A Study of the Structure-Property Relationship of Azole-Azine Based Homoleptic Platinum(II) Complexes and Tunability of the Photo-physical Properties

Malaviarachchige Rabel Ranga Prabhath

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Advanced Technology Institute
Faculty of Engineering and Physical Sciences
University of Surrey
Guildford, Surrey, GU2 7XH, United Kingdom.

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Dedicated to my Wife, Family and Teachers
ABSTRACT

Owing to superior energy efficiency, Light Emitting Diode (OLED) technology has become considerably commercialised over the last decade. Innovations in this field have been spurred along by the discovery of new molecules with good stability and high emission intensity, followed through by intense engineering efforts. Emissive transition metal complexes are potent molecular emitters as a result of their high quantum efficiencies related to facile intersystem crossing (ISC) between excited-state manifolds (efficient spin orbit coupling (SOC)) and resultant efficient emission from the triplet state (phosphorescence). These also allow rational tuning of the emission wavelengths. Tuning of the ground and excited state energies, and thus emission wavelength of these complexes can be achieved by subtle structural changes in the organic ligands. Pyridyl-triazole ligands have started receiving increasing attention in recent years as strong field ligands that are relatively straightforward to synthesise.

In this study we explore the emission tunability of a newly synthesised series of 5-substituted-Pyridyl-1,2,3-triazole-based ligands and their Pt(II) complexes. Studies have shown, substitution at the triazole moiety is less effective in achieving emission tunability. Alternatively we carried out the substitution at the 5th position of the pyridine ring with a wide range of electronically diverse, donor-acceptor groups (-N(CH$_3$)$_2$, -H, -CHO, -CHC(CN)$_2$). The target ligands were approached through the serial application of the Sonogashira carbon–carbon coupling and the Sharpless copper-catalyzed Huisgen’s 1,3-dipolarcycloaddition procedures.

As a result, coarse tunability of excimer emission was observed in thin-films, generating blue-(486 nm), green-(541 nm), orange-(601 nm) and red-(625 nm) luminescence respectively. This “turned-on” substituent effect was accounted for metallophilic Pt—Pt interaction-induced aggregates in the solid state. Excited state calculations reveal that the solid state emission is associated with $^1$MMLCT transitions. Lifetime measurements revealed the existence of two decay processes: one being fluorescence and the other process, either phosphorescence or delayed fluorescence. Further a linear-relationship between the Hammett parameters of the substituents and emission wavelengths was established. This allows a reliable emission predictability for any given substituent of 5-substituted pyridyl-1,2,3-triazole platinum complexes. In conclusion, we show a new approach in achieving coarse emission tunability in pyridyl-1,2,3-triazole based platinum complexes via subtle changes in the molecular structure and the importance of metallophilic interactions in the process.
During the second phase of the study, the scope was broadened to examine the effects of heterocyclic nitrogens in the ligand skeleton. Fifteen different combinations of azole-azine linked ligand systems were synthesized, by systematically increasing the number of nitrogens and changing the ring position of the nitrogens in the skeleton. Later, the homoleptic platinum complexes of the respective ligands were synthesised, and the photo-physical characteristics were studied. The above mentioned changes in the ligand structure resulted in a 264 nm emission tunability, in the thin films of the complexes. Theoretical studies on the complexes revealed that based on the structure of the ligand, different metallophilic stacking behaviours and different origins of emission (fluorescence and phosphorescence) can result, which in turn give rise to tunable emission wavelengths.
DECLARATION

This thesis and the work to which it refers are the results of my own efforts, other than the areas explicitly noted as being conducted collaboratively. The Theoretical calculations discussed in Chapter 5 and Chapter 7 were performed / assisted by Dr. Julia Romanova. The Lifetime measurements were carried out by Prof. Richard Curry. The analysis of the data published, was done by the author. Any ideas, data, images or text resulting from the work of others (whether published or unpublished) are fully identified as such within the work and attributed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in whole or in part for any other academic degree or professional qualification. I agree that the University has the right to submit my work to the plagiarism detection service TurnitinUK for originality checks. Whether or not drafts have been so-assessed, the University reserves the right to require an electronic version of the final document (as submitted) for assessment as above.

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M. R. Ranga Prabath

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<table>
<thead>
<tr>
<th>Abbreviation</th>
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<tr>
<td>bpy</td>
<td>2,2’-bipyridine</td>
</tr>
<tr>
<td>CFSE</td>
<td>crystal field stabilisation energy</td>
</tr>
<tr>
<td>DMF</td>
<td>N, N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>EA</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>en</td>
<td>ethylene diamine</td>
</tr>
<tr>
<td>ESI/APCI</td>
<td>electron spray ionization/ atmospheric pressure chemical ionization</td>
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<tr>
<td>FTIR</td>
<td>fourier transformed infrared</td>
</tr>
<tr>
<td>Hex</td>
<td>hexane</td>
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<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
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<td>h</td>
<td>hours</td>
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<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ISC</td>
<td>inter system crossing</td>
</tr>
<tr>
<td>LC/MS</td>
<td>liquid chromatography / mass spectrometry</td>
</tr>
<tr>
<td>Liq.</td>
<td>liquid</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<tr>
<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>min</td>
<td>minutes</td>
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<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>n-BuLi</td>
<td>n-butyl lithium</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic spectroscopy</td>
</tr>
<tr>
<td>OLED</td>
<td>organic light emitting diode</td>
</tr>
<tr>
<td>P.D.U.</td>
<td>process defined units</td>
</tr>
<tr>
<td>Φ</td>
<td>fluorescence yield</td>
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<tr>
<td>QE</td>
<td>quantum efficiency</td>
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<tr>
<td>R.T.</td>
<td>room temperature</td>
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<tr>
<td>SOC</td>
<td>spin orbit coupling</td>
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<tr>
<td>TEA</td>
<td>Trimethylamine</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>UV/VIS</td>
<td>ultraviolet/ visible</td>
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PUBLICATIONS

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CHAPTER 1

INTRODUCTION

1.1 Luminescence

Nature has provided many examples of light emission in our environment. In the biological world bioluminescence is common. Examples include fireflies, jellyfish, shells and glow-worms, to name a few in the animal world, while certain bacteria, plants and mushrooms (*Omphalotus olearius*) also express luminescence in a biological process.¹ The discovery of Bolognian stone, which emits light after exposure to sunlight, in 1603 by Vincenzo Casciarolo² and isolation of the element phosphorus in 1669 were the first steps in the quest for materials that emit light at low temperatures (“cold light”). This differentiated from the emission of light from a heated object (‘hot light’, incandescence),³ which emits a broad spectrum extending out to the IR (infrared) region the electromagnetic spectrum and is thus associated with heat loss and low efficiency. Cold light emission is now known as “luminescence” having been termed in 1888 by Eilhardt Wiedemann, a German physicist.¹,⁴ Luminescence is now known to originate from emission of light by an excited molecule, atom or a substance that is not resulting from heat; it is thus a form of cold body radiation, which Wiedemann recognised as the anti-thesis of incandescence.¹ Wiedemann went further and categorised the luminescent materials into six classes based on the mode of excitation; photoluminescence, thermoluminescence, electroluminescence, crystalloluminescence, triboluminescence, and chemiluminescence. Photoluminescence is excited by light itself and is subdivided into two main categories, fluorescence and phosphorescence. Thermoluminescence is the generation of light from gentle heating. Electroluminescence appears from excitation with an electric field; crystalloluminescence and triboluminescence occur when solutions crystallise or when crystals are crushed or broken (pressurised), and chemiluminescence may appear during chemical reactions.

Today the phenomenon of luminescence has expanded not only into simple applications in everyday life but also into the more advanced realms of ‘Engineering’ and ‘Biology’. Applications in this area may vary from simple applications such as glow sticks, security markings on bank notes to more complex applications such as light emitting diodes, light emitting transistors, bio-imaging applications etc. The disciplines of Quantum Physics and Chemistry are important for the understanding of the origins and mechanisms involved in the luminescence process, whereas the understanding of the physical-organic chemistry aspect of
the luminescent materials is important to study the trends in behaviour as a function of structure towards further control and design. Identifying the principles associated with luminescence while establishing structure-property relationships from a chemical perspective will help to enhance materials design, allowing the manipulation of the photo-physical properties of luminescent materials leading towards more targeted and efficient production of new materials and compounds.

1.2 Luminescent materials

The drive for luminescent materials started with inorganic chemistry. Inorganic materials are mainly of three classes;\(^5\) (1) atomic emitters like Neon in neon lights, (2) large band gap semiconductors like ZnS which emits from dopant levels to the ground level upon doping with various metal ions like Mn\(^{2+}\), Ag\(^+\), Cu\(^{2+}\) and (3) inorganic materials involving insulators, which again emit by introduction of dopant levels in between the valence and conduction bands of the insulator. A known example of inorganic material is Cr\(^{3+}\) doped Al\(_2\)O\(_3\), better known as ruby. Inorganic materials have been able to show high performance levels for luminescence. Despite the many appealing properties of inorganic materials, recently, organic materials have gained considerable attention as potential replacements for inorganic counterparts in luminescent applications such as flat panel lighting applications.\(^6\) Organic luminescent materials can be of different classes of compounds including aromatic hydrocarbons, arylethylenes, polyenes, divinylbenzenes, stilbenes, trivinylbenzenes, aryl acetylenes etc.\(^5\) Organic materials deliver simple and cost effective processing techniques such as spin coating, doctor blading and ink jet printing. In addition, they also offer more flexibility and lighter weight to materials, which are crucial in the miniaturisation process of the luminescent devices. While organic materials deliver many promising attributes, they also have a number of disadvantages, including poor thermal and mechanical stability. In addition, room temperature charge mobility is limited in organic materials by their weak van der Waals interactions that are the primary effects that drive crystallisation for organic molecules.\(^6\) This effect limits the extent of the special wavefunction of organic materials, whereas inorganic materials can be often considered as fully electron-delocalised continuum structures.

In order to address these drawbacks in both organic and inorganic materials a new class of materials known as organic-inorganic hybrid materials has gained attraction with the intention of combining the desirable properties of both organic and inorganic materials within a single entity. These hybrid materials are not the simple sum of two components but their synergistic combination.\(^7\) Organic-inorganic hybridised materials are usually
metallopolymer or metal complex. The inorganic component is usually a transition metal ion while the organic component can be either a polymer or a small molecular ligand system. Small molecular systems deliver nano-scale changes at the molecular level of the hybrid materials while polymeric materials, having properties strongly dependent on macrostructure, are less predictable to design. In addition to the previously discussed advantages that both inorganic and organic components can deliver, the methodologies of synthetic organic chemistry, in particular, provide a wealth of possible ligand molecules that offer an even greater wealth of physical properties and structural diversity. Thus, systems with organic components can be widely tunable in their photo-physical properties by changing these organic building blocks (fine tuning) while also using different metal centres (coarse tuning) within the hybrid component.

![Image of organic-inorganic hybridised materials](image)

Figure 1.1- Design concept of organic-inorganic hybridised materials

In the development process of new luminescent materials many important aspects should be considered. Some of the most important aspects are listed below.

i. High quantum efficiency of the material
ii. Wide range of tunability of photo-physical properties (i.e., emission colour)
iii. Stability of the material
iv. Cost effectiveness
The improvement of the efficiencies of materials has been very successfully addressed in the literature (more than 30,000 publications on this topic – sci-finder). Compared to that, the tunability of the properties in luminescent materials, especially colour tunability, is less explored (only around 4,000 publications – sci-finder). Property tunability of luminescent materials/devices is generally approached by synthetic based modifications at the molecular level and/or post-synthetic processing involving material level alterations (engineering). The latter is primarily based on the alteration in device fabrication parameters like film thickness of the materials, temperature, transport layer assembly etc. This has delivered promising results often of great significance but has lacked the repeatability and the predictability accustomed to in synthetic chemistry efforts. The synthetic approach delivers the freedom of changing the molecular level construction (bottom-up design) of the material and the fundamental desired properties in a more direct manner. Hence the study of structure-property relationships is also vital in the field of luminescent materials. A remaining challenge is the greater understanding of how the molecular properties transfer to their respective materials. This issue is also of central importance in the context of our current work.

1.3 Objective of the study

Heavy metal containing complexes are potent molecular emitters due to their high quantum efficiencies related to facile intersystem crossing between excited-state manifolds (efficient spin orbit coupling) and resultant efficient emission from the triplet state (phosphorescence). Rational tuning of the emission wavelengths based on structural modifications of the ligands, has been demonstrated in a number of octahedral complexes of d\textsuperscript{6} metals including predominantly iridium, rhodium and ruthenium and with a large range of structurally diverse ligands. The square-planar d\textsuperscript{8} complexes have also received some considerable interest since the seminal work of Gray, Vlcek and Miskowski. Square-planar platinum complexes present excellent emissive properties and allow for a more minimal planar structural motif with less diasteromeric diversity. However, anticipated deleterious excitonic self-quenching of planar complexes brought on by enhanced intermolecular electronic coupling through π-π stacking interactions implies considerable design difficulties for this class of phosphors. Nonetheless, for Pt(II) this negative aspect is largely offset by the propensity of these systems to engage in metallophilic Pt---Pt interactions, which give rise to new and interesting photo-physics involving transitions between metallophilic bonds and ligands (metal-metal to ligand charge-transfer (MMLCT)).
and supramolecular design potential for further property tunability.\textsuperscript{20-23} Indeed, a number of studies have shown strong emissivity despite strong metallophilic stacking.\textsuperscript{24, 25} A better understanding and control of such interaction may lead to materials with increased quantum yields and potential anisotropic ordering arranged through a discrete non-covalent interaction. Further studies of the excimer states of such systems through systematic alteration of the ligands would reveal important design criteria towards these goals.

Heterocyclic azole-azine ligand based systems are popular in the literature for their luminescent metal complexes. In the first phase of this study the photo-physical properties of the novel pyridyltriazolyl complexes of platinum(II) are explored. Compared to other pyridyl azoles,\textsuperscript{24, 26, 27} pyridyl-1,2,3-triazoles are less studied. Moreover, most of the examples related to pyridyl-1,2,3-triazoles involve substitution at N of the triazolyl ring in order to affect the energy of the highest occupied molecular orbital (HOMO). However, triazolyl is electronically insulating and thus substituent effects have not been very pronounced.\textsuperscript{28, 29} A more effective tuning route might target the lowest unoccupied molecular orbital (LUMO) that is found on the pyridyl ring and is anticipated to be more closely associated with the excited-state.\textsuperscript{27} Thus, in the present work, pyridyl-1\textit{H}-1,2,3-triazole ligands were prepared using efficient reactions to build a structurally homologous series of donor and acceptor 5-pyridyl substituted anionic ligands via deprotonation of the 1\textit{H}-triazolyl moiety to give strong field ligation (suppressed \textit{d-d} transitions)\textsuperscript{30} in final neutral complexes.

During the second phase, the scope of the study is expanded to examine the effects of heterocyclic nitrogens in the ligand skeleton to fine tune the energy levels in their homoleptic platinum complexes thereby changing the emission wavelengths in a systematic manner and to improve the quantum yields. Fifteen different ligands systems were synthesized by systematically increasing the number of nitrogens and changing the ring position of the nitrogens in the azole (pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tertazole) and azine (pyridine, pyrimidine, pyrazine) rings. Then the photo-physical properties of the novel homoleptic platinum complexes were studied to establish structure–property relationships.

Therefore the main goal in this project is to systematically explore the molecular and supramolecular design space of heterocyclic azole-azine ligands and their platinum complexes and to develop materials with predictable luminescent properties.

1.4 Arrangement of the thesis

Following the introduction in this chapter, \textbf{Chapter 2} involves a review of fundamental concepts involved in this study. A further discussion based on the previous work reported so
far in the scientific literature is presented. **Chapter 3** is an overview of the experimental techniques and synthetic protocols used during the study. **Chapter 4** involves discussion on the reaction mechanisms and structural characterisation of the novel pyridyl-1H-1,2,3-triazole ligands and their homoleptic platinum complexes. **Chapter 5** focuses on the photo-physical properties of the ligands and the platinum complexes and the study of the substituent effects related to the structure-property relationship. Observed experimental data is further elaborated based on theoretical simulations to identify ground state and excited state properties. Finally a relationship between the Hammett parameters and the emission wavelengths was established. **Chapter 6** is dedicated to the reaction mechanisms involved and the structural characterisation of the 15 ligands and 15 metal complexes in the second phase of the project. **Chapter 7** discusses the photo-physical properties of the ligands and platinum metal complexes described in Chapter 6 and the investigation of heterocyclic effects in the ligands and their involvement in the tunability of photo-physical properties of the metal complexes. Finally, **Chapter 8** summarises the conclusions made from the work and possible future avenues for investigation.
CHAPTER 2
LITERATURE REVIEW

2.1 Metal complexes

Metal complexation is a wide area of interest which spans from inorganic chemistry, organic chemistry, biochemistry, molecular biology, pharmacology, materials engineering to, and beyond, environmental science.

A metal complex is a chemical structure that contains at least one metal atom or a cation surrounded by an array of bound neutral molecules or anions, which are called ligands or complexing agents. In metal-ligand bond formation, the interactions between the empty/electron deficient metal orbitals and electron rich orbitals of the surrounding ligands originate through non-bonding electrons (lone pairs) or pi bonding electrons of the ligands. In the case of transition metal complexes, the properties of the complex are different from the individual properties of its constituent metal atoms or ligands. Depending on the nature of the ligands attached, metal complexes are broadly classified under the categories below:

i. Classical / Werner Complexes: Ligands are bound to the metal centre through lone pairs of electrons residing on the main group atoms of the ligands (e.g. [Co(NH$_3$)$_6$]Cl$_3$, [Fe(C$_2$O$_4$)$_3$]K$_3$).

ii. Organometallic / Metallorganic complexes: Surrounding ligands are organic or organic-like (e.g. (C$_5$H$_5$)Fe(CO)$_2$CH$_3$).

iii. Cluster complexes: The cluster contains metal-metal bonds where the metal act as the electron acceptor as well as the ligands and at least one organic moiety directly bonded to a metal atom (e.g. Ru$_3$(CO)$_{12}$).

iv. Bioinorganic complexes: Complexes formed between metal ions and ligands present in biological systems (e.g. heme in hemoglobin, which is a complex of porphyrins and iron).

2.1.1 Coordination complexes

Coordination complexes are formed as a result of a Lewis acid-base reaction where the central transition metal atom or ion is bonded to ligands via coordinate covalent bonds. A coordinate covalent bond is a type of covalent bond where one atom provides (donor atom) both electrons for bond formation. The difference between a covalent bond and a coordinate covalent bond is that, in a covalent bond two atoms donate one electron each for bond formation. Metal atoms or ions act as Lewis acids (acceptors) due to their ability to accept
pairs of electrons from ligands (Lewis bases). Ligands act as Lewis bases (donors) as they contain at least one pair of electrons available for donation to the metal centre (Lewis acid).\textsuperscript{35}

Within a coordination compound, a number of spheres are defined. The part where the ligands are directly attached (via dative bonds) to the metal centre is called the first coordination sphere. When the ligand atoms are non-covalently attached to the metals this is called the second coordination sphere. Usually, the interactions between the first and second coordination spheres involve hydrogen bonding and for charged complexes, ion-pairing interactions play an important role.\textsuperscript{36} For example, in hexamminecobalt(III) chloride ([Co(NH$_3$)$_6$]Cl$_3$), Co$^{3+}$ and the six ammonia ligands comprise the first coordination sphere. The three Cl$^-$ anions belong to the second coordination sphere.

The influence of the first coordination sphere is greater than that of the second coordination sphere toward the reactivity and chemical properties of the metal complex. Nonetheless, the second coordination sphere is possibly more relevant to understanding reaction mechanisms of the metal complex, including ligand exchange and catalysis.

The coordination number is defined as the number of donor atoms bonded to the central metal atom/ion.\textsuperscript{35} In a typical complex, the metal ion is bound to several donor atoms which can be of the same type or different. The number of bonds depends on the electronic configuration, size and the charge of the metal ion and the ligands.

2.1.2 Geometry of metal complexes

The spatial geometry of transition metal complexes is dominated by the coordination number, which is mainly determined by the orbital overlap of the $s$ and $p$ orbitals of the ligand atom and the $d$ orbitals of the metal centre. According to the 18 electron rule, the $s$, $p$ and $d$ orbitals of the metal can accommodate up to a maximum of 18 electrons which limits the maximum coordination number of a transition metal complex to be 9.\textsuperscript{35, 37} Moreover, the ratio of the size of the metal and the ligands plays an important role in deciding the coordination number of a metal complex. For example, a large metal centre and small ligands form a higher coordination complex whereas, a smaller metal centre and larger ligands gives
rise to a lower coordination number. In addition to the above two factors, ligand-ligand repulsions also affect the geometry of a coordination complex. Other factors that influence the geometry of a complex are the nature of the ligands leading to irregular bond lengths (e.g. use of different types of ligands) and electronic effects (e.g. Jahn-Teller distortion in six coordinated octahedral geometries). The most common spatial geometries based on the coordination number of complexes are given in Table 2.1 below.

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Geometry of the metal complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral, Square planar</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal, Square pyramidal</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral, Trigonal prismatic</td>
</tr>
<tr>
<td>7</td>
<td>Pentagonal bipyramidal</td>
</tr>
<tr>
<td>8</td>
<td>Square antiprismatic</td>
</tr>
<tr>
<td>9</td>
<td>Tri-capped trigonal prismatic</td>
</tr>
</tbody>
</table>

2.1.3 Stereoisomerism of metal complexes

Stereoisomers are molecules that have the same molecular formula and atomic sequences but different three-dimensional spatial orientation. Stereoisomerism can be further
subdivided to: *cis-trans*, *facial-meridional* and optical isomerism.\(^{35}\) When two ligands are adjacent to each other the ligands are assigned to be *cis* and when they are facing opposite to each other, they are called *trans*. *cis-trans* isomerism is observed only in octahedral and square planar complexes. *mer-fac* isomerism is a notation assigned to octahedral complexes. When three identical ligands occupy one face of an octahedron, the isomer is assigned as *fac*, and if three identical ligands and the metal centre lies on the same plane, the isomer is called *mer*. In a *fac* isomer, any two identical ligands are *cis* to each other and a *mer* isomer contains both *cis* and *trans* pairs of identical ligands.

### 2.1.4 Optical isomerism

If two molecules are non-superimposable mirror images of each other, they are called optical isomers. The two optical isomers are also referred to as enantiomers and these differ only by the direction of rotation of plane polarized light i.e. enantiomers rotate the plane of polarised light in opposite directions.\(^{35}\) Different assignments are used to denote the absolute configuration of enantiomers such as, \( \text{R (clockwise)} / \text{S (anti-clockwise)} \) and \( \Lambda (\text{left-handed}) / \Delta (\text{right-handed}) \).

![Figure 2.3 - \( \Lambda \) and \( \Delta \) optical isomers](image)

### 2.1.5 Thermodynamics of formation of metal complexes

Standard free energy, or the Gibbs free energy, \( \Delta G^\circ \) of formation is the change of free energy (energy that can be used to do work) when a product is formed from its elements that are in their most thermodynamically stable physical states at standard conditions (1 atm, 298 K). \( \Delta G^\circ \) is related to enthalpy, \( \Delta H^\circ \) and entropy, \( \Delta S^\circ \) changes according to the following equation:\(^{38}\)

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

(2.1)

If,

- \( \Delta G^\circ < 0 \), reaction is spontaneous in the forward direction
- \( \Delta G^\circ = 0 \), reaction is in equilibrium
\[ \Delta G^\circ > 0, \text{ reaction is spontaneous in the reverse direction} \]
Hence, according to the equation 2.1, the spontaneity of a reaction is governed by the magnitude of both \( \Delta H^\circ \) and \( \Delta S^\circ \). Another important thermodynamic relationship is that, if
\[ \Delta S^\circ > 0, \text{ reaction is spontaneous in the forward direction} \]
\[ \Delta S^\circ = 0, \text{ reaction is in equilibrium} \]
\[ \Delta S^\circ < 0, \text{ reaction is non-spontaneous in the forward direction} \]
where, \( \Delta S^\circ \) is the change in the entropy of the system.
Hence, for an exothermic reaction (\( \Delta H^\circ < 0 \)), the reaction is most feasible if \( \Delta S^\circ > 0 \).
Generally, bond forming reactions are exothermic in nature.\(^{38}\) For a metal complex formation reaction of the type:
\[ M^{3+} + 3L \rightleftharpoons ML_3 \]  \hspace{1cm} (2.2)
And
\[ \Delta G^\circ = -RT \ln \beta = -2.303 \ R T \log \beta \]  \hspace{1cm} (2.3)
Where, \( M^{3+} \) is the metal ion, \( L \) is the free ligand, \( \beta \) is the overall formation constant for the reaction, \( R \) is the gas constant and \( T \) is the absolute temperature (in K).\(^{38}\) In solution, free metal ions do not exist in the isolated charged form and they are generally surrounded by solvent molecules. Hence, there is a competition between the solvent molecules and free ligands in a metal complexation reaction. For simplicity, if the presence of solvent molecules is ignored, the step-wise formation of \( ML_3 \) complex can be written as;\(^{39}\)
\[ M^{3+} + L \rightleftharpoons [ML]^{2+} \; ; \; K_1 = \frac{[ML]^{2+}}{[M^{3+}][L]} \]  \hspace{1cm} (2.4)
\[ [ML]^{2+} + L \rightleftharpoons [ML_2]^+ \; ; \; K_2 = \frac{[ML_2]^+}{[[ML]^{2+}][L]} \]  \hspace{1cm} (2.5)
\[ [ML_2]^+ + L \rightleftharpoons ML_3 \; ; \; K_3 = \frac{[ML_3]}{[[ML_2]^+][L]} \]  \hspace{1cm} (2.6)
Where, \( K_1, K_2 \) and \( K_3 \) are step-wise formation constants. Stability constants are an indication of the strength of the interactions between the involved components when forming a metal complex. Further,
\[ \beta = K_1 K_2 K_3 = \frac{[ML_3]}{[M^{3+}][L]^3} \]  \hspace{1cm} (2.7)
Therefore, for a metal complex formation reaction, if \( \Delta H^\circ \) is determined (by calorimetry), by substituting \( \beta \) in equation 2.2 a, value for \( \Delta S^\circ \) can be obtained using equation 2.1.\(^{38,39}\)
2.1.6 Factors affecting the stability of metal complexes

2.1.6.1 The chelate effect

Denticity of ligands

Denticity is defined as the number of donor atoms in a single ligand that binds to a metal centre in a complex.\textsuperscript{40} Hence;

i. A monodentate ligand has one donor atom that links to a central metal atom / ion (Cl\textsuperscript{−}, OH\textsuperscript{−}, NH\textsubscript{3}, H\textsubscript{2}O)

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]

\textbf{Figure 2.4 – Structure of [CuCl\textsubscript{4}]^{2−}}

ii. A bidentate ligand has two donor atoms bonding to a metal centre at two points (ethylenediamine (en), oxalate ion (ox))

\[
\begin{array}{c}
\text{H}_2\text{O} \\
\text{H}_2\text{N} \\
\text{Cu} \\
\text{H}_2\text{N} \\
\text{H}_2\text{O}
\end{array}
\]

\textbf{Figure 2.5 – Structure of [Cu(en)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}]^{2+}}

iii. A polydentate ligand consists of more than a single donor atom and the number of donor atoms involving in binding to a central metal atom / ion varies (ethylenediamminetetraacetic acid / EDTA, maximum denticity = 6)

\[
\begin{array}{c}
\text{M} \\
\text{N} \\
\text{O} \\
\text{N} \\
\text{O}
\end{array}
\]

\textbf{Figure 2.6 – Structure of a [M-EDTA]\textsuperscript{2−} complex where, M=Cu\textsuperscript{2+}}

Chelation

Chelation is a thermodynamically driven process where a polydentate ligand binds to a central metal atom / ion forming up to a 5 or 6 membered ring.\textsuperscript{39, 41} The polydentate ligand
that undergoes chelation is referred to as the chelating ligand. Thermodynamic data proves that a complex resulting from a reaction with a chelating ligand is much more stable than a complex formed with monodentate ligands. For example, adding one bidentate ligand results in a thermodynamically more stable complex than when two monodentates are used for complexation. If the following two reactions are considered:\(^\text{39}\)

\[
\text{Cd}^{2+} + 4\text{MeNH}_2 \rightleftharpoons [\text{Cd(MeNH}_2)_4]^{2+} \quad (2.8) \\
\text{Cd}^{2+} + 2\text{en} \rightleftharpoons [\text{Cd(en)}_2]^{2+} \quad (2.9)
\]

In equation 2.8, four monodentate methylamine ligands are attached to the \(\text{Cd}^{2+}\) centre while in equation 2.9, two ethylene diamine (en) bidentate ligands form a chelate complex with the \(\text{Cd}^{2+}\) centre resulting in two five-membered ring formations. The donor power of both these ligands being similar, the enthalpy of formation of \(\text{Cd-N}\) bonds of both reactions are approximately the same. However, the magnitude of the equilibrium / stability constants for the two reactions are: \(\beta_1 \ll \beta_2\). Hence, when the concentration of methylamine is twice than that of ethylene diamine (provided the concentration of \(\text{Cd}^{2+}\) is the same in both reactions), the concentration of \([\text{Cu(en)}]^{2+}\) is much greater than the concentration of \([\text{Cu(MeNH}_2)_2]^{2+}\). As the enthalpy of formation of \(\text{Cd-N}\) bonds is similar in both cases, the difference in stability constants is believed to be due to an entropic effect. For example, in equation 2.8, the number of components on the left hand side (LHS) of the reaction is 5 and the number of components on the right hand side (RHS) is 1. When equation 2.9 is considered, the number of components on the LHS of the reaction is 3 and on the RHS is 1. Therefore, a lower entropy of disorder is lost during the formation of the chelate complex in comparison to the formation of the complex with monodentate ligands. Entropy being the main factor in deciding the stability constants of the reactions, other factors such as solvation changes and ring formation effects play a significant role.\(^{39}\) The following Table 2.3 illustrates the effect of chelation on the stability constants and the \(\Delta G^\circ\) values of the reactions 2.8 and 2.9 at 298 K.\(^{39}\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log (\beta)</th>
<th>(\Delta G^\circ / \text{kJ mol}^{-1})</th>
<th>(\Delta H^\circ / \text{kJ mol}^{-1})</th>
<th>(T\Delta S^\circ / \text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>6.55</td>
<td>-37.2</td>
<td>-57.3</td>
<td>20.1</td>
</tr>
<tr>
<td>2.9</td>
<td>10.62</td>
<td>-60.7</td>
<td>-56.5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Some general phenomena of chelation are:

i. The chelate effect increases with the number of atoms in a chelate ring - \([\text{Ni(dien)}_2]^{2+}\) is more stable than \([\text{Ni(en)}_3]^{2+}\). The reason being, diethylenetriamine-1,4,7-
triazaheptane (dien) is tridentate and ethylene diamine (en) is bidentate, although both complexes are octahedral with 6 nitrogen atoms around the metal centre.

ii. 5- and 6-membered chelate rings form the most stable complexes – For example EDTA with 6 donor atoms form stable 5-membered rings with metal ions such as Cu$^{2+}$. 4-membered rings are destabilised due to bond strains when forming the ring. When rings become larger than 6-membered a reduced chelation effect is observed; the bond strains increase, the enhancement of the local concentration is diminished and ligands are positioned further away from the metal ion.

### 2.1.6.2 Effect of Temperature

According to van’t Hoff equation;\(^{38}\)

\[
\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}
\]  \hspace{1cm} (2.10)

Where,
- \(K\) is the equilibrium constant of the equilibrium reaction
- \(\Delta H\) is the enthalpy of formation
- \(R\) is the gas constant
- \(T\) is the absolute temperature (in K)

Hence, if a reaction is exothermic (\(\Delta H < 0\)), \(K\) decreases with temperature and for an endothermic reaction (\(\Delta H > 0\)), \(K\) increases with temperature.

### 2.1.6.3 Nature of Metal Ions / HSAB Theory

The Hard and Soft Acids and Bases (HSAB) theory introduced by Ralph Pearson is used to describe the stability of metal complexes.\(^{37, 42}\)

i. **Hard acids** are Lewis acids that have small ionic radii, high positive charge, contain empty valence shell orbitals, high energy LUMOs and generally are highly solvated.

ii. **Soft acids** are Lewis acids that have large ionic radii, low positive charge, completely filled valence shell atomic orbitals and low energy LUMOs.

iii. **Hard bases** are Lewis bases that have small ionic radii, high electronegativity, weak polarizability, high energy HOMOs and are highly solvated.

iv. **Soft bases** are Lewis bases that have large ionic radii, low electronegativity, high polarizability and low energy HOMOs.

v. **Borderline acids or bases** Lewis acids or bases that contain intermediate properties.
According to the HSAB theory, hard acids prefer binding with hard bases, forming ionic complexes (due to the large electronegativity difference). While soft acids tend to bind with soft bases, forming covalent complexes (due to the negligible electronegativity difference). The interactions between a hard acid and a soft base (or vice versa) are generally polar covalent are less stable (more reactive). The reactivities of polar covalent complexes are high and hence, if allowed these tend to be converted to more ionic or more covalent complexes.

The theory behind the HSAB concept is explained using the Klopman’s FMO (Frontier Molecular Orbitals) analysis. According to this, the nature of the interactions between acids and bases are governed by the relative energies of the participating FMOs (HOMO and LUMO).

2.1.7 Crystal field stabilisation energy

Crystal field stabilization energy (CFSE) is the stability introduced by the splitting of degenerate orbitals when a transition metal ion is placed in an environment surrounded by a set of ligands due to a static electric field created by the ligands. In a hypothetical spherical field, all five $d$-orbitals of a transition metal ion are degenerate. In the presence of a ligand field, the $d$-orbitals split and the energy of some orbitals become lower than in the case of being under a spherical field. As a result, if any of the metal ion electrons are occupying these low lying orbitals, the metal ion is more stable in the ligand field than in the case of being in a spherical field. The amount of stabilisation is referred to as the CFSE. On the other hand, if any of the electrons are occupying the orbitals which are higher in energy than in the case of degenerate orbitals, this lowers the CFSE.

![Figure 2.7 – Crystal field splitting diagrams of octahedral, tetrahedral and square planar complexes](image-url)
Initially, a ligand is attracted to a metal ion due to the attraction between non-bonding electrons of the ligand and the positive charge of the metal cation. As the ligand approaches the metal ion the ligand electrons will be closer to some of the metal d-orbitals and farther away from the rest of the orbitals. This is the cause for the loss of degeneracy of d-orbitals. Due to repulsion between like charges, the d-electrons closer to the approaching ligand electrons go higher in energy than those further away. This results in splitting of d-orbitals in energy. The extent of splitting (Δ) is affected by:  

i. The metal ion

ii. The metal ion’s oxidation state - higher the oxidation state larger the splitting:  
A higher positive charge means the ligand will be attracted closer to the metal ion centre. This results in a shorter distance between the metal electrons and ligand electrons generating greater repulsions and hence a higher Δ.

iii. Nature of the ligands:
Spectrochemical series – (weak field ligands) I⁻ < Br⁻ < S₂⁻ < SCN⁻ < Cl⁻ < NO₃⁻ < N₃⁻ < F⁻ < OH⁻ < C₂O₄²⁻ < H₂O < NCS⁻ < CH₃CN < py < NH₃ < en < 2,2'-bipyridine < phen < NO₂⁻ < PPh₃ < CN⁻ < CO (strong field ligands) (The ligand that produce larger splitting are the ones that can participate in metal to ligand back bonding)

iv. Ligand arrangement / geometry around the metal centre
Figure 2.7 illustrates the crystal field splitting diagrams of three of the most commonly encountered geometries of metal complexes; tetrahedral, octahedral and square planar. The reason for the Δₜₜ < Δₐₜₖ is that, unlike octahedral geometry, the ligand electrons in tetrahedral geometry are not directly oriented towards the metal d-orbitals (hence, less repulsion between like charges).

2.1.7.1 High spin and low spin complexes

When metal complexes are formed with strong field ligands (large Δ), the lower energy orbitals are completely filled prior to occupying the higher energy orbitals (Aufbau principle) as populating the higher energy states is energetically unfavourable. Such complexes are called “low spin”. Conversely, when weak field ligands are involved in the formation of metal complexes (low Δ), the energy required to populate higher energy orbitals is less than that of paring two electrons in the same energy level. Hence, electrons start occupying all energy levels prior to pairing (Hund’s rule). These complexes are referred to as “high spin”. This is the reason why tetrahedral complexes are generally high spin (low Δₜₜ).
2.1.7.2 Calculation of CFSE

In the case of an octahedral geometry, the $t_{2g}$ orbitals are stabilised by $2/5 \Delta_{\text{oct}}$ and $e_g$ orbitals are destabilised by $3/5 \Delta_{\text{oct}}$ relative to the case of under a spherical field. If a metal complex with d$^5$ configuration is considered, in the case of it forming a low spin complex (all 5 electrons in $t_{2g}$ level), the CFSE is $5 \times 2/5 \Delta_{\text{oct}} = 2 \Delta_{\text{oct}}$. If a high spin complex of the same is considered (3 electrons occupying $t_{2g}$ level and 2 electrons occupying $e_g$ level), the CFSE is $(3 \times 2/5 \Delta_{\text{oct}}) - (2 \times 3/5 \Delta_{\text{oct}}) = 0$. Hence, the net stabilisation or destabilisation is zero.\textsuperscript{35} Very large CFSE is considered to be the reason for d$^8$ complexes to form square planar geometries over others.

2.1.8 Colours of transition metal complexes

The principle phenomena behind the vast number of colours observed in transition metal complexes are either due to; (i) d-d transitions or (ii) charge transfer processes.\textsuperscript{35}

2.1.8.1 d-d transitions

As described above, according to the crystal field theory (CFT) d orbitals are split in energy in an environment of a ligand field. Hence, based on the $\Delta$, different complexes absorb different wavelengths (\(\lambda\)) of photons which in turn produce various colours. For example, metal complexes with a larger $\Delta$ absorb photons with shorter $\lambda$ whereas, complexes with a smaller $\Delta$ absorb photons of longer $\lambda$. However, electron-electron repulsions and Jahn-Teller effects also play an important role in deciding the splitting of d orbitals and hence the colours of complexes. Typical $\varepsilon$ (absorption coefficient) values of metal complexes with d-d transitions fall in the range of $\varepsilon < 20$ dm$^3$ mol$^{-1}$ cm$^{-1}$.\textsuperscript{44}

According to the “Laporte Selection Rule” ($\Delta l = \pm 1$) d-d transitions are forbidden and hence weakly intense. Laporte allowed are the transitions that occur with a change in parity (i.e. $s \rightarrow p$ and $p \rightarrow d$) and Laporte forbidden are the ones where the parity remains unchanged (i.e. $p \rightarrow p$ and $d \rightarrow d$).\textsuperscript{35}
In general, if only a particular wavelength is absorbed the observed colour is complementary to the actual colour (wavelength) absorbed by the metal complex and is illustrated by the colour wheel given in fig 2.8.

2.1.8.2 Charge Transfer Complexes

Atoms or ions which have low ionisation potentials (readily oxidizable) have high HOMO levels and the ones with high electron affinities (readily reducible) have relatively low lying LUMO levels. If a complex between a readily oxidizable metal and a readily reducible ligand is formed, the energy gap between the HOMO of the metal and LUMO of the ligand will be relatively small. If the energy gap is too small (less than 10,000 cm\(^{-1}\)), a total electron transfer from the metal atom to the ligand occurs resulting in oxidation of the metal and the reduction of the ligand. For a transition to generate colours in the visible region, the energy separation between the relevant states should be in the range of 14,000-28,000 cm\(^{-1}\). If the energy gap is high enough for the complex to be stable, a charge transfer absorption band is observed which is denoted as metal-to-ligand charge transfer (MLCT).\(^{45}\)

\[
M^{(n+1)+} - L^- \leftrightarrow M^{n+} - L
\]

Conversely, if a readily reducible metal atom forms a complex with a readily oxidizable ligand or an anion, a ligand-to-metal charge transfer (LMCT) is observed.

\[
M^{(n-1)+} - L \leftrightarrow M^{n+} - L^-
\]

The difference between total electron transfer and charge transfer transitions is that, in total electron transfer an electron is completely transferred from one atom to another, whereas in the latter case an electron in a molecular orbital primarily located at one atom is transferred to a molecular orbital primarily located at another atom.\(^{45}\)

The absorption wavelength of charge transfer bands or the charge transfer transition energy is characteristic of the donor and the acceptor atoms involved. The energy gained in a spontaneous charge transfer (\(\Delta E\)) could be represented by;\(^{46}\)

\[
\Delta E = E_A - E_I + J \tag{2.11}
\]

Where, \(E_A\) is the electron affinity of the acceptor, \(E_I\) is the ionisation potential of the donor and \(J\) is the resulting electrostatic attraction between the donor and the acceptor. The position of the charge transfer band in the electromagnetic spectrum is dependent on \(\Delta E\) and the balance of resonance contributions of dative and non-bonded states in the resonance equilibrium.
2.1.8.2.1 Ligand-to-Metal Charge Transfer (LMCT)

Ligand-to-metal charge transfer (LMCT) is a phenomenon observed in the close proximity of the visible region when an oxidizable ligand and a reducing metal (metals in a higher oxidation state) form a complex. More polarisable ligands such as I⁻ and S²⁻ favour LMCT transitions as they have low ionisation potentials. In halides, for a given metal the energy of the LMCT rises in the order of I⁻ < Br⁻ < Cl⁻ < F⁻ according to the ease of oxidation along the group. Similarly, an electron donation ligand forms LMCT bands of lower energies while electron accepting ligands give rise to higher energy LMCT bands.⁴⁵

2.1.8.2.2 Metal-to-Ligand Charge Transfer (MLCT)

In the case of metal-to-ligand charge transfer (MLCT), the charge transfer band shifts to a lower energy with a decrease in oxidation state of the metal, when the electronegativity of the ligand increases and with an increase in the coordination number. The more commonly observed phenomenon is LMCT, where ligands with empty orbitals of suitable energy and symmetry give rise to MLCT in close proximity to the visible region are less common. Some examples of ligands that show MLCT bands are, unsaturated ligands such as acetylacetone, aromatic ligands such as pyridine, dipyridyl, pyrazine, oxidising ligands such as pyridine N-oxides via their K anti-bonding levels. In the case of unsaturated ligands, if the charge transfer occurs at a very high energy the charge transfer band could be masked by the intense internal π-π* transitions of the ligand. Therefore, MLCT bands are generally less intense than LMCT bands (the intensities of MLCT bands rarely exceeds 10⁴ dm³ mol⁻¹ cm⁻¹) and are less prominent than the latter in nature.⁴⁵

2.2 Azine and Azole Heterocyclic Ligands

Based on the size of the ring, nitrogen containing aromatic heterocycles can be divided into; (i) six-membered azines and (ii) five-membered azoles. Azines are generally π deficient, with low lying π* orbitals, and hence tend to form stable transition metal complexes through metal-ligand back bonding (metal d-orbitals to the ligand π orbitals). In contrast, azoles are π rich (π donors) and form anionic ligands by deprotonation of acidic N-H in the free ligand. When a heterocyclic ligand contains more than one nitrogen atom, they are called diazines, triazines, diazoles, triazoles, etc. The electronic properties of these are

![Chemical structure of pyridine]

Figure 2.9 – Chemical structure of pyridine
different to that of azines and azoles.\textsuperscript{47}

**Pyridine**

Pyridine is a basic heterocyclic ligand with the chemical formula, C\textsubscript{5}H\textsubscript{5}N (Figure 2.9) which is categorised in the family of azines. According to the Hückel rule,\textsuperscript{48} pyridine falls under the category of “aromatic systems” as the molecule is planar and contains six delocalised $\pi$-electrons over the ring. However, unlike benzene the uneven electron density distribution over the ring causes a negative inductive effect on the N atom. Hence, pyridine has a dipole moment and a weaker resonance stabilisation than that of benzene (pyridine resonance energy = 117 kJ mol\textsuperscript{-1} and benzene resonance energy = 150 kJ mol\textsuperscript{-1})\textsuperscript{49}. Due to this electron localisation effect, the C-N bond distance is 137 pm, whereas the C-C bond length in both pyridine and benzene is 139 pm.\textsuperscript{50} The ring atoms in the molecule are sp\textsuperscript{2} hybridised where the N atom donates one of the hybridised electrons to the aromatic ring while its lone pair projects outward lying in-plane with the molecule. As the free lone pair of the N in pyridine, does not participate in the aromatic ring and, the ligand acts as a Lewis base. When reacted with Lewis acids, it acts similar to a tertiary amine and forms a positively charged pyridinium ion.

**Reactivity of Pyridines**

Generally, pyridines show a reluctance to undergo electrophilic substitutions and such
reactions are facilitated by functionalisation with electron donors.\textsuperscript{49} As shown above in Figure 2.11, the most electron rich position is the 3- position. Substitutions at the 2- or 4- position result in an energetically unfavorable σ complex.

Unlike benzene, pyridines readily undergo nucleophilic substitution reactions, the reason being the lower electron density of the C atoms of the ring.\textsuperscript{49} Pyridines tend to direct nucleophiles to 2-, 4- and 6- positions and can be explained using Figure 2.12. Pyridine nucleophilic substitutions are more favoured when the ring is functionalised with good leaving groups such as, F, Cl or Br.\textsuperscript{49} Generally, the nucleophilic reactions proceed at reduced rates when pure pyridine is used as the hydride ion is a poor leaving group.\textsuperscript{51} In general, the occurrence of $\eta^6$ coordination mode as in benzene is only seen in pyridine when the N centre is sterically hindered.\textsuperscript{50}

**Pyrimidine**

Pyrimidine is another aromatic heterocyclic ligand which falls into the category of diazines (six-membered heterocycles with two N atoms). Substitution of C atoms with electronegative N atoms increases the $\pi$ electron deficiency and reduces the basicity of the ring. Hence, the $\pi$ electron deficiency of pyrimidine is further increased from pyridines resulting in enhanced nucleophilic reactions and reduced electrophilic attacks.

In pyrimidine, protonation occurs at only one N atom due to the presence of a second N atom which deactivates the process.\textsuperscript{49} Therefore, the electron lone pair availability and the

![Figure 2.12 - Resonance structures of pyridine under nucleophilic attack at 2-, 3- and 4- positions](image)

![Figure 2.13 – Chemical structure of pyrimidine](image)
basicity of pyrimidine is decreased compared to pyridine (protonated pyrimidine $pK_a = 1.23$ and protonated pyridine $pK_a = 5.30$). As in the case with pyridines, resonance stabilisation in pyrimidines is further reduced compared to both benzene and pyridines, which facilitates addition and ring cleavage reactions than substitutions.

**Reactivity of pyrimidines**

Due to the reduced basicity of pyrimidines, electrophilic substitution is less pronounced than in the case of pyridines. Protonation or alkylation generally occurs at only one of the N atoms. The 5-position is the most electron rich and therefore, electrophilic substitution reactions (nitration, halogenation, sulfonation, formylation, etc.) take place at the 5 position.

Nucleophilic substitutions occur at the 2-, 4-, and 6-positions as these are the most electron deficient positions in the ring.

**Pyrazine**

Pyrazine is a symmetric, planar aromatic heterocyclic molecule (point group $D_{2h}$) with a zero dipole moment and is also known as 1,4-diazine. Similar to the case of pyrimidine, due to the presence of two N atoms in the ring, pyrazine is less basic than pyridine.

In the same way as other aromatic heterocycles, pyrazines undergo electrophilic substitution reactions. The most electron deficient positions in the ring are 2-, 3-, 5- and 6-positions. Hence, these are the positions at which nucleophilic substitution takes place. Studies have proven that nucleophilic substitution only happens in the presence of a strong electron donating group such as, OH, NH$_2$ and SH attached to the ring.

**Pyrrole**

Pyrrole is a five-membered heterocyclic aromatic compound classified under azoles.
Pyrrole has a dipole moment and is weakly basic with a \( pK_a \) of -3.8. The basicity of pyrroles is increased through the introduction of alkyl groups to the ring. It is also weakly acidic at the N-H position, with a \( pK_a \) of 17.5.

**Reactivity of Pyrrole**

Pyrroles undergo electrophilic attack at the 2- and 5- positions. Thermodynamically, the most stable pyrrolium ion is formed by protonation at the 2- or 5- position. Pyrroles readily undergo reactions with nitrating, sulfonating and halogenating reagents at 2- or 5-positions. However, the less reactive 3- or 4- positions can also be halogenated by silylation of the N atom. Under acidic conditions, pyrroles undergo rapid polymerization, and hence, many electrophiles that are used in benzene chemistry cannot be used with pyrroles. Pyrroles do not undergo nucleophilic reactions.

![Resonance structures of pyrrole](image)

**Pyrazole**

Pyrazole is a five-membered aromatic heterocyclic compound consisting of three C atoms and two N atoms (C₃H₃N₂H) and which falls under the category of diazoles. The N atom at 1-position contributes the lone pair of electrons in its \( p \) orbital (perpendicular to the plane of the ring) to the aromatic ring (pyrrole-like). The N atom at 2-position is pyridine-like where it donates one \( sp^2 \) electron to the aromatic ring. The basic lone pair (on N-2) does not participate in the aromatic system laying in-plane with the ring. Pyrazole is N-H acidic with a \( pK_a \) of 14.2 and the basicity (\( pK_a = 2.5 \)) arising from the pyridine-like N atom is less than that of pyridine (\( pK_a = 5.2 \)). It also has lower resonance energy than does pyrrole.

![Chemical structure of pyrazole](image)

**Reactivity of Pyrazole**

As in the case of azines and diazines, the presence of an additional N atom reduces the overall electron density on the ring C atoms and as a result of the structure, the electron delocalization is uneven around the ring. Position 4- is the most electron rich while 3- and 5-
are the most electron deficient. Pyrazole is more susceptible toward electrophilic substitution reactions than benzene (and less reactive than pyrrole).

**Imidazole**

Imidazole is a planar, five-membered aromatic heterocycle which comes under the category of diazoles.\(^{56}\) It exists in two tautomeric forms as the H could reside on either of the two N atoms. The contribution of electrons to the aromatic ring is similar to pyrazole. Imidazole is a highly polar molecule. Imidazole is known to be an amphoteric molecule, where it can act both as an acid and a base. The \(pK_a\) of the acidic N-H is 14.5 and as a base (pyridine-like N) the \(pK_a\) value is around 7. Therefore, the basicity of imidazole is approximately 60 times greater than that of pyridine.

![Chemical structure of imidazole](image)

**Reactivity of Imidazole**

Imidazoles show a high reactivity towards electrophilic attack, greater than the case for pyrazoles. Under electrophilic attack, the electrophile approaches the 3- position N atom and not the 1- position N atom as this is a part of the aromatic sextet. The imidazole ring is more prone to electrophilic attack at 4- or 5- position C atoms (attack at 2- position C atom involves a canonical form which is highly unfavorable with a positively charged 3- position N atom) while 2- position C (electron deficient) is more susceptible to nucleophilic attacks. However, under special circumstances, 4- and 5- positions become favourable for electrophilic attack when a strong electron withdrawing group is attached to elsewhere in the ring.

**1,2,3-Triazole**

1,2,3-Triazole is an aromatic heterocycle which is one of a pair of molecules that are isomeric in nature with the molecular formula of \(\text{C}_2\text{H}_3\text{N}_3\).\(^{57}\) The \(\pi\) electron densities are

![Chemical structure of 1,2,3-triazole](image)
highest on the heteroatoms and the π deficiency on the C atoms is similar to pyrazoles. When acidic, the $pK_a$ is 1.2 and when basic, the $pK_b$ is 9.4.$^{58}$

1,2,4-Triazole

![Figure 2.20 – Chemical structure of 1,2,4-triazole](image)

1,2,4-Triazole is the other isomeric form with a chemical formula of $\text{C}_2\text{H}_3\text{N}_3$. Since every C atom in the molecule is linked to two N atoms, the C atoms are π electron deficient. The $pK_a$ value of the compound is 10.3 and the $pK_b$ is 11.8.$^{58}$ Electrophilic attack occurs preferentially on the N atoms of the ring.

Tetrazole

Tetrazole is a five-membered synthetic aromatic heterocyclic compound with four N atoms and one C atom (CH$_2$N$_4$). The $pK_a$ of the compound is 4.9.$^{58}$ Thus, in the class of azoles, tetrazole is the weakest base but by far the strongest N-H acid.

![Figure 2.21 - Chemical structure of tetrazole](image)

In solution, annular tautomerism is observed for 1H-tetrazoles and the two forms in equilibrium are illustrated in Figure 2.22. However, NMR spectroscopy has revealed that one form slightly dominates the other in solution.

![Figure 2.22 – Tautomerism of tetrazoles](image)

Electrophilic attack preferentially occurs on 1- or 2- position N atoms and the proportion depends on the nature of the 5- position substituent.$^{58}$

2.2.1 Chelating Heterocyclic Ligands

As explained previously in Section 2.1.6, the stability of metal complexes increases when chelating ligands are involved in complexation. In agreement with this phenomenon, heterocyclic ligands also tend to form bidentate ligands through linkage of two ligand atoms.
The 2,2’-bipyridine (bpy) ligand is the most widely studied chelate, and was first synthesised in 1888.\textsuperscript{59}

\[ \text{Figure 2.23 - Chemical structure of bipyridine} \]

It forms stable transition metal complexes and \([\text{Ru(bpy)}_3]^{2+}\) is one such well known compound where the photophysical properties are studied extensively.\textsuperscript{60} When one or more of the bpy ligands are replaced by another chelating ligand (azole or azine), the properties of the complex such as the HOMO-LUMO gap changes significantly. Therefore, the nature of the chelating ligands play an important role in tuning the ground and excited state properties of metal complexes.\textsuperscript{61}

Based on a series of 2-azinyl-2H-benzotriazoles (azinyl = 2-pyridinyl, 2-pyrazinyl, 2-pyrimidinyl, 6-methoxy-3-pyridazinyl, 5-methyl-2-pyridinyl), Obijalska \textit{et al.}\textsuperscript{62} have shown that the HOMO-LUMO gap changes with the number and position of the nitrogen atoms in the azine ring. Based on theoretical calculations it was seen that the LUMO is localised on the azine ring. The study was carried out to observe the effect of changing the heterocyclic system in the azine ring. As the reference 2-phenyl-2H-benzotriazoles (Figure 2.24 (a)) was used and the LUMO is determined as -2.02 eV. Upon changing the phenyl ring to pyridine, LUMO is changed to -2.12 eV (b). With further nitrogen substitutions the change in LUMO energy was observed as; to pyrimidine ((c) - LUMO -2.24 eV), to pyrazine ((d) -2.42 eV), pyridazine ((e) -2.37 eV) and to triazine ((f) -2.69 eV). The authors proved that the LUMO energy of the ligands decreases with the number of N atoms in the azine ring. Furthermore, the study has shown that the introduction of nitrogen atoms to the azine ring reduces the electron density at the coordinated nitrogen atom and hence lowers the electron donating

\[ \text{Figure 2.24 – Chemical structures of the 2-azinyl-2H-benzotriazoles based Ruthenium complexes} \]
power of the ligand. Therefore, the chelating ability is reduced with increasing number of nitrogen atoms in the azine ring. However, the introduction of an electron donating group such as OMe to the heterocyclic ring increases the electron density and the chelating power of the coordinating nitrogen atom (higher enthalpy of formation).

In addition to the nature of the heterocyclic ligand, another factor that affects the HOMO-LUMO gap of a metal complex is the nature of the substituents attached to the heterocyclic ring system. It has been reported that for Ru(II) based 4,4’-dicarboxylic acid-2,2’-bipyridine (dcbpy) complexes, substitution of a dcbpy ligand by a highly conjugated bipyridine ligand substituted with alkyl thiophene groups (Figure 2.25), a red-shift in the MLCT band and an increase in the absorption coefficient is observed.63

![Figure 2.25 – Chemical structure of the conjugated alkyl substituted cis-di(thiocyanato)bis(2,2’-bipyridyl)ruthenium(II) complex](image)

An extensive discussion on the alteration of HOMO-LUMO gaps based on the electron donating and withdrawing capabilities of the substituents and the effect of the conjugation length is given later in Section 2.4.

### 2.3 Photoluminescence

Photoluminescence (PL) is the phenomenon of light emission from atoms or molecules, which is initiated by photoexcitation through light absorption. The process involved in photoluminescence are explained below using a Jablonski diagram (Figure 2.26, appendix 1). Following light absorption, several processes of internal energy transfer occur within a molecule before emitting radiation. The time lag between absorption and emission ranges from short femtosecond regime to milliseconds and in some circumstances may be
minutes or hours. PL is studied under two major categories of light emission; (i) fluorescence and (ii) phosphorescence. 38, 64-66

![Jablonski diagram](image)

**Figure 2.26 – Jablonski diagram illustrating radiative and non-radiative processes in a molecule. S represents singlet-states and T represents triplet-states (explained in the appendix 1)**

### 2.3.1 Fluorescence and phosphorescence

Electronic states of molecules can be grouped into singlet (\(S\)) and triplet (\(T\)) states. A singlet state is one in which all of the spins of electrons in a molecule are paired whereas a triplet state is one in which one set of electron spins is unpaired. Singlet and triplet states differ in properties and energies where a triplet state always lies lower in energy than its corresponding singlet state. 26, 65

#### 2.3.1.1 Non-Radiative Transitions

**Vibrational Relaxation**

From absorption to emission, there is an often complicated pathway in molecules. Post absorption, there are non-radiative processes which compete with photon emission. Immediately after excitation, there are two processes that a molecule could undergo; (i) Emit a photon from the same vibrational level that it was excited to or (ii) Undergo changes in the vibrational level prior to emission. Which process dominates, depend on the environment that the molecule is present in. For a molecule excited in gas phase at low pressures, losing vibrational energy *via* releasing an IR photon is less probable than returning to the ground state by undergoing electronic transition. Hence, the emission spectra under such conditions originate from higher vibrational levels of the excited state. In solution phase, due to the possibility of transferring the excess vibrational energy (as heat) from the solute molecules to
the solvent molecules, rapid vibrational relaxation (in $10^{-11}$ to $10^{-13}$ s) occurs prior to emission. As a result, emission will always originate from the lowest vibrational level ($0^{th}$) of the excited state. \textsuperscript{26,66}

**Internal Conversion**

Internal conversion is a process where electrons in a singlet excited state relaxes back to the ground state without emission of a photon but converting excitation energy into heat (phonons). If a molecule is excited beyond the first excited state ($S_1$) to a higher vibrational level of the second excited state ($S_2$), the molecule will undergo vibrational relaxation and reside on the lowest vibrational level ($0^{th}$) of the $S_2$ state. Generally, the energy separation between $S_1$ and $S_2$ states is less than that of the separation between $S_0$ and $S_1$ states. Hence, there’s a high possibility that the lower vibrational levels of $S_2$ will overlap with the upper vibrational levels of $S_1$. This coupling creates a highly efficient path for the molecule to cross from $S_2$ to $S_1$ that it takes the same amount of time ($10^{-3}$ s) for a molecule to cross from $S_2$ to the $0^{th}$ vibrational level of $S_1$, and for the process of transition from a higher vibrational level of $S_1$ to the $0^{th}$ vibrational level. \textsuperscript{26,66}

### 2.3.1.2 Fluorescence

As discussed previously, post absorption a molecule will undergo vibrational relaxation and reach the lowest vibrational energy level of the excited state. The process of an electron in the lowest vibrational level of a singlet excited state relaxing back to the ground state is called fluorescence. Due to the loss of energy through vibrational relaxation, the wavelength of emitted photon is generally less than the absorbed radiation and is called a Stokes shift. \textsuperscript{38,26,66} In addition to vibrational energy loss, relaxation could also occur through interaction with a molecule such as $O_2$. This is called fluorescence quenching. Molecular $O_2$ is an excellent fluorescence quencher due to its unusual triplet ground state.

**Fluorescence Lifetime** - Fluorescence lifetime is defined as the average time that a molecule resides in the excited state before emitting a photon. Fluorescence typically follows 1\textsuperscript{st} order kinetics: \textsuperscript{26}

$$[S_1] = [S_1]_0 e^{-\tau t}$$

\([S_1]\) is the concentration of the excited molecule at time \(t\), \([S_1]_0\) is the concentration at the beginning \(\tau\) is the decay rate where \(\tau = 1/\text{fluorescence lifetime}\). Under real conditions, as non-radiative processes compete with radiative emission, the total rate of decay \(\tau_{tot}\) is given by,

$$\tau_{tot} = \tau_{rad} + \tau_{nrad}$$

(2.13)
Where, $\tau_{rad}$ is the radiative decay rate and $\tau_{nrad}$ is the non-radiative decay rate. Fluorescence is a rapid process and generally (for emissions between near-IR to UV) the decay time lies in the range of 0.5 to 20 ns.

2.3.1.3 Phosphorescence

Generally, transitions between the ground state $S_0$ level and triplet state $T_1$ are forbidden and hence are considered improbable. The probability of an $S \rightarrow T$ transition is calculated to be of the order of $10^{-6}$ that of a corresponding $S \rightarrow S$ or $T \rightarrow T$ transition. However, a more efficient process to populate the triplet states from the lowest energy singlet state ($S_1$) exists in many molecules and is called intersystem crossing. Intersystem crossing is a spin dependent, internal conversion process which involves vibrational coupling between the two states.\textsuperscript{38,26,66}

Subsequent to intersystem crossing (ISC), the molecule undergoes internal conversion and falls to the $0^{th}$ vibrational level of the $T_1$ state. It should be noted that, typically the energy difference between the $T_1 0^{th}$ vibrational level and the $0^{th}$ vibrational level of $S_1$ is larger than the thermal energy, and hence, repopulation of a $S$ state from a $T$ state is improbable.

Once the molecule is residing on the $0^{th}$ vibrational level of the $T_1$ state, there are competing non-radiative transitions between the lowest triplet state and the $S_0$ state: (i) as the energy difference between the $T_1$ and $S_0$ is smaller than that of the difference between $S_1$ and $S_0$ there is a tendency of $T_1$ and $S_0$ vibrational coupling which results in enhanced internal conversion, (ii) the lifetime of a $T$ state ($10^{-4}$ to $10$ s) is much longer than for an excited $S$ state, which leads to loss of excitation energy by collisional transfer. Latter is the dominant non-radiative path for triplet emitters in solution phase under room temperature.

However, if a molecule is present in a rigid medium where collisional non-radiative losses are minimised, radiative emission while the molecule relaxes from the $T_1$ state to the $S_0$ state is observed and is called phosphorescence. The phosphorescence decay time is similar to the lifetime of the $T_1$ state which is $10^{-4} – 10$ s.

2.3.1.4 Delayed Fluorescence

Delayed fluorescence is a non-collisional energy transfer process, where it has an emission spectrum characteristic to fluorescence and a lifetime a little longer than phosphorescence. Delayed fluorescence is considered as a biphotonic process involving two $T$ states as the intensity of emission is proportional to the square of intensity of both exciting
radiation and phosphorescence intensity. There are three types of mechanisms for delayed fluorescence;\textsuperscript{67,68}

i. \textit{P}-type delayed fluorescence: the mechanism of delayed fluorescence is thought to be along the steps of:

\begin{align*}
S_0 + h\nu & \rightarrow S_1 & (2.14) \\
S_1 & \rightarrow T & (2.15) \\
T + T & \rightarrow S_1 + S_0 & (2.16) \\
S_1 & \rightarrow S_0 + h\nu_f & (2.17)
\end{align*}

A molecule in the $S_0$ ground state is excited to the lowest singlet excited state $S_1$ (equation 2.13) followed by intersystem crossing to the $T$ state (equation 2.14). The long lifetime of these excited $T$ states allow the particles to diffuse through the crystal and interact ($T$-$T$ annihilation) generating a singlet excited state ($S_1$) and a ground $S_0$ state (equation 2.15). The formed $S_1$ state then emits radiation in the form of fluorescence (equation 2.16). The lifetime of delayed fluorescence is typically half the value of the concomitant phosphorescence process.

ii. \textit{E}-type delayed fluorescence: the $S_1$ state becomes populated by a thermally activated non-radiative transition from the $T_1$ state. The lifetimes of delayed fluorescence and the concomitant phosphorescence are equal as the population of the $S_1$ and $T_1$ states are under thermal equilibrium.

iii. Recombination fluorescence: The $S_1$ state becomes populated by recombination of radical ions of opposite charge or radical cations with electrons.

\textbf{2.4 Photoluminescence of Metallorganic Complexes}

Photoresponsive organic molecules have clearly distinct properties in contrast to their inorganic counterparts: (i) isolated organic molecules have well defined singlet and triplet spin states and the luminescence is linked to the excited state of the molecule. In inorganic materials, luminescence is associated with defects, impurities in the host lattice or with the excited states of the isolated atom or ion.\textsuperscript{69} (ii) in organic materials, subsequent to photo-absorption, Frenkel type excitons are created where the electron-hole pair is bound by strong coulombic forces.\textsuperscript{70} The binding energy of these excitons varies between 0.1 to 1 eV and hence, the excitons could be localised on the generating molecule.\textsuperscript{70} In contrast, inorganic materials generate free electrons and holes which are easily delocalised throughout the lattice.\textsuperscript{70}
During the past decade, significant activity has been reported in producing novel luminescent materials for organic light emitting diodes (OLED) with desired photophysical properties and the capability to withstand manufacturing processes. For OLED applications, metallorganic complexes offer several advantages over purely organic emissive materials;\(^7\)

i. Increased fluorescence emission and high phosphorescence emission due to the mixing of \(S\) and \(T\) states via spin-orbit coupling (SOC) - Generally, molecular rigidity reduces the probability of non-radiative transitions by decreasing vibrational relaxation, inter-system crossing to \(T\) states as well as collisional heat loss. Hence, with the enhanced rigidity introduced by complexation of metal ions to organic ligands, the fluorescence probability and intensity is increased. Moreover, the involvement of metal orbitals in the excited state induces novel photo-physical properties such as efficient phosphorescence in pure organic compounds. For example, heavy metal ions such as Ir(III) and Pt(II) facilitate inter-system crossing and hence allow spin-forbidden phosphorescence.

ii. Tunable molecular orientation - The presence of coordination centres on the metal ions allows tailoring of stereochemistry and geometries of metal complexes which is vital to the control over thermodynamic, mechanical and opto-electronic properties of metallorganic complexes.

iii. Ease of device fabrication as metallorganic complexes (small molecules) are easily sublimable compared to high molecular weight polymers.

iv. The metal centre leads to mixing of metal centred and ligand centred orbitals forming new bands and hence, by careful selection of the ligands tunable light emissivity can be achieved with pre-determined excited/emission state.

v. Improved charge transport characteristics - Effective charge transport / high charge carrier mobilities of organic semiconductor materials is key in device performance. Transition metals contain delocalised valence electrons and variable oxidation states which influence high charge carrier injection and transport.

In transition metal complexes four types of transitions could be observed; (i) \(d-d\), (ii) \(d-\pi^*\), (iii) \(\pi-\pi^*\) and \(n-\pi^*\), and (iv) \(\pi-d\).

i. \(d-d\) transition states - These are generated via metal-centred (MC) transitions. As discussed in Section 2.1.5, ligand coordination results in \(d-d\) splitting. This type of an excited state arises when an electron is transferred from a lower \(d\) orbital to an upper \(d\) orbital.
ii. $d-\pi^*$ transition states - These are generated via metal-to-ligand charge transfer (MLCT) transitions. These are formed when a metal centred $d$ electron is transferred to a ligand anti-bonding $\pi^*$ orbital.

iii. $\pi-\pi^*$ and $n-\pi^*$ transition states - These are generated via intra-ligand transitions. Electrons are transferred from a $\pi$ bonding or non-bonding orbital to a higher anti-bonding $\pi$ orbital.

iv. $\pi-d$ transition states - These are generated via ligand-to-metal charge (LMCT) transfer transitions. Electrons are transferred from a ligand centred $\pi$ orbital to a metal centred $d$ orbital.

As noted previously, transition metal complexes tend to show phosphorescence emission as they fascilitate spin orbit coupling (SOC) followed by inter-system crossing (ISC). Hence, observation of fluorescence in these materials is rare. However, a number of reports on fluorescent emissive metal complexes are available in the literature.\textsuperscript{73}

2.4.1 Iridium Complexes

Iridium(III) complexes are among the most important metal complexes studied in the
field of emissive materials. One of the greatest challenges of tailoring luminescent molecules is the achievement of white light. One approach of white light generation is the mixing of blue, red and green phosphors and another is to mix yellow and blue emitting phosphors which results in a “white” spectrum.\textsuperscript{1} Several methods are used to synthesise blue phosphorescent materials and two of which are: (i) increasing the HOMO–LUMO energy gap through elevating/destabilising the LUMO level or by lowering/stabilising the HOMO level\textsuperscript{74}, (ii) introduction of strong field ancillary ligands\textsuperscript{75}, and (iii) by shortening the effective conjugation length of the molecules.

Lee and Kim\textsuperscript{76} have reported that by the introduction of an electron-donating methoxy (OMe) group to the phenylpyridine based Ir(III) complex (Figure 2.28), the LUMO level is destabilised, resulting in a blue-shift in the emission. In parallel, Seo et al.\textsuperscript{77} have reported that through the attachment of an electron withdrawing trifluoromethyl (CF\textsubscript{3}) group to a similar phenylpyridine based Ir(III) complex, the HOMO level is stabilised, compared to the –H substituted version (Figure 2.29) resulting in a bright blue emission at 454 nm.

Ancillary ligands strongly interact with the metal centre and play an important role in optoelectronic properties of the metal complex. Di Censo et al.\textsuperscript{78} have reported a series of
cyano-stabilized Ir(III) complexes where replacement of a phenylpyridine ligand with two cyano groups blue-shifts the emission spectrum of the resulting complex by 10 nm (Figure 2.30 (a)). Kim et al.\textsuperscript{79} and Ha et al.\textsuperscript{80} have also published reports on blue-emitting Ir(III) phosphors based on triphenylphosphine or triazolopyridine as the ancillary ligand. Furthermore, Chen et al.\textsuperscript{81} have also synthesised blue phosphors using N-heterocyclic carbene ancillary ligands ((fpmi)\textsubscript{2}Ir(dmpypz)) (Figure 2.30 (b)) with very high triplet energy levels and emission at 455 nm.\textsuperscript{82}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{figure231.png}
\caption{Controlling the concentration quenching by introducing dendrimers}
\end{figure}

A great challenge in designing OLEDs is the luminescent quenching effect caused by inter-molecular interactions. Hence, an approach taken to avoid concentration quenching is through the use of dendrimers. These highly branched molecular structures serve as dynamic internal cavities where luminescent complexes are embedded (protected metal centres). In 2008, Leo et al.\textsuperscript{83} proved that dendron-modified phenyltriazole Ir(III) complexes can host the metal in the interior site to suppress quenching. The same group has also reported similar dendrimer-modified complexes with added fluorine and methyl groups.\textsuperscript{84} The presence of fluorine shifts the emission to deep-blue while the methyl group provides steric hindrance to mitigate the quenching effect caused by the fluorine atom.

Introduction of sterically hindered bulky groups to Ir(III) complexes has been shown to be an effective approach in minimising self-quenching.\textsuperscript{85-88} Liu et al.\textsuperscript{89} have shown this using an amidinate ligand where the weak intermolecular interactions and the short

\begin{figure}[h]
\centering
\includegraphics[width=0.2\textwidth]{figure232.png}
\caption{Controlling the self quenching by introducing bulky groups}
\end{figure}
phosphorescence lifetime of 0.34 μs are attributed to a minimised quenching effect.

The effect of conjugation length on the optoelectronic properties of metal complexes have been reported by Bettington et al., based on 2-carbazolylpyridine (Figure 2.33 (a)) (500 nm) and 3-carbazolylpyridine (Figure 2.33 (b)) (590 nm) Ir(III) complexes. Interestingly, the difference in emission wavelength is readily eliminated when an oligofluorene linker is introduced between the carbozyl and pyridine moieties. With increasing numbers of fluorenyl units the emission of both complexes shifts to 550 nm.

Figure 2.34 – green and yellow emitting Ir(III) complexes
A much studied green emitting Ir(III) complex is Ir(bt)acac, which gives emission at 557 nm with a quantum yield of 26%. The emission could be shifted to 564 and 554 nm when the benzothiazole unit is substituted with a CF$_3$ (CF$_3$-bt)Ir(acac) (Figure 2.34 (a)) or a Fluorine atom (F-bt)Ir(acac) (Figure 2.34 (b)) respectively. When it is substituted by an electron donating naphthylphenylamine group the emission shows a bathochromic/red-shift by >20 nm (Figure 2.34 (c) and (d)). This shift is mainly governed by the increase of HOMO levels promoted by the aryl amine group. In contrary, Chou et al. have reported bright yellow emitting Ir(bipz)$_3$ (Figure 2.34 (e)) (567 nm) and Ir(fipz)$_3$ (Figure 2.34 (f)) (545 nm) complexes using high-field ligands to induce a blue-shift in the emission wavelength.

Lamansky et al. have reported a series of highly phosphorescent bis-cyclometalated Ir(III) complexes; bis(2-phenylpyridinato-$N,C^2$)iridium(acetylacetonate) [$ppy_2$Ir(acac)], bis(2-phenyl benzothiozolato-$N,C^2$)iridium(acetylacetonate) [bt$_2$Ir(acac)] and bis(2-(2'-benzothienyl)-pyridinato-N,C$^3$)iridium(acetylacetonate) [btp$_2$Ir(acac)]. By changing the C$^N$ moiety, the authors have demonstrated phosphorescence ranging from green to red.

2.4.2 Ruthenium Complexes

Among luminescent ruthenium complexes, [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine) is the most extensively studied compound as it shows high phosphorescence emission from a spin-forbidden triplet excited state. In a solution of acetonitrile at room temperature, [Ru(bpy)$_3$]$^{2+}$ shows high photoluminescence yields of 6.1%. The complex shows two intense MLCT absorption bands at 428 and 454 nm emitting phosphorescence in the blue region.

Ru(II) complexes with N-based ligands have attracted a lot of attention during the past few years for application in OLEDs as red emitting phosphors. Zhu et al. have reported a class of phosphorescent Ru(II) complexes with peripheral carbazole ligands (intense deep red emission at 660 nm) (Figure 2.36). The HOMO level is increased by 0.1 eV while the

![Chemical structure of [Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2'-bipyridine)](image)
LUMO is decreased by 0.4 eV leading to red emission.

Tsui et al.\textsuperscript{97} have reported a luminescent Ru(II)-cyanide complex with N-heterocyclic carbene pincer ligand \(\text{C}^\text{N}^\text{C}=2,6\text{-bis(1-butylimidazol-2-ylidene)pyridine}\) and 2,2'-bipyridine \((\text{bpy})\) (\([\text{Ru(II)}(\text{C}^\text{N}^\text{C})(\text{bpy})(\text{CN})]^+\)). Emission is observed at 464 nm, which is assigned to a \(d_x\) (Ru(II)) – \(\pi^*(\text{bpy})\) MLCT transition.

Although, the complexes of \([\text{Ru(bpy)}_3]^{2+}\) and \([\text{Ir(ppy)}_3]\) are the most extensively studied phosphorescent metal complexes,\textsuperscript{61, 98-101} the observation of fluorescence in these is highly rare. The reason being the extremely short lifetime of the singlet excited state of these complexes i.e. 100 fs for \([\text{Ir(ppy)}_3]\) and 15 ± 10 fs for \([\text{Ru(bpy)}_3]^{2+}\).\textsuperscript{102-104} The fast ISC rates of the order of \(10^{12}\) s\(^{-1}\) in these complexes, leads to high phosphorescence yields and extremely low fluorescence yields. For example the fluorescence yield (\(\Phi\)) of \([\text{Ru(bpy)}_3]^{2+}\) is \(9\times10^{-5}\).\textsuperscript{105}

In addition to OLED technology, various Ru(II) based luminescent complexes have
been synthesised for a variety of applications ranging from solar photovoltaics to bio-imaging and sensors.\textsuperscript{106-110}

### 2.4.3 Palladium Complexes

Weissman et al.\textsuperscript{111} have reported perylene tetracarboxylic acid diimide (PDI) ligand based Pd(II) complexes with strong fluorescence and phosphorescence emission (Figure 2.37 (a) and (b)). Both complexes have shown similar emission with an intense peak at 584 nm. The emission is assigned to fluorescence due to the small Stokes shift, the nanosecond time scale (compound (a); $\Phi = 0.65$ in dichloromethane, lifetime ($\tau$) = 7.5 ns and compound (b); $\Phi = 0.22$, $\tau = 2.8$ ns) and as the absorption and emission properties of both complexes being identical in open air. In addition to intense fluorescence, the authors prove that the two complexes have triplet excited states with yields of 0.06 and 0.21 for (a) and (b) respectively. TDDFT calculations have proven that the HOMO and LUMO of the complexes are localised on the ligand. Hence, the $\sigma$-bond between the Pd(II) and ligand is dominant and the $\pi$-bond between the Pd(II) and ligand is weak. This results in a reduced heavy-atom effect of Pd(II) and a decreased rate of ISC. However, from the observed emission yields it is clear that the rate of ISC in (b) $>$ (a). It is also believed that the $d_{z^2}$ orbital of Pd(II) in complex (b) has more participation in HOMO than the one in complex (a).

![Figure 2.37 – Fluorescent Palladium complexes of Pd(II) perylene diimide ligands](image)

### 2.4.4 Rhodium Complexes

Since the 1980s, photophysical properties of $[\text{Rh(bpy)}_3]^{3+}$ have been extensively studied. In solution at room temperature the complex is non-emissive and only emits radiation at 448 nm at 77 K on a rigid glass.\textsuperscript{112} The high intensity bands below 350 nm in the
Marder et al.\textsuperscript{114, 115} have reported a series of Rh containing metallocyclic complexes (2,5-bis(ditolylethynyl) rhodacyclopentadienes) with a $\lambda_{\text{max}}$ of emission in the region 496-590 nm ($\Phi = 0.01-0.18$). The nanosecond scale lifetimes (0.45–1.21 ns) and the small Stokes shifts (1870-2390 cm$^{-1}$) have been used to assign the luminescence to fluorescence. The study has further proven that the ISC rate for the complex is slow ($10^8$ s$^{-1}$), which leads to a long-lived $S_1$ state and fluorescence emission. This is in contrast to heavy atom (SOC constant of Rh, $\chi = 1200$ cm$^{-1}$) containing organometallics where fast ISC ($10^{12}$ s$^{-1}$), is facilitated followed by phosphorescence emission.

In 2010, the Marder group published another type of rhodacycle complexes with high fluorescence $\Phi$ of 0.07-0.69 and a of $\tau$ 0.4-3.0 ns\textsuperscript{116} Using picosecond time-resolved IR (TRIR) vibrational spectroscopy, the authors have proven that a triplet excited state with a $\tau$ of $1.6 \pm 0.6$ ns is formed ((ISC rate = $5x10^8$ s$^{-1}$), although it does not emit as phosphorescence emission.

### 2.4.5 Rhenium Complexes

Despite high phosphorescence emission, Re(I) complexes have not been able to gather a great deal of attention due to their poor processability which limits their use in device applications. Mauro et al.\textsuperscript{117} have recently published a paper on diazine ligand based Re(I) complexes with emission tunability from yellowish green to orange and $\Phi$ of 0.22.

Aly et al.\textsuperscript{118} have observed ligand based fluorescence for the Re(I) based complex [[(OTC)Re-(CO)$_3$Cl]. The compound exhibits intra-ligand fluorescence at 750 nm with a $\Phi$ of 0.002. This report claims that ISC facilitated by the heavy atom effect of Re(I) is only observed when the ligand is an efficient $\pi$-acceptor. The phenolate ligand used in this
complex is not a \( \pi \)-acceptor and hence phosphorescence is not generated. Further it is mentioned that the fluorescence emission intensity increases with complexation, which is attributed to the removal of a phenolic proton in the ligand with metal ion binding (upon deprotonation, the charge transfer donor strength increases).

Sun et al.\textsuperscript{119} have also reported a series of Re(I) containing macrocyclic compounds (fac-[Re(CO)]\( _x \)X] (X = Cl, Br)) with bipyridyl bridging ligands where the observed fluorescence emission is attributed to ligand based \( ^1\pi-\pi^* \) transitions.

### 2.4.6 Copper Complexes

Cu(I) complexes are an important class of luminescent materials due to their low cost and high reliability. However, tetrahedral Cu(I) complexes suffer from a common problem of weak luminescence (or pronounced non-radiative decay) as a result of distortion of excited states. A solution for this is to increase the rigidity of the complex by adding bulky ligand moieties. Hashimoto et al.\textsuperscript{120} have reported a series of highly symmetric, strongly green emissive three-coordinate Cu(I) complexes with high \( \Phi \) of 0.57-0.71 in amorphous films.

Liu et al.\textsuperscript{121} have reported a method of co-depositing 3,5-bis(carbazol-9-yl)pyridine (mCPy) and CuI to form a green emissive (530 nm) [CuI(mCPy)]\(_2\) complex for OLEDs (Figure 2.40). In this case, the pyridine-based ligand plays a dual role; (i) a ligand for stabilising the metal centre and (ii) an accommodating host material for the complex, thereby forming a uniform film of the complex.
Furthermore, Hsu et al.\textsuperscript{122} have performed a systematic investigation to determine the effect of group 11 $d$-orbitals on luminescence properties of corresponding metal complexes. The authors have proven that Cu(I) complexes exhibit a substantially higher ISC rate and show more efficient phosphorescence emission than their Ag(I) and Au(I) analogues.

### 2.4.7 Zinc Complexes

Son et al.\textsuperscript{123} have published a series of Zn based complexes (Figure 2.41 (1-6)) where the emission is tuned from blue to green by varying the substituents at the 4-position of the oxazolylphenolate ligand. The authors attribute the colour tunability to the influence of the substituents on the HOMO of the complex, as electron donating groups induce a significant bathochromic effect and electron withdrawing groups only make a slight shift of the emission wavelength.

Xu et al.\textsuperscript{124} have reported blue emitting Zn(II) complexes with phenylbenzoimidazole ligand (Figure 2.42). It is stated that the peripheral $N$-hexylcarbazole group in complex (c) introduces a deep blue emission at 422 nm (the HOMO level elevates by 0.6 eV) with a $\Phi$ of 0.64, provides improved color purity and enhanced thermal stability.

Fluorescence emission in Zn(II) complexes has also been widely reported in the literature with many of them being used in cell imaging and fluorescence probe applications.\textsuperscript{125-128}
2.5 Platinum Complexes for Luminescence Harnessing

Up until the late 1980s, there were no reports on luminescent square planar Pt complexes due to the high rates of non-radiative decay. As a result of crystal field stabilisation, Pt complexes tend to highly prefer a square planar geometry. In square planar geometries the unoccupied $d_{x^2-y^2}$ orbital lies high in energy and is strongly anti-bonding. Populating this orbital involves elongation of Pt-ligand bonds and hence severe distortion of the metal complex. This promotes non-radiative decay of metal centred ($d-d$) excited states to the ground state at the isoenergetic intersection point of the potential energy surfaces (Figure 2.43). Even if other excited states such as LC ($\pi-\pi^*$) or MLCT ($d-\pi^*$) reside at lower energies than $d-d$ states, and if the latter states are thermally accessible, this results in adverse effects/non-radiative decay processes.

In order to overcome this problem, ligands with low lying excited states or those with high electron donor capacities are used. These being strong field ligands, they further raise the $d-d$ orbital up in energy making this a thermally non-accessible state. Hence this results in reduced non-radiative decay and enhanced luminescence of Pt complexes.

In recent years much attention has been given to Pt(II) containing square planar

![Diagram of Potential energy surface of the d-d excited state in Pt(II) complexes which is displaced relative to the ground state. Thick arrow represents absorption and the thin ones indicate vibrational relaxation and non-radiative decay](image)

Figure 2.43 – Potential energy surface of the d-d excited state in Pt(II) complexes which is displaced relative to the ground state. Thick arrow represents absorption and the thin ones indicate vibrational relaxation and non-radiative decay.
complexes as highly luminescent materials.\textsuperscript{8, 129, 130} The reasons that make Pt(II) an attractive metal centre for phosphorescent emitters include:\textsuperscript{8, 9, 11}

i. High SOC of the Pt nucleus ($\chi = 4481 \text{ cm}^{-1}$) due to Pt being a heavy atom.\textsuperscript{131}

Theoretically, this means emission originates from states of triplet character so that unitary efficiency can be approached. However, this depends on the extent of contribution of the metal orbitals to the excited states. If the excited state involves significant metal character, the rate of radiative decay constant of triplet emission can be accelerated by a factor of $10^6$. On the other hand if the excited state consists of significant ligand character, ligand-based singlet state emission is observed.\textsuperscript{132}

ii. Pt(II) based phosphors possess a high triplet quantum yield

iii. Relatively short triplet lifetime

iv. Rational tunability of emission colours based on structural modifications with concomitant control of the quantum efficiency (QE)

v. Square planar complexes allow for a more minimal planar structural motif with less diasteromeric diversity. This allows for an approach based on controlled structural changes tied to molecular properties.

However, anticipated deleterious excitonic self-quenching of planar complexes brought on by enhanced intermolecular electronic coupling through $\pi-\pi$ stacking interactions implies considerable design difficulties for this class of phosphors. Nonetheless, for Pt(II) this
negative aspect is largely offset by the propensity of these systems to engage in metallophilic Pt---Pt interactions, which give rise to new and interesting photophysics involving transitions between metallophilic bonds and ligands (metal-metal to ligand charge-transfer (MMLCT), and supramolecular design potential for further property tunability.\textsuperscript{20-23} Indeed, a number of studies have shown strong emissivity despite clear metallophilic stacking.\textsuperscript{24, 25}

The square-planar $d^8$ complexes received some considerable interest since the seminal work of Gray, Vlcek and Miskowski on binuclear Pt(II) complexes in 1987. The work involved studying the photochemistry and excited states of Tetrakis(pyrophosphito)diplatinate(II) \([\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^+\) complexes.\textsuperscript{16-18}

Chang \textit{et al.}\textsuperscript{24} have reported a series of luminescent Pt(II) azolate complexes (Figure 2.44) with the formula of \([\text{Pt}(\text{N}^\text{N})_2]\) where (N$^\text{N}$) could be: 3-methyl-5-(2-pyridyl) pyrazole (mppz), 3-tert-butyl-5-(2-pyridyl) pyrazole (bppz), 3-tert-butyl-5-(2-pyrazine) pyrazole (bzpz), 3-tert-butyl-5-(5-methyl-2-pyrazine) pyrazole (bmpz), 1-(5-tert-butyl-2H-pyrazol-3-yl) isoquinoline (bqpz), 3-trifluoromethyl- and 3-heptafluoropropyl-substituted 5-(2-pyridyl) pyrazoles (fppz) and (hppz), 5-tert-butyl-3-(pyridin-2-yl)-1H-1,2,4-triazole (bptz) or 5-heptafluoropropyl-3-(pyridin-2-yl)-1H-1,2,4-triazole (hptz). The authors have observed high phosphorescent emission in the series of complexes with short lifetimes of several $\mu$s and tuneable tendency to form aggregates depending on the nature of the azolate ligands. The structure of complexes (a – e) (Figure 2.44), is determined as “slipped-stack” with negligible inter-molecular Pt---Pt contact and the emission is assigned to be originated from $^3\text{MLCT}$, $^3\pi^*$ or mixed $^3\text{MLCT}$/\text{\textcircled{$^3\pi^*$}}$ transitions. In contrast, the complexes (f – i) show strong inter-molecular $\pi-\pi$ stacking interactions between the electron rich azolate and the electron deficient pyridyl fragments giving a “linear columnar stacking” structure in the solid state. It is stated that the existence of inter-molecular Pt---Pt contacts give rise to $^3\text{MMLCT}$ type excited states that account for different photophysical properties of these 4 complexes.

In 2009, Hudsen \textit{et al.}\textsuperscript{133} have reported a triarylboron-Pt(II) (\([\text{Pt}(\text{N,N-Si-BNPA})\text{Ph}_2]\)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure245.png}
\caption{Conversion of Pt(N,N-Si-BNPA)Ph$_2$ to Pt(N,C-Si-BNPA)(SMe$_2$)Ph}
\end{figure}
complex displaying unusual white singlet-triplet dual emissions at 77 K. When reacted with \( \text{SMe}_2 \) this unstable complex has a six-membered non-planar \( \text{N}^\text{N} \) chelate ring which undergoes intramolecular “roll-over” C-H activation forming a stable five-membered \( \text{N,C} \) complex \( ([\text{Pt(N,C-Si-BNPA)(SMe}_2\text{)}\text{Ph}]) \) (Figure 2.45).

The \([\text{Pt(N,N-Si-BNPA)Ph}_2]\) complex shows a singlet emission peak at \( \lambda_{\text{max}} = 399 \text{ nm} \) with a shoulder at 362 nm and a very weak triplet emission peak 494 nm. The \([\text{Pt(N,C-Si-BNPA)(SMe}_2\text{)}\text{Ph}]) \) complex gives a singlet emission peak at \( \lambda_{\text{max}} = 392 \text{ nm} \), with a shoulder at 348 nm and a strong triplet emission at 495 nm. The peaks at 399 and 392 nm in the two complexes have been assigned as fluorescence peaks originating from the Si-BNPA ligand, which is due to the mesityl→boron charge transfer transition. The peaks at 494 and 495 nm have been assigned to phosphorescence originating from a NPA centred \( 3\pi\rightarrow\pi^\ast \) transition.

Using the excitation profiles at 77 K, the authors showed that the dual emission originates from the same molecule. Further studies show that the unusual singlet-triplet dual emissive nature of the complexes is due to the heavy atom effect of Pt(II) which facilitates the ISC resulting in phosphorescence at ambient temperature. Moreover, the study reveals the effect of the chelate mode (\( \text{N}^\text{N} \)- vs. \( \text{N}^\text{C} \)-) on the singlet and triplet emission intensities.

Lentijo et al.\(^{134}\) have reported a series of Pt(II) complexes containing perylene (per) and perylene monoimide (PMI) ligands. The complexes show intense fluorescent emissions (\( \Phi = 0.3 \text{ – } 0.8 \text{ and } \tau = 1.9 \text{ - } 5.0 \text{ ns} \)) in solutions at room temperature. The Stokes shift of the complexes are \(< 1000 \text{ cm}^{-1} \) and are assigned to an intra-ligand \( \pi\rightarrow\pi^\ast \) singlet transition. In order to prove that the emissions are due to singlet transitions, the authors have obtained the emission spectra at low temperatures and in the presence of \( \text{O}_2 \). The unchanged nature of the spectra under these conditions and the ns time scale of emission lifetime further shows that transitions are singlet in nature. The reduced heavy atom effect of Pt(II) is thought to be due to the poor interaction of filled d\( \pi \) orbitals of Pt(II) with the empty frontier \( \pi^\ast \) orbitals of Per or PMI ligands. Hence, the interaction between the Pt-C bonds is mainly governed by \( \sigma \) interactions of the 5d\( _z \) orbitals of Pt(II) with the aryl group of the ligands.

![Figure 2.46 – Structures of (a) [PtL²(acac)] and (b) [PtL³(acac)]](image-url)
Kozhevnikov et al.\textsuperscript{135} have synthesised two Pt(II) complexes ([PtL\textsuperscript{n}(acac)] (Figure 2.46) where L\textsuperscript{n} = 2 or 3. 2 = 5-(2-pyridyl)-5′-dodecyl-2,2′-bithiophene; and 3 = 5-(2-pyridyl)-5″-dodecyl-2,2′:5′2″-terthiophene). The authors have compared the emission of these complexes with [PtL\textsuperscript{1}(acac)] (1 = 2-(2-thienyl)pyridine) which is known to be an intense phosphorescence emitter. The two complexes [PtL\textsuperscript{2}(acac)] and [PtL\textsuperscript{3}(acac)] show both weak phosphorescence ((\(\tau = 2.3 \mu s\) for [PtL\textsuperscript{2}(acac)]) and fluorescence (\(\tau < 0.5\) ns for [PtL\textsuperscript{2}(acac)]). The reason for dual emission was attributed to the low participation of the metal d orbitals in the HOMO of [PtL\textsuperscript{2}(acac)] and [PtL\textsuperscript{3}(acac)] reducing SOC and hence a decreased rate of ISC. It is also noted that with increased conjugation of the complex (addition of a thiophene group), the S\textsubscript{1}-T\textsubscript{1} energy gap increases which in turn decrease the rate of ISC.\textsuperscript{32} In a separate study, similar results have been observed by Liu et al.\textsuperscript{137} where increased ligand size results in a decrease of the rate of ISC.

Durrell et al.\textsuperscript{19} have published the synthesis of a diplatinum (II,II) complex (per(difluoroboro)tetrakis(pyrophosphito)diplatinate(II), [Pt(pop-BF\textsubscript{2})\textsuperscript{4−}]\textsuperscript{4−}) showing intense dual emission. Fluorescence emission is observed at 393 nm (\(\tau = 1.6\) ns, \(\Phi = 2.7\times10^{-1}\) and Stokes shift = 1760 cm\(^{-1}\)) and phosphorescence at 512 nm (\(\tau = 8.4\) \(\mu s\) and Stokes shift = 2460 cm\(^{-1}\)). It is reported that the ISC of this complex is much slower than that of its parent complex [Pt(pop)]\textsuperscript{4−} as the perfluoroboration of the complex increases the rigidity of the BF\textsubscript{2} covalent bonds resulting in an increase in energy of LMCT states. The electron withdrawing power of BF\textsubscript{2} which increases the barrier of \(^1\text{A}_{2u} - ^3\text{Eu}\) (decreased SOC) is attributed as another reason for the lower ISC observed.

Nguyen et al.\textsuperscript{138} have reported fluorescence emission of dinuclear Pt(II) complexes with the 5,12-diethynyltetracene ligand (Figure 2.47). Observation of emission in the range of 561-608 nm, \(\Phi = 0.13–0.97\), small Stokes shift of 290-800 cm\(^{-1}\) and short \(\tau\) of 2.0-9.3 ns has resulted in assigning the emission to singlet excited states. The authors have attributed the low ISC rate to the large ligand π conjugation, long-lived S\textsubscript{1} excited state and the presence of

\[
\begin{align*}
\text{PEt}_3 & \text{Pt} & \text{X} & \text{PEt}_3 \\
\text{PEt}_3 & \text{Pt} & \text{X} & \text{PEt}_3 \\
\text{X} = \text{neutral, } \pi \text{ accepting ligand or anionic, } \pi \text{ donating ligands}
\end{align*}
\]

\textbf{Figure 2.47 – Chemical structure of the dinuclear Pt(II) complex with 5,12-diethynyltetracene}
the ligand tetracene which is an “alternant hydrocarbon” that has a large $S_1$-$T_1$ energy gap (10,800 cm$^{-1}$) creating a Franck-Condon barrier for ISC.

Tridentate ligands of the types $N^N^C^-$, $N^C^N^-$, $N^N^N^-$ and $C^N^C^-$ are generally rigid and form cyclometalated Pt(II) complexes. One of the advantages of using such rigid ligands is the higher $\Phi$, when incorporated in Pt(II) complexes due to suppression of $D_{2d}$ distortions.\textsuperscript{30}

Lu et al.\textsuperscript{25, 139} have reported several studies on cycometalated $N^N^C^-$Pt(II) complexes where the authors have shown that the emission colour tuneability of $\sigma$-alkynyl auxiliary ligand containing Pt(II) complexes depend on the steric and electronic effects of the ligands. They have further shown that the phosphorescence $\Phi$ increases with the $\pi$ conjugation of the ligands.

As stated above, higher rigidity of the molecular skeleton results in higher phosphorescence $\Phi$. Williams et al.\textsuperscript{140} have published that the Pt–C bond lengths in $N^C^N^-$Pt(II) (Figure 2.48) to be around 1.90 Å, which is nearly 0.14 Å shorter than those in typical $N^N^C^-$Pt(II) complexes.\textsuperscript{140} Moreover, the shorter Pt–C bond length is thought to deactivate the d-d states by raising their energy and leading to better performance. This has been proven in a series of $N^C^N^-$Pt(II) complexes bearing aryl substituents where the phosphorescence $\Phi$ values are around 0.46 to 0.65, with emission in the range 481-588 nm.\textsuperscript{141}

Owing to the structural rigidity, Jabbour et al.\textsuperscript{142} have reported a blue phosphor with a maximum $\Phi$ of 0.8 in degassed dichloromethane. In addition to the rigid nature of the triplet state configuration, the very high ligand-field strength which destabilises the metal centered $d$-$d$ excited states was also attributed to the observed high $\Phi$. 

![Figure 2.48 – Chemical structures of high performance $N^C^N$-Pt(II) phosphors](image)

48
Chen et al.\textsuperscript{143} have studied Pt(II) complexes of 6-(5-trifluoromethyl-pyrazol-3-yl)-2,2'-bipyridine (PtNNN-1 and PtNNN-2) (Figure 2.49) which emit phosphorescence at 524 and 604 nm respectively. The red-shift of energy of PtNNN-2 is thought to be due to the stronger electron donor ability and the longer π-conjugation involving the nitrogen and the carbonyl group of the acetamide group. Strassert et al.\textsuperscript{144} have also published several N^N^N-Pt(II) type complexes (Figure 2.50) with high phosphorescence Φ values of up to 0.73 in de-aerated chloroform which are amongst the highest Φ values reported for tridentate chelates.

Pt(II) complexes with C^N^C type ligands have been rarely published in the literature, due to their inherent poor luminescence properties.\textsuperscript{145, 146} In 2012, for the first case, Kui et al.\textsuperscript{146} reported Pt(II) complexes (Figure 2.51) of this type with intense
phosphorescence (Φ up to 0.26) in solutions at room temperature (PtCNC-1 and PtCNC-2). The performance has been attributed to the σ-donating ability of the C≡NR ancillary ligand and the triplet state rigidity due to the presence of the carbazole, fluorene or thiophene heterocyclic units in the main ligand.

J. Brooks et al.\textsuperscript{135} have reported a series of Pt(II) containing 2-phenylpyridine-type (ppy-type) phosphorescent complexes (Ptpy-1 to Ptpy-8) (Figure 2.52) with intense emission at room temperature. The key in this study is the emission colour tuneability of the complexes. By introducing electron donating groups to the pyridyl ring and electron withdrawing groups to the phenyl moiety in the ppy ligand, a blue-shift in the $\lambda_{\text{max}}$ (Ptpy-1 = 486 nm, Ptpy-3 = 484 nm, Ptpy-2 = 466 nm, Ptpy-6 = 456 nm and Ptpy-7 = 440 nm) has been observed, while electron donating groups on the phenyl ring cause a red shift (Ptpy-4 = 525 nm and Ptpy-5 = 480 nm) in emission frequency. The contribution by the phenyl ring π orbitals and the Pt(II) $d_\pi$ orbital in the formation of HOMOs and LUMOs on the pyridyl ring π orbitals is thought to be the reason behind the observed colour tuneability.

Chang et al.\textsuperscript{24, 147} have synthesised a series of Pt(II) containing $N$-heterocycle

![Chemical structures of Ptpy-1 to Ptpy-8](image)

Figure 2.52 – Chemical structures of Ptpy-1 to Ptpy-8
substituted pyrazole ligands (PtNN-1 and PtNN-2) (Figure 2.53) which has been successfully used to fabricate OLEDs. However, a common problem observed for these complexes is the self-aggregation at high concentrations. Omary et al. have also reported a turquoise-blue complex (PtNN-3), where N^N is a pyridyltriazolate derivative. Due to the strong polarity induced by pyridyltriazolate and the square planar geometry, the complex shows intense Pt---Pt inter-molecular interactions.

Pt(II) phosphors constituting of carbene-type moieties have also been studied. Unger et al. have published a deep blue emissive (UV region) homoleptic Pt(II) biscarbene complexes (PtCC-1, λ_max = 386 nm, Φ = 0.45 under a nitrogen atmosphere) (Figure 2.54). Due to the unsuitability of the complex for OLED applications (emission in the UV region), a new modified complex (PtCC-2) has been subsequently published, with a Φ of 0.9 under nitrogen.

2.6 Summary

Metal complex formation and phenomena related to the photoluminescence of metal complexes have been discussed, with examples from the literature on widely used metal ions and their complexes. Strategies were analysed that have been used to manipulate the emission
properties of the respective complexes, especially in respect to the tunability of the emission energy. In this thesis the main focus will be given to study of the systematic tunability of the emission energy in azole-azine ligands in related Platinum(II) complexes and to their structure-property relationship.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 General

All precursor reagents, solvents and high purity NMR solvents were purchased from commercial sources (Sigma Aldrich and Acros) and used as supplied unless otherwise stated. All reactions that are air or moisture sensitive were carried out under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Tetrahydrofuran (THF) and triethylamine (TEA) solvents were distilled over Na/Benzophenone. Reaction completion was monitored by thin layer chromatography (TLC) on pre-coated TLC sheets (silica gel 60 with Fluorescent indicator UV254) purchased from Macherey-Nagel. Product purification was carried out by normal phase column chromatography using silica gel (pore size 60 Å, particle size 0.04-0.063 mm, technical grade, Sigma - Aldrich). Melting points were recorded using a Stuart SMP 30 melting point apparatus within an aluminium optimised heating block with variable ramp rates between 0.5 and 10 °C in 0.1 °C increments. Liquid chromatography/mass spectrometry (LC/MS) was performed on an analytical Agilent system running an inline 1260 series quaternary pump VL, a 1260 diode array detector and a 6120 Single Quadrupole Mass detector with dual mode ESI/APCI source. LCMS was performed with a C18 column (100 x 4.6 mm; 3.5 μm pore size) using atmospheric pressure photo ionization (APPI) or electrospray ionization (ESI). High resolution Mass spectra (HRMS) were measured at MEDAC Ltd and National Mass Spectrometry Facility. $^1$H and $^{13}$C NMR spectra were obtained using Bruker AVANCE II-300 (300 MHz) NMR instrument. The NMR chemical shifts (δ) are reported in parts per million (ppm) with reference to residual proton and carbon signals of chloroform-d (δ = 7.24 ppm (singlet) in $^1$H, 77.00 ppm (triplet) in $^{13}$C), dichloromethane-d$_2$ (δ = 5.32 ppm (triplet) in $^1$H, 54.00 ppm (quintet) in $^{13}$C), DMF-d$_7$ (δ = 2.75 ppm (quintet), 2.92 ppm (quintet) and 8.03 ppm (broad) in $^1$H and 29.76 ppm (septet), 34.89 ppm (septet) and 163.15 ppm (triplet) in $^{13}$C ) or DMSO-d$_6$ (2.50 ppm (quintet) in $^1$H and 39.51 ppm (septet) in $^{13}$C) depending on the solvent used. $^1$H NMR coupling multiplicity is indicated as follows: s (singlet), d (doublet), dd (doublet of a doublet), td (triplet of a doublet), dt (doublet of a triplet), ddd (doublet of a doublet of a doublet), m (multiplet). All the IR measurements were carried out using Varian 660 FTIR spectrometer equipped with Class II 1mW 633 nm laser in combination with a ZnSe ATR reflectance sample holder from Pike Technologies. Prior to each sample scan, background
scans were undertaken between 4000 – 400 cm\(^{-1}\). UV/Vis spectra were recorded with a Cary 5000 UV-Vis-NIR spectrophotometer equipped with Pb-Smart detector. All the measurements were carried out in ethanolic medium using Hellma suprasil quartz cuvettes (limit 200-2,500 nm spectral range, path length 10 mm, chamber volume 3,500 μL). All the photoluminescence spectral data were obtained from Cary Eclipse Plus spectrometer, which is equipped with a halogen lamp as the excitation source. All the excitations were carried out at 350 nm with a 295 – 395 nm excitation filter and the emissions were detected in the presence of 360 – 1100 nm emission filter. The accuracy of the PL measurements were confirmed using Coherent Innova 300C Ar-ion laser (25 mW) coupled with a Newport 818-IG detector. For solution measurements samples Hellma 101-QS cuvettes (Suprasil\textsuperscript{®} quartz, limit 200 – 2,500 nm spectral range, path length 10 mm, chamber volume 3,500 μL) were used. Solid samples were measured on silicon substrates. Emission lifetimes were measured using a tunable pulsed laser with a pulse width of ~8 ns at an excitation wavelength of 350 nm with the emission being dispersed in a monochromator and detected using a S20 photomultiplier detector.

3.2 Synthesis of derivatised 1H-(1,2,3-triazol-4-yl)pyridine Ligand Series

3.2.1 Synthesis of donor ligand series (3pyaz(1,2,3)-N(CH\textsubscript{3})\textsubscript{2})

![Synthetic scheme for the donor ligand series](image)
3.2.1.1 Synthesis of 3-N,N-dimethylaminopyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$–s1) (1)$^{152}$

To a round bottom flask containing formaldehyde (55.0 ml, 37% water) and formic acid (65.0 ml) was slowly introduced 3-aminopyridine (25.000 g, 0.266 mol, 1 eq.) under vigorous stirring. The system was then refluxed for 19 h. After refluxing, the system was cooled to R.T. and the pH was adjusted to be less than 2 by adding 6 M HCl. The volume of the mixture was reduced to around 50 ml under rotary evaporation. To this was added a concentrated mixture of sat. NaHCO$_3$ followed by 2 M NaOH in small aliquots until the pH was greater than 10. The resulting mixture was then extracted with CHCl$_3$ (100 ml x 3). Combined CHCl$_3$ layers were dried over anhydrous MgSO$_4$ and concentrated in vacuo to obtain the crude product. The product (1) was further purified via vacuum distillation at 98 – 100 °C at < 8 Torr.

3.2.1.2 Synthesis of 3-(N,N-dimethylamino)-6-bromopyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$–s2) (2)$^{153}$

3-(N,N-dimethylamino)pyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$-S1) (5.000 g, 0.041 mol, 1 eq.) was placed in a three-necked flask containing 50 ml of CH$_2$Cl$_2$ maintained at -25 °C. The mixture was allowed to stir for 15 min and a suspension of N-bromosuccinimide (7.2930 g, 1 eq.) in about 150 ml of CH$_2$Cl$_2$ was introduced dropwise over 3 h. The temperature was always maintained well below 0 °C inside the flask during the addition. The system was stirred overnight. The resulting mixture was washed with 0.1 M NaOH and water. The organic layer was dried over MgSO$_4$ and concentrated in vacuo. The pure product 3-(N,N-dimethylamino)-6-bromopyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$-S2) was obtained via column chromatography (hexane: ethyl acetate 1:1) followed by recrystallization from hexanes.

3.2.1.3 Synthesis of 5-N,N-dimethylamino-2-((trimethylsilyl)ethynyl)pyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$–s3) – Sonogashira coupling (3)$^{154}$

Pd(PPh$_3$)$_2$Cl$_2$ (7.5 mol%) and CuI (10 mol%) were introduced to a pressure tube flushed with N$_2$. A portion of 25 ml of dry triethylamine (TEA) was cannulated to the pressure tube followed by addition of 3-(N,N-Dimethylamino)-6-bromopyridine(1a)(3.000g, 0.015 mol, 1 eq.) dissolved in a portion of 25 ml of dry THF. The system was then lowered into a liquid nitrogen bath and trimethylsilylacetylene (1 eq.) was added drop wise. The mixture was allowed to warm to R.T. the system was degassed three times by the ‘freeze-pump-thaw’ technique and the tube was placed in an oil bath maintained at 100 °C. After stirring for 24 h at 100 °C under nitrogen, the tube was cooled to R.T. and the completion of the reaction was monitored by TLC. The contents were filtered through celite and the filter cake was washed thoroughly with CH$_2$Cl$_2$. The organic layer was then washed with saturated
NH₄Cl and deionized water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated in vacuo. The crude product was purified by column chromatography (hexane: ethyl acetate − 2:1) to obtain pure product (3pyaz(1,2,3)-N(CH₃)₂-S₃).

3.2.1.4 Synthesis of 5-N,N-dimethylamino-2-ethynylpyridine (3pyaz(1,2,3)-N(CH₃)₂ − s₄) − desilylation (4)

5-N,N-dimethylamino-2-((trimethylsilyl)ethynyl)pyridine (3pyaz(1,2,3)-N(CH₃)₂-S₃) (1.500 g, 0.007 mol, 1 eq.) was placed in a 50 ml round bottom flask and was dissolved in 20 ml of methanol followed by slow addition of 1.1 eq. of 1 M KOH. The system was stirred for approx. 30 min at R.T. The completion of the reaction was monitored by TLC. Once completed, the methanol layer was evaporated under a flow of N₂. The resulting mixture was diluted with deionized water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated in vacuo. The crude product was further purified via column chromatography (hexane:ethyl acetate − 3:1).

3.2.1.5 Synthesis of Azidomethylpivalate (5)

![Figure 3.2 – Synthesis of azidomethyl pivalate](image)

Sodium azide (6.350 g, 0.105 mol) was added to a suspension of chloromethylpivalate (10.6 g, 0.700 mol) in H₂O and the mixture was stirred for 12 h at 90 °C. The resulting mixture was separated between ethyl acetate and H₂O and the organic layer was dried over anhydrous MgSO₄. The solvent was evaporated and the pure product was obtained as a clear liquid. The product was not further analysed for safety considerations and was stored at reduced temperatures wet. The mixture was used in excess in further reactions.

3.2.1.6 Synthesis of (4-(5-(dimethylamino)pyridine-2-yl)-1H-1,2,3-triazol-1-yl)methyl pivalate (3pyaz(1,2,3)-N(CH₃)₂ − s₅) – 1,3-dipolar cycloaddition (6)

5-N,N-dimethylamino-2-ethynylpyridine (3pyaz(1,2,3)-N(CH₃)₂-S₄) (0.900 g, 0.006 mol, 1 eq.) and azidomethylpivalate (1 eq.) were suspended in 1:1 H₂O: t-Butanol (10 ml). To this was added CuSO₄.5H₂O (5 mol%) and sodium ascorbate (33 mol%). The mixture was stirred at R.T. for 24 h. The completion of the reaction was observed with TLC. The reaction mixture was partitioned between ethyl acetate and water. The organic layer was separated and washed with 7% NH₄OH, brine and deionized water. The resulting organic layer was dried
over anhydrous MgSO$_4$ and the solvent was evaporated in vacuo. The crude product was purified via column chromatography (hexane: ethyl acetate – 2:1).

3.2.1.7 Synthesis of 5-N,N-dimethylamino-2-(1H-1,2,3-triazol-4-yl)pyridine (3pyaz(1,2,3)-N(CH$_3$)$_2$) (7)$^{155}$

To a solution of (4-(5-(dimethylamino)pyridin-2-yl)-1H,1,2,3-triazol-1-yl)methyl pivalate (3pyaz(1,2,3)-N(CH$_3$)$_2$-S5) (1.500 g, 0.005 mol, 1 eq.) suspended in 7.5 ml of methanol was added 6 ml of 1 M KOH and stirred at R.T. until completion observed by TLC. The solution was subsequently neutralized with 1 M HCl and diluted with water (20 ml). The resulting precipitate was filtered and washed thoroughly with hexane. The crude product was purified via column chromatography (hexane: ethyl acetate – 1:1) and was recrystallized from hexane to obtain the pure product (7).

3.2.2 Synthesis of basic ligand series (3pyaz(1,2,3))

3.2.2.1 Synthesis of 2-(trimethylsilyl)ethynylpyridine (3pyaz(1,2,3) – s1) (8)$^{154}$

Following the Sonogashira coupling protocol described in Section 3.2.1.3 synthesis was carried out with 2-bromopyridine (3.000 g, 0.019 mol, 1 eq.). The crude product was purified by column chromatography (hexane: ethyl acetate– 9:1).

3.2.2.2 Synthesis of 2-ethynylpyridine (3pyaz(1,2,3) – s2) (9)$^{154}$

According to the procedure described in 3.2.1.4 desilylation of 2-(trimethylsilyl)ethynlypyridine (3pyaz(1,2,3)-S1) (2.000g, 0.011 mol, 1 eq.). The purification was carried out on a silica column (hexane: ethyl acetate – 2:1).
3.2.2.3 Synthesis of \( (4-(\text{pyridin}-2\text{-y})l-1\text{H}-1,2,3\text{-triazol}-1\text{-y})\text{methyl pivalate} \) \( (3\text{pyaz}(1,2,3) \text{ -- s3}) \) (10)

The 1,3-dipolar cycloaddition was performed as stated in Section 3.2.1.6, starting with 2-ethynylpyridine \( (3\text{pyaz}(1,2,3)-\text{S2}) \) (1.000 g, 0.010 mol, 1 eq.). The purification was carried out via column chromatography (hexane: ethyl acetate – 2:1).

3.2.2.4 Synthesis of \( 2-\text{(1H}-1,2,3\text{-triazol}-4\text{-y})\text{pyridine} \) \( (3\text{pyaz}(1,2,3)) \) (11)

The deprotection of methyl pivalate group was carried out as in Section 3.2.1.7 with \( (4-(\text{pyridin}-2\text{-y})l-1\text{H}-1,2,3\text{-triazol}-1\text{-y})\text{methyl pivalate} \) \( (3\text{pyaz}(1,2,3)-\text{s3}) \) (2.000 g, 0.008 mol, 1 eq.). The crude product was purified via column chromatography (hexane: ethyl acetate – 1:1). The product was further purified by sublimation.

3.2.3 Synthesis of acceptor ligand series \( (3\text{pyaz}(1,2,3)-\text{CHO and } 3\text{pyaz}(1,2,3)-\text{CHC(CN)}_2) \)

3.2.3.1 Synthesis of \( 6\text{-bromopyridine-3-carbaldehyde} \) \( (3\text{pyaz}(1,2,3)-\text{CHO -- s1}) \) (12)

2,5-dibromopyridine (5.000 g, 0.021 mol, 1 eq.) was placed in a 500 ml round bottom flask and was purged with N\(_2\). A 200 ml portion of freshly dried diethylether (dried over Na/ Benzophenone) was cannulated to the flask. The mixture was swirled for 15 min at a temperature below -78 °C (hexane/ liq. N\(_2\) = -94 °C) and n-BuLi (13.7 ml, 1.05 eq.) was added to the mixture over 20 min while stirring vigorously. The mixture was allowed to stir for 1 h and 1.76 ml (1.1 eq.) of dry DMF (Dried over 4a molecular sieves overnight and...
vacuum distilled) was introduced drop wise to the mixture at the same temperature and allowed another 1 h of stirring. Finally the mixture was warmed to R.T. followed by addition of a portion of 40 ml of 1 M HCl and was stirred for another 15 min. The mixture was subsequently washed with water and brine and the organic layer was dried over MgSO₄. The resulting organic layer was evaporated in vacuo. The crude product was purified by column chromatography (hexane: ethyl acetate – 3:1).

3.2.3.2 Synthesis of 6-((trimethylsilyl)ethynyl)pyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO – s2) (13)\\(^{154}\)

Sonogashira coupling was carried out for 6-bromopyridine-3-carbaldehyde (2.000 g, 0.011 mol, 1 eq.) as in Section 3.2.1.3. Column chromatography was carried out to purify the compound (hexane: ethyl acetate – 3: 1).

3.2.3.3 Synthesis of 6-Ethynylpyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO – s3) (14)\\(^{154}\)

The protection of the trimethylsilyl group from 6-((trimethylsilyl)ethynyl)pyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO-S2) (1.500 g, 0.007 mol, 1 eq.) was carried out as described in Section 3.2.1.4. Resulting crude product was purified through a silica column (hexane: ethyl acetate – 2:1).

3.2.3.4 Synthesis of (4-(5-formylpyridin-2-yl)-1H-1,2,3-triazol-1-yl)methyl pivalate (3pyaz(1,2,3)-CHO – s4) (15)\\(^{155}\)

6-Ethynylpyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO-S3) (0.900 g, 0.007 mol, 1 eq.) was reacted with azidomethyl pivalate as stated in Section 3.2.1.6. The purification was carried out by column chromatography (hexane: ethyl acetate – 2:1).

3.2.3.5 Synthesis of 6-(1H-1,2,3-triazol-4-yl)pyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO) (16)\\(^{155}\)

The methyl pivalate group on 6-(1H-1,2,3-triazol-4-yl)pyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO) (1.500 g, 0.005 mol, 1 eq.) was deprotected as in Section 3.2.1.7. The crude product was purified by column chromatography (hexane: ethyl acetate 1: 1).

3.2.3.6 Synthesis of 3-Dicyanovinyl-6-[1H-(1,2,3-triazol-4-yl)]pyridine (3pyaz(1,2,3)-CHC(CN)₂) (17)

To 6-[1H-(1,2,3-triazol-4-yl)]pyridine-3-carbaldehyde (3pyaz(1,2,3)-CHO) (0.400 g, 0.002 mol, 1 eq.) dissolved in 5 ml of THF was added malononitrile (0.1517 g, 1 eq.) and;

Method 1\\(^{157}\) - basic alumina (3g) followed by malononitrile (0.1517 g, 1 eq.) and heated at 50°C for 10 min while stirring. The completion of the reaction was observed by TLC. The
resulting mixture was filtered and the solvent was evaporated. Further purification was carried out via column chromatography using 3:2 Hex:EA mobile phase.

**Method 2** – a catalytic amount of piperidine and the mixture was allowed to stir at R.T. for 3 h under inert conditions. The completion of the reaction was observed by TLC. The solvent was evaporated and the crude product was washed thoroughly with hexane and petroleum ether and was further purified by column chromatography (hexane: ethyl acetate 3: 2).

### 3.3 Synthesis of derivatised ligand series with changing nitrogen content in the azole and pyridyl rings

Table 3.1 – Derivatised ligands by varying the nitrogen content in the ring systems (tautomeric structures are not listed) (In future reference pyridine may termed as – ‘py’, pyrimidine as – ‘pm’ and pyrazine as – ‘pz’)

<table>
<thead>
<tr>
<th>(1,2)diazole (pyrazole)</th>
<th>(1,3)diazole (imidazole)</th>
<th>(1,2,3)triazole</th>
<th>(1,2,4)triazole</th>
<th>(1,2,3,4)tetrazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2pyaz(1,2)</td>
<td>2pyaz(1,3)</td>
<td>3pyaz(1,2,3)</td>
<td>3pyaz(1,2,4)</td>
<td>4pyaz</td>
</tr>
<tr>
<td>Pyrimidine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2pmaz(1,2)</td>
<td>2pmaz(1,3)</td>
<td>3pmaz(1,2,3)</td>
<td>3pmaz(1,2,4)</td>
<td>4pmaz</td>
</tr>
<tr>
<td>Pyrazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2pzaz(1,2)</td>
<td>2pzaz(1,3)</td>
<td>3pzaz(1,2,3)</td>
<td>3pzaz(1,2,4)</td>
<td>4pzaz</td>
</tr>
</tbody>
</table>

#### 3.3.1 Synthesis of (1,2) diazole / pyrazole series

**3.3.1.1 Synthesis of 2-(1H-pyrazol-5-yl)pyridine (2pyaz(1,2)) (18)**

3-(dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (2.200 g, 12.5 mmol, 1 eq.) was dissolved in ethanol (10 ml) and hydrazine monohydrate (2 ml) was added slowly to the solution. The reaction was stirred at R.T. for 4 h. The resulting brown solution was partitioned between water and CH₂Cl₂. The organic layer was evaporated in vacuo and the resulting crude product was purified by column chromatography (mobile phase - hexane: ethyl acetate – 1:1).
3.3.1.2 Synthesis of 1-(pyrimidine-2-yl)ethanone/2-acetylpyrimidine (19)\textsuperscript{158}

A solution of 2-cyanopyrimidine (7.500 g, 71.4 mmol, 1 eq.) in THF (75 ml) was cooled to -5 °C and a portion of 3 M methyl magnesium bromide (35.7 ml, 1.5 eq.) dissolved in 75 ml of THF was slowly introduced. The reaction mixture was stirred at 0 °C for 5 h. The resulting yellow suspension was added to a rapidly stirring mixture of saturated ammonium chloride (75 ml) and 4 M HCl (45 ml). Following this, the pH of the mixture was further reduced to pH 1 by adding 2M HCl. The mixture was stirred for 40 min at R.T. The pH of the resulting mixture was adjusted to between 6 and 7 by adding a saturated solution of K$_2$CO$_3$ and was extracted into ethyl acetate. The solvent was evaporated \textit{in vacuo} and the crude product was purified by column chromatography (mobile phase hexane: ethyl acetate – 1:8).

3.3.1.3 Synthesis of 3-(dimethylamino)-1-(pyrimidin-2-yl)prop-2-en-1-one (2pmaz(1,2) – s1) (20)\textsuperscript{159}

1-(pyrimidin-2-yl)ethanone (5.000 g, 41.0 mmol, 1 eq.) and DMF – DMA (3.650 ml, 1.5 eq.) were refluxed at 100 °C on a short distillation bridge for 1 h. A small amount of distillate was collected during this time. The resulting brown coloured mixture was concentrated and recrystallized from benzotrifluoride.

3.3.1.4 Synthesis of 2-(1H-pyrazol-5-yl)pyrimidine (2pzaz(1,2)) (21)\textsuperscript{159}

3-(dimethylamino)-1-(pyrimidin-2-yl)prop-2-en-1-one (4.500 g, 25.4 mmol, 1 eq.) was heated under reflux at 90 °C for 3 h with hydrazine monohydrate (1.850 ml, 1.5 eq.) in 100 ml of ethanol. The reaction mixture was concentrated and separated between CH$_2$Cl$_2$ and water. The organic layer was evaporated \textit{in vacuo} and the resulting crude product was recrystallized from benzotrifluoride.

3.3.1.5 Synthesis of 3-(dimethylamino)-1-(pyrazin-2-yl)prop-2-en-1-one – (2pzaz(1,2) – s1) (22)\textsuperscript{159}

2-acetylpyrazine (5.000 g, 41.0 mmol, 1 eq.) was reacted with DMF – DMA (3.64 ml, 1.5 eq.) under reflux for 10 h at 100 °C. The resulting green – brown mixture was concentrated and recrystallized from a mixture of CHCl$_3$ and hexane.

3.3.1.6 Synthesis of 2-(1H-pyrazol-5-yl)pyrazine (2pzaz(1,2)) (23)\textsuperscript{159}

3-(dimethylamino)-1-(pyrazin-2-yl)prop-2-en-1-one (4.000 g, 22.6 mmol, 1 eq.) was refluxed with hydrazine monohydrate (4.000 ml, 1.5 eq.) for 3 h at 90 °C. The reaction mixture was cooled and partitioned between CH$_2$Cl$_2$ and water. The organic layer was evaporated \textit{in vacuo} to obtain the crude product, which was recrystallized from a mixture of CH$_2$Cl$_2$ and hexane.
3.3.2 Synthesis of (1,3) diazole / imidazole series

**Figure 3.6 – Synthetic scheme for (1,3) diazole / imidazole series**

3.3.2.1 Synthesis of 2-(1H-imidazol-2-yl)pyridine (2paz(1,3)) (24)

To a 250 ml round bottom flask containing 2-cyanopyridine (5.205 g, 50.0 mmol, 1 eq.) in 20 ml of methanol was added a 30% solution of NaOMe in methanol (0.270 g, 10 mol%). The mixture was stirred for 60 min at 40 °C. To the resulting suspension 2,2-dimethoxyethanamine (a) (5.257 g, 1 eq.) was introduced followed by slow addition of acetic acid (5.5 ml, 1.92 eq.). The reaction mixture was heated to reflux at 50 °C for 30 min After cooling the mixture to R.T., 30 ml of methanol and 25 ml of 6 M HCl in water were added and refluxed for another 4.5 h. The resulting solution was evaporated in vacuo and a portion of freshly prepared, warm solution (50 °C) of K₂CO₃ (27.5 g in water 27.5 g) was added carefully to the residue bringing the pH of the system to 10. The resulting suspension was cooled to R.T. and filtered while washing the filter cake with water to obtain the crude product. The crude product was recrystallized from ethyl acetate.

3.3.2.2 Synthesis of 2-(1H-imidazol-2-yl)pyrimidine (2pmaz(1,3)) (25)

To a 250 ml round bottom flask containing 2-cyanopyrimidine (5.255 g, 50.0 mmol, 1 eq.) in 20 ml of methanol was added a 30% solution of NaOMe in methanol (0.207 g, 10 mol%). The mixture was stirred for 1.5 h at R.T. 2,2-dimethoxyethanamine (a) (5.257 g, 1 eq.) was introduced to the resulting mixture followed by slow addition of AcOH (5.5 ml, 1.92 eq.). The reaction mixture was heated to reflux at 50 °C for 30 min After allowing the system to cool to R.T., 30 ml of methanol and 25 ml of 6 M HCl in water were added and refluxed for another 5 h. Once completed, the solution was evaporated in vacuo and a portion of freshly prepared warm solution (50 °C) of K₂CO₃ (27.5 g in water 27.5 ml) was introduced carefully by bringing the pH to 10. The resulting suspension was cooled to R.T. and filtered while washing the filter cake with water to obtain the crude product. The crude product was recrystallized from methanol.
3.3.2.3 Synthesis of 2-(1H-imidazol-2-yl)pyrazine (2pzaz(1,3)) (26)

To a 100 ml round flask containing 2-cyanopyrazine (5.255 g, 50.0 mmol, 1 eq.) in 10 ml of methanol was added a 30 % solution of NaOMe in methanol (0.207 g, 10 mol%) and the mixture was stirred for 20 min at R.T. 2,2-diethoxyethanamine (b) (6.660 g, 1 eq.) was introduced to the resulting mixture followed by slow addition of AcOH (5.5 ml, 1.92 eq.). The reaction mixture was heated to 50 °C for 1 h. After cooling the mixture to R.T., 30 ml of methanol and 25 ml of 6 M HCl in water were added and refluxed for another 5 h. Once the reaction was completed solution was evaporated in vacuo and aqueous NaOH was added carefully to the residue bringing the pH to between 8 and 9. The resulting suspension was filtered and recrystallized from ethyl acetate.

3.3.3 Synthesis of (1,2,3) triazole series154,155

![Synthetic scheme for (1,2,3) triazole series](image)

3.3.3.1 Synthesis of 2-(1H-1,2,3-triazol-4-yl)pyridine (3pyaz(1,2,3)) (11)

The procedure reported earlier in the Section 3.2.2 was followed for the synthesis of the compounds listed below.

3.3.3.2 Synthesis of 2-((trimethylsilyl)ethynyl)pyrimidine (3pmaz(1,2,3) – s1) (27)

Pd(PPh3)2Cl2 (1.179 g, 7.5 mol%) and CuI (0.299 g, 10 mol%) were introduced to a pressure tube flushed with N2. A portion of 25 ml of dry TEA was cannulated to the pressure tube followed by addition of 2-bromopyrimidine (2.500 g, 15.7 mmol, 1 eq.) dissolved in a portion of 25 ml of dry THF. Trimethylsilylacetylene (1.544 g, 1 eq.) was added drop wise to the mixture while the pressure tube is immersed in a liquid nitrogen bath. The mixture was warmed to R.T., degassed by ‘freeze-pump-thaw’ method, and heated at 100 °C for 24 h under nitrogenous atmosphere. The completion of the reaction was monitored by TLC. The contents were filtered through celite and the filter cake was rinsed with CH2Cl2. The organic layer was washed with saturated NH4Cl, water and the solvent was evaporated in vacuo. The
crude product was purified by column chromatography (mobile phase hexane: ethyl acetate – 4:1).

3.3.3.3 Synthesis of 2-ethynylpyrimidine (3pmaz(1,2,3) – s2) (28)

To a flask containing 2-((trimethylsilyl)ethyl)pyrimidine (1.800 g, 10.2 mmol, 1 eq.) in 20 ml of methanol was introduced 1.1 eq. of 1 M KOH. The mixture was stirred at R.T. for approx. 30 min. The completion of the reaction was observed by TLC. The methanol layer was evaporated under a flow of N₂. The resulting mixture was diluted with deionized water and extracted with CH₂Cl₂. The organic layer was evaporated in vacuo. The crude product was further purified by column chromatography (mobile phase - hexane: ethyl acetate – 6:1).

3.3.3.4 Synthesis of pyrimidin-2-yl-1H-1,2,3-triazol-1-yl)methyl pivalate (3pmaz(1,2,3) – s3) (29)

2-ethynylpyrimidine (0.700 g, 6.7 mmol, 1 eq.) and azidomethylpivalate (1.057 g, 1 eq.) were suspended in a mixture of 1:1 H₂O: t-Butanol (10 ml). To this was added CuSO₄.5H₂O (0.084 g, 5 mol%) and sodium ascorbate (0.440 g, 33 mol%) and the mixture was stirred at R.T. for 24 h. The resulting solution was partitioned between ethyl acetate and water. The organic layer was separated and washed with 7% NH₄OH, brine and deionized water. The solvent was evaporated in vacuo and the crude product was purified by column chromatography (mobile phase - hexane: ethyl acetate – 3:1).

3.3.3.5 Synthesis of 2-(1H-1,2,3-triazol-4-yl)pyrimidine (3pmaz(1,2,3)) (30)

To a solution of pyrimidin-2-yl-1H-1,2,3-triazol-1-yl)methyl pivalate (1.200 g, 5.8 mmol, 1 eq.) in 7.5 ml of methanol was added 6 ml of 1 M KOH and the mixture stirred at R.T. for 20 min. The solution was subsequently neutralized with 1 M HCl and diluted with water 20 ml of water. The resulting precipitate was filtered and washed thoroughly with hexane. The crude product was purified by column chromatography (mobile phase – hexane: ethyl acetate – 1:1) to obtain the final product.

3.3.3.6 Synthesis of 2-((trimethylsilyl)ethyl)pyrazine (3pzaz(1,2,3) – s1) (31)

Pd(PPh₃)₂Cl₂ (1.011 g, 7.5 mol%) and CuI (0.366 g, 10 mol%) were introduced to a pressure tube flushed with N₂. A portion of 25 ml of dry TEA was cannulated to the pressure tube followed by addition of 2- chloropyrazine (2.200 g, 19.2 mmol, 1 eq.) dissolved in a portion of 25 ml of dry THF. Trimethylsilylacetylene (1.890 g, 1 eq.) was added drop wise to the mixture while the pressure tube was immersed in a liquid nitrogen bath. The mixture was warmed to R.T., degassed by ‘freeze-pump-thaw’ method, and heated at 100°C for 24 h under
nitrogenous atmosphere. The completion of the reaction was monitored by TLC. The contents were filtered through celite and the filter cake was rinsed with CH₂Cl₂. The organic layer was washed with saturated NH₄Cl, water and the solvent was evaporated in vacuo. The crude product was purified by column chromatography (mobile phase hexane: ethyl acetate – 4:1.

3.3.3.7 Synthesis of 2-ethynlypyrazine (3pzaz(1,2,3) – s2) (32)

To a flask containing 2-((trimethylsilyl)ethynyl)pyrazine (2.200 g, 12.5 mmol, 1 eq.) in 20 ml of methanol was introduced 1.1 eq. of 1 M KOH. The mixture was stirred at R.T. for approx. 30 min. The completion of the reaction was observed by TLC. The methanol layer was evaporated under a flow of N₂. The resulting mixture was diluted with deionized water and extracted with CH₂Cl₂. The organic layer was evaporated in vacuo. The crude product was further purified via column chromatography (mobile phase - hexane: ethyl acetate – 3:1).

3.3.3.8 Synthesis of pyrazin-2-yl-1H-1,2,3-triazol-1-yl)methyl pivalate (3pyaz(1,2,3) – s3) (33)

2-ethynlypyrazine (0.950 g, 9.1 mmol, 1 eq.) and azidomethylpivalate (1.434 g, 1 eq.) were suspended in a mixture of 1:1 H₂O: t-Butanol (10 ml). To this was added CuSO₄·H₂O (0.114 g, 5 mol%) and sodium ascorbate (0.597 g, 33 mol%) and the mixture was stirred at R.T. for 24 h. The resulting solution was partitioned between ethyl acetate and water. The organic layer was separated and washed with 7 % NH₄OH, brine and deionized water. The solvent was evaporated in vacuo and the crude product was purified by column chromatography (mobile phase - hexane: ethyl acetate – 5:1).

3.3.3.9 Synthesis of 2-(1H-1,2,3-triazol-4-yl)pyridine (3pzaz(1,2,3)) (34)

To a solution of pyridin-2-yl-1H-1,2,3-triazol-1-yl)methyl pivalate (1.500 g, 5.7 mmol, 1 eq.) in 7.5 ml of methanol was added 6 ml of 1 M KOH and the mixture stirred at R.T. for 20 min. The solution was subsequently neutralized with 1 M HCl and diluted with water 20 ml of water. The resulting precipitate was filtered and washed thoroughly with hexane. The crude product was purified via column chromatography (mobile phase – hexane: ethyl acetate – 1:1) to obtain the final product.
3.3.4 Synthesis of (1,2,4) triazole series

3.3.4.1 Synthesis of pyrimidine-2-carboximidhydrazide/ pyrimidylamidrazone (3pmaz(1,2,4) – s1) (35)\(^\text{161}\)

\[
\begin{align*}
\text{py} - X_1 &= N, X_2 = C; \quad \text{pm} - X_1 &= N, X_2 = C; \quad \text{pz} - X_1 &= C, X_2 = N
\end{align*}
\]

Figure 3.8 – Synthetic scheme for (1,2,4) triazole series

To a solution containing 2-cyanopyrimidine (10.000 g, 95.2 mmol, 1 eq.) in 40 ml of ethanol was slowly introduced hydrazine monohydrate (4.800 g, 1 eq.) and the mixture was stirred at R.T. for 1h. The reaction mixture was stored overnight at -30 °C. The resulting yellow/orange precipitate was filtered and washed with cold ethanol. Recrystallization from ethanol yielded the purified product.

3.3.4.2 Synthesis of 2-(1H-1,2,4-triazol-3-yl)pyrimidine (3pmaz(1,2,4)) (36)

Pyrimidine-2-carboximidhydrazide (5.000 g, 36.5 mmol, 1 eq.) was added slowly to a stirring portion of 16.6 ml of formic acid (10 eq.) at 0 °C. The mixture was warmed to R.T. and refluxed for 2 h. The excess formic acid was evaporated in vacuo and the resulting residue was neutralised with a saturated solution of Na\(_2\)CO\(_3\). The product was purified by column chromatography (mobile phase – hexane: ethyl acetate 1:9) and recrystallized from a mixture of ethyl acetate and hexane to obtain the final product.

3.3.4.3 Synthesis of pyrazine-2-carboximidhydrazide/ pyrazinylamidrazone (3pzaz(1,2,4) – s1) (37)\(^\text{162}\)

To a solution containing 2-cyanopyrazine (10.000 g, 95.2 mmol, 1 eq.) in 40 ml of ethanol was slowly introduced hydrazine monohydrate (4.800 g, 1 eq.) and the mixture was stirred at R.T. for 1h. The yellow reaction suspension was stored overnight at -30 °C. The resulting yellow precipitate was filtered and washed with cold ethanol. Recrystallization from ethanol yielded the final product.

3.3.4.5 Synthesis of 2-(1H-1,2,4-triazol-3-yl)pyrazine (3pzaz(1,2,4)) (38)\(^\text{162}\)

Pyrazine-2-carboximidhydrazide (5.000 g, 36.5 mmol, 1 eq.) was added in small portions to formic acid (16.6 ml, 10 eq.) while stirring at 0 °C. The mixture was warmed to
R.T. and refluxed for 2 h. The excess formic acid was evaporated in vacuo and the resulting residue was neutralised with a saturated solution of Na$_2$CO$_3$. The product was purified by column chromatography (mobile phase – methanol: CH$_2$Cl$_2$ 1:3).

### 3.3.5 Synthesis of tetrazole series

#### 3.3.5.1 Synthesis of 2-(1H-tetrazol-5-yl)pyridine (4pyaz) (39)

To a flask containing 60 ml of dry DMF was introduced 2-cyanopyridine (10.000 g, 96.2 mmol, 1 eq.) followed by NH$_4$Cl (6.700 g, 1.3 eq.) and NaN$_3$ (8.130 g, 1.3 eq). The mixture was refluxed at 120 °C for 24 h. The resulting yellow suspension was allowed to cool to R.T. and the pH was adjusted to 2 by adding conc. HCl. The precipitate was filtered and recrystallized from ethanol to obtain white needle shaped crystals (Yield – 96%, 13.651 g).

#### 3.3.5.2 Synthesis of 2-(1H-tetrazol-5-yl)pyrimidine (4pmaz) (40)

To a solution containing 2-cyanopyrimidine (2.00 g, 19.0 mmol, 1 eq.) and NaN$_3$ (2.476 g, 2 eq.) in dry DMF (50 ml) was added Sb$_2$O$_3$ (0.554 g, 10 mol%) and refluxed at 120 °C for 7 h. The resulting mixture was separated between ethyl acetate and water. The organic layer was stirred vigorously with 40 ml of 6 M HCl. The resulting organic layer was separated and the aqueous layer was re-extracted with another portion of ethyl acetate. The combined organic layers were evaporated in vacuo and the crude product was recrystallized from ethanol to obtain a white crystalline powder (Yield – 73%, 2.061 g).

#### 3.3.5.3 Synthesis of 2-(1H-tetrazol-5-yl)pyrazine (4pzaz) (41)

To a solution containing 2-cyanopyrazine (2.00 g, 19.0 mmol, 1 eq.) and NaN$_3$ (2.476 g, 2 eq.) in dry DMF (50 ml) was added Sb$_2$O$_3$ (0.554 g, 10 mol%) and refluxed at 120 °C for 5 h. The resulting mixture was separated between ethyl acetate and water. The organic layer was stirred vigorously with 40 ml of 6 M HCl. The resulting organic layer was separated and the aqueous layer was re-extracted with another portion of ethyl acetate. The combined
organic layers were evaporated in vacuo and the crude product was recrystallized from ethanol to obtain a white crystalline powder (Yield – 81%, 2.280 g).

### 3.4 Synthesis of the platinum(II) metal complexes

**Figure 3.10 – Generic synthetic scheme for Platinum(II) metal complexes**

**General Procedure**

To a portion of 4 eq. of the ligand dissolved in 3 ml of ethoxy-ethanol, was added 4 eq. of 0.1 M Na₂CO₃ and stirred under N₂ atmosphere for 10 min. 1 eq. of dissolved in 2 ml of deionised water was slowly introduced and the system was stirred at 50 °C overnight (12 h) under N₂ atmosphere. The resulting solid was filtered and washed thoroughly with ethanol, water and acetone respectively. The complex was obtained as pure product after vacuum drying at 50 °C for 48 h.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Complex</th>
<th>Complex no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3pyaz(1,2,3) – N(CH₃)₂</td>
<td>Pt[3pyaz(1,2,3) – N(CH₃)₂]₂</td>
<td>42</td>
</tr>
<tr>
<td>3pyaz(1,2,3)</td>
<td>Pt[3pyaz(1,2,3)]₂</td>
<td>43</td>
</tr>
<tr>
<td>3pyaz(1,2,3) – CHO</td>
<td>Pt[3pyaz(1,2,3) – CHO]₂</td>
<td>44</td>
</tr>
<tr>
<td>3pyaz(1,2,3) – CHC(CN)₂</td>
<td>Pt[3pyaz(1,2,3) – CHC(CN)₂]₂</td>
<td>45</td>
</tr>
<tr>
<td>2pyaz(1,2)</td>
<td>Pt[2pyaz(1,2)]₂</td>
<td>46</td>
</tr>
<tr>
<td>2pzaz(1,2)</td>
<td>Pt[2pzaz(1,2)]₂</td>
<td>47</td>
</tr>
<tr>
<td>2pyaz(1,3)</td>
<td>Pt[2pyaz(1,3)]₂</td>
<td>48</td>
</tr>
<tr>
<td>2pzaz(1,3)</td>
<td>Pt[2pzaz(1,3)]₂</td>
<td>49</td>
</tr>
<tr>
<td>2pmaz(1,3)</td>
<td>Pt[2pmaz(1,3)]₂</td>
<td>50</td>
</tr>
<tr>
<td>3pzaz(1,2,3)</td>
<td>Pt[3pzaz(1,2,3)]₂</td>
<td>51</td>
</tr>
<tr>
<td>3pyaz(1,2,3)</td>
<td>Pt[3pyaz(1,2,3)]₂</td>
<td>52</td>
</tr>
<tr>
<td>3pzaz(1,2,4)</td>
<td>Pt[3pzaz(1,2,4)]₂</td>
<td>53</td>
</tr>
<tr>
<td>3pmaz(1,2,4)</td>
<td>Pt[3pmaz(1,2,4)]₂</td>
<td>54</td>
</tr>
<tr>
<td>3pzaz(1,2,4)</td>
<td>Pt[3pzaz(1,2,4)]₂</td>
<td>55</td>
</tr>
<tr>
<td>4pyaz</td>
<td>Pt[4pyaz]₂</td>
<td>56</td>
</tr>
</tbody>
</table>
### 3.5 Computational procedures

The ground-state geometries of the ligands (anion forms), neutral complexes and their intermolecular dimers were fully optimized with the PBE0 functional, 6-31G* basis set for the organic parts and SDD basis set for Pt atom.\(^{165,166}\) The choice of the PBE0 functional is dictated by recently published results demonstrating the good performance of the functional in the simulation of optical properties of Pt complexes and their dimers.\(^{167}\) The polarizable continuum model (PCM) was used to account for the solvent effects.\(^{168}\) Ground state vibrational frequencies were calculated in order to confirm that optimized structures are true minima on the potential energy surface. The vertical excitation and oscillator strengths for all compounds were determined by TDDFT calculations with the same method as for geometry optimization. Then, we have performed Time Dependent Density Functional Theory (TDDFT) optimizations of the lowest-energy singlet (S\(_1\)) and triplet (T\(_1\) and/or T\(_2\)) excited states of the neutral complexes and their dimers and the vertical emission energies were estimated. When the TDDFT geometry optimization of the T\(_1\) state of dimers was hampered, an alternative approach was applied in order to estimate the T\(_1\)→S\(_0\) emission energies. This alternative approach comprises DFT optimization of T\(_1\) and then single point TDDFT estimation of DT\(_1\) energies on the T\(_1\) geometry with singlet wave-function. The accuracy of the alternative approach is demonstrated in the case of 4b-4b and 4c-4c dimers. The results reveal good agreement between the T\(_1\)→S\(_0\) emission energies obtained with the TDDFT optimization and alternative approach. The state specific solvation was taken into account only for geometry optimization steps. All quantum-chemical calculations were carried out with the Gaussian 09 program package. The molecular orbitals were visualized with Jmol 14.2.4 and Molekel 5.4.0.

<table>
<thead>
<tr>
<th>4pmaz</th>
<th>Pt[4pmaz](_2)</th>
<th>58</th>
</tr>
</thead>
<tbody>
<tr>
<td>4pzaz</td>
<td>Pt[4pzaz](_2)</td>
<td>59</td>
</tr>
</tbody>
</table>
CHAPTER 4
SYNTHESIS AND CHARACTERISATION OF NOVEL PYRIDYL-1,2,3-TRIAZOLE LIGANDS

4.1 Design and selection of donor, neutral and acceptor ligands

As stated in Chapter 1, one of the main objectives of this study is the synthesis and analysis of hybrid-metal complexes and to study their photo-physical characteristics in a structure-property perspective. To realise an efficient design strategy, it was necessary to base the approach on both efficient elementary synthetic steps as well as convergent synthetic routes. Additionally, the molecular design needed to be effective in delivering noticeable and predictable changes in spectroscopic properties. Therefore, ligand systems that can deliver a significant degree of freedom to alter photo-physical characteristics in simple and efficient manner are important. Since triazole based ligands emerge as potential candidates for such applications, in this study the photo-physical properties of novel pyridyl-triazolate complexes are explored. Compared to other pyridyl azoles,24, 26 pyridyl-1,2,3-triazoles are less studied. Moreover, most of the examples related to pyridyl-1,2,3-triazoles involve substitution at the N of the triazole ring in order to affect the energy of the highest occupied molecular orbital (HOMO). However, triazole is electronically insulating and thus substituent effects have not been very pronounced.29, 169 A more effective tuning route might target the lowest unoccupied molecular orbital (LUMO) that is found on the pyridyl ring and is anticipated to be more closely associated with the excited-state.170 Thus, in the present work, pyridyl-1H-1,2,3-triazole ligands were prepared to build a structurally homologous series of donor and acceptor 5-pyridyl substituted ligands. Another important aspect in leaving the N of the triazole unsubstituted, is to exploit the protic nature of the 1H-triazolyl moiety to give strong field ligation (suppressed d-d transitions in metal complexes)171 in the final neutral complexes. The design of structurally homologous series is an important approach that maintains synthetic efficiency and avoids complications that result due to incompatible materials in optoelectronic applications.

Keeping synthetic efficiency in mind, the target ligands were approached through the serial application of the Sonogashira carbon-carbon coupling and the Sharpless copper-catalysed Huisgen’s 1,3-dipolar cycloaddition protocols starting from the 2-bromopyridyl derivatives. Sonogashira coupling with trimethylsilylacetylene produced the terminal alkynylated pyridines after nearly quantitative basic desilylation with KOH. Following this,
copper catalysed reaction of these terminal alkynes with azidomethylpivalate gave the N-protected 1,4-disubstituted-1,2,3-triazoles which were subsequently proto-deprotected to yield the intended 1H-1,2,3-triazole ligands. The final ligand in the acceptor series was synthesised by Knövenagel condensation with malononitrile in the presence of catalytic basic alumina.

Another important aspect is the selection of organic substituents as donor and acceptor groups. Therefore, the Hammett parameters that describe the donating and accepting capability of the functional groups are considered. Since the donor and acceptor groups are substituted at the para-position to the triazole ring, the Hammett $\sigma_p$ parameter (para-substituted) is considered. A positive value of $\sigma_p$ indicates accepting character, whereas a negative value indicates donating character. The $\sigma_p$ values of some known donor, acceptor groups are listed in Table 4.1.

Table 4.1 - Hammett ($\sigma_p$) parameters for common organic donor and acceptor groups

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\sigma_p$</th>
<th>Acceptor</th>
<th>$\sigma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3$-</td>
<td>-0.17</td>
<td>$-F$</td>
<td>0.06</td>
</tr>
<tr>
<td>$t$-$\text{C}_4\text{H}_9$-</td>
<td>-0.20</td>
<td>$-\text{CHO}$</td>
<td>0.42</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}$-</td>
<td>-0.27</td>
<td>$-\text{CN}$</td>
<td>0.66</td>
</tr>
<tr>
<td>$\text{HO}$-</td>
<td>-0.37</td>
<td>$-\text{NO}_2$</td>
<td>0.78</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{N}$-</td>
<td>-0.61</td>
<td>$-\text{CH}=\text{C}(\text{CN})_2$</td>
<td>0.84</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_2\text{N}$-</td>
<td>-0.91</td>
<td>$-\text{C}(\text{CN})_3$</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-\text{C}(\text{CN})=\text{C}(\text{CN})_2$</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Tertiary nitrogen based donor groups exhibit the highest donating capability in the series. The donating ability of tertiary amino groups also varies depending on the $R$ group attached to amino-nitrogen. Due to synthetic efficiency, *dimethyamino* (-$\text{C}(\text{NH}_3)_2$) group was selected as the donor group in this study. Poly-nitrile based organic substituents are important in considering the acceptor groups. In this study *dicyanovinyl* (-$\text{CHC}(\text{CN})_2$) group was used as the acceptor due to the ease of synthesis via Knövenagel condensation. Also an *aldehyde* (-$\text{CHO}$) based ligand was explored to study intermediate accepting nature of the ligands. As a standard to study the effect of the functional groups, and the impact of them on the final complexes, unsubstituted –$H$ based ligand was also included.
4.2 Reaction mechanisms and compound characterisation

4.2.1 Synthesis of bromo derivatives

4.2.1.1 Synthesis of 3-(N,N-Dimethylamino)pyridine (3pyaz(1,2,3) – N(CH$_3$)$_2$ – s1)

Synthesis of 3pyaz(1,2,3) – N(CH$_3$)$_2$ – s1 follows Eschwieler–Clarke reaction mechanism,\textsuperscript{173,174} which involves reductive amination. This is important in the preparation of tertiary amines via methylation of primary or secondary amines, in the presence of excess formaldehyde and formic acid. The mechanism of the reaction is shown below (Figure 4.1).

![Mechanism of Eschwieler-Clarke reaction](image)

i. The methylation initiates with an imine formation via a nucleophilic attack on the carbonyl carbon of the formaldehyde, by the nitrogen of the primary amine.

ii. Negatively charged oxygen accepts a proton from formic acid and forms an imine, releasing a water molecule.

iii. The imine is then reduced to a secondary amine by a hydride ion attack from the formate ion, which oxidises to CO$_2$.

iv. The same set of steps is taking place again to methylate the secondary amine into a tertiary amine.

The reaction will not continue to form quaternary ammonium salt since the tertiary amine is not capable of forming an imine. Therefore, addition of excess formaldehyde or formic acid will not lead to undesired side products.

3-Aminopyridine was used as the primary amine source in this study. After refluxing, the pH of the system was increased to deprotonate the nitrogen in the pyridine ring to make it possible to extract into CHCl$_3$. The crude product was a brown waxy substance, which
yielded light yellow, clear oil upon vacuum distillation (yield – 67%, 21.9234 g). TLC analysis of the purified product with hexane: ethylacetate 3:2 mobile phase indicated an \( R_f \) value of 0.49, suggesting a decrease in the polarity compared to the reactant, with the introduction of methyl groups (reactant - \( R_f = 0.20 \)). GC/MS spectrum exhibited a molecular ion peak at m/z 122.1, confirming the formation of the product (Figure 4.2 – a). The reactant contains a primary amine group, which produce two IR absorption bands due to symmetric and asymmetric bond stretching of N-H groups, around 3300 - 3500 cm\(^{-1}\) region (Figure 4.2– b), sometimes with a shoulder peak due to N-H stretching overtone. N-H bending peak is observed around 1650 – 1580 cm\(^{-1}\). Since the product is a tertiary amine, it will not produce the peaks mentioned above. As expected in the IR spectrum of the product ((Figure 4.2– b (−)) the peaks observed for the reactant (Figure 4.2 – b (---)) are absent. The product also exhibits a novel peak at 2885 cm\(^{-1}\) which corresponds to C-H stretching of tertiary amine – methyl groups.

In \(^1\)H NMR spectrum (Figure 4.3 – a) of the product; four aromatic protons of the pyridyl ring are observed in the region 6.5 – 7.8 ppm with the expected splitting patterns. The singlet at 2.46 ppm resembles the protons in the dimethyl amino group (\(^1\)H NMR in chloroform-d (300 MHz): \( \delta = 2.76 \) (s, 6H, M04), 6.77 (ddd, 3H, J=8.5, 3.1, 1.4 Hz, M05), 6.93 (ddd, 5H, J=8.5, 4.5, 0.6 Hz, M03), 7.82 (dd, 1H, J=5.1, 0.2 Hz, M02), 7.98 (dd, 8H, J=3.4, 0.2 Hz, M01)). Five aromatic carbons are observed in the region 118 – 147 ppm in the \(^{13}\)C NMR spectrum (Figure 4.3 – b). The dimethyl amino group carbons are visible at 39.97 ppm (\(^{13}\)C NMR in chloroform-d (75 MHz): \( \delta = 39.97(9, 8), 118.52(4), 123.36(5), 135.05(2), 137.74(6), 146.16(3) \)).

![Figure 4.2 – (a) Low resolution mass spectrum (b) IR spectrum of 3-(N,N-Dimethylamino)pyridine](image-url)
4.2.1.2 Synthesis of 3-(N,N-Dimethylamino)-6-bromopyridine (3pyaz(1,2,3)–N(CH3)2 – s2)

The bromination of 3-(N,N-dimethylamino)pyridine to get 3-(N,N-Dimethylamino)-6-bromopyridine from NBS follows a radical substitution mechanism\textsuperscript{175} as shown in the Figure 4.4. Upon irradiation to light, NBS forms bromine and succinimide radicals, the step which is known as the initiation. The succinimide radical cleaves the C-H bond of the alkyl/aryl compound homolytically, to generate succinimide and alkyl/ aryl radical. The alkyl / aryl radical then react with the bromine radical to give the brominated product.
In this particular reaction system, 3pyaz(1,2,3) – N(CH$_3$)$_2$ – s1 is brominated using NBS. NBS is preferred over molecular bromine due to high toxicity and high vapour pressure of bromine, which make it hazardous and cumbersome to handle. In contrast, NBS is easy to handle and cost effective. Succinimide forms as the by-product of the reaction that can easily be removed from the system. The addition of NBS was carried out very slowly at a very low temperature to prevent over bromination of the pyridine ring. The resulting mixture was washed with aqueous NaOH, to extract the succinimide from the system as a salt.

The purified product via column chromatography and recrystallisation produced white, flake like crystals in 68% yield (5.6135 g). $R_f$ value of the product was 0.64 with 3:2 hexane: ethylacetate mobile phase indicating a further decrease in polarity compared to the reactant ($R_f$ 0.49). The molecular weight of the product was calculated to be 201.06 g mol$^{-1}$. The mass spectrum of the product (Figure 4.5 – a) exhibits two close lying molecular ion peaks at m/z 199.9 and 201.9. This is characteristic to mass spectroscopy of brominated

![Figure 4.4 - Mechanism of bromine substitution via a radical mechanism](image)

In this particular reaction system, 3pyaz(1,2,3) – N(CH$_3$)$_2$ – s1 is brominated using NBS. NBS is preferred over molecular bromine due to high toxicity and high vapour pressure of bromine, which make it hazardous and cumbersome to handle. In contrast, NBS is easy to handle and cost effective. Succinimide forms as the by-product of the reaction that can easily be removed from the system. The addition of NBS was carried out very slowly at a very low temperature to prevent over bromination of the pyridine ring. The resulting mixture was washed with aqueous NaOH, to extract the succinimide from the system as a salt.

The purified product via column chromatography and recrystallisation produced white, flake like crystals in 68% yield (5.6135 g). $R_f$ value of the product was 0.64 with 3:2 hexane: ethylacetate mobile phase indicating a further decrease in polarity compared to the reactant ($R_f$ 0.49). The molecular weight of the product was calculated to be 201.06 g mol$^{-1}$. The mass spectrum of the product (Figure 4.5 – a) exhibits two close lying molecular ion peaks at m/z 199.9 and 201.9. This is characteristic to mass spectroscopy of brominated

![Figure 4.5 - (a) Low resolution mass spectrum (b) IR spectrum of 3-(N,N-Dimethylamino)-6-bromopyridine](image)
Since bromine consists of two isotopes, $^{79}$Br and $^{81}$Br, with a natural abundance of approximately 1:1 ratio, bromine containing compounds generate two peaks with 2 m/z units apart from each other as observed in this spectrum. In the IR spectrum (Figure 4.5 – b) of the product, a notable change cannot be expected since the introduction of bromine will not produce significant peaks in the functional group region.

The $^1$H NMR spectrum (Figure 4.6 – a) indicates the disappearance of one aromatic multiplet observed in the reactant due to the substitution by bromine. The aromatic peaks are comparatively downfield as bromine withdraws electron density from the pyridyl ring. The
spectrum indicates nine protons; three in the region 6.9 – 7.9 ppm and another singlet at 2.96 ppm resembling the six dimethyl amino protons (1H NMR in chloroform-d (300 MHz): δ = 2.98 (s, 6H, M04), 6.90 (dd, 1H, J=8.8, 3.4 Hz, M03), 7.27 (dd, 1H, J=8.8, 0.5 Hz, M02), 7.86 (d, 1H, J=3.3 Hz, M01)). In the 13C NMR spectrum (Figure 4.6 – b), peaks in the region 122 – 146 ppm correspond to pyridyl carbons whereas the peak at 40.30 ppm resembles dimethylamino group carbons (13C NMR in chloroform-d (75 MHz): δ = 40.30(9, 10), 122.04(4), 127.50(3), 127.65(2), 134.59(6), 145.80(5)).

4.2.1.3 Synthesis of 6-bromopyridine-3-carbaldehyde (3pyaz(1,2,3) – CHO – s1)

The synthesis of 6-bromopyridine-3-carbaldehyde was carried out based on Li – halogen exchange reaction mechanism,176 followed by an electrophilic attack on the organo-lithium bond to furnish the desired product.

The first step of the process is a nucleophilic attack on the bromine atom by the n-butyl group, leaving a Li+ ion in the system (A). The complex formed between the organo-bromide and n-butyl group is referred to as an “-ate complex” (B).

i. The “-ate complex” decomposes on the C-Br bond by attacking the Li+ ion. The attack is preferred on the bond, which would form the most stable organo-lithium bond. In this case, the preferred bond is aryl-bromide bond, since more electronegative sp2 carbons on the aryl ring allow the delocalisation of the positive charge on the Li+ ion by imparting more stability.

ii. Finally, the organo-lithium complex undergoes an electrophilic attack (C), to give the desired product, D. In carbaldehyde formation reactions, the final electrophile is a carbonyl source.

Figure 4.7 – Mechanism of lithium-halogen exchange followed by electrophilic substitution
In this reaction 2,5-dibromopyridine was subjected to carbaldehyde formation. DMF was used as the final electrophile, which acts as the carbonyl source. Anhydrous conditions were important since \( n \)-BuLi reacts violently with water forming \( n \)-BuH and LiOH. A nitrogenous environment was employed as \( n \)-BuLi reacts with oxygen to give \( n \)-BuOLi. The temperature was maintained well below -78 °C as the reaction is highly exothermic and \( n \)-BuLi decomposes at high temperatures.

The purified product via column chromatography appeared as yellow-white, needle shaped crystals giving a yield of 55% (2.186 g). The product exhibited an \( R_f \) value of 0.66 with 3:2 hexane: ethylacetate mobile phase, indicating increased polarity of the product compared to the reactant (reactant - \( R_f \) = 0.89). The melting point was 94 – 96 °C. The mass spectrum (Figure 4.8 - a) of the product shows two closely aligned molecular ion peaks at \( m/z \) 184.9 and 186.9 with two \( m/z \) units apart, which is characteristic to brominated compounds. Two closely aligned baseline peaks were observed at 155.9 and 157.9. These are 29 \( m/z \) units less than the molecular ion peaks which are analogous to loss of –CHO group.

Substitution with an aldehyde group is expected to result in a new IR peak corresponding to C=O bond stretching, which was observed at 1681 cm\(^{-1}\) (Figure 4.8 - b). C=O stretching frequency is less in aromatic aldehydes compared to their aliphatic counterparts, as \( \alpha - \beta \) unsaturation in aromatic aldehydes results in lowering of C=O stretching frequency.

In the \(^1\)H NMR spectrum (Figure 4.9 - a) of the product, three peaks were observed in the aromatic region, 7.7 – 8.9 ppm, corresponding to the three aromatic protons in the pyridyl ring. The singlet appearing at 10.11 ppm corresponds to the proton of the aldehyde group (\(^1\)H NMR in dichloromethane-\(d_2\) (300 MHz): \( \delta = 7.72 \) (dd, 1H, J=8.3, 0.5 Hz, M04), 8.05 (dd, 1H, J=8.2, 2.5 Hz, M03), 8.84 (dd, 1H, J=2.1, 0.5 Hz, M02), 10.12 (s, 1H, M01)). The

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![Figure 4.8 – (a) Low resolution mass spectrum (b) IR spectrum of 6-bromopyridine-3-carbaldehyde](image)
carbonyl carbon is observed at 189.87 ppm in the $^{13}$C NMR spectrum, while five pyridyl carbons were observed in the region 129 – 153 ppm ($^{13}$C NMR in dichloromethane-$d_2$ (75 MHz): $\delta = 129.10(3), 130.86(5), 137.79(4), 148.16(2), 152.48(6), 189.87(8)$) (Figure 4.9 – b).

4.2.2 Sonogashira carbon – carbon coupling

Sonogashira carbon – carbon coupling reaction has become one of the most widely explored reactions in forming a carbon – carbon bond between aryl or vinyl halides or triflates and terminal alkynes. The reaction was first reported in 1975 by Kenkichi
Sonogashira, Yasuo Tohda and Nobue Hagihara.\textsuperscript{178} This was an extension of Heck\textsuperscript{179}, Deik\textsuperscript{179} and Cassar\textsuperscript{180} reactions where a palladium based catalyst was employed to promote the reaction. The modification to the previous protocols was introduced in the Sonogashira coupling by using copper(I) iodide as a co-catalyst, which enhanced the performance of the reaction greatly while allowing to use less-demanding reaction conditions.

While the mechanism of the Sonogashira coupling is still not unequivocally proven,\textsuperscript{177} plausible mechanistic studies suggests that the reaction proceeds through two catalytic cycles \textit{viz}, palladium cycle and copper cycle (Figure 4.10).

**Palladium cycle**

The palladium cycle involves intermediates $A$, $B$, $C$ and $D$ as shown above.

i. First step of the palladium cycle is usually, the fast oxidative addition of aryl or vinyl halides to Pd(0) complex, $A$, to generate square-planar Pd(II) intermediate, $B$. The active palladium catalyst is thought to be involved with 14-electron Pd(0)L\textsubscript{2} species,
formed *in-situ* by reduction of different Pd(II) complexes, such as Pd(PPh$_3$)$_2$Cl$_2$ and Pd(OAc)$_2$. It is known that n-electron donors, such as phosphanes, ethers, and amines, used as ligands and solvents, can reduce Pd(II) species. The efficiency of this step is also governed by the nature of the aryl/vinyl halide involved.

ii. $B$ reacts with copper acetylide from the copper cycle via transmetallation to yield $C$ in which the $R_1$ and the alkyne ($R_2$) is *trans* oriented to each other. This is believed to be the rate-limiting step in the reaction.

iii. Third step is the *cis-trans* isomerisation to give *cis* oriented $R_1$ and alkyne groups which facilitates the elimination.

iv. The final step in the process is the regeneration of the catalyst via reductive elimination.

**Copper cycle**

The copper cycle involves steps, $E$, $F$ and $G$.

i. Copper(I) halides form *pi*-alkyne complex ($E$), with terminal alkynes via bonding and back bonding interactions. This enhances the acidity of the terminal alkyne leading to the formation of copper acetylide, ($F$). The base is important in the removal of proton from the terminal alkyne.

ii. The copper acetylide participates in the transmetallation with $B$ (from palladium cycle), regenerating Cu(I) co-catalyst ($G$).

Another important experimental consideration in the Sonogashira coupling is the use of air and moisture free conditions. It is known that copper acetylides promotes the formation of homo-coupled product of terminal alkynes as a by-product via Glaser-Hay coupling in the presence of oxidative agents or air.

During this study Pd(PPh$_3$)$_2$Cl$_2$ was used as the Pd(II) source (pre-catalyst) and CuI was used as the co-catalyst. A mixture of triethylamine and tetrahydrofuran was employed as the reaction medium. Triethylamine also acts as the base during the reaction. The reaction was

![Figure 4.11 - Sonogashira coupling of 2-bromopyridyl derivatives](image-url)
carried out between 2-bromopyridyl derivatives and trimethylsilylacetylene (terminal alkyne).

Fresh solvents were used by drying over Na/ benzophenone to remove moisture and oxygen. The system was maintained under nitrogenous atmosphere to maintain oxygen free conditions. Freeze-pump-thaw technique was performed to remove any further traces of oxygen present in the system. A pressure tube was used as the reaction vessel, since it allows maintaining high pressures and temperatures, while maintaining air free conditions more conveniently than normal refluxing apparatus.

The resulting mixture from the reaction was filtered through celite to remove any solid residues. The filtrate was washed with NH₄Cl to remove remaining copper co-catalyst by complexation. Further washing with water was carried out to remove traces of polar impurities.

4.2.2.1 Structural characterisation of 3pyaz(1,2,3)–N(CH₃)₂ – s1

The purified product was yellow, crystalline flakes with a yield of 68 % (3.343 g). TLC analysis with 3:2 – hexane: ethylacetate mobile phase gave an Rf of 0.54, which indicates an increase of polarity of the product compared to bromo-substituted reactant (3pyaz(1,2,3) – N(CH₃)₂ – s2). A sharp melting point of 72 °C was observed. GC/MS mass spectrum (Figure 4.12 – a) exhibits a molecular ion peak at m/z 218.1, which corresponds to the expected molecular weight of the product. In the spectrum a base line peak is observed at 203.1, corresponding to loss of a methyl group from the TMS group. An IR spectrum corresponding to the product is expected to obtain a peak around 2100 – 2260 cm⁻¹ region for the internal alkyne. The peak at 2143 cm⁻¹ is indicative of the C≡C stretching of the internal alkyne as expected (Figure 4.12 – b).

![Figure 4.12 – (a) Low resolution mass spectrum (b) IR spectrum of 3pyaz(1,2,3) – N(CH₃)₂](image)

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In the $^1$H NMR spectrum (Figure 4.13 – a), the singlet peak appearing at 0.20 ppm corresponds to the protons of the trimethylsilyl group, which integrates to nine protons. Six protons appear at 3.05 ppm which relate to the protons in the dimethylamino group. The aromatic protons appeared in the region $6.8 - 8.0$ ppm that integrates to three protons. The spectrum altogether shows presence of 18 protons as expected. $^1$H NMR in Chloroform-$d$ (300 MHz); $\delta = 0.28$ (s, 9H, M05), 3.05 (s, 6H, M04), 6.93 (dd, 1H, J=8.8, 3.1 Hz, M03), 7.36
84 (dd, 1H, J=8.8, 0.7 Hz, M02), 8.08 (dd, 1H, J=2.7, 0.4 Hz, M01) ppm. The \(^{13}\)C NMR spectrum (Figure 4.13 - b) shows a peak at 0.1 ppm corresponding to the methyl groups in the trimethylsilyl moiety, whereas the peak at 40.00 ppm resembles the methyl groups in the dimethylamino portion. Two alkyne carbons are represented by the peaks at 92.66 and 104.32 ppm. Peaks corresponding to five carbons in the pyridyl ring are visible in the region 118 – 146 ppm (Chloroform-\textit{d} (75 MHz): \(\delta = 0.10(10, 13, 14), 40.00(12, 15), 92.66(8), 104.32(7), 118.11(4), 127.82(3), 129.68(2), 134.37(6), 145.39(5))

4.2.2.2 Structural characterisation of 3pyaz(1,2,3) – s1

The final product was a brown oil with a yield of 73 % (2.455 g). TLC exhibited an \(R_f\) of 0.69 with 4:1 – hexane: ethylacetate mobile phase, indicating a decrease of polarity of the product compared to the reactant. GC/MS mass spectrum (Figure 4.14 – a) exhibits two significant peaks; one being the molecular ion peak at m/z 175.0, and the next being, the base line peak observed at 160.0 corresponding to the fragmentation of a methyl group from the TMS group. The IR spectrum of the product generates a peak at 2163 cm\(^{-1}\) corresponding to the C≡C stretching of the internal alkyne as expected (Figure 4.14 – b).

The final product was a brown oil with a yield of 73 % (2.455 g). TLC exhibited an \(R_f\) of 0.69 with 4:1 – hexane: ethylacetate mobile phase, indicating a decrease of polarity of the product compared to the reactant. GC/MS mass spectrum (Figure 4.14 – a) exhibits two significant peaks; one being the molecular ion peak at m/z 175.0, and the next being, the base line peak observed at 160.0 corresponding to the fragmentation of a methyl group from the TMS group. The IR spectrum of the product generates a peak at 2163 cm\(^{-1}\) corresponding to the C≡C stretching of the internal alkyne as expected (Figure 4.14 – b).
In the $^1$H NMR spectrum (Figure 4.15 – a), singlet appearing at 0.28 ppm corresponds to the protons of the trimethylsilyl group, which integrates into nine protons. The four aromatic protons appeared in the region 7.2 – 8.6 ppm exhibiting the expected splitting patterns ($^1$H NMR in Chloroform-d (300 MHz): $\delta = 0.28$ (s, 9H, M05), 7.24 (ddd, 1H, J=7.6, 4.9, 1.2 Hz, M04), 7.47 (dt, 1H, J=7.8, 1.1 Hz, M03), 7.66 (td, 1H, J=7.7, 1.8 Hz, M02), 8.58 (ddd, 1H, J=4.9, 2.5, 0.9 Hz, M01) ppm). The $^{13}$C NMR spectrum (Figure 4.15 - b) shows a peak at 0.13 ppm that corresponds to the methyl groups in the trimethylsilyl moiety whereas the peaks at 95.26 and 103.64 ppm resemble two carbons of the alkyne. Peaks corresponding
to five carbons in the pyridyl ring are visible in the region 123 – 150 ppm ($^{13}$C NMR in Chloroform-d (75 MHz): $\delta = 0.13(10, 11, 12), 95.26(8), 103.64(7), 123.21(5), 127.47(3), 136.38(4), 143.10(2), 149.95(6))$).

4.2.2.3 Structural characterisation of $3$pyaz(1,2,3) – CHO – s2

The purified product appeared as white, needle shaped crystals with a yield of 70 % (1.530 g). TLC analysis gave an $R_f$ value of 0.66 (3:2 – hexane: ethylacetate mobile phase). The melting point of the product was found to be 80 – 82 °C. The molecular ion peak is observed at m/z 203.0, whereas the base line peak corresponding to loss of a methyl group from the TMS moiety is observed at 188.0 (Figure 4.16 – a). The IR spectrum exhibits a peak at 2163 cm$^{-1}$ corresponding to the C≡C stretching of the internal alkyne, and the carbonyl peak at 1682 cm$^{-1}$ (Figure 4.16 – b).

![Figure 4.16](image)

In the $^1$H NMR spectrum (Figure 4.17 - a), the singlet appearing at 0.34 ppm corresponds to the protons of the trimethylsilyl group which integrates into nine protons. The three pyridyl protons appeared in the region 7.6 –9.1 ppm.$^{13}$C NMR spectrum shows a peak at 0.64 ppm that resembles the methyl groups in the trimethylsilyl moiety and the two peaks at 99.28 and 103.25 ppm correspond to the alkyne carbons. Peaks corresponding to the five carbons in the pyridyl ring are visible in the region 127 – 153 ppm. The carbonyl carbon is seen at 190.19 ppm ($^{13}$C NMR in Dichloromethane-d2 (75 MHz): $\delta = -0.64(10, 13, 14), 99.28(8), 103.25(7), 127.68(3), 130.24(5), 135.98(4), 147.79(2), 152.09(6), 190.19(11))$. 

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4.2.3 Desilylation of the TMS group

The de-protection of TMS group was carried out by base hydrolysis with KOH in methanolic medium; methanol in basic medium forms methoxide ions, which promotes the deprotection process (Figure 4.18). The methoxide ion carries out a nucleophilic attack on silyl group of the protected alkyne, generating TMS-methoxide and the terminal alkyne by subsequent hydrolysis. Base is acting as the catalyst during the process. The reaction was
carried out at R.T., since heating of KOH in methanol forms glycerol as a by-product which makes it impossible to recover the product.

4.2.3.1 Structural characterisation of 3pyaz(1,2,3)–N(CH₃)₂–s4

The purified product was off-white crystals with a yield of 97% (0.976 g). TLC analysis produced an $R_f$ value of 0.20 (mobile phase – 3:2 hexane: ethylacetate), indicating further increase of polarity due to the removal of non-polar TMS group. Melting point range was in the region 94 – 96 °C. The molecular ion peak was observed at m/z 146.1, which corresponds to the expected molecular weight of the product (Figure 4.19 – a). The deprotection of TMS group is expected to generate a novel peak for C-H stretching of the terminal alkyne around 3300 cm⁻¹ in the IR spectrum. The peaks at 2084 and 3201 cm⁻¹ indicate the C≡C stretching and C-H stretching of the terminal alkyne respectively (Figure 4.19 – b). Aromatic conjugation is known to lower the IR frequencies of functional groups. Therefore, the aromatic alkyne generates a lower C-H stretching frequency than expected for a non-conjugated alkyne.

Five peaks are observed in the ¹H NMR spectrum (Figure 4.20 – a), integrating to 15 protons that is compatible with the product. New singlet appearing at 3.15 ppm corresponds
to the proton in the terminal alkyne ($^1$H NMR in Chloroform-d (300 MHz): $\delta = 3.04$ (s, 6H, M05), 3.07 (s, 1H, M04), 6.89 (dd, 1H, J=8.8, 3.1 Hz, M03), 7.35 (dd, 1H, J=8.8, 0.4 Hz, M02), 8.10 (d, 1H, J=3.1 Hz, M01) ppm). $^{13}$C NMR spectrum (Figure 4.20 – b) shows two peaks corresponding to the alkyne at 75.06 and 83.66 ppm. Two methyl groups of the dimethyl amino group appear at 39.98 ppm, whereas the aromatic carbons appear in the region 117 – 146 ppm. $^{13}$C NMR in Chloroform-d (75 MHz): $\delta = 39.98$(10, 11), 75.06(8), 83.66(7), 117.84(4), 127.81(3), 129.20(2), 134.93(6), 145.59(5).
4.2.3.2 Structural characterisation of 3pyaz(1,2,3) – s2

The final product was a yellow oil with a yield of 97% (1.139 g). TLC exhibited an $R_f$ of 0.57 with 3:2 – hexane: ethylacetate mobile phase. GC/MS mass spectrum (Figure 4.21 - a) shows the molecular ion peak at 103.0 representing the terminal alkyne. In the IR spectrum (Figure 4.21 – b), C≡C stretching and C-H alkyne stretches are represented by the peaks at 2114 and 3286 cm⁻¹.

![Figure 4.21](image)

**Figure 4.21** (a) Low resolution mass spectrum (b) IR spectrum of 3pyaz(1,2,3) – s2

In the $^1$H NMR spectrum (Figure 4.22 – a), the singlet at 3.25 ppm corresponds to the proton of the terminal alkyne. Five protons of the pyridyl ring are observed in the region 7.3 – 8.7 ppm ($^1$H NMR in Dichloromethane-d2 (300 MHz): $\delta = 3.25$ (s, 1H, M05), 7.31 (ddd, 1H, J=7.6, 4.9, 1.2 Hz, M04), 7.52 (dt, 1H, J=7.8, 1.1 Hz, M03), 7.71 (td, 1H, J=7.7, 1.8 Hz,
M02), 8.60 (ddd, 1H, J=4.9, 2.3, 0.9 Hz, M01) ppm). Two peaks at 76.83 and 83.00 ppm in the $^{13}$C NMR spectrum correspond to the two alkyne carbons. All the pyridyl carbons appear in 123 – 151 ppm region. ($^{13}$C NMR in Dichloromethane-d2 (75 MHz): $\delta$ = 76.83(8), 83.00(7), 123.64(5), 127.69(3), 136.29(4), 142.41(2), 150.22(6)).

4.2.3.3 Structural characterisation of 3pyaz(1,2,3) – CHO – s3

The purified product appeared as white, needle shaped crystals with a yield of 98% (0.950 g). TLC analysis gave an $R_f$ value of 0.43 (3:2 – hexane: ethylacetate mobile phase). The melting point of the product was 128 – 130 °C. The molecular ion peak is observed at m/z 203.0, whereas the base line peak corresponding to loss of a methyl group from the TMS moiety is observed at 188.0 (Figure 4.23 – a). The IR spectrum exhibits peaks at 2098 and
3194 cm⁻¹ corresponding to the C≡C stretching and C-H stretching of the terminal alkyne along with the carbonyl peak at 1682 cm⁻¹ (Figure 4.23 – b).

In the ¹H NMR spectrum (Figure 4.24 - a), the singlet appearing at 3.47 ppm corresponds to the terminal alkyne proton. Three protons of the pyridine ring appear in the region 7.6 – 9.1 ppm. The aldehyde proton is represented by the singlet at 10.15 ppm (¹H NMR in Dichloromethane-d₂ (300 MHz): δ = 3.47 (s, 1H, M05), 7.69 (dt, 1H, J=8.0, 0.7 Hz, M04), 8.18 (dd, 1H, J=8.1, 2.1 Hz, M03), 9.06 (dd, 1H, J=2.0, 0.8 Hz, M02), 10.15 (s, 1H, M05).

Figure 4.24 – (a) ¹H NMR spectrum (b) ¹³C NMR spectrum of 3pyaz(1,2,3) – CHO – s²
M01) ppm). The aldehyde proton is represented by the singlet at 10.15 ppm (1H NMR in Dichloromethane-d2 (300 MHz): δ = 3.47 (s, 1H, M05), 7.69 (dt, 1H, J=8.0, 0.7 Hz, M04), 8.18 (dd, 1H, J=8.1, 2.1 Hz, M03), 9.06 (dd, 1H, J=2.0, 0.8 Hz, M02), 10.15 (s, 1H, M01) ppm). Two alkyne carbons appear at 80.47 and 82.38 ppm in the 13C NMR spectrum (Figure 4.24 – b) Peaks corresponding to five carbons in the pyridyl ring are visible in the region 127 – 153 ppm. The carbonyl carbon is seen at 190.17 ppm (13C NMR in Dichloromethane-d2 (75 MHz): δ = 80.47(8), 82.38(7), 127.96(3), 130.62(5), 136.14(4), 147.09(2), 152.05(6), 190.17(9)).

4.2.4 1,3–Dipolar cycloaddition reaction

The triazole formation is carried out by a “click reaction” between 2-Ethynylpyridine and azidomethylpivalate via copper(I) catalysed azide alkyne dipolar cycloaddition reaction mechanism (CuAAC) (Figure 4.25). This method was chosen due its high efficiency, selectivity, cost-effectiveness and less demanding reaction conditions.

i. Studies have shown the reaction is second order with respect to copper. Therefore, it is suggested that the mechanism involves two copper ions, which exist in dimer form, A.

![Figure 4.25 – Suggested mechanism of CuAAC reaction](image-url)
ii. Cu(I) dimer forms a pi-alkyne complex with the terminal alkyne giving complex B.

iii. In the presence of a base, the proton in the terminal alkyne, being the most acidic is deprotonated first to give a copper acetylide intermediate, C.

iv. The copper acetylide interacts with the azide forming complex D. One Cu(I) ion is bonded to the acetylide while the other Cu(I) ion serves to activate the azide. The copper ion interacts with the terminal nitrogen of the azide. Importantly, the azide and the acetylide are not coordinated to the same copper ion.

v. The third nitrogen on the azide attaches to the second carbon of the alkyne initiating the cyclisation producing complex E.

vi. The complex E, rearranges to give copper substituted 1,2,3-triazole forming compound F. This followed by protonation generates the final triazole product, G, while regenerating the Cu(I) catalyst.

When Cu(I) forms a pi-alkyne complex, the acidity of the terminal alkyne proton is dramatically increased. Thus, under certain conditions, the reaction may be carried out even in the absence of a base.

In this reaction, the terminal alkyne, 2-ethynylpyridine derivatives were reacted with azidomethylpivalate, which was taken as the azide source for triazole formation due to its simple purification, ability for deprotection easily under basic conditions, and good thermal stability up to around 80 °C. The Cu(I) catalyst was generated in situ during the reaction, by reduction of CuSO₄·5H₂O / Cu(II) from sodium ascorbate, which acts as a reducing agent. This eliminates the requirement of oxygen free reaction conditions. 1:1 mixture of H₂O to t-butanol was used as the solvent, while t-butanol acts as a base as well. The employment of a base allowed the reaction to take place at R.T. The resulting reaction mixture was washed with aqueous NH₃ to remove Cu(I) catalyst from the medium, whereas, washings with brine and water helped to remove polar impurities.

4.2.4.1 Structural characterisation of 3pyaz(1,2,3)−N(CH₃)₂−s5

The purified product was white, needle shaped crystals with a yield of 90% (1.683 g). TLC analysis produced an Rf value of 0.40 (mobile phase −1:1 hexane: ethylacetate. Melting point of the compound was over the range 102–104 °C. The molecular ion peak was observed at m/z 303.1, which corresponds to the expected molecular weight of the product (Figure 4.26 – a). The protected triazole contains an ester group in the methyl pivalate moiety, which generates two IR peaks at 1743 and 1126 cm⁻¹ corresponding to C=O and C-O bond stretchings respectively (Figure 4.26 – b). The absence of the C≡C and C-H stretching of the
terminal alkyne (reactant), further confirms the formation of the product.

In the $^1$H NMR spectrum (Figure 4.27 – a), the peak appeared at 1.22 ppm (singlet), corresponds to the nine protons in the t-butyl group. Singlet at 3.06 ppm represents the six protons in the dimethyl amino group. Two hydrogens on -CH$_2$ of the methylpivalate group are represented by the singlet at 6.30 ppm. Three protons in the pyridyl ring and one proton in the triazole ring appeared in the region 6.3 – 8.4 ppm ($^1$H NMR in chloroform-d (300 MHz): $\delta$ = 1.22 (s, 9H, M08), 3.05 - 3.07 (m, 6H, M07), 6.31 (s, 2H, M05), 7.13 (dd, 1H, J=8.7, 3.0 Hz, M04), 8.06 (dd, 1H, J=8.9, 0.3 Hz, M03), 8.12 (d, 1H, J=3.1 Hz, M02), 8.35 (s, 1H, M01) ppm). $^{13}$C NMR spectrum (Figure 4.27 – b) shows a peak at 27.01 ppm corresponding to the methyl groups in the t-butyl group. Peaks at 38.96 and 40.22 ppm resemble the tertiary
carbon in the t-butyl group and the methyl groups in dimethylamino group respectively. The CH₂ carbon in the methylpivalate group appears at 70.11 ppm. Seven aromatic protons are observed in 119 – 149 ppm region. Carbonyl carbon in the methylpivalate ester group appears at 177.62 ppm (¹³C NMR in chloroform-d (75 MHz): δ = 27.01(17, 20, 21), 38.96(16), 40.22(19, 22), 70.11(6), 119.74(5), 121.05(15), 121.78(14), 133.50(12), 137.54(13), 145.98(4), 148.90 (10), 177.62(8)).

4.2.4.2 Structural characterisation of 3pyaz(1,2,3) – s3

Figure 4.28 – (a) Low resolution mass spectrum (b) IR spectrum of 3pyaz(1,2,3) – s3
The purified product was white, needle shaped crystals with 80% yield (2.023 g). TLC analysis produced an $R_f$ value of 0.42 (mobile phase – 3:2 hexane: ethylacetate). Melting point of the compound was over the range 119 – 121 °C. The molecular ion peak was observed at m/z 260.1 which corresponds to the expected molecular weight of the product (Figure 4.28 – a). The baseline peak at m/z 57 appears to arise from the t-butyl fragment. IR peaks at 1728 and 1142 cm$^{-1}$ correspond to C=O and C-O bond stretchings respectively (Figure 4.28 - b).

![NMR spectra](image_url)

Figure 4.29 – (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pyaz(1,2,3) – s3
In the $^1$H NMR spectrum (Figure 4.29 – a), the peak was seen at 1.24 ppm corresponds to the protons in the $t$-butyl group. Two hydrogens on -CH$_2$ of the methylpivalate group appeared at 6.34 ppm. Four protons in the pyridyl ring and one proton in the triazole ring appeared in the region 7.3 – 8.7 ppm ($^1$H NMR in dichloromethane-$d_2$ (300 MHz): d = 1.24 (s, 9H, M05), 6.34 (s, 2H, M06), 7.29 (ddd, 1H, J=7.6, 4.9, 1.2 Hz, M04), 7.83 (td, 1H, J=7.8, 1.8 Hz, M03), 8.18 (dt, 1H, J=7.9, 1.0 Hz, M02), 8.42 (s, 1H, M07), 8.62 (ddd, 1H, J=4.8, 1.8, 0.9 Hz, M01) ppm). $^{13}$C NMR spectrum (Figure 4.29 – b) shows a peak at 26.72 ppm corresponding to the methyl groups in the $t$-butyl group. The peak at 38.84 ppm resembles the tertiary carbon in the $t$-butyl group. The -CH$_2$ carbon in the methylpivalate group appears at 70.13 ppm. Seven aromatic carbons were observed in 120 – 150 ppm region. The carbonyl carbon in the methylpivalate ester group appeared at 177.60 ppm. ($^{13}$C NMR in dichloromethane-$d_2$ (75 MHz): d = 26.72(17, 18, 19), 38.84(16), 70.13(6), 120.19(15), 123.19(5), 123.51(13), 136.95(14), 149.05(12), 149.77(4), 150.11(10), 177.60(8)).

4.2.4.3 Structural characterisation of 3pyaz(1,2,3) – CHO – s4

The purified product was yellow needle shaped crystals with 82% yield (2.023 g). TLC analysis gave an $R_f$ value of 0.31 (3:2 – hexane: ethylacetate mobile phase). The melting point of the product was 121 – 123 °C. The molecular ion peak is observed at m/z 288.0, which correspond to the molecular weight of the product (Figure 4.30 – a). IR peak at 1142 cm$^{-1}$ correspond to C-O stretching of the ester group. It is expected to observe two peaks around 1700 cm$^{-1}$ for the two carbonyl groups, but only one peak was observed at 1697 cm$^{-1}$, which may arise due to overlapping of the two carbonyl IR peaks (Figure 4.30 – b).
In the $^1$H NMR spectrum (Figure 4.31 – a), the peak appeared at 1.24 corresponds to the protons in the $t$-butyl group. Two hydrogens on the -CH$_2$ of the methypivalate group appeared at 6.35 ppm. Three protons in the pyridyl ring and the other aromatic proton in the triazole ring are observed in the region 8.2 – 9.1 ppm. The proton of the aldehyde group is seen at 10.15 ppm ($^1$H NMR in dichloromethane-d$_2$ (300 MHz): d = 1.24 (s, 9H, M07), 6.35 (s, 2H, M06), 8.29 (dd, 1H, J=8.0, 2.1 Hz, M05), 8.37 (dd, 1H, J=8.0, 0.2 Hz, M04), 8.54 (s, 1H, M03), 9.08 (dd, 1H, J=2.1, 0.8 Hz, M02), 10.15 (s, 1H, M01) ppm). $^{13}$C NMR spectrum (Figure 4.31 – b) shows a peak at 26.71 ppm corresponding to the methyl groups in the $t$-butyl group. Peaks at 38.87 ppm represent those for the tertiary carbon in the $t$-butyl group.

Figure 4.31 – (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pyaz(1,2,3) – CHO – s4

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The -CH₂ carbon in the methylpivalate group appears at 70.13 ppm. Seven aromatic protons are observed in 120 – 155 ppm region. The two carbonyl carbons in the methylpivalate ester group and the aldehyde appeared at 177.65 and 190.41 ppm. (¹³C NMR in dichloromethane-d₂ (75 MHz): d = 26.71(17, 20, 21), 38.87(16), 70.13(6), 120.35(5), 125.13(15), 130.84(13), 137.11(14), 148.08(12), 152.13(4), 154.70(10), 177.65(8), 190.41(18)) 9.1 ppm.

4.2.5 Deprotection of the triazole

4.2.5.1 Structural characterisation of 3pyaz(1,2,3)–N(CH₃)₂

The purified product was white, needle shaped crystals with a yield of 95% (1.683 g). TLC analysis produced an Rᵢ value of 0.20 (mobile phase –1:1 hexane: ethylacetate), indicating an increase in the polarity due to the removal of pivaloyloxymethyl protecting group. Melting point of the compound was over the range 172 – 174 °C. High resolution mass spectrum (Figure 4.32 – a) of the compound produced the [M + H⁺] ion peak at 190.1084 (theoretical [M+ H⁺] – 190.1087), which confirms the formation of the product. Another peak is seen at 212.0905 which correspond to the [M + Na⁺] ion. In the IR spectrum (Figure 4.32 – b), peaks are not observed at 1728 cm⁻¹ and 1141 cm⁻¹, indicating the removal of methylpivalate group. No characteristic IR peaks would be identified as N=N and stretching peaks in the triazole can overlap with C=C bond stretching in the aromatic system (both appear in 1600 cm⁻¹ region).

In the ¹H NMR spectrum (Figure 4.33 – a) singlet at 3.07 ppm corresponds to the six protons in the dimethyl amino group. Four aromatic protons in the pyridyl and triazole ring are seen in the region 7.2 – 8.3 ppm. The triazole N-H proton is not observed, as it may be too downfield due to its highly acidic nature (¹H NMR in DMF-d7 (300 MHz): δ = 3.07 (s,

![Figure 4.32](image-url) • High resolution mass spectrum (b) IR spectrum of 3pyaz(1,2,3)–N(CH₃)₂
The carbon atom in the dimethyl amino group is seen at 39.49 ppm, and the pyridyl and triazole carbons are seen in the region 119 – 150 ppm (\(^{13}\)C NMR in DMF-\(\text{d7}\) (75 MHz): \(\delta = 39.49(13, 14), 119.21(11), 120.55(10), 132.13(5), 134.34(8), 137.81(9), 146.28(4), 149.45(6))

Figure 4.33 – (a) \(^1\)H NMR spectrum (b) \(^{13}\)C NMR spectrum of 3pyaz(1,2,3) – N(CH\(_3\))\(_2\)
4.2.5.2 Structural characterisation of 3pyaz(1,2,3)

The purified product was a white powder with 90% yield (2.023 g). TLC analysis showed an $R_f$ value of 0.28 (mobile phase – 1:1 hexane: ethylacetate). Melting point of the compound was over the range 117 – 120 °C. High resolution mass spectrum (Figure 4.34 – d) gave [M + H$^+$] peak at 147.0663 m/z (theoretical [M + H$^+$] – 147.0665 m/z) confirming the formation of the product (other high mass peaks are due to background). The absence of the IR peaks corresponding to C=O and C-O bond stretching indicates the removal of methylpivalate group (Figure 4.34 - b).
The \(^1\)H NMR spectrum (Figure 4.35 – a) indicates the absence of peaks corresponding to the protons in the methylpivalate. Five aromatic protons in the pyridyl and triazole rings are appeared in 7.3 – 8.8 ppm region giving an integration value of 5H’s (\(^1\)H NMR in DMF-d7 (300 MHz): \(\delta = 7.36 - 7.49\) (m, 1H, M05), 7.92 - 8.01 (m, 1H, M04), 8.04 - 8.19 (m, 1H, M03), 8.33 (s, 1H, M01), 8.64 - 8.75 (m, 1H, M02) ppm). Seven aromatic carbon peaks are seen in the region 120 – 151 ppm in the \(^{13}\)C NMR spectrum (Figure 4.35 – b) (\(^{13}\)C NMR in DMF-d7 (75 MHz): \(\delta = 120.51(9), 123.74(11), 133.39(10), 137.46(5), 148.83(8), 149.97(4), 150.01(6))

4.2.5.3 Structural characterisation of 3pyaz(1,2,3) – CHO

Figure 4.36 – (a) High resolution mass spectrum (b) IR spectrum of 3pyaz(1,2,3) - CHO
The purified product was white, crystalline powder (yield 95%, 2.023 g). TLC analysis gave an $R_f$ value of 0.31 (1:1 – hexane: ethylacetate mobile phase). The melting point of the product was 178 – 180 °C. The high resolution mass spectrum indicated the $[\text{M + H}^+]$ peak at 175.0612 m/z (theoretical $[\text{M + H}^+]$ – 175.0614 m/z) (Figure 4.36 – a). The IR spectrum shows the removal of methylpivalate group and absence of the peak at 1697 cm$^{-1}$ corresponding to the C=O stretching of the aldehyde group (Figure 4.36 – b).

In the $^1$H NMR spectrum, four aromatic protons appear in the region 8.2 – 9.3 and the

![Figure 4.37 – (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pyaz(1,2,3) – CHO](image-url)
aldehyde proton is seen at 10.25 ppm (1H NMR in DMF-d7 (300 MHz): \( \delta = 8.28 - 8.36 \) (m, 1H, M05), 8.39 - 8.47 (m, 1H, M04), 8.63 (s, 1H, M03), 9.16 - 9.26 (m, 1H, M02), 10.25 (s, 1H, M01)) (Figure 4.37 – a). \(^{13}\)C NMR spectrum (Figure 4.37 – b) shows aromatic carbons in 120 – 155 ppm region and the carbonyl carbon at 191.76 ppm (\(^{13}\)C NMR in DMF-d7 (75 MHz): \( \delta = 120.46(11), 131.10(5), 134.45(9), 137.19(10), 147.88(8), 152.42(4), 154.92(6), 191.76(12) \).

### 4.2.6 Knövenagel condensation\(^{185}\)

The final product of the series was achieved by converting the carbonyl group of the 3pyaz(1,2,3) – CHO, to a dicyanovinyl group via Knövenagel condensation. The mechanism of the reaction is shown above (Figure 4.38).

i. In the first step of the reaction, a base which acts as the catalyst removes \( \alpha \) – proton from the methylene group of the malanonitrile to generate a carbanion.

ii. The carbanion, then attacks the carbonyl carbon to generate alkoxide ion, which abstracts a proton to form hydroxyl compound.

iii. The hydroxyl compound will subsequently undergo dehydration to generate \( \alpha-\beta \) unsaturated condensation product.

In this reaction 3pyaz(1,2,3) – CHO was reacted with malononitrile using basic alumina (Al\(_2\)O\(_3\)) as the catalyst (method 1 – Section 3.2.3.6). The same reaction was carried out using catalytic amounts of piperidine as well (method 2 – Section 3.2.3.6). From both catalysts product was obtained, but the use of alumina catalyst was more efficient and the product was then easy to purify. Yields from both methods were comparable.
4.2.6.1 Synthesis of 3-dicyanovinyl-6-[1H-(1,2,3-triazol-4-yl)]pyridine (3pyaz(1,2,3) – CHC(CN)₂)

The purified product was a yellow powder with an $R_f$ value of 0.34 (mobile phase – hexane: ethylacetate – 1:1). The melting point of the product was 174 – 176 °C. High resolution mass spectrum indicated the formation of the product under negative detection mode, with the [M – H⁺] peak at 221.0582 m/z (theoretical [M – H⁺] – 221.0581 m/z) (Figure 4.39 – a). The IR spectrum showed C≡N bond stretching peak at 2113 cm⁻¹, and C=C bond stretching at 1680 cm⁻¹. The peak corresponding to C=O stretching of the carbonyl peak in the reactant, is absent indicating the complete formation of the product (Figure 4.39 – b).

In the $^1$H NMR spectrum (Figure 4.40 – a) of the product, the singlet corresponding to the aldehyde group of the reactant is absent, and a new singlet corresponding to the proton on the dicyanovinyl group is seen at 8.15 ppm. Four aromatic protons of the pyridyl and triazole rings were detected in the region 8.3 – 9.0 ppm region ($^1$H NMR in DMSO-$d_6$ (300 MHz): $\delta$ = 8.15 (s, 1H, M05), 8.35 (d, 1H, J=8.2 Hz, M04), 8.52 (dd, 1H, J=8.5, 2.4 Hz, M03), 8.73 (s, 1H, M02), 8.95 (d, 1H, J=2.5 Hz, M01)). In the $^{13}$C NMR spectrum of the compound, two cyano carbons were seen at 113.29 and 114.29 ppm, whereas the two vinyl carbons were observed at 85.41 and 158.30 ppm (Figure 4.40 – b). Aromatic carbons were detected in the region 127 – 156 ppm ($^{13}$C NMR in DMSO-$d_6$ (75 MHz): $\delta$ = 85.41(13), 113.29(16), 114.29(14), 127.78(11), 129.60(9), 131.56(5), 146.87(8), 152.92(4), 155.14(6), 158.30(12)).
Figure 4.40 – (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pyraz(1,2,3) – CHC(CN)$_2$
4.3 Characterisation of the Metal Complexes

During the synthesis of the metal complexes a mixture of solvents was used to enhance the mixing of the reactants. The ligands were solubilised in 2-ethoxy ethanol, and the K₂PtCl₄ was solubilised in water. The medium was basified prior to the addition of the Pt²⁺, to form the anionic versions of the respective ligands. Once the reactions were completed, the resulting complexes were washed with ethanol, water and acetone to remove excess ligands and any polar/ nonpolar impurities. Vacuum drying was carried out to remove any solvent traces remaining in the complexes. Due to poor solubility of the complexes recrystallisation could not be carried out.

The structural characterisation of the metal complexes was carried out by mass spectrometry, ¹H NMR, and IR spectroscopy. High Resolution Mass analysis could only be obtained for Pt[3pyaz(1,2,3)-N(CH₃)₂]₂ and Pt[3pyaz-(1,2,3)]₂, as Pt[3pyaz(1,2,3)-CHO]₂ and Pt[3Pyaz(1,2,3)-CHC(CN)₂]₂ were only sparsely soluble in DMSO, which is incompatible with the mass spectrometer. Only Low Resolution Mass data were obtained for Pt[3pyaz(1,2,3)-CHO]₂ and Pt[3Pyaz(1,2,3)-CHC(CN)₂]₂ by injecting a small portion of the compounds dissolved in DMSO, despite its “incompatibility” with the spectrometer. The mass spectroscopic data are stated below.

Pt[3pyaz(1,2,3)-N(CH₃)₂]₂ – yellowish white powder (Yield – 95%) ((M+H⁺) Calc. Mass 572.1599 Observed Mass 572.1609)

Pt[3pyaz-(1,2,3)]₂ – yellow powder (yield – 94%) ((M+H⁺) Calc. Mass 485.0733 Observed Mass 485.0761)

Pt[3pyaz(1,2,3)-CHO]₂ – white orange powder (96%) ((M+H⁺) Calc. Mass 542.07 Observed Mass 542.1)

Pt[3Pyaz(1,2,3)-CHC(CN)₂]₂ – yellow orange powder (90%) ((M+H⁺) Calc. Mass 638.09 Observed Mass 638.0)

Again due to solubility issues of the complexes, only ¹H NMR could be obtained. The spectral comparison of the complexes with the free ligands indicates, clear de-shielding effects of the corresponding NMR peaks due to the electron withdrawal from the Pt²⁺ ion (Figure 4.41). This indicates the complexation process. The poor solubility of the complexes and the peak broadening effects incurred by Pt²⁺ ion, result in poorly resolved peaks in the NMR spectra.¹⁸⁶,¹⁸⁷ The complexation process is confirmed further, however, by analysis of IR spectral shifts associated with C-H vibronic bands of the free ligands and the complexes (Figure 4.42).
Figure 4.1 - $^1$H NMR spectra of the metal complexes and a comparison of the peaks with relevant free ligands.
Summary

Within this chapter we show the synthesis of 5-substituted, pyridyl-1,2,3-triazole ligands (4 ligands including 16 intermediates) and their homoleptic Platinum complexes. Substitution with a range donor acceptor groups (-N(CH₃)₂, -H, -CHO, -CHC(CN)₂) was carried out on the pyridyl ring, to influence the energy of the LUMO levels of the ligands. Triazole ring was left with the acidic N-H proton to achieve ligands with strong field ligation ability. The mechanisms involved in the reactions were discussed and structural characterisation of each compound is presented. Homoleptic platinum complexes were characterised by mass spectrometry and ¹H NMR. Poor solubility of the complexes hindered further characterisation of the complexes.
CHAPTER 5
PHOTOPHYSICAL PROPERTIES OF THE PYRIDYL-1,2,3-TRIAZOLE LIGANDS AND THE HOMOLEPTIC PLATINUM COMPLEXES

5.1 Introduction
In the first section of this chapter the effects of the substituents on the ligand structures are considered with respect to the acid dissociation constants. Later in the chapter the photo-physical properties of the ligands and their respective homoleptic platinum(II) complexes will be discussed based on the absorption and emission characteristics. The trends observed are analysed in relation to the donor – acceptor strengths of the substituents on the ligands and will further be discussed using theoretical calculations to understand the origin and molecular level aspects related to the trends observed.

5.2 Determination of the acid dissociation constants of the ligands
Acid dissociation constant ($K_a$), is important in analysing the effects of substitution on the donor-acceptor strength of the ligands. $K_a$ is derived as follows for a generic acid having the formula of HA, what is known as the Henderson – Hasselbalch equation;\textsuperscript{188-190}

$$HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)}$$

For this equilibrium assuming the equilibrium constant / acid dissociation constant is $K_a$,

$$K_a = \left[ A^-_{(aq)} \right] / \left[ H^+_{(aq)} \right]$$

$$log_{10}K_a = log_{10} \left( \left[ A^-_{(aq)} \right] / \left[ H^+_{(aq)} \right] \right)$$

Since $-log_{10}K_a = pK_a$ and $-log_{10} \left[ H^+_{(aq)} \right] = pH$,

$$-pK_a = -pH + log_{10} \left[ A^-_{(aq)} \right] / \left[ HA_{(aq)} \right]$$

$$pK_a = pH + log_{10} \left[ HA_{(aq)} \right] / \left[ A^-_{(aq)} \right]$$

At a point where $\left[ A^-_{(aq)} \right] = \left[ HA_{(aq)} \right]$,

$$pK_a = pH$$

The 2-pyridyl-1H-1,2,3-triazole ligands display two acid dissociation constants as shown below in Figure 5.1.
Determination of the acid dissociation constants can be carried out via two approaches: (1) acid – base / neutralisation titrimetry and (2) spectrometric analysis at different pH values. In general the sensitivity of titrimetry is less compared to other analytical methods. The first associated difficulty arises when titrating solutions of low concentration. When the concentration of the titrant and the titrand are lower than 0.01 mol dm\(^{-3}\) the accurate location of the equivalence point and thereby the end-point becomes less readily achieved. The next difficulty arises with the associated free-energy change during the titration. When the free-energy change is larger it is easier to locate the end-point. Most weak acids are associated with low free-energy changes. Thus, titrimetry is not a suitable method for our set of ligands as they are expected to be fairly weak acids and their solubility is a persistent problem. Spectrometric analysis is preferred over titrimetry in such cases, especially as we have clear and strong absorption for our ligands that is related directly to the site of protonation. Protonated and deprotonated entities will thus have discernible differences in their charge transfer properties that can be analysed by their respective absorption bands at different pH values.

5.2.1 Analysis of absorption spectra and determination of \(K_a\) of 3pyaz(1,2,3) – N(CH\(_3\))\(_2\)
The absorption spectra of 3pyaz(1,2,3) – N(CH₃)₂ at some selected pH values (for clarity) are given above in Figure 5.2 (a). The intention of this was to identify the absorption bands that change with the pH of the medium. Once the bands are located absorption was measured for a series of pH values as needed (pH 1 – 13 of 10⁻⁵ M solutions). Starting from highly acidic conditions and moving towards basic conditions the peak appearing at 380 nm at pH 1 starts to disappear (Figure 5.2 (b)). This is associated with the acid dissociation of the protonated pyridyl ring. Further measurements of the absorption band at 380 nm at more elaborated pH ranges are given in Table 5.1. According to the graph between the absorption at 380 nm and the pH of the medium (Figure 5.3), a drastic change is observed in the region pH 2 – 4. At the half way of the vertical portion of the graph it is assumed the protonated and the deprotonated

<table>
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<th>pH</th>
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<th>pH</th>
<th>Absorption at 380 nm</th>
</tr>
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<td>1.2721</td>
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</table>

Figure 5.3 – Graph of absorption at 380 nm vs. pH
entities exist in the same concentrations where the pH of the medium equals the $pK_a$. According to the calculation $pK_{a_1}$ of the ligand was calculated as 2.8, where $K_{a_1}$ would be $1.58 \times 10^{-3}$ mol dm$^{-3}$.

The next deprotonation is from the triazole forming the triazolate anion. According to the calculation of $pK_{a_1}$, after pH 4 it can be assumed that the protonated pyridyl species is completely deprotonated and therefore species existing after pH 4 are considered to calculate $pK_{a_2}$. No significant change in the absorption profiles are noticed. The only changes that can be seen are the slight blue shift of the major absorption band in the region 285 – 295 nm (Figure 5.2 (c)) and the disappearance of the peak around 225 nm (Figure 5.2 (d)). A graph of the maximum absorption wavelength of the absorption band around 285 – 295 nm as a function of the pH of the medium estimated the $pK_{a_2}$ as 9.4 where $K_{a_2}$ is $3.98 \times 10^{-10}$ mol dm$^{-3}$ (Table 5.2 and Figure 5.4).

<table>
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Table 5.2 - Absorption wavelength at different pH values

Figure 5.4 - Graph of absorption wavelength around 290 nm vs. pH
By considering the disappearance of the peak around 225 nm a graph can be plotted to determine the $pK_{a2}$. Since the peak around 225 nm is overlapped, the difference between the absorption maximum around 225 nm (Figure 5.2 (c); point $y$) and the absorption minimum (Figure 5.2 (c); point $x$) is considered as a function of the pH (with increasing pH, peak disappears and flat region results; thus the difference between $x$ and $y$ decreases) (Table 5.3 and Figure 5.5). According to the analysis of the 225 nm peak the $pK_{a2}$ was calculated to be 9.3 and the $K_{a2}$ is to be $5.01 \times 10^{-10}$ mol dm$^{-3}$.

<table>
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<th>pH</th>
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Table 5.3 – $\Delta$ Absorption ($y$-$x$) at different pH values

By considering the disappearance of the peak around 225 nm a graph can be plotted to determine the $pK_{a2}$. Since the peak around 225 nm is overlapped, the difference between the absorption maximum around 225 nm (Figure 5.2 (c); point $y$) and the absorption minimum (Figure 5.2 (c); point $x$) is considered as a function of the pH (with increasing pH, peak disappears and flat region results; thus the difference between $x$ and $y$ decreases) (Table 5.3 and Figure 5.5). According to the analysis of the 225 nm peak the $pK_{a2}$ was calculated to be 9.3 and the $K_{a2}$ is to be $5.01 \times 10^{-10}$ mol dm$^{-3}$.

**5.2.2 Acid dissociation constants of 3pyaz(1,2,3)**

In the same manner explained previously, the acid dissociation constants of the 3pyaz(1,2,3) ligand were also determined. The analysis of the absorption spectra reveal moving from pH 1 to 4 exhibits a rapid decrease in the absorption profile around 298 nm indicating the deprotonation of the pyridyl ring and again an increase in the absorption at 295 nm from around pH 7 indicating the second proton dissociation to form the triazolate.
Therefore to calculate $pK_{a_1}$ absorption at 298 nm from pH 1 – 6 will be considered and to calculate $pK_{a_2}$ absorption at 295 nm are considered from pH 4 – 13. The absorption at 298 and 295 nm are shown in the Table 5.4 and the graphs corresponding to each are shown in the Figure 5.7 (●) and (▲). According to the calculation $pK_{a_1}$ is calculated to be 2.4 and ($K_{a_1}$ 3.98 x 10$^{-3}$ mol dm$^{-3}$) and the $pK_{a_2}$ 8.3 ($K_{a_2}$ 5.01 x 10$^{-9}$ mol dm$^{-3}$).

<table>
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</tr>
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</tr>
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5.2.3 Acid dissociation constants of 3pyraz(1,2,3) - CHO

The analysis of the absorption spectra (Figure 5.9) moving from pH 1 to 13 reveal two significant changes in the maximum absorption wavelengths at 297 and 330 nm. A continuous decrease in the absorption is observed for the peak at 297 nm. Except for the lowering in the absorption peak at 297 nm no significant change in the absorption profiles are observed in the acidic medium making it difficult to determine the $pK_{a1}$. A graph (Table 5.5 and Figure 5.9) was plotted for the absorption at 297 nm exhibiting a continuous decrease in the absorption from pH 1 – 3 and a flat region till pH 6, which then starts to decrease further.
Table 5.5 - Absorption at 298 and 295 nm at different pH values

<table>
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<tr>
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<th>Absorption at 330 nm</th>
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</tr>
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</table>

until pH 10, and concludes with another flat region. Since there is no flat region below pH 1 another solution was prepared with 1 mol dm$^{-3}$ HCl and the absorption was recorded and the graph was plotted with the data point inserted for pH 0 which shows signs of a flat region from pH 0 – 1. Therefore the calculation of $pK_{a_1}$ was possible. From the graph $pK_{a_1}$ was calculated to be 1.8 where $K_{a_1}$ is $1.58 \times 10^{-2}$ mol dm$^{-3}$. From the next vertical portion of the

![Graph of absorption at 297 nm vs. pH](image-url)
Graph $pK_{a_2}$ was calculated to be 7.7 where $K_{a_2}$ is $2.00 \times 10^{-8}$ mol dm$^{-3}$. By considering the absorption at 330 nm another graph (Table 5.5 and Figure 5.11) was plotted using the absorption at 330 nm to determine the $pK_{a_2}$ in an alternative manner and it was determined to be 7.5 where $K_{a_2}$ is $3.16 \times 10^{-8}$ mol dm$^{-3}$.

5.2.4 Acid dissociation constants of $3$pyaz(1,2,3) – CHC(CN)$_2$
The absorption spectra (Figure 5.11) of the 3pyaz(1,2,3) – CHC(CN)₂ indicate two regions where a significant change in the absorption profiles can be observed. Moving from pH 1 – 4 a peak is appearing at 290 nm and starts to disappear with further increase of the pH/basicity of the medium. Also with the increase of pH a new peak is observed at 392 nm (Figure 5.11 and Table 5.6). From the spectra it is evident that from pH 1 – 4 the first

<table>
<thead>
<tr>
<th>pH</th>
<th>Absorption at 290 nm</th>
<th>pH</th>
<th>Absorption at 392 nm</th>
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Figure 5.12 - Graph of absorption at 290 nm vs. pH (●) and graph of absorption at 392 nm vs. pH (▲)
proton dissociation takes place and the second proton dissociation takes place at higher pH conditions. Therefore to calculate the $pK_{a1}$ the absorption at 290 nm is considered (pH 1–4) (Figure 5.12 (●)) and to calculate $pK_{a2}$ absorption at 392 nm will be considered (Figure 5.12 (▲)). From the graph $pK_{a1}$ was calculated to be 1.6 where $K_{a1}$ is $2.51 \times 10^{-2}$ mol dm$^{-3}$ and the $pK_{a2}$ was calculated to be 6.9 where $K_{a2}$ is $1.27 \times 10^{-7}$ mol dm$^{-3}$.

In summary, the $pK_a$ values obtained for each ligand are tabulated in the Table 5.7. When the $pK_a$ values are calculated from more than one method the average value was considered. Plotting a graph between the Hammett parameters$^{172}$ of the substituents and the $pK_a$ values of the ligands to see whether there is an impact from the substituent, it is revealed that with increasing donor strength of the substituent, dissociation of the protons becomes difficult and with the increasing acceptor strength of the substituents the reverse is taking place. In selecting the Hammett parameters, $\sigma_m$ is considered for the $pK_{a1}$ and $\sigma_p$ is considered for $pK_{a2}$ plots separately. This can be explained as the increasing electron density on the ring systems and its withdrawal of electrons from the N-H hydrogen, therefore the potential of releasing a proton, becomes difficult making them less strong acids. Also by looking at the graphs, the gradients for $pK_{a2}$ and $pK_{a1}$ are similar, indicating the sensitivity of the substituents are in equal contributions for both dissociations; but the $pK_{a2}$ is associated with the triazole ring whereas the $pK_{a1}$ is associated with the pyridine ring. In the first instance it would seem that since the substituents are attached to the pyridine ring, more effect from the substituents should be on the $pK_{a1}$ rather than the $pK_{a2}$. However, upon looking at the structure, the substituents are placed meta to the pyridyl N-H and para to the triazole ring. According to the Hammett parameters it can be seen that the effect of having meta-substituent is less than that for having a para-substituent. Especially in the case of donor substituent, which (Hammett parameter) is highly altered from -0.83 to -0.16. This is also seen from the $pK_a$ values. The difference in the $pK_{a2}$ values between the donor and the

<table>
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<th>Ligand</th>
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<th>$pK_{a2}$</th>
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<td>3pyaz(1,2,3) – N(CH$_3$)$_2$</td>
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<td>9.35</td>
</tr>
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<td>3pyaz(1,2,3)</td>
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<td>8.3</td>
</tr>
<tr>
<td>3pyaz(1,2,3) – CHO</td>
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<td>7.6</td>
</tr>
<tr>
<td>3pyaz(1,2,3) – CHC(CN)$_2$</td>
<td>1.6</td>
<td>6.9</td>
</tr>
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</table>
standard ligand is 1 unit, whereas the difference in $pK_{a1}$ values are just 0.4 units. Also, the pyridine ring is less electron dense than the triazole ring and therefore the triazole ring also acts as donor to the pyridine ring. This removes some of the effects from the accepting groups, making the pyridyl ring less sensitive towards the acceptors, and may be an enhanced contribution towards the donors.

This analysis shows that there is a direct impact of the nature of the substituents on the properties of the ligands. This also suggests substituents can influence the electron densities of the ring systems, thereby on the distribution of energy levels (HOMO and LUMO) which are crucial in determining the photo-physical properties of the ligands and resulting complexes.

In the final section of this chapter the relationship between the determined $pK_{a}$ values and the photo-physical properties of the ligands will be discussed.
5.3 Photo-physical properties of the free ligands

The absorption spectra of the free ligands in basic ethanolic solutions (10^{-5} \text{ mol dm}^{-3}) are given in Figure 5.14 to allow a direct comparison of the free ligand (in the triazolate form) to the complexed ligand (absorption and emission data of the neutral/protonated ligands are given in Appendix 1). According to the spectra the lowest energy absorption band red-shifts with increasing acceptor power of the substituent over a range of approximately 100 nm, from 295 (3pyaz(1,2,3)), to 330 (3pyaz(1,2,3) - CHO) and to 392 nm (3pyaz(1,2,3) – CHC(CN)₂), while, the introduction of the donating group (3pyaz(1,2,3) – N(CH₃)₂) causes absorption at 332 nm. In addition to the first absorption bands, transitions were observed at ca. 280, 250 and 220 nm with relatively less sensitivity to substitution.

The analysis of the structures of the free ligands indicates the possibility of intramolecular charge transfer properties where the triazolate donates to the accepting pyridine ring and its substituents. In order to confirm the experimentally observed trend, PBE0/BS1 (BS1 = 6-31G*, C,H,N & SDD Pt) in ethanol, calculations were performed and the results are given in Table 5.8. These data predicts the first absorption bands at 281 (3pyaz(1,2,3)), 338 (3pyaz(1,2,3) - CHO), 421 (3pyaz(1,2,3) – CHC(CN)₂) and 313 nm (3pyaz(1,2,3) – N(CH₃)₂) which agree well with the experimental values.

The molecular orbital (MO) analysis (Figure 5.15) of the ligands 3pyaz(1,2,3), 3pyaz(1,2,3) – CHO and 3pyaz(1,2,3) – CHC(CN)₂, reveals that the intra-molecular charge
transfer occurs from the triazolate (HOMO) to the pyridine and its substituent (LUMO). This also shows the HOMO level of the three ligands remains invariant over the effects of substitution as they share no electron density with the respective substituents. This will lead them to HOMO levels arranged close in energy. In contrast, the substituent effects are more pronounced for the three ligands in the LUMO level. It can be observed that with increasing accepting power of the substituents, enhanced delocalisation of the LUMO electron density over the pyridyl ring and the substituents results. This introduces more stabilisation to the LUMO levels (depending on the substituent) allowing loose arrangement of energy levels compared to HOMO levels, resulting in a concurrent red-shift in the first absorption bands.

Moreover, the analysis of MO’s of the $3\text{pyaz}(1,2,3) – \text{N(CH}_3)_2$ gives insight into the slightly different behaviour observed for the donor substituent. The effect of the donor substituent is more pronounced in the HOMO level, which comprises both the triazolate and N(CH$_3$)$_2$ group. Since the electron densities are localised on the triazolate and the substituent, this would not help the delocalisation of the electron density over the molecule. In contrast this increases the electron density in the HOMO level which leads to an increase in the HOMO energy. The LUMO is localised mainly on the pyridyl ring, exhibiting no contribution from the substituent. Therefore, it can be assumed that the LUMO of $3\text{pyaz}(1,2,3) – \text{N(CH}_3)_2$, stays closer to the energy of the $3\text{pyaz}(1,2,3)$. This scenario leads to the detection of relatively longer wavelength absorption than expected in the case of the

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<th>E</th>
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<td>S$_9$</td>
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donor substituents. This behaviour can be further elaborated qualitatively by the energy level diagram shown in Table 5.9 and Figure 5.16. The energies of the corresponding levels were calculated by DFT/PBE0 method.

The emission / photoluminescence (PL) spectra of the free ligands give emission transitions for 3pyaz(1,2,3) – N(CH₃)₂ (400 nm) and 3pyaz(1,2,3) (402 nm) at the same energy, but with a considerable bathochromic shift for 3pyaz(1,2,3) – CHO (431 nm) and 3pyaz(1,2,3) – CH(CN)₂ (469 nm) (Figure 5.14). These PL bands are well overlapped with the first absorption bands and are thus reasonably assigned as fluorescence. The trend that was observed with the absorption is also closely followed in the emission except for the case of the 3pyaz(1,2,3) – N(CH₃)₂ which is blue-shifted slightly by 2 nm compared to

Figure 5.15 – Leading molecular orbitals involved in the lowest energy $S_2$→$S_1$ transitions for the free ligands (anionic forms). Donating (left) and accepting (right) molecular orbitals
3pyaz(1,2,3). This can be due to different solvent interactions associated with the ligands and vibronic broadening of the states causing the overlap. This effect was not further studied since it lies out of the scope of this study.

Table 5.9 - Energies of the HOMO and LUMO levels of the free ligands

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<tr>
<th>3pyaz(1,2,3) – N(CH₃)₂</th>
<th>3pyaz(1,2,3)</th>
<th>3pyaz(1,2,3) – CHO</th>
<th>3pyaz(1,2,3) – CHC(CN)₂</th>
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<td>HOMO [eV]</td>
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<tr>
<td>Δ E (HOMO-LUMO) [eV]</td>
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<td>5.16</td>
<td>4.12</td>
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</table>

Figure 5.16 – Computed HOMO-LUMO energy level arrangement of the free ligands
5.4 Photo-physical properties of the homoleptic complexes

Absorption profiles of the homoleptic platinum complexes of the ligands; Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$], Pt[3pyaz(1,2,3)$_2$], Pt[3pyaz(1,2,3)-CHO], Pt[3pyaz(1,2,3)-CHC(CN)$_2$] in ethanolic solutions (10$^{-5}$ mol dm$^{-3}$) are given in Figure 5.17. Irrespective of the substituents and the effects observed in the free ligands, complexes at low concentrations exhibit almost the same absorption profiles. All of them present intense high energy absorption bands at 225 and 275 nm, followed by a shoulder at a ca. 282 nm. These bands are of similar energy to the higher energy absorption of the free ligands but with a blue / hypsochromic shift of about 20 nm and show a similar immovability upon substitution. Further scanning into the 300 – 400 nm region show low-energy absorption bands with values of 331 and 377 nm (Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$]), 342 and 377 nm (Pt[3pyaz(1,2,3)$_2$]), 348 and 377 nm (Pt[3pyaz(1,2,3)-CHO]) and 352 nm (Pt[3pyaz(1,2,3)-CHC(CN)$_2$]). In contrast to the free ligands, these bands express a lowered tunability with changing substituent with a range of only a few nanometers for the lowest energy absorptions. In order to understand the effects of complexation TDDFT (TDDFT/PBE0/BS1 (BS1 = 6-31G*$_{C,H,N}$ & SDD$_{Pt}$) in ethanol) calculations were carried out. The results (Table 5.10) also confirm the trends observed experimentally which reveal absorption bands located at 311 and 376 nm (Pt[3pyaz(1,2,3)-CHC(CN)$_2$]), 301 and 338 nm (Pt[3pyaz(1,2,3)$_2$]), 326 and 370 nm (Pt[3pyaz(1,2,3)-CHO]), as well as at 365 and 416 nm (Pt[3pyaz(1,2,3)-CHC(CN)$_2$]).
Table 5.10 – Excited states ES, vertical excitation energies E [eV], wavelengths λ [nm] and oscillator strength f computed with TDDFT/PBE0/6-31G* & SDD in ethanol

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</table>

With the intention of understanding the photo-physical properties, molecular orbital (MO) analysis of the complexes were carried out. This identifies these bands as having metal-to-ligand charge transfer character (1MLCT) involving the d$_{xz}$ and d$_{yz}$ (Figure 5.18). According to the analysis, HOMO levels are located mainly in the metal centre and the triazole ring where the pyridyl ring shares no electron density. The only exception is Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$]$_2$ where the -N(CH$_3$)$_2$ substituent shares electron density in the HOMO level. Electron density in the LUMO levels is distributed in the pyridyl ring and the substituents as in the case of free ligands; no electron density is shared by the metal centre. Since the substituents are involved in the LUMO levels, one would expect to see the same tunability of the first absorption bands as in free ligands. The fact that it is not seen must be associated with the metal-ligand interaction (since the process involves 1MLCT) which is controlled by ligation ability that depends on the nature of the substituent. The energy level distribution and the reason for the lack of tunability involved in the monomer complexes will be discussed later in this chapter.

Another aspect to study was whether there is an effect from the concentration of the sample on the absorption profiles of the complexes. Interestingly, upon increasing the concentration of the ethanolic solutions, no noticeable change in the absorption spectra was
observed (Appendix 2). This observation indicates that there are no strong ground-state intermolecular interactions/ aggregations.
Pt[3pyaz(1,2,3)-CHO]$_2$ $S_0 \rightarrow S_1$ Charge transfer from Pt and triazolate to Pyridine and CHO

Pt[3pyaz(1,2,3)-CHO]$_2$ $S_0 \rightarrow S_1$ Charge transfer from Pt and triazolate to Pyridine and CHO

Pt[3pyaz(1,2,3)-CH(CN)$_2$]$_2$ $S_0 \rightarrow S_1$ Charge transfer from Pt and triazolate to Pyridine and CH=CN(CN)$_2$

Pt[3pyaz(1,2,3)-CH(CN)$_2$]$_2$ $S_0 \rightarrow S_1$ (1) Excitation localized in the ligand – charge transfer from Triazolate to Pyridine and CH=CN(CN)$_2$ (2) Charge transfer from Pt and triazolate to Pyridine and CH=CN(CN)$_2$

Figure 5.18 – Leading molecular orbitals involved in the lowest energy $S_0 \rightarrow S_n$ transitions for the monomer complexes. Donating (left) and accepting (right) molecular orbitals.
PL spectra of dilute solutions (10^{-6} mol dm^{-3}) of the complexes (Figure 5.19) were recorded at the excitation wavelength of 350 nm. The complexes display emission maxima for Pt[3pyaz(1,2,3)-N(CH_3)_2]_2 (397 nm), Pt[3pyaz(1,2,3)]_2 (400 nm) Pt[3pyaz(1,2,3)-CHO]_2 (405 nm) and Pt[3pyaz(1,2,3)-CHC(CN)]_2 (408 nm) that are nearly coincident with each other. Additionally, for Pt[3pyaz(1,2,3)-N(CH_3)_2]_2 and Pt[3pyaz(1,2,3)]_2 the emissions are strikingly similar to those of the ligands 3pyaz(1,2,3)-N(CH_3)_2 and 3pyaz(1,2,3) whereas for Pt[3pyaz(1,2,3)-CHO]_2 and Pt[3pyaz(1,2,3)-CHC(CN)]_2 the complex emissions are blue-shifted compared to 3pyaz(1,2,3)-CHO and 3pyaz(1,2,3)-CHC(CN). Therefore complexes at

Table 5.11 - Calculated emission properties of 4a-d complexes. Excited states ES, vertical emission energies E (eV), wavelengths λ (nm) and oscillator strength f computed with TDDFT/PBE0/6-31G* & SDD in ethanol. * Above 528 nm - estimated on the basis of S0→T1 upper excitations.

<table>
<thead>
<tr>
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<td></td>
<td>T_2</td>
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<td>T_2</td>
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<td></td>
<td>T_2</td>
<td>1.73</td>
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</table>

Figure 5.19 – Photoluminescence spectra of the metal complexes (10^{-6} M, in ethanol, excitation at 350 nm); Blue – Pt[3Pyaz(1,2,3)-N(CH_3)_2], Green – Pt[3Pyaz(1,2,3)]_2, Orange – Pt[3Pyaz-CHO]_2 – 4c, Red – Pt[3Pyaz-CHC(CN)]_2.
Figure 5.20 – Leading molecular orbitals involved in the lowest energy $S_1 \rightarrow S_0$ transitions for the monomer complexes. Donating (left) and accepting (right) molecular orbitals.
low concentrations exhibit lack of tunability in the emission profiles as well. Emissions around 400 nm allow for good spectral overlap with the lowest energy absorption bands of the complexes. Thus, the small spectral shifts compared to the complex absorption, point to fluorescence despite the proximity and strong interaction with the heavy platinum cation. To investigate the origins of the emission, TDDFT excited-states optimizations have been performed for the lowest singlet ($S_1$) and triplet ($T_1, T_2$) states of the complexes (Table 5.11). The results indicate good qualitative agreement between the experimental PL maxima and the calculated $S_1 \rightarrow S_0$ emission energies: 416 nm ($\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$), 375 nm ($\text{Pt[3pyaz(1,2,3)]}_2$), 413 nm ($\text{Pt[3pyaz(1,2,3)-CHO]}_2$) and 461 nm ($\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2}$).

In contrast, the predicted phosphorescence energies are considerably lower in energy at 686 nm ($\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$), 473 nm ($\text{Pt[3pyaz(1,2,3)]}_2$), 517 nm ($\text{Pt[3pyaz(1,2,3)-CHO]}_2$) and 956 nm ($\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2}$). Therefore phosphorescence should not be related to the observed emissive processes. Thus, the computational and experimental results together identify the emission at the molecular level as fluorescence from $^1\text{MLCT}$ state. Analysis of the leading MO’s involved in the process, follows the same trend observed for absorption (Figure 5.20).

Key to our findings, however, is that the substituent effects on the emission properties are restored in more concentrated solutions ($10^{-4}$ M) of the complexes revealing a coarse tunability (Figure 5.21 (---)). Emission can be observed across a large portion of the visible spectrum with PL peaks found at: $\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$ (459 nm); $\text{Pt[3pyaz(1,2,3)]}_2$ (540 nm); $\text{Pt[3pyaz(1,2,3)-CHO]}_2$ (575 nm); and $\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2}$ (599 nm). The detected tunability in concentrated solution indicates that the aggregation causes a significant change in the excited-state character and suggests the existence of excited dimer (excimer) states. Both the monomer emission and excimer emission can be observed in concentrated solutions of the complexes simultaneously to different degrees suggesting that the excimerisation equilibrium is affected by the substituent. $\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$, $\text{Pt[3pyaz(1,2,3)]}_2$, $\text{Pt[3pyaz(1,2,3)-CHO]}_2$ emit strongly from the excimeric state while $\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2}$ shows a strong residual monomer emission. For these emissions, red shifts are increasingly large (from $\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$ to $\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2$) compared to the lowest energy absorption bands and the spectral overlap correspondingly decreasing. In the thin films (deposited through drop casting) there is an additional, and varying, red shift of the PL maxima (Figure 5.23 (−)) with a comparable range from 487 to 625 nm: $\text{Pt[3pyaz(1,2,3)-N(CH}_3\text{)]}_2$ (487 nm), $\text{Pt[3pyaz(1,2,3)]}_2$ (540 nm), $\text{Pt[3pyaz(1,2,3)-CHO]}_2$ (575 nm), and $\text{Pt[3pyaz(1,2,3)-CHC(CN)\text{)]}_2$ (599 nm).
Pt\[3\text{pyaz}(1,2,3)\]_2 (541 nm), Pt\[3\text{pyaz}(1,2,3)\text{-CHO}\]_2 (602 nm) and Pt\[3\text{pyaz}(1,2,3)\text{-CHC(CN)}\]_2 (625 nm) emitting in the blue, green, orange and red regions.

The corresponding photoluminescence excitation (PLE) spectra of the complexes (10^{-4} M, in ethanol) (Figure 5.22) show strong excitation maxima in the 300 to 400 nm range; Pt\[3\text{pyaz}(1,2,3)\text{-N(CH}_3)_2\]_2 (322 nm); Pt\[3\text{pyaz}(1,2,3)\]_2 (340 nm); Pt\[3\text{pyaz}(1,2,3)\text{-CHO}\]_2 (348 nm); and Pt\[3\text{pyaz}(1,2,3)\text{-CHC(CN)}\]_2 (359 nm). Interestingly any resemblance between the absorption and PLE spectra is hard to find except for the lowest energy absorption band.
This suggests the main absorption band at 275 nm is not responsible for the excimer/low energy emission.

The Pt$^{2+}$ complexes exhibit metallophilic interactions due to its square planar geometry. All experimental observations suggest the formation of excimers which results as function of metallophilic interactions. In order to understand the restored substituents effect at higher concentration, theoretical calculation on the Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$]$_2$ --- Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$]$_2$ (4a-4a), Pt[3pyaz(1,2,3)]$_2$ --- Pt[3pyaz(1,2,3)]$_2$ (4b-4b), Pt[3pyaz(1,2,3)-CHO]$_2$ --- Pt[3pyaz(1,2,3)-CHO]$_2$ (4c-4c) and Pt[3pyaz(1,2,3)-CHC(CN)$_2$]$_2$ --- Pt[3pyaz(1,2,3)-CHC(CN)$_2$]$_2$ (4d-4d) dimers have been carried out and the results are summarised in Table 5.12 and Figure 5.23 (a detailed procedure of the simulation was provided in Chapter 3).

The results indicate that upon excitation an enhancement of the metallophilic

Table 5.12 - Calculated emission properties of 4a-d complexes and their intermolecular dimers. Excited states ES, vertical emission energies E [eV], wavelengths $\lambda$ [nm] and oscillator strength $f$ computed with TDDFT/PBE0/6-31G* & SDD in ethanol. *Estimated on DFT optimised $T_1$ geometry, i.e. by the alternative approach (refer Chapter 3)

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<th>E</th>
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<th>$f$</th>
<th>ES$^a$</th>
<th>E$^a$</th>
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<td>-</td>
<td>T$_1$</td>
<td>1.56</td>
<td>796</td>
</tr>
</tbody>
</table>

Figure 5.23 - Equilibrium Pt-Pt distance [Å] in ground DS$_0$ and in excimeric states (DS$_1$, DT$_1$), DS$_1$ --- DS$_0$ and DT$_1$ --- DS$_0$ emission wavelengths for the dimers of 4a - d obtained with TDDFT/PBE0 method in ethanol.
interaction is observed and the Pt-Pt distance, Computed $R_{\text{Pt-Pt}}$ changes from 3.515-3.754 Å (DS$_0$) to 2.791-2.877 Å (DS$_1$ and DT$_1$). These interactions seem to enhance in the excited state. Moreover, the significantly shortened Pt-Pt distance in excited states indicates a covalent interaction (vdW radius of Pt: ~1.8 Å) and hence confirms the formation of the excimeric states. The molecular orbital analysis shows that this covalent interaction originates from the sigma type overlap between the $d_{z^2}$ atomic orbitals of the two Pt centers (Figure 5.25). Indeed, at higher concentration $^{1/3}$MLCT emitting states of the monomers are replaced by excimer states with metal-to-metal-to-ligand charge transfer character ($^{1/3}$MMLCT) and the emission is associated with transitions from ligand-centered molecular orbitals to metal-centered molecular orbitals representing the antibonding ($d_{z^2}$-$d_{z^2}$)* combination. The quantum-chemical results also reveal better tunability for the DS$_1$ → DS$_0$ emission energies from 524 (4a-4a), 554 (4b-4b), 587 (4c-4c) to 745 nm (4d-4d) and relatively narrow range of DT$_1$ → DS$_0$ emission energies from 584 (4a-4a), 591 (4b-4b), 613 (4c-4c) and 796 nm (4d-4d). Therefore, the observed tunability is more likely to be associated with fluorescence or a mixed singlet – triplet state. Moreover, the simulations reveal that due to the excimerisation process the DS$_1$ state is stabilised with respect to the DT$_1$ state and that the energy difference between them decreases as a function of the acceptor strength (up to 0.1 eV in 4d-4d). The latter may suggest that the modification of the substituent leads also to an increase in the probability for thermally delayed fluorescence and therefore could affect positively the quantum yield.
Understanding the changes in photo-physical behaviour of the homoleptic platinum complexes and the tunability aspects in a structure-property perspective is important. This can be studied qualitatively by looking at the energy level diagram generated from TDDFT calculations (Figure 5.25). As discussed previously, the ligands exhibit a good tunability in the photo-physical properties (absorption and photoluminescence) due to the changes introduced mainly on the LUMO levels by the substituents. The first aspect to be addressed is the lack of tunability of the photo-physical properties in the monomer complexes. By looking at the energy level diagram it can be seen in the monomers ($S_0$) that all the energy levels are reduced in energy as the system is stabilised upon complexation. The HOMO levels of all the four complexes (monomer) are stabilised virtually by the same amount of energy maintaining comparatively a similar energy distribution to the free ligands (a subtle variation is associated with 3pyaz(1,2,3) – N(CH₃)₂ which can be due to the contribution from the –N(CH₃)₂ substituent to the HOMO level). Compared to the HOMO levels, LUMO levels in the monomers show different degrees of stabilisation upon complexation. The LUMO level of Pt[3pyaz(1,2,3) – N(CH₃)₂]₂ shows the highest stability from the free ligand compared to that of the other complexes, suggesting with increasing donor ability of the substituent the stabilisation of the LUMO levels of the complexes is enhanced. Substituents that increase the
electron density in the pyridyl ring (associated with the LUMO), enable a stronger interaction with the platinum metal ion which stabilises the LUMO level of the complex.

This effect is greater with donor substituents than with the acceptors. This can also be seen in the energy level diagram which shows 1.76 eV stabilisation for the –N(CH$_3$)$_2$ moving from the ligand (S$_0$) and to monomer (S$_0$), whereas the –CHC(CN)$_2$ group shows only 0.75 eV stabilisation. This results in decreasing the energy difference between the LUMO levels of the complexes resulting in lack of tunability in the monomer complexes. This effect is further enhanced for the excited states of the monomer complexes which can be confirmed by noting the bond lengths between the pyridyl nitrogen and triazole nitrogen and the metal. The analysis indicates in going from S$_0$ to S$_1$, an increased ligand – metal interaction results as the

| Table 5.13 – Calculated bond lengths of the monomer and dimer complexes |
|---|---|---|---|
| Complex | S$_0$ | S$_1$ |
|   | N$_{py}$-Pt | N$_{tr}$-Pt | N$_{py}$-Pt | N$_{tr}$-Pt |
| Pt[3pyaz(1,2,3)-N(CH$_3$)$_2$]$_2$ | 2.05852 | 2.01496 | 2.03092 | 1.99732 |
| Pt[3pyaz(1,2,3)]$_2$ | 2.05525 | 2.01361 | 2.04181 | 1.96393 |
| Pt[3pyaz(1,2,3)-CHO]$_2$ | 2.05426 | 2.01070 | 2.05117 | 1.96057 |
| Pt[3pyaz(1,2,3)-CHC(CN)$_2$]$_2$ | 2.05491 | 2.00873 | 2.06357 | 1.96419 |
| 4a---4a | 2.05873 | 2.01559 | 2.05410 | 2.02090 |
| 4b---4b | 2.05491 | 2.01339 | 2.05252 | 2.01853 |
| 4c---4c | 2.05472 | 2.01025 | 2.05591 | 2.01303 |
| 4d---4d | 2.05422 | 2.00930 | 2.06521 | 2.01529 |
bond lengths decrease. This is greater with the donor substituents compared to the acceptors ($S_0 \rightarrow S_1$; $\Delta$ bond length ($\Delta N_{py-Pt}$); (N(CH$_3$)$_2$ – 0.027 Å) (H – 0.013 Å) (CHO – 0.003 Å) (CHC(CN)$_2$ – -0.009 Å)) (Table 5.13). This further restricts the dispersion of the LUMO levels restricting the emission tunability to 13 nm in the monomer excited complexes.

In the dimer/ excimer form the tunability is reinstated which follows substituent effects showing more sensitivity towards the substituents. The energy level diagram in Figure 5.26 (excimer S$_1$) indicates a slight enhancement in the spread of LUMO levels compared to the monomer S$_1$ which can positively contribute to regaining the tunability. Most importantly the effect of the LUMO level distribution based on the substituent effects are “turned-on” with the change in the HOMO level from $\pi_{\text{try}} - d_{xy}$ to ($d_{z^2} - d_{z^2}$)* orbital. The strong interaction of the two platinum centres along the $d_{z^2}$ orbitals increases the energy of the ($d_{z^2} - d_{z^2}$)* orbital, shifting it to the upper valence introducing a new HOMO level in the dimer. In the dimers Pt-Pt bond distance significantly changes as function of substituents (Figure
enhancing the tunability in the HOMO levels. As a synergistic effect of both HOMO and LUMO changes in the excited dimer pronounced substituent effect can be observed leading to an enhanced emission tunability. The changes in the orbitals from free ligands to dimers are given in Figure 5.26.

In order to study the relationship between the Hammett parameters of the substituents and the emission energies a graph was plotted between the two variables as show in Figure 5.27. The linear relationship indicates a good agreement between the two parameters suggesting the predictability of the emission energy base on the substituents used. Also the slopes of the two graphs ((●) monomer emission (▲) dimer/ excimer emission) show that the dimers are more sensitive toward the substitution. Figure 5.28 shows the relationship between the calculated $pK_a$ values and the emission energies of the monomer and dimer complexes ((●) monomer emission (▲) dimer/ excimer emission). This also indicates a linear relationship and provides another parameter that can be used to predict emission energies of the complexes.
5.5 Lifetime measurement data

Lifetime measurements are used to identify the origins of emission processes. As stated in Chapter 2, since fluorescence is a fast process compared to phosphorescence, when the emission process involves fluorescence, lifetime is shorter compared to that of phosphorescence. As a preliminary photodynamic investigation the emission lifetime data of the ligand 3pyaz(1,2,3) and the corresponding complex, [Pt(3pyaz(1,2,3)₂] in solution and thin-film are given in Figure 5.29. According to the data it can be confirmed the fluorescent nature of the ligand emission (16 ns measured at 390 nm) having a lifetime limited by the resolution of the detection system. In a solution of [Pt(3pyaz(1,2,3)₂] where both the high/monomer and low/excimer energy emissions are present, high energy emission (measured at 390 nm) lifetime was measured as a single exponential decay with a 15 ns lifetime. This confirms that the related high energy emission of the monomers involves a fluorescence process strengthening our earlier assignment. Interestingly, the low energy/excimer emission (measured at 530 nm) in the solution displays a bi-exponential decay with lifetime values of 42 and 153 ns, respectively. In the same manner, lifetime of emission in thin film of [Pt(3pyaz(1,2,3)₂] (measured at 540 nm) was observed as bi-exponential decay with two distinct lifetimes; 89 and 223 ns. This observation may lead to the conclusion of two emission processes contributing to the low energy/excimer emission.

Figure 5.29 – Lifetime measurement of 3pyaz(1,2,3) and [Pt(3pyaz(1,2,3)₂]: black – ligand emission (390 nm), red – complex solution – high energy emission (390 nm), green – complex solution – low energy emission (530 nm), blue – thin film emission (540 nm)
The difference in the lifetimes in solution and solid phase can be associated with the solvent effects of the medium. The comparatively shorter lifetime process may involve fluorescence whereas the longer lifetime process may involve either phosphorescence or a delayed fluorescence. The supposed fluorescence process in the excimer emission exhibits comparatively longer lifetime than that of monomers and the ligands may be due to the fact that the excimer emission involves excited state aggregations, which would expand over a considerable length of time. The distinction between the phosphorescence and delayed fluorescence for the longer lifetime process requires low temperature lifetime measurements which will be made in the future.

**Summary**

Innovations in the field of emissive materials have been motivated by the discovering of new emissive materials. Desirable candidates present tunable emission wavelengths and large quantum efficiencies. Tuning of the ground and excited state energies, and thus emission wavelength of these complexes can be achieved by subtle structural changes in the organic ligands. In this study we explore the emission tunability of a newly synthesised series of 5-substituted-pyridyl-1,2,3-triazole-based ligands and their Pt(II) complexes. Despite the substitution effects, the emission of the complexes in diluted solutions is restricted to around 13 nm. In contrast, a coarse tunability of the emission was observed in concentrated solutions and in thin films, spanning over a range in the 150 nm region. This “turned-on” substituent effect in the thin films was accounted for by metallophilic Pt---Pt interaction-induced aggregates in the excited state. Excited state calculations reveal a change in the excited state character going from isolated complexes/ monomers (1MLCT) to dimers (1MMLCT). Further, a linear-relationship between the Hammett parameters of the substituents and emission energies was established. This allows a reliable emission predictability for any given substituent of 5-substituted-pyridyl-1,2,3-triazole platinum complexes. In conclusion, we show a new approach in achieving coarse emission tunability in pyridyl-1,2,3-triazole based platinum complexes via subtle changes in the molecular structure and the importance of metallophilic interactions in the process.
6.1 Design of a library of heterocyclic azoles

As explained in the Chapter 2, heterocyclic systems introduce different characteristics depending on the number and the position of the heteroatoms in the molecular skeleton. In this chapter the synthesis and characterisation of a library of different ligands based on combinations of different six membered azines (pyridine, pyrimidine, pyrazine) and different five membered azoles (pyrazoles, imidazoles, 1,2,3-triazoles, 1,2,4-triazoles and tetrazoles) will be considered. The changes in the photo-physical properties of the ligand systems and their concomitant impact on the properties of the metal complexes will be discussed in the next chapter.

6.2 Reaction mechanisms and compound characterisation

6.2.1 Synthesis of (1,2)diazole / pyrazole series

6.2.1.1 Synthesis of acetyl pyrimidine

Acetyl pyrimidine was synthesised by acetylation of 2-cyanopyrimidine. The reaction takes place between a nitrile compound and a nucleophilic Grignard reagent. The mechanism of the reaction is shown in Figure 6.1

1. Nucleophilic carbon on the Grignard reagent attacks the carbon of the polar nitrile group forming intermediate imine salt complex.
2. On addition of an acid, the intermediate imine salt protonates generating the imine

![Figure 6.1 – Mechanism of acetylation of a nitrile](image)
144

compound.

3. Further protonation (acid catalysis) activates the imine, which undergoes a nucleophilic attack by a water molecule.

4. Deprotonation of the oxygen of the water molecule, neutralises the positive charge on the compound.

5. Further protonation of the nitrogen makes it a better leaving group releasing a neutral molecule of ammonia, which subsequently deprotonates the oxygen to produce the desired ketone.

Since the ketone is not formed until after the addition of an aqueous acid, the Grignard reagent does not get the opportunity to react with the ketone product. It is important to maintain low temperatures upon introduction of the Grignard reagent, and during the reaction as the process is highly exothermic.

The purified product from column chromatography appeared as yellow needle shaped crystals (Yield 70%, 6.100 g). The product exhibits an $R_f$ value of 0.33 with hexane: ethyl acetate 1:5 mobile phase. Mass spectrum (Figure 6.2 – a) exhibited the [M+H$^+$] peak at m/z 123.1, indicating the formation of the product. IR spectrum (Figure 6.2 – b) shows the introduction of carbonyl group by the strong peak at 1703 cm$^{-1}$.

The $^1$H NMR spectrum (Figure 6.3 – a) shows a triplet at 7.46 and a doublet of doublets at 8.92 ppm accounting for the protons in the pyrimidine ring. Methyl protons in the acetyl group were seen at 2.77 ppm ($^1$H NMR (300 MHz, chloroform-$d$) δ ppm 2.77 (s, 3 H) 7.46 (t, $J$=4.90 Hz, 1 H) 8.92 (dd, $J$=4.86, 1.93 Hz, 1 H)). The carbonyl carbon was seen at 197.66 ppm indicating the introduction of the acetyl group. The four carbons in the pyrimidine ring were observed by three peaks appearing at 122.7, 157.57 and 159.97 ppm, where the peak at 157.57 ppm corresponds to the two equivalent carbons in the ring. Methyl

![Figure 6.2](image)

**Figure 6.2** – (a) Low resolution mass spectrum (b) IR spectrum of 2-acetylpurimidene
carbon was observed at 26.72 ppm ($^{13}$C NMR (75 MHz, Chloroform-$d$) δ ppm 26.72, 122.91, 157.57, 159.97, 197.66).
6.2.1.2 Synthesis of eneaminone derivatives

Formamide acetals like DMF-DMA, are useful reagents in organic synthesis; their reaction with active methylene compounds lead to the formation of eneamine compounds that are instrumental in heterocyclic synthesis. The reaction takes place as follows.

At high temperatures, DMF-DMA is in equilibrium with $\text{OCH}_3^-$, which removes a proton from the ketone (active methylene compound) to generate a nucleophile at the $\alpha$-carbon of the ketone. This nucleophile attacks the $\text{OCH}_3(\text{H})\text{C} = N^+(\text{CH}_3)_2\alpha$–carbon, neutralising the positive charge on the nitrogen. Finally, a loss of methanol molecule generates the desired eneaminone derivative.

6.2.1.2.1 Structural characterisation of 3-(dimethylamino)-1-(pyrimidin-2-yl)prop-2-en-1-one

Recrystallisation from benzotrifluoride yielded a brown crystalline powder (Yield 69%, 5.003 g). TLC with hexane: ethyl acetate – 1:5 produced an $R_f$ value of 0.33. The melting point of the compound was 98 – 100 °C. Mass spectrum (Figure 6.6 – a) of the compound exhibited [M+H+] peak at m/z 178.1, indicating the product formation. IR spectrum (Figure 6.6 – b) shows two important peaks at 1643 and 1543 cm$^{-1}$ corresponding
to C=C stretch and C=O stretch, respectively. The C=O stretching frequency is less than that expected for a carbonyl group due to conjugation with the C=C bond.

The $^1$H NMR spectrum (Figure 6.7 – a) of the compound shows two singlets at 2.89 and 3.16 ppm, corresponding to the protons on the two methyl groups of the dimethylamino group. Two protons of the alkene appear at 6.14 and 7.78 ppm. Three protons on the pyrimidyl ring appear at 7.55 and 8.90 ppm as a triplet and a doublet of a doublet, where the later corresponds to the two equivalent protons. $^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 2.89 (s, 3 H) 3.10 - 3.31 (m, 3 H) 6.14 (br. s., 1 H) 7.55 (t, $J$=4.86 Hz, 1 H) 7.78 (br. s., 1 H) 8.90 (dd, $J$=4.86, 0.60 Hz, 2 H). The $^{13}$C NMR spectrum (Figure 6.7 – b) of the compound exhibited two peaks at 37.14 and 44.64 ppm corresponding to the carbons of the dimethylamino group. Two alkene carbons were seen at 92.11 and 154.92 ppm. Four
pyrimidyl carbons were observed at 121.94, 157.35 and 163.23 ppm. The carbonyl carbon was detected at 183.33 (\(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) \(\delta\) ppm 37.14, 44.64, 92.11, 121.94, 154.92, 157.53, 163.23, 183.33).

**6.2.1.2.2 Structural characterisation of 3-(dimethylamino)-1-(pyrazin-2-yl)prop-2-en-1-one**

Recrystallised product was brown crystals (Yield 80%, 5.800 g). TLC with ethyl acetate exhibited an \(R_f\) value of 0.2. The melting point of the compound was 123 – 125 °C. Mass spectrum (Figure 6.8 – a) of the compound exhibited [M+H\(^+\)] peak at m/z 178.1 indicating the product formation. The IR spectrum (Figure 6.8 – b) shows two important peaks at 1635 and 1543 cm\(^{-1}\) corresponding to C=C stretch and C=O stretch respectively.
The $^1$H NMR spectrum (Figure 6.9 – a) of the compound, shows two singlets at 2.93 and 3.19 ppm, corresponding to the protons on the two methyl groups of the dimethylamino group. Two protons of the alkene appear at 6.25 and 7.86 ppm as doublets. Pyrazinyl protons appear at 8.68, 8.75 and 9.12 ppm ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 2.93 (s, 3 H) 3.19 (s, 3 H) 6.25 (d, $J$=12.20 Hz, 1 H) 7.86 (d, $J$=12.56 Hz, 1 H) 8.68 (dd, $J$=2.34, 0.96 Hz, 1 H) 8.75 (d, $J$=2.48 Hz, 1 H) 9.12 (s, 1 H)). The $^{13}$C NMR spectrum (Figure 6.9 – b) of the

Figure 6.9– (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3-(dimethylamino)-1-(pyrazine-2yl)prop-2-en-1-one
compound exhibited two peaks at 37.24 and 44.74 ppm corresponding to the carbons of the dimethylamino group. Two alkene carbons were seen at 89.75 and 154.79 ppm. Four pyrazinyl carbons were observed in the range of 143 – 150 ppm. The carbonyl carbon was detected at 183.33 (\(^{13}\text{C} \text{NMR (75 MHz, DMSO-}d_6\)) \(\delta\) ppm 37.24, 44.74, 89.75, 142.98, 143.36, 146.38, 150.00, 154.79, 183.33).

6.2.1.3 Synthesis of (1,2) diazoles / pyrazoles via cyclisation of enaminone derivatives\(^{197}\)

![Figure 6.10 – Synthesis of pyrazole derivatives from enaminones](image)

Hydrazine drives a nucleophilic attack on the carbonyl carbon of the enaminone to form hydrazinium enolate (B), which rearranges internally to give hydrazinyl-enol (C). Loss of a water molecule from C produces hydrazono-enamine (D), which cyclises to form dimethylamino substituted pyrazole. Further internal rearrangements and removal of a dimethylamine molecule gives the final pyrazole version (G).

![Figure 6.11 – Reaction mechanism of pyrazole formation](image)

6.2.1.3.1 Structural characterisation of 2-(1H-pyrazol-5-yl)pyridine-(2pyraz(1,2))

The final product was obtained as white crystalline powder (Yield - 77%, 1.400 g). The product showed an \(R_f\) value of 0.46 with hexane: ethyl acetate – 1:5 mobile phase. The melting point range of the compound was 122 – 124 °C. The mass spectrum (Figure 6.12 - a) of the product exhibited \([M+H]^+\) peak at \(m/z\) 146.1. Further analysis from high resolution mass spectrometry gave \([M+H]^+\) peak at \(m/z\) 146.0710 (theoretical \([M+H]^+\) - 146.0713)
confirming the product formation. The peaks in the IR spectrum (Figure 6.12 - b) around 2900 – 3150 cm$^{-1}$ correspond to the C-H stretching peaks of the pyridine and pyrazole rings.

The $^1$H NMR spectrum (Figure 6.13-a) indicates formation of two tautomers, where the acidic proton of pyrazole ring would be on either of the nitrogen atoms. By comparing the peak integration values corresponding to the N-H proton / acidic proton on the pyrazole ring, it is evident that the 2H isomer dominates over 1H isomer (approx. 7:3 ratio). The acidic proton on the 1H would be more de-shielded as it exists closer to the electron withdrawing pyridyl ring. The acidic proton of the 2H and 1H isomers are detected at 13.07 and 13.54 ppm respectively. The proton on the 3$^{rd}$ carbon of the pyrazole ring is also affected by the position of the acidic proton. At 7.58 and 7.79 ppm values, C-H proton of the 3$^{rd}$ carbon of the pyrazole ring can be seen corresponding to 1H and 2H isomers respectively. All other protons seems to share an equivalent chemical environment for both isomers. At the same time poor multiplet separation and broadness in the peaks may result from the peak overlap for the two isomers ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 6.86 (d, $J=1.70$ Hz, 1 H) 7.19 - 7.39 (m, 1 H) 7.58 (br. s., 0.31 H) 7.72 - 7.91 (m, 1 H) 7.99 (d, $J=7.84$ Hz, 0.71 H) 8.57 (d, $J=3.68$ Hz, 1 H) 13.07 (br. s., 0.68 H) 13.54 (br. s., 0.28 H)). The $^{13}$C NMR spectrum shows the effect of having a mixture of isomers resulting very close lying pairs of peaks corresponding to the aromatic carbons in the two rings. All the carbons were observed in the region 103 – 153 ppm ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 103.14, 119.24, 122.37, 129.86, 136.82, 149.15, 151.09, 152.42).

Although the final product was obtained as a mixture of isomers, it would not introduce any complications during metal complexation as the complexation occurs under basified conditions, where the acidic proton would be removed.
6.2.1.3.1 Structural characterisation of 2-(1H-pyrazol-5-yl)pyrimidine-(2pmaz(1,2))

The final product was yellow/orange, rod shaped crystals (yield – 85%, 3.155 g). Product exhibited an $R_f$ value of 0.28 with hexane: ethyl acetate – 1:5 mobile phase. The melting point of the compound was 133 °C. The mass spectrum (Figure 6.14 - a) of the product exhibited [M+H$^+$] peak at m/z 147.1. The high resolution mass spectrometry also
Figure 6.14 – (a) Low resolution mass spectrum (b) IR spectrum of 2-(1H-pyrazol-5-yl)pyrimidine – (2pmaz(1,2)) showed [M+H\(^+\)] peak at m/z 147.0665 (theoretical [M+H\(^+\)] -147.0665). The peaks corresponding to C-H stretching of the two aromatic rings were observed around 3000 cm\(^{-1}\) region the IR spectrum (Figure 6.14 - b).

As in the case of the pyridyl derivative, the pyrimidyl derivative also indicates an isomeric mixture of 1H and 2H pyrazoles in the final product. By comparing the peak integration values corresponding to the N-H proton / acidic proton of the pyrazole ring, it can be derived as approx. 6:4 mixture of 1H : 2H isomers. The acidic proton of the 2H and 1H isomers are detected at 13.26 and 13.79 ppm respectively. The proton on the 3\(^{rd}\) carbon of the pyrazole ring is also affected by the position of the acidic proton. At 7.62 and 7.85 ppm values, C-H proton of the 3\(^{rd}\) carbon of the pyrazole ring was observed corresponding to 1H and 2H isomers respectively. As previously with the pyridyl version, the chemically equivalent protons in the pyrimidyl pyrazole also exhibited poor multiplet separation and
broadness in the peaks due to the effects of isomerization ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 6.95 (d, $J$=1.23 Hz, 1 H) 7.29 - 7.52 (m, 1 H) 7.62 (br. s., 1 H) 7.85 (br. s., 1 H) 8.85 (d, $J$=4.06 Hz, 2 H) 13.26 (br. s., 1 H) 13.79 (br. s., 1 H)). Replacing the pyridyl ring with more electronegative pyrimidyl ring (due to higher number of heteroatoms), increases the acidity of the N-H proton of the pyrazole ring.

The $^{13}$C NMR spectrum also shows the effect of having a mixture of isomers, resulting in very close lying pairs of peaks corresponding to the aromatic carbons in the two rings. All the carbons were observed in the region 106 – 163 ppm ($^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ ppm 106.19, 119.97, 140.16, 157.13, 157.75, 162.84).
6.2.1.3.1 Structural characterisation of 2-(1H-pyrazol-5-yl)pyrazine - (2pzaz(1,2))

The final product was yellow/orange, cubic shaped crystals (Yield 70%, 2.310 g). \( R_f \) – 0.22 (hexane: ethyl acetate – 1:2). The melting point of the compound was 148 °C. The [M+H⁺] peak of the product was observed at m/z 147.1 (Figure 6.16 - a). High resolution mass spectrometry also showed [M+H⁺] peak at m/z 147.0664 (theoretical [M+H⁺] - 147.0665). The peaks corresponding to C-H stretching of the two aromatic rings were observed in the 2900 – 3200 cm⁻¹ region the IR spectrum (Figure 6.16 - b).

As in previous situations, the pyrazinyl derivative also exhibited the existence of isomeric forms having approx. 8:2 ratio of 2H: 1H pyrazoles in the final product. The acidic proton of the 2H and 1H isomers are detected at 13.29 and 13.76 ppm respectively. Compared to pyrimidine derivative, pyrazinyl-pyrazole also indicated an increase in the
acidity of the N-H proton. Both pyrazinyl and pyrimidyl versions seem to have the same acidity by comparing the shift of the acidic proton in the $^1$H NMR spectrum. The proton on the 3$^{rd}$ carbon of the pyrazole ring is also affected by the position of the acidic proton. At 7.64 and 7.90 ppm values, C-H proton of the 3$^{rd}$ carbon of the pyrazole ring was observed corresponding to 1H and 2H isomers respectively ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 6.75 - 7.29 (m, 1 H) 7.64 (br. s., 1 H) 7.90 (s, 1 H) 8.43 - 8.82 (m, 2 H) 9.19 (s, 1 H) 13.29 (br. s., 1 H) 13.76 (br. s., 1 H)). The $^{13}$C NMR spectrum shows the aromatic carbons of the two rings in the region 103 – 149 ppm ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 103.83, 130.39, 138.14, 141.21, 143.09, 144.16, 148.55).

6.2.2 Synthesis of (1,3)diazoles / imidazoles

The reaction initiates via the formation of an amidate, which follows the Pinner reaction mechanism. The amidate subsequently reacts with a dialkoxyethylamine equivalent and eventually cyclises in to the imidazole by releasing two alcohol equivalents. From the amidate to the imidazole the reaction follows the Pomeranz-Fritsch reaction mechanism, which is a modification of the Schilittle-Muller reaction.

1. The Pinner reaction proceeds via base catalysed nucleophilic addition of an alkoxide equivalent to nitriles, to form an amidate of the respective nitrile.
2. Methoxide ion attacks the electrophilic nitrile in methanolic medium to form the amidate, (B). Generally this is a very fast reaction, which requires mild reaction conditions.

3. Amidate is activated in the presence of a diluted acid (C) which reacts with dialkoxyethylamine by releasing a methanol equivalent, (D).

4. Removal of a proton to neutralise the positive charge, generates amidine, (E) equivalent. Imidates contain both amide and imine functional groups which are considered to be the nitrogen equivalent of the respective carboxylic acid. Amidines are also considered as organic bases.

5. Addition of a proton to the alkoxy group activates the carbon atom bearing the alkoxy groups, making it susceptible for nucleophilic attacks, (F). Intramolecular nucleophilic attack by the imine nitrogen cyclises the imidamide into an imidazole, (G) by releasing an equivalent of alcohol.

6. Removal of another alcohol equivalent from H, results in the formation of 1H-imidazole (I).

In this reaction series sodium methoxide acts as the base during the formation of the

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Figure 6.18 – Reaction mechanism for (1,3)diazole/ imidazole formation

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Figure 6.19 – Synthesis of amino-ene-one derivatives
imidamide derivative. With pyrazinyl and pyrimidyl derivatives, Pinner reaction was performed at R.T. whereas pyridyl derivative required gentle heating to 40 °C. This can be due to greater electron withdrawal from pyrimidine and pyrazine activating the nitrile carbon more than that from the pyridine. Mild heating was required during the formation of the amidate. Compared to that more drastic conditions were used for amidine formation. This is due to the fact that carboxylic acid-equivalent carbon in the amidate is more active and susceptible for nucleophilic attacks than the electrophilic carbon in the imidamide. The crude products were washed with water to remove any salt residues remaining in the product.

6.2.2.1 Structural characterisation of 2-(1H-imidazol-2-yl)pyridine – (2pyaz(1,3))

The final product was faint brown/white crystals (Yield 41%, 2.995 g). Product showed an $R_f$ value of 0.19 with hexane: ethyl acetate – 1:2 mobile phase. The melting point of the compound was 131 °C. Mass spectrum (Figure 6.20 - a) of the product showed the [M+H$^+$] peak at m/z 146.1. High resolution mass spectrometry gave the [M+H$^+$] peak at m/z 146.0710 (theoretical [M+H$^+$] -146.0713) confirming the product formation. The peaks in the IR spectrum (Figure 6.20 - b) around 2900 – 3100 cm$^{-1}$ correspond to the C-H stretching peaks of the pyridine and pyrazole rings.

The $^1$H NMR spectrum (Figure 6.21 -a) indicates the two protons in the imidazole ring that share the similar chemical environment, exhibiting broad singlet/ unresolved multiplet at 7.14 ppm. All the protons in the pyridyl ring appear in the region 7.3 – 8.6 ppm. The acidic proton in the imidazole ring is represented by a broad singlet/ unresolved multiplet at 12.18 ppm. This value suggests that the acidic proton in the pyrazole is more deshielded (around 13.5 ppm) and hence more acidic than the imidazole ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 6.86 (d, $J=1.70$ Hz, 1 H) 7.19 - 7.39 (m, 1 H) 7.58 (br. s., 0.31 H) 7.72 - 7.91 (m, 1 H) 7.99.

![Figure 6.20 – (a) Low resolution mass spectrum (b) IR spectrum of 2-(1H-imidazol-2-yl)pyridine – (2pyaz(1,3))](image)
(d, J=7.84 Hz, 0.71 H) 8.57 (d, J=3.68 Hz, 1 H) 13.07 (br. s., 0.68 H) 13.54 (br. s., 0.28 H)). The $^{13}$C NMR spectrum (Figure 6.21 - b) shows the equivalent imidazole ring carbons at 121.97 ppm. All the carbons in the pyridine ring were observed in the region 123 – 164 ppm ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 121.97, 123.02, 125.09, 136.70, 148.59, 148.81, 163.56).

Figure 6.21 - (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 2-(1H-imidazol-2-yl)pyridine – (2pyaz(1,3))
6.2.2.2 Structural characterisation of 2-(1H-imidazol-2-yl)pyrimidine – (2pmaz(1,3))

The final product was white, cubic shaped crystals (Yield 31%, 2.288 g). Product exhibited an \( R_f \) value of 0.17 with ethyl acetate mobile phase. The melting point of the compound was in the range of 204 – 206 °C. Mass spectrum (Figure 6.22 - a) of the product exhibited \([M+H^+]\) peak at m/z 147.1. High resolution mass spectrometry also showed \([M+H^+]\) peak at m/z 147.0663 (theoretical \([M+H^+]\) -147.0665). The peaks corresponding to C-H stretching of the two aromatic rings were observed around 3000 cm\(^{-1}\) region the IR spectrum (Figure 6.22 - b).

The two equivalent protons in the imidazole ring appear at 7.25 ppm as a broad singlet/unresolved multiplet. Protons in the pyrimidine ring appear at 7.42 as a triplet, and at 8.86 ppm as a doublet (two equivalent protons). The acidic proton in the imidazole appears at
13.12 ppm suggesting a slight decrease in the acidity compared to the analogous pyrazole version (1H NMR (300 MHz, DMSO-d$_6$) δ ppm 7.25 (br. s., 2 H) 7.42 (t, $J$=4.80 Hz, 1 H) 8.86 (d, $J$=4.82 Hz, 2 H) 13.12 (br. s., 1 H)). All the aromatic carbons in the two rings were observed in the region 120 – 158 ppm region (13C NMR (75 MHz, DMSO-d$_6$) δ ppm 120.00, 124.91, 144.37, 156.91, 157.67).

6.2.2.3 Structural characterisation of 2-(1H-imidazol-2-yl)pyrazine – (2pzaz(1,3))

The final product was white, needle shaped crystals (Yield 40 %, 2.923 g). $R_f$ – 0.33 (ethyl acetate). The melting point of the compound was 196 – 198 °C. Mass spectrum (Figure
6.24 - a) of the product gave the [M+H⁺] peak at m/z 147.1. High resolution mass spectrometry also showed the [M+H⁺] peak at m/z 147.0664 (theoretical [M+H⁺] - 147.0665). The peaks corresponding to C-H stretching of the two aromatic rings were observed around 3100 cm⁻¹ region the IR spectrum (Figure 6.24 - b).

As previous, the imidazole protons were observed as a broad singlet/ unresolved multiplet at 7.26 ppm. Pyrazine ring protons appear in the region 8.5 – 9.3 ppm. The acidic

![Figure 6.25 - (a) ¹H NMR spectrum (b) ¹³C NMR spectrum of 2-(1H-imidazol-2-yl)pyrazine – (2pzaz(1,3))]
imidazole proton was observed at 13.07 ppm, also suggesting a decrease in the acidity compared to its analogous pyrazole version ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 7.26 (br. s., 2 H) 8.44 - 9.06 (m, 2 H) 9.24 (d, $J$=1.51 Hz, 1 H) 13.07 (br. s., 1 H)). The carbons in the imidazole ring were observed at 119.74 ppm whereas the carbons in the pyrazine ring were seen in the region 130 – 145 ppm ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 119.74, 130.04, 141.36, 143.47, 143.77, 144.44).

6.2.3 Synthesis of (1,2,3) triazole series

Reaction mechanisms involved with this series were discussed in the Section 4.2. An overview of the reaction scheme is shown in Figure 6.26

![Reaction scheme](image)

**Figure 6.26 – Synthesis of (1,2,3) triazoles**

6.2.3.1 Synthesis of the protected alkyne derivative via Sonogashira coupling

6.2.3.1.1 Structural characterisation of 2-((trimethylsilyl)ethynyl)pyridine – 3pyaz(1,2,3) - s1

Structural characterisation related to 3pyaz(1,2,3) was discussed in the Section 4.2.

6.2.3.1.2 Structural characterisation of 2-((trimethylsilyl)ethynyl)pyrimidine – 3pmaz(1,2,3) - s1

The purified product was a brown oil (yield 72%, 2.000 g). TLC analysis revealed an $R_f$ value of 0.43 (mobile phase – hexane: ethyl acetate – 1:3). Mass spectrum (Figure 6.26 – a) exhibited the [M+H$^+$] peak at 177.1. IR spectrum (Figure 6.27 – b) showed weak C≡C stretching peak at 2121 cm$^{-1}$, corresponding to the internal alkyne.

![Mass spectrum](image)

**Figure 6.27 – (a) Low resolution mass spectrum (b) IR spectrum of 2-((trimethylsilyl)ethynyl)pyrimidine – (3pmaz(1,2,3) – s1)**
In the $^1$H NMR spectrum (Figure 6.28 – a), singlet peak appearing at 0.05 ppm corresponds to the protons of the trimethylsilyl group, which integrates into nine protons. Two peaks corresponding to the pyrimidyl aromatic protons appear at 6.90 and 8.47 ppm as a triplet and a doublet respectively ($^1$H NMR (300 MHz, chloroform-$d$) $\delta$ ppm 0.05 (s, 9 H) 6.90 (t, $J$=4.86 Hz, 1 H) 8.47 (d, $J$=4.90 Hz, 1 H)). $^{13}$C NMR spectrum (Figure 6.28 –b) shows a peak at 3.00 ppm, corresponding to the methyl groups in the trimethylsilyl moiety. Two alkyne carbons are represented by the peaks at 77.18 and 90.63 ppm. Peaks corresponding to the four carbons of the pyrimidyl ring were observed in the region 121 –
159 ppm \(^{13}\text{C} \text{NMR}\) (75 MHz, Chloroform-\(d\)) \(\delta\) ppm 3.00, 77.18, 90.63, 121.08, 153.25, 158.09).

6.2.3.1.3 Structural characterisation of 2-((trimethylsilyl)ethynyl)pyrazine – 3pzaz(1,2,3) - s1

The final product was a yellow oil (yield 73%, 2.537 g). TLC exhibited an \(R_f\) = 0.71 with hexane: ethyl acetate – 1:3 mobile phase. Mass spectrum (Figure 6.29 – a) exhibits the \([M+H^+]\) peak at m/z 177.1. It is hard to see the C≡C stretching of the internal alkyne as expected on the IR spectrum, as that stretching mode sometimes is very weak and hard to observe (Figure 6.29 – b).

In the \(^1\text{H} \text{NMR}\) spectrum (Figure 6.30 – a), singlet appearing at 0.23 ppm corresponds to the protons of the trimethylsilyl group. The four aromatic protons appeared in the region 8.42 – 8.62 ppm \(^{1}\text{H} \text{NMR}\) (300 MHz, chloroform-\(d\)) \(\delta\) ppm 0.23 (s, 9 H) 8.42 (d, \(J=2.50\) Hz,
1 H) 8.47 (dd, J=2.50, 1.65 Hz, 1 H) 8.62 (d, J=1.70 Hz, 1 H). $^{13}$C NMR spectrum shows a peak at 0.83 ppm that corresponds to the methyl groups in the trimethylsilyl moiety whereas the peaks at 99.21 and 100.39 ppm reflect the two carbons of the alkyne. Peaks corresponding to the four carbons in the pyrazinyl ring are visible in the region 139 – 148 ppm ($^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ ppm 0.83, 99.21, 100.39, 139.48, 142.72, 143.95, and 147.51).

6.2.3.2 Desilylation of the TMS group

6.2.3.2.1 Structural characterisation of 2-ethynylpyridine – 3pyaz(1,2,3) – s2

Structural characterisation related to 3pyaz(1,2,3) – s2 was discussed in the Section 4.2.

6.2.3.2.1 Structural characterisation of 2-ethynylpyrimidine – 3pmaz(1,2,3) – s2

The purified product is separated as white, needle shaped crystals. (yield 71%, 0.760
g). $R_f = 0.78$ (hexane: ethyl acetate – 1:3). The melting point of the compound was in the range of 88 – 91 °C. The mass spectrum indicated the [M+H$^+$] peak at -105.1 (Figure 6.31 – a). IR spectrum shows (Figure 6.31 – b) C≡C stretching peak of the terminal alkyne at 2121 cm$^{-1}$, indicating the deprotection of the TMS group, and at 3247 cm$^{-1}$ C-H terminal alkyne stretching can be seen.

In the $^1$H NMR spectrum (Figure 6.32 – a), the alkyne proton was seen at 3.17 and the pyrimidyl protons were observed in the region 7.3 – 8.8 ppm ($^1$H NMR (300 MHz,
chloroform-\(d\)) $\delta$ ppm 3.17 (s, 1 H) 7.31 (t, $J$=4.95 Hz, 1 H) 8.75 (d, $J$=4.95 Hz, 2 H)). In the $^{13}$C NMR spectrum (Figure 6.32 – b), the two alkyne carbons were observed at 75.87 and 81.70 ppm, whereas the aromatic carbons were found in the region 120 – 158 ppm ($^{13}$C NMR (75 MHz, Chloroform-\(d\)) $\delta$ ppm 75.87, 81.70, 120.48, 152.14, 157.26).

6.2.3.2.2 Structural characterisation of 2-ethynylpyrazine – 3pzaz(1,2,3) – s2

The purified product is separated as yellow, needle shaped crystals. (yield 71%, 0.760 g). $R_f$ – 0.54 (hexane: ethyl acetate – 1:3). The melting point of the compound was 45 – 47 °C. The mass spectrum indicated the [M+H$^+$] peak at - 105.1 (Figure 6.33 – a). IR spectrum shows (Figure 6.33 – b) C≡C stretching peak of the terminal alkyne at 2114 cm$^{-1}$ indicating the deprotection of the TMS group and at 3217 cm$^{-1}$ C-H terminal alkyne stretching can be seen.

In the $^1$H NMR spectrum (Figure 6.34 – a), the alkyne proton was seen at 3.17 and the
pyrimidyl protons were observed in the region 7.3 – 8.8 ppm (\textsuperscript{1}H NMR (300 MHz, chloroform-\textit{d}) δ ppm 3.36 (s, 1 H) 8.54 (d, J=2.50 Hz, 1 H) 8.57 (dd, J=2.52, 1.51 Hz, 1 H) 8.72 (d, J=1.38 Hz, 1 H). In the \textsuperscript{13}C NMR spectrum (Figure 6.34–b), the two alkyne carbons were observed at 79.95 and 81.18 ppm, whereas the aromatic carbons were found in the region 139 – 149 ppm (\textsuperscript{13}C NMR (75 MHz, Chloroform-\textit{d}) δ ppm 79.95, 81.18, 139.23, 143.59, 144.45, 148.04).

6.2.3.3 Synthesis of protected triazole via 1,3–Dipolar cycloaddition reaction\textsuperscript{183,184}

6.2.3.3.1 Structural characterisation of 3pyaz(1,2,3) – s3

Structural characterisation related to 3pyaz(1,2,3) – s3 was discussed in the Section 4.2.

6.2.3.2.1 Structural characterisation of 3pmaz(1,2,3) – s3

Figure 6.35 – (a) Low resolution mass spectrum (b) IR spectrum of 3pmaz(1,2,3) – s3
The purified product was white, needle shaped crystals with 76% yield (1.334 g). TLC analysis produced an $R_f$ value of 0.32 (mobile phase – 1:3 hexane: ethylacetate). Melting point of the compound was over the range 177 –179 °C. The [M+H$^+$] peak was observed at m/z 262.1 (Figure 6.35 – a). IR peaks at 1719 and 1149 cm$^{-1}$ correspond to the C=O and C-O bond stretchings respectively (Figure 6.35 - b).

![Figure 6.36 - (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pmaz(1,2,3) – s3](image)

In the $^1$H NMR spectrum (Figure 6.36 – a), the peak observed at 1.20 ppm corresponds to the protons in the $t$-butyl group. Two hydrogens on -CH$_2$ of the
methylpivalate group appeared at 6.33 ppm. Three protons in the pyrimidyl ring and one proton in the triazole ring appeared in the region 7.2 – 8.9 ppm (1H NMR (300 MHz, chloroform-d) δ ppm 1.20 (s, 6 H) 6.33 (s, 2 H) 7.25 (t, J=4.91 Hz, 1 H) 8.52 (s, 1 H) 8.83 (d, J=4.95 Hz, 2 H)). 13C NMR spectrum (Figure 6.36 – b) shows a peak at 26.78 ppm corresponding to the methyl groups in the t-butyl group. Peak at 38.78 ppm reflects the tertiary carbon in the t-butyl group. -CH2 carbon in the methylpivalate group appears at 69.78 ppm. Seven aromatic carbons are observed in the 119 – 159 ppm region. Carbonyl carbon in the methylpivalate ester group appears at 177.67 ppm. (13C NMR (75 MHz, Chloroform-d) δ ppm 26.78, 38.78, 69.78, 119.88, 126.36, 147.73, 157.56, 158.78, 177.67).

6.2.3.2.2 Structural characterisation of 3pzaz(1,2,3) – s3

![Figure 6.37](image)

**Figure 6.37** – (a) Low resolution mass spectrum (b) IR spectrum of 3pzaz(1,2,3) – s3

The purified product was white, needle shaped crystals (yield 71%, 1.692 g). TLC analysis produced an Rf value of 0.68 (mobile phase – 1:3 hexane: ethylacetate. Melting point of the compound was over the range 128 – 130 °C. The [M+H+] peak was observed at m/z 262.1 (Figure 6.37 – a). IR peaks at 1743 and 1134 cm⁻¹ correspond to C=O and C-O bond stretchings respectively (Figure 6.37 – b).

In the 1H NMR spectrum (Figure 6.38 – a), the peak appeared at 1.21 ppm corresponds to the protons in the t-butyl group. Two hydrogens on -CH2 of the methylpivalate group appeared at 6.33 ppm. Three protons in the pyrazinyl ring and the proton in the triazole ring appeared in the region 8.4 – 9.5 ppm (1H NMR (300 MHz, chloroform-d) δ ppm 1.21 (s, 9 H) 6.33 (s, 2 H) 8.44 (s, 1 H) 8.54 (d, J=2.60 Hz, 1 H) 8.56 (dd, J=2.60, 1.50 Hz, 1 H) 9.43 (d, J=1.50 Hz, 1 H)). 13C NMR spectrum (Figure 6.38 – b) shows a peak at 26.80 ppm corresponding to the methyl groups in the t-butyl group. The peak at 36.80 ppm resembles that for the tertiary carbon in the t-butyl group. -CH2 carbon in the
methympivalate group appears at 69.79 ppm. Seven aromatic carbons are observed in 124 – 147 ppm region. Carbonyl carbon in the methympivalate ester group appears at 177.66 ppm ($^{13}$C NMR (75 MHz, Chloroform-$d$) δ ppm 26.80, 38.81, 69.79, 124.39, 142.23, 143.91, 144.07, 145.50, 146.48, 177.66).

Figure 6.38 - (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 3pzaz(1,2,3) – s3
6.2.3.4 Synthesis of 1H-(1,2,3)triazole derivative

6.2.3.4.1 Structural characterisation of 3pyaz(1,2,3)

Structural characterisation related to 3pyaz(1,2,3) was discussed in the Section 4.2.

6.2.3.4.2 Structural characterisation of 3pmaz(1,2,3)

![Image of mass spectrum and IR spectrum](image)

Figure 6.39 – (a) Low resolution mass spectrum (b) IR spectrum of 3pmaz(1,2,3)

The purified product was a white, crystalline powder with 92 % yield (0.621 g). TLC analysis showed an $R_f$ value of 0.18 (mobile phase – 1:3 hexane: ethylacetate). Melting point of the compound was over the range 135 – 136 °C. Mass spectrum (Figure 6.39 – a) indicated the \([M + H^+]\) peak at m/z 148.1. High resolution mass analysis generated the \([M+H^+]\) peak at m/z 148.0617 (theoretical \([M + H^+]\) – 148.0618 m/z), confirming the formation of the product. The absence of the IR peaks corresponding to C=O and C-O bond stretching indicates the removal of methylpivalate group (Figure 6.39 – b).
The $^1$H NMR spectrum (Figure 6.40 – a) indicates the absence of peaks corresponding to the protons in the methylpivalate group. Four aromatic protons in the pyrimidyl and triazole rings appeared in the range 7.4 – 9.0 ppm giving an integration value of 4H’s. A broad singlet appearing at 15.48 ppm indicates a very acidic proton which would resemble the N-H triazole proton. This shows that the increase in the nitrogen content in the azole ring increases the acidity of the N-H proton (compared to diazole versions) ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 7.47 (t, $J=4.91$ Hz, 1 H) 8.46 (s, 1 H) 8.90 (d, $J=4.82$ Hz, 1 H) 15.48 (br. s., 1 H)). Seven aromatic carbon peaks were seen in the region 120 – 159 ppm in the $^{13}$C NMR spectrum (Figure 6.40 – b) ($^{13}$C NMR in DMF-$d_7$ (75 MHz): $\delta = 120.51(9), 123.74(11), 133.39(10), 137.46(5), 148.83(8), 149.97(4), 150.01(6)$).

6.2.3.4.3 Structural characterisation of 3pzaz(1,2,3)

The purified product was a white, crystalline powder with 84 % yield (0.710 g). TLC analysis showed an $R_f$ value of 0.45 (mobile phase – 1:3 hexane: ethylacetate). Melting point of the compound was over the range 146 – 148 °C. Mass spectrum (Figure 6.41 – a) showed $[M + H^+]$ peak at m/z 148.1. High resolution mass analysis indicated $[M+H^+]$ peak at m/z 148.0617 (theoretical $[M + H^+]$ – 148.0618 m/z). As previous the absence of the IR peaks corresponding to C=O and C-O bond stretching indicates the removal of methylpivalate group (Figure 6.41 – b).
The $^1$H NMR spectrum (Figure 6.42 – a) indicates the absence of the peaks corresponding to the protons in the methylpivalate group. Aromatic protons in the pyrazinyl and triazole rings were observed in the region 8.5 – 9.3 ppm. Broad singlet appearing at 15.55 ppm resembles the N-H triazole proton. This again shows that the increase in the nitrogen content in the azole ring increases the acidity of the N-H proton (compared to the analogous diazole versions) ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 8.53 (s, 1 H) 8.62 (d, $J$=2.55 Hz, 1 H) 8.69 (dd, $J$=2.45, 1.50 Hz, 1 H) 9.22 (d, $J$=1.51 Hz, 1 H) 15.55 (br. s., 1 H)).

Seven aromatic carbon peaks were seen in the region 123 – 146 ppm in the $^{13}$C NMR spectrum (Figure 6.42 – b) ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 123.76, 138.01, 141.61, 143.95, 144.50, 145.48).
6.2.4 Synthesis of (1,2,4) triazole series

6.2.4.1 Synthesis of amidrazone derivatives

The synthesis of the 1,2,4-triazoles proceeds via formation of amidrazones. Amidrazones are, in general, monoacidic bases, which can be regarded as the bis-nitrogen analogue of the carboxylic acids and esters. Amidrazones are capable of exhibiting tautomeric structures as shown in Figure 6.43.

![Figure 6.43 – Tautomeric structures of amidrazones](image)

Synthesis of the amidrazones involves a nucleophilic attack on a nitrile or a cyanamide, by hydrazine. Since nitrile compounds were used as the precursors in the synthesis, the mechanism will be explained using a nitrile (Figure 6.44).

![Figure 6.44 – Reaction mechanism for amidrazone formation](image)
Hydrazine drives a nucleophilic attack on the nitrile carbon, forming a structure containing azomethine like C=N double bond, and amide like C-N single bond. An internal proton transfer results in the formation of the corresponding amidrazone. The reaction mixture was kept overnight to allow the internal rearrangement.

6.2.4.1.1 Structural characterisation of pyrimidine-2-carboximidhydrazide / pyrimidylamidrazone 3pmaz(1,2,4) – s1

Figure 6.45 – (a) Low resolution mass spectrum (b) IR spectrum of 3pmaz(1,2,4) – s1

The final product was yellow/orange, needle shaped crystals (yield 88%, 11.480 g), which showed an $R_f$ value of 0.27 with ethylacetate mobile phase. The melting point of the compound was 105 – 107 °C. The mass spectrum indicated the formation of the product with the [M+H$^+$] peak at m/z 138.1 (Figure 6.45 - a). The IR peak at 1623 cm$^{-1}$ corresponds to the
N-H bend of the primary amine, whereas N-H stretch of the amine is given by the peaks at 3348 and 3433 cm⁻¹ (Figure 6.45 - b). The presence of two peaks in the region 3300 – 3500 cm⁻¹, correspond to the N-H stretch that may indicate the dominance of the isomer containing two primary amino groups.

In the ¹H NMR spectrum of the compound (Figure 6.46 – a), protons in the two primary amino groups were seen at 4.77 and 5.13 ppm, which again confirms the existence of the isomer containing two primary amino groups. The pyrimidyl protons were observed in the region 7.4 – 8.9 ppm (¹H NMR (300 MHz, chloroform-d) δ ppm 4.77 (br. s., 2 H) 5.13 (br. s., 2 H) 7.40 (t, J=4.88 Hz, 1 H) 8.85 (d, J=4.91 Hz, 2 H)). Amidrazone carbon was observed at 144.97 ppm, whereas pyrimidyl carbons were seen 121.60, 155.82 and 157.36 ppm (Figure 6.46 - b) (¹3C NMR (75 MHz, Chloroform-d) δ ppm 121.60, 144.97, 155.82, 157.36).

6.2.4.1.2 Structural characterisation of pyrazine-2-carboximidhydrazide / pyrazinylamidrazone 3pzaz(1,2,4) – s1

The final product was yellow, needle shaped crystals (yield 90%, 11.738 g), which showed an $R_f$ value of 0.26 with ethylacetate mobile phase. The melting point of the compound was over the range 124 – 126 °C. The mass spectrum indicated the formation of the product with $[M+H^+]$ peak at m/z 138.1 (Figure 6.47 - a). The IR peak at 1643 cm⁻¹ corresponds to the N-H bend of the primary amine, whereas N-H stretch of the amine is presented by peaks at 3189 cm⁻¹, 3309 cm⁻¹, 3386 cm⁻¹ (N-H stretch primary amine). A peak
at 3386 cm⁻¹ can be considered as a shoulder peak, which is common for primary amines (Figure 6.47 - b). This also suggests the dominance of the isomer containing two primary amino groups.

In the ¹H NMR spectrum of the compound (Figure 6.48 – a), protons in the two primary amino groups were seen at 4.76 and 5.16 ppm. The pyrazinyl protons were observed in the region 8.4 – 9.3 ppm (¹H NMR (300 MHz, chloroform-d) δ ppm 4.76 (br. s., 2 H) 5.16 (br. s., 2 H) 8.45 (dd, J=2.57, 1.56 Hz, 1 H) 8.52 (d, J=2.57 Hz, 1 H) 9.28 (d, J=1.47 Hz, 1 H)). Amidrazone carbon was observed at 146.35 ppm, whereas pyrazinyl carbons were seen in the region 142 – 147 ppm (¹³C NMR (75 MHz, Chloroform-d) δ ppm 142.16, 142.59, 143.87, 146.23, 146.35).
6.2.4.2 Cyclisation of amidrazone derivatives to form (1,2,4) triazoles

At the final step, the amidrazone cyclises to form the respective 1,2,4-triazole derivative (Figure 6.49). The reaction initiates with a nucleophilic attack on the carbon of the formic acid by the nitrogen in the primary amine group, giving B. Loss of a water molecule from (B), generates \(N\)-formyl-imidohydrazide (C). Another nucleophilic attack on the formyl carbon by the nitrogen of the imido group, completes the cyclisation giving (D). Internal rearrangement in (D) gives 1,2,4-triazol-3-ol (E). Loss of another water molecule gives the final 1H-(1,2,4)triazole, (F).

![Reaction mechanism for the cyclization amidrazone generating 1,2,4-triazole](image)

Figure 6.49 – Reaction mechanism for the cyclization amidrazone generating 1,2,4-triazole
The addition of formic acid was carried out slowly at 0 °C, as the formation of $B$ is highly exothermic. Refluxing was important in the removal of water molecules and to supply energy required for the cyclisation. Na$_2$CO$_3$ was used to neutralise the excess formic acid in the reaction mixture.

6.2.4.2.1 Structural characterisation of 2-(1H-1,2,4-triazol-5-yl)pyrimidine

The final product was orange, needle shaped crystals (yield – 57%, 3.053 g) giving an $R_f$ value of 0.27 with ethylacetate mobile phase. The melting point of the compound was 226 – 229 °C. The mass spectrum indicated the [M+H$^+$] peak at m/z 148.1 (Figure 6.50 – a). High resolution mass analysis gave the [M+H$^+$] peak at m/z 148.0617 (theoretical [M+H$^+$] m/z – 148.0618). The IR spectrum indicates the absence of the peaks related to amino groups of the amidrazone (Figure 6.50 – b).
In the $^1$H NMR spectrum of the compound (Figure 6.51 – a) the four aromatic protons in the pyrimidyl and triazole rings were observed in the region 7.6 – 9.2 ppm. The acidic proton of the triazole N-H was not detected, indicating the high acidity of the proton ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 7.62 (t, $J=4.80$ Hz, 1 H) 8.93 (d, $J=4.82$ Hz, 2 H) 9.12 (s, 1 H)). In the $^{13}$C NMR spectrum of the compound the aromatic carbons were detected in the region 122 – 158 ppm except for the 3rd carbon in the triazole ring ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 122.26, 145.21, 155.84, 157.79).

6.2.4.1.2 Structural characterisation of 2-(1H-1,2,4-triazol-5-yl)pyrazine

The final product was orange, needle shaped crystals (yield – 52%, 2.786 g) giving an
$R_f$ value of 0.27 with ethylacetate mobile phase. The melting point of the compound was over the range 217 – 220 °C. The mass spectrum indicated the [M+H$^+$] peak at m/z 148.1 (Figure 6.52 - a). High resolution mass analysis gave the [M+H$^+$] peak at m/z 148.0614 (theoretical [M+H$^+$] m/z – 148.0618). The IR spectrum also indicates the absence of the peaks related to amino groups of the amidrazone (Figure 6.52 - b).

In the $^1$H NMR spectrum of the compound (Figure 6.53 – a), the four aromatic

Figure 6.53 - (a) $^1$H NMR spectrum (b) $^{13}$C NMR spectrum of 2-(1H-1,2,4-triazol-5-yl)pyrazine - 3pzaz(1,2,4)
protons in the pyrazinyl and triazole rings were observed in the region 8.5 – 9.3 ppm. The acidic proton of the triazole N-H was also not detected in the pyrazine version as well ($^1$H NMR (300 MHz, DMSO-$d_6$) δ ppm 7.62 (t, $J$=4.80 Hz, 1 H) 8.93 (d, $J$=4.82 Hz, 2 H) 9.12 (s, 1 H)). In the $^{13}$C NMR spectrum of the compound all the aromatic carbons were detected in the region 142 – 156 ppm (Figure 6.53 – b) ($^{13}$C NMR (75 MHz, DMSO-$d_6$) δ ppm 122.26, 145.21, 155.84, 157.79).

6.2.5 Synthesis of the tetrazole series

The tetrazoles functionality is widely studied due to its widespread applications. The most direct method of synthesising tetrazoles is via thermally activated (2+3) cycloaddition of sodium azide to respective nitrile derivatives. Although the reaction has long been proven to work with variety of nitriles, the yield has not been consistent with different nitrile compounds. Therefore the activation of the nitrile functionality is important. This is usually carried out by protonation or by activation using a Lewis acid. In the synthesis of pyridyl tetrazole, $\text{NH}_4\text{Cl}$ was used to activate the nitrile by protonation.

![Reaction mechanism of 1H-tetrazole synthesis via activation of nitrile by protonation](image)

Heating of sodium azide with ammonium chloride yields ammonium azide, which acts as the proton donor to activate the nitrile compound. A concerted type cyclisation between the azide and the nitrile gives the tetrazolate which protonates to give the 1H-tetrazole. In the case of pyrimidine and pyrazine versions, activation via protonation of the
compound was not revealed to be efficient. Therefore, antimony oxide, Sb$_2$O$_3$, was used as a Lewis acid to activate the nitrile.$^{164}$ The activated compound proceeds via (2+3) cycloaddition mechanism as shown in Figure 6.55.

6.2.5.1 Structural characterisation of 2-(1H-tetrazol-5-yl)pyridine (4pyaz)

![Figure 6.56 - (a) Low resolution mass spectrum (b) IR spectrum of 2-(1H-tetrazol-5-yl)pyridine – (4pyaz)](image)

The final product was white, needle shaped crystals (yield – 96%, 13.651 g) giving an $R_f$ value of 0.22 with ethylacetate mobile phase. The melting point of the compound was 212 – 214 °C. The mass spectrum indicated the [M+H$^+$] peak at m/z 148.1 (Figure 6.56 - a). High resolution mass analysis gave the [M+H$^+$] peak at m/z 148.0615 (theoretical [M+H$^+$] m/z – 148.0618). In the IR spectrum no significant functional group peaks were expected (Figure 6.56 - b).
In the $^1$H NMR spectrum of the compound (Figure 6.57 – a), the four aromatic protons in the pyridine ring were observed in the region 7.6 – 8.9 ppm. The acidic proton of the triazole N-H was not detected ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 7.64 (ddd, $J$=7.60, 4.86, 1.13 Hz, 1 H) 8.09 (td, $J$=7.74, 1.70 Hz, 1 H) 8.23 (dt, $J$=7.84, 1.10 Hz, 1 H) 8.80 (ddd, $J$=4.90, 1.80, 0.80 Hz, 1 H)). In the $^{13}$C NMR spectrum of the compound the six aromatic carbons of the two rings were detected in the region 122 – 155 ppm (Figure 6.57 -b) ($^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ ppm 122.63, 126.09, 138.22, 143.72, 150.06, 154.83).

6.2.5.2 Structural characterisation of 2-(1H-tetrazol-5-yl)pyrimidine (4pyaz)

The final product was white, crystalline powder (yield – 73%, 2.061 g) giving an $R_f$
value of 0.17 with ethylacetate mobile phase. The melting point of the compound was 226 – 228 °C. The mass spectrum indicated the [M+H⁺] peak at m/z 149.1 (Figure 6.58 - a). High resolution mass analysis gave the [M+H⁺] peak at m/z 149.0570 (theoretical [M+H⁺] m/z – 149.0567).

In the ¹H NMR spectrum of the compound (Figure 6.59 – a), the three aromatic protons in the pyrimidine ring were observed in the region 7.6 – 9.1 ppm. As previous, the

Figure 6.59 - (a) ¹H NMR spectrum (b) ¹³C NMR spectrum of 2-(1H-tetrazol-5-yl)pyrimidine
acidic proton of the triazole N-H was not detected ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 7.66 (t, $J$=3.90 Hz, 1 H) 9.02 (dd, $J$=3.90, 1.00 Hz, 2 H)). In the $^{13}$C NMR spectrum of the compound the six aromatic carbons of the two rings were detected in the region 122 – 159 ppm (Figure 6.59 -b) ($^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ ppm 122.72, 153.74, 154.51, 158.44).

6.2.5.3 Structural characterisation of 2-((1H-tetrazol-5-yl)pyrazine (4pzaz)

The final product was white crystalline powder (Yield = 81%, 2.280 g) giving an $R_f$ value of 0.19 with ethylacetate mobile phase. The melting point of the compound was 193 – 195 $^\circ$C. The mass spectrum indicated the [M+H$^+$] peak at m/z 149.1 (Figure 6.60 - a). High resolution mass analysis gave the [M+H$^+$] peak at m/z 149.0570 (theoretical [M+H$^+$] m/z –
In the $^1$H NMR spectrum of the compound (Figure 6.61 – a), the three aromatic protons in the pyrimidine ring were observed in the region 8.8 – 9.4 ppm. As previous, the acidic proton of the triazole N-H was not detected ($^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ ppm 8.86 (d, $J$=3.60 Hz, 2 H) 9.37 (d, $J$=1.04 Hz, 1 H)). In the $^{13}$C NMR spectrum of the compound the six aromatic carbons of the two rings were detected in the region 140 – 154 ppm (Figure 6.61 – b) ($^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ ppm 140.00, 143.39, 144.89, 146.83, 153.53).

6.3 Characterisation of the metal complexes

The metal complexes were characterized by high resolution mass spectrometry as shown in the Table 6.1. Mass spectra were not possible to obtain for tetrazole complexes and Pt[3pmaz(1,2,4)]$_2$ due to poor solubility. The obtained spectra are given in Appendix 3. Also NMR analysis was also not successful due to the poor solubility of the compounds.

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<td>Mass 2</td>
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**Summary**

Within this chapter, the synthesis of a library of azole-azine ligands with varying contents of ring nitrogen atoms (15 ligands) and their homoleptic platinum complexes (15 complexes) has been discussed. The mechanisms involved in the reactions were discussed accordingly and the structural characterisation of each compound is presented. Homoleptic platinum complexes were characterised by high resolution mass spectrometry and the poor solubility of the complexes hindered further characterisation of the complexes.
CHAPTER 7
PHOTO-PHYSICAL CHARACTERIZATION OF AZOLE LIGANDS AND HOMOLEPTIC PLATINUM COMPLEXES

7.1 Introduction

In the first section of this chapter the effects incurred by the number and position of ring nitrogen atoms in the ligands will be discussed with respect to the absorption and emission properties and further will be analysed using theoretical calculations. Once the effects on the ligands and the trends are understood the photo-physical characteristics of the platinum complexes will be explored to investigate whether the same trends are observed upon complexation. These will also be further investigated by theoretical simulations to understand the molecular level origins of such behaviour.

7.2 Photo-physical properties of the Ligands

The absorption data of the free ligands in their anionic forms (basic ethanolic solutions at $10^{-4}$ mol dm$^{-3}$) are presented in Figure 7.1 as series based on the six-membered ring (pyridyl series, pyrimidyl series, pyrazinyl series) and five-membered ring ((1,2)-diazole, (1,3)-diazole, (1,2,3)-triazole, (1,2,4)-triazole and tetrazole series) for the convenience of future reference. The absorption peaks of each ligand are listed in Table 7.1. Basic ethanolic solutions were prepared by adding 0.1 M NaOH to the ethanolic ligand solutions until the pH

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<td>3pzaz(1,2,3)</td>
<td>240, 266, 300, 322</td>
</tr>
<tr>
<td>3pzaz(1,2,4)</td>
<td>234, 259, 297, 314</td>
</tr>
<tr>
<td>4pzaz</td>
<td>237, 287, 307</td>
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</tbody>
</table>
was 11.

Figure 7.1 – Absorption spectra of anionic free ligands (a) pyridyl azole series (b) pyrimidy1 azole series (c) pyrazinyl azole series. In (a), (b) and (c); black – (1,2) diazole, red – (1,3) diazole, green – (1,2,3) triazole, orange – (1,2,4) triazole, blue – tetrazole. (d) (1,2) diazole series, (e) (1,3) diazole series, (f) (1,2,3) triazole series, (g) (1,2,4) triazole series, (h) tetrazole series. In (d), (e), (f), (g) and (h); pyridyl series, pyrimidyl series and pyrazinyl series

Figure 7.2 – (a) Experimental lowest energy absorptions (b) Calculated lowest energy absorption
Different absorption profiles are seen with the change of number and position of the nitrogen atoms in the azole and azine rings. In general with increasing number of nitrogen atoms in the azole ring, the whole absorption profiles of the ligands are blue-shifted indicating increased HOMO-LUMO gaps. Further, increase in the number of N-N links (number of adjacent nitrogen atoms) in the azole ring, promotes blue-shift of the absorption profiles. This effect becomes less sensitive with increasing nitrogen content in the azole ring (2az(1,2) vs. 2az(1,3) and 3az(1,2,3) vs. 3az(1,2,4)). In contrast to the azole ring variations, with increasing nitrogen atoms in the azine ring/ six-membered ring, promotes red-shift of the absorption profiles indicating decrease in the HOMO-LUMO gaps.

To discuss the experimental data, TDDFT calculations were performed using the PBE0 functional and 6-31G*\textsubscript{C,H,N} basis set (Table 7.2). A graph of experimentally obtained and calculated lowest energy absorption values indicates the same trend revealing a good agreement between the experimental and calculated data (Figure 7.2). In order to understand the nature and the origin of the electronic transitions, a molecular orbital (MO) analysis was carried out (Table 7.2 and Figure 7.3). According to the analysis, the lowest energy transitions are associated with a charge transfer processes, which in most of the cases originate from a dominantly azole centred HOMO level to a LUMO level concentrated on the pyridine (pyrimidine/ pyrazine) ring. Only in some cases, calculations show the HOMO to LUMO charge transfer is not favourable. Even in those cases the lowest energy transition is a charge transfer process from the azole to the six-membered heterocycle.

<p>| Table 7.2 – Excited states ES, vertical excitation energies E [eV], wavelengths λ [nm] and oscillator strength f computed with TDDFT/PBE0/6-31G*&amp;SDD in ethanol |
|-----------------|---------|------|------|
| ES   | E(eV) | λ (nm)   | f    |
| 2pyaz(1,2)  | S\textsubscript{1} | 4.15  | 299  | 0.1906 |
|          | S\textsubscript{3} | 4.47  | 277  | 0.3282 |
|          | S\textsubscript{3} | 4.92  | 252  | 0.0835 |
| 2pmaz(1,2) | S\textsubscript{3} | 4.30  | 289  | 0.2741 |
|          | S\textsubscript{3} | 4.46  | 278  | 0.1653 |
|          | S\textsubscript{6} | 4.50  | 276  | 0.2446 |
| 2pzaz(1,2) | S\textsubscript{1} | 3.70  | 335  | 0.1596 |
|          | S\textsubscript{1} | 4.41  | 281  | 0.3999 |
|          | S\textsubscript{7} | 4.76  | 260  | 0.0911 |
|          | S\textsubscript{10} | 5.88  | 211  | 0.0542 |
| 2pyaz(1,3) | S\textsubscript{1} | 3.88  | 319  | 0.1873 |
|          | S\textsubscript{2} | 4.18  | 296  | 0.4562 |
|          | S\textsubscript{6} | 5.27  | 235  | 0.0136 |
|          | S\textsubscript{8} | 5.59  | 222  | 0.0272 |
| 2pmaz(1,3) | S\textsubscript{2} | 4.08  | 304  | 0.6809 |
|          | S\textsubscript{6} | 5.10  | 244  | 0.0328 |</p>
<table>
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2pyaz(1,2,3)
$S_0 \rightarrow S_1$ (285 nm)

2pmaz(1,2,3)
$S_0 \rightarrow S_1$ (295 nm)

2pzaz(1,2,3)
$S_0 \rightarrow S_1$ (317 nm)

2pyaz(1,2,4)
$S_0 \rightarrow S_1$ (281 nm)

2pmaz(1,2,4)
$S_0 \rightarrow S_1$ (295 nm)

2pzaz(1,2,4)
$S_0 \rightarrow S_1$ (313 nm)
Energies of the leading MO of the ligands were calculated and are presented in Table 7.3. According to the data, a structure property relationship can be established to discuss the trends observed for the changes in HOMO and LUMO levels as a function of the ring nitrogen atoms. From the molecular orbital analysis, the HOMO levels are mainly associated
with the structure of the azole ring whereas the LUMO levels are localised on the six-membered heterocycle. Therefore, the changes in HOMO and LUMO levels are assumed to be more related to five and six-membered rings separately.

**Table 7.3 - Energies of the valence molecular orbitals**

<table>
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<tr>
<th>Ligand</th>
<th>2pyaz(1,2)</th>
<th>2pyaz(1,3)</th>
<th>3pyaz(1,2,3)</th>
<th>3pyaz(1,2,4)</th>
<th>4pyaz</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO+1 (eV)</td>
<td>-0.16</td>
<td>0.23</td>
<td>0.033</td>
<td>0.027</td>
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<td>LUMO (eV)</td>
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<td>-0.09</td>
<td>-0.30</td>
<td>-0.31</td>
<td>-0.52</td>
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<tr>
<td>HOMO (eV)</td>
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<td>-4.69</td>
<td>-5.46</td>
<td>-5.44</td>
<td>-6.09</td>
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<tr>
<td>HOMO-1 (eV)</td>
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<td>-6.13</td>
<td>-6.34</td>
<td>-6.27</td>
<td>-6.71</td>
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<th>3pmaz(1,2,3)</th>
<th>3pmaz(1,2,4)</th>
<th>4pmaz</th>
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<tr>
<td>LUMO+1 (eV)</td>
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<td>-0.50</td>
<td>-0.53</td>
<td>-0.72</td>
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<td>-0.56</td>
<td>-0.55</td>
<td>-0.77</td>
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<tr>
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<td>-6.38</td>
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<tr>
<td>HOMO-1 (eV)</td>
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<td>-6.09</td>
<td>-6.36</td>
<td>-6.25</td>
<td>-6.79</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ligand</th>
<th>2pzaz(1,2)</th>
<th>2pzaz(1,3)</th>
<th>3pzaz(1,2,3)</th>
<th>3pzaz(1,2,4)</th>
<th>4pzaz</th>
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</thead>
<tbody>
<tr>
<td>LUMO+1 (eV)</td>
<td>-0.13</td>
<td>-0.06</td>
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<td>-0.31</td>
<td>-0.50</td>
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<tr>
<td>LUMO (eV)</td>
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<td>-0.69</td>
<td>-0.92</td>
<td>-0.92</td>
<td>-1.12</td>
</tr>
<tr>
<td>HOMO (eV)</td>
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<td>-4.84</td>
<td>-5.64</td>
<td>-5.60</td>
<td>-6.28</td>
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<tr>
<td>HOMO-1 (eV)</td>
<td>-5.71</td>
<td>-6.23</td>
<td>-6.45</td>
<td>-6.39</td>
<td>-6.75</td>
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![Figure 7.4 – Leading molecular energy level arrangement in free anionic ligands](image-url)
In Figure 7.4 energy level arrangement of the ligands are presented as series of 
(1,2)diazole/ pyrazole, (1,3)diazole/ imidazole, (1,2,3)triazole, (1,2,4) triazole and tetrazole. 
Within each series (dashed box) the variation of the energy levels is shown as a function of 
the six-membered ring (in the order of pyridine, pyrimidine and pyrazine).

**Variation of HOMO energy**

According to the Figure 7.4 (moving from one series to another) the energy of the 
HOMO levels exhibits a strong dependence on the structure of the azole ring whereas they 
show only minor changes with the change of six-membered ring. It can be seen that in the 
azole rings, the increase in the nitrogen content tends to stabilize the HOMO level in the 
molecule. This has also been observed previously, the increase in the number of pyridine-
like nitrogen atoms (donating one pi electron to the ring) increases the stability of the HOMO 
levels in azoles. Apart from the aromatic stabilization of the azole ring, in the case of anionic 
versions, the stabilization is also by inductive effects incurred by the electronegative nitrogen 
atoms that help to delocalize the negative charge. The resonance stabilization of the anion is 
not effective as it disturbs the aromaticity of the ring according to the Hückle rule, and is 
restricted by the steric factors as the second lone pair on the anionic nitrogen is co-planar to 
the ring plane. Our results indicate that even with the same number of nitrogen atoms in the 
ring, the HOMO levels are varied based on the position of the nitrogen atoms as well 
(pyrazole and imidazole, 1,2,3-triazole and 1,2,4-triazole). This is also related to the effects 
of delocalization, where placing a pyridine-like nitrogen adjacent (α) to the anionic/ pyrrole-
like nitrogen induces more delocalization compared to a nitrogen placed β to the pyrrole-like 
nitrogen.

In order to study the delocalization effects, the charge on the anionic nitrogen can be 
investigated (the higher the delocalization, the lower the charge on the anionic nitrogen of the 
azole ring). The charge on the most negatively charged nitrogen in each azole ring is selected 
(Table 7.4) and 1/N_{charge} was plotted as a function of the azole ring structure (Figure 7.5). 
Compared with the trend observed for HOMO level changes, the variation of the negative 
charge/ delocalization coarsely follows the same trend. Apart from the trend observed, the 
HOMO levels show enhanced stabilization effects with increasing number of nitrogen atoms 
suggesting more factors contribute for the enhanced effects. This can be due to;

i. enhanced aromatic stabilization with increasing number of nitrogen atoms

ii. the MO analysis shows delocalization of the HOMO level into the six-membered ring, 
   with increasing number of nitrogen atoms in the azole ring, which wasn’t accounted
previously (highest in the case of tetrazoles).

Table 7.4 - Muliken atomic charges on the N anions of different azole rings

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<thead>
<tr>
<th></th>
<th>2pyaz(1,2)</th>
<th>2pyaz(1,3)</th>
<th>3pyaz(1,2,3)</th>
<th>3pyaz(1,2,4)</th>
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<td><strong>Charge on N</strong></td>
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<td>-0.572</td>
<td>-0.454</td>
<td>-0.574</td>
<td>-0.458</td>
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<tr>
<td><strong>1/N charge</strong></td>
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<td>-1.745</td>
<td>-2.202</td>
<td>-1.742</td>
<td>-2.179</td>
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<td><strong>Charge on N</strong></td>
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<td>-0.564</td>
<td>-0.447</td>
<td>-0.567</td>
<td>-0.449</td>
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<tr>
<td><strong>1/N charge</strong></td>
<td>-2.141</td>
<td>-1.770</td>
<td>-2.236</td>
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<td><strong>1/N charge</strong></td>
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Also the suggested variation in the HOMO levels is overestimated by the delocalization analysis in the case of 1,2,3-triazole and 1,2,4-triazoles. This suggests, having a pyridine-like nitrogen at the α position to the anionic/ pyrrole-like nitrogen is more significant compared to the β (3rd) position / β’ (4th) position in determining the HOMO energy.

**Variation of the LUMO as function of the ring structure**

Within each series (py, pm, pz – Figure 7.4), it is clear that the LUMO levels of the ligands vary significantly compared to the HOMO level. As discussed previously, the HOMO’s are mainly associated with the five-membered/ azole rings, which stay constant through a series leading to minor changes in the HOMO energy. In contrast, the six-membered ring varies through a series resulting in significant changes in the arrangement of LUMO energy, which again indicates the dependence of the LUMO on the structure of the six-membered ring.
Systematically, in each series the stabilization of the LUMO is increased in the order of pyridine < pyrimidine < pyrazine. This hints that the stabilization effect varies as a function of both number and position of the nitrogen atoms in the six-membered azine ring. This can be assumed to be associated with the electron delocalization effects by the nitrogen atoms.

Since this involves the LUMO level, considering the electron distribution at the ground level would not be effective. Therefore, the excited state charge distribution needs to be considered. Alternatively, since the LUMO levels in most cases are restricted to the six-membered ring, the ground state of pyridine, pyrimidine and pyrazine rings can be optimized, assuming they are equivalent to the excited states, where electrons are filled in the six-membered ring. The calculated, $1/N_{\text{avg. charge}}$ of pyridine, pyrimidine and pyrazine rings are tabulated in the Table 7.5. Comparison of the LUMO energies of each series with $1/N_{\text{avg. charge}}$ exhibit the similar trend, indicating the effect of delocalization on the arrangement of LUMO levels (Figure 7.6). It is known that by increasing the number of pyridine-like nitrogen atoms in a six-membered ring makes the ring/ carbons pi-deficient systems. This is indicative of the accepting nature of the azine ring and therefore, the stabilization of the LUMO levels in the order of pyrazine > pyrimidine > pyridine. This is in good agreement with the LUMO level

Table 7.5 - Avg. charge on ring nitrogen and avg. bond length of C-N in optimized pyridine, pyrimidine and pyrazine rings (PBE0 functional and 6/31G* basis set optimized in ethanol assuming pcm model)

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<th>Avg. charge on nitrogen</th>
<th>$1/N_{\text{avg. charge}}$</th>
<th>Energy of the LUMO (eV)</th>
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<td>pyrazine</td>
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<td>-2.385186086</td>
<td>-0.04829</td>
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Figure 7.6 - (a) $1/\text{avg. charge}$ on N of pyridine/pyrimidine/pyrazine (b) LUMO energies of pyridine/pyrimidine/pyrazine
variation within the ligand series.

**Emission profiles of the free ligands**

The PL emission spectra of the free anionic ligands are given in Figure 7.7. They indicate good tunability ranging over 68 nm for pyridyl series, 150 nm for pyrimidyl series and 138 nm for pyrazinyl series. In general, all the series follow the similar trend as with the change of number and position of the nitrogen atoms in the azole and azine rings.

![Emission spectra](image)

**Figure 7.7** – Anionic free ligand emission spectra (a) pyridyl azole series (b) pyrimidyl azole series (c) pyrazinyl azole series. In (a), (b) and (c); black – (1,2)diazole, red – (1,3)diazole, green – (1,2,3)triazole, orange – (1,2,4)triazole, blue – tetrazole.
7.3 Photo-physical properties of the Homoleptic platinum complexes

The absorption spectra of the homoleptic platinum complexes in solution (ethanol, $10^{-4}$ mol dm$^{-3}$) are given in the Figure 7.8, as series based on the six-membered ring (a, b, c) and the five-membered ring (d, e, f, g, h). The corresponding absorption peaks are given in Table 7.6. All the spectra exhibit intense absorption bands below 300 nm region, which are of similar energy as the corresponding free ligand absorption bands. In the region above 300 nm, new absorption bands are observed, which were not present in the free ligands. This may suggest charge transfer transitions involving the platinum metal centre. As a function of changing nitrogen content and position in the five and six-membered rings, different absorption profiles are observed. As a general feature, with the increasing number of nitrogen atoms in the five-membered ring, the first absorption bands are blue-shifted except in the case of (1,2,4)-triazoles, where the first absorption bands are considerably red-shifted. The reason for such behaviour will be discussed later in this section. With the increasing nitrogen content in

![Absorption spectra](image)

**Figure 7.8** – Absorption spectra of homoleptic platinum series (a) pyridyl azole series (b) pyrimidyl azole series (c) pyrazinyl azole series. In (a), (b) and (c): black – (1,2)diazole, red – (1,3)diazole, green – (1,2,3)triazole, magenta – (1,2,4)triazole, blue – tetrazole. (d) (1,2) diazole series, (e) (1,3) diazole series, (f) (1,2,3) triazole series, (g) (1,2,4) triazole series, (h) tetrazole series. In (d), (e), (f), (g) and (h): ___ pyridyl series, ______ pyrimidyl series and ______ pyrazinyl series.
the six-membered ring, the first absorption bands are red-shifted in pyrimidine and pyrazine compared to that of pyridine. Based on the previous observations in Chapter 5, the new complexes can also be assumed to have the HOMO localised in the azole ring and the metal centre, whereas the LUMO is localised in the six-membered ring. As explained with free ligands, the increasing number of nitrogen atoms in the azole ring and the six-membered azine ring, the HOMO and LUMO levels are stabilized respectively due to the effects of increasing aromaticity and delocalisation. These effects are responsible for the observed outcomes in the absorption of the complexes. Upon considering the effects of the position of the nitrogen in the six-membered rings it can be seen that the pyrazine absorption profile is red-shifted compared to pyrimidine. This is also due to the better stabilization of the LUMO in pyrazine compared to pyrimidine due to delocalisation effects.

In order to understand the observed effects, PBE0/BS1 (BS1 = 6-31G*_{C,H,N} /SDD_{Pt} ) (in ethanol) calculations were performed. Due to time restrictions and technical difficulties, monomer complexes in the pyridine series were analysed to understand the effects of the change in the five-membered ring, and the (1,2,3)-triazole series, to analyse the effects of the change of six-membered ring. According to the simulations (Table 7.7), the first absorption bands for the pyridine series were predicted to be in the region 300 – 400 nm. In contrast,

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption peak (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt[2pyaz(1,2)]$_2$</td>
<td>265, 274 (shoulder), 314, 337 (shoulder), 416</td>
</tr>
<tr>
<td>Pt[2pyaz(1,3)]$_2$</td>
<td>268, 293, 311, 327 (shoulder), 397, 409 (shoulder)</td>
</tr>
<tr>
<td>Pt[3pyaz(1,2,3)]$_2$</td>
<td>225, 275, 282 (shoulder), 342, 377</td>
</tr>
<tr>
<td>Pt[3pyaz(1,2,4)]$_2$</td>
<td>232, 274, 285 (shoulder), 322 (shoulder), 349 (shoulder), 423, 457, 513</td>
</tr>
<tr>
<td>Pt[4pyaz]$_2$</td>
<td>224, 276, 282 (shoulder), 323 (shoulder), 362 (shoulder)</td>
</tr>
<tr>
<td>Pt[2pmaz(1,2)]$_2$</td>
<td>222, 273, 282 (shoulder), 336, 369, 418, 444, 468 (shoulder)</td>
</tr>
<tr>
<td>Pt[2pmaz(1,3)]$_2$</td>
<td>268, 305, 330 (shoulder), 410</td>
</tr>
<tr>
<td>Pt[3pmaz(1,2,3)]$_2$</td>
<td>263, 325 (shoulder), 386 (shoulder), 432 (shoulder)</td>
</tr>
<tr>
<td>Pt[3pmaz(1,2,4)]$_2$</td>
<td>223, 275, 282 (shoulder), 330 (shoulder), 488 (shoulder)</td>
</tr>
<tr>
<td>Pt[4pmaz]$_2$</td>
<td>224, 272, 283 (shoulder), 303 (shoulder), 336 (shoulder)</td>
</tr>
<tr>
<td>Pt[2pzaz(1,2)]$_2$</td>
<td>222, 275, 282 (shoulder), 395, 482 (shoulder), 512 (shoulder), 584</td>
</tr>
<tr>
<td>Pt[2pzaz(1,3)]$_2$</td>
<td>228, 278, 309, 354 (shoulder), 402 (shoulder), 461, 539 (shoulder)</td>
</tr>
<tr>
<td>Pt[3pzaz(1,2,3)]$_2$</td>
<td>224, 275, 284 (shoulder), 319 (shoulder), 463 (shoulder)</td>
</tr>
<tr>
<td>Pt[3pzaz(1,2,4)]$_2$</td>
<td>243, 294, 329, 445, 496, 553</td>
</tr>
<tr>
<td>4pzaz</td>
<td>224, 279, 340, 393 (shoulder)</td>
</tr>
</tbody>
</table>
Experimental results indicate considerably red-shifted bands spanning into the region 400 – 500 nm. This can be associated with the formation of ground state dimers/ oligomers at the given concentration. Especially in the case of (1,2,4)-triazole series highly red-shifted absorption bands can be observed spanning into 500 – 550 nm region. The ground state dimerisation is observed in the mass spectroscopic analysis as well (Appendix 3). As observed earlier in Chapter 5, dimerisation is probable with square planar platinum complexes. Apart from the red-shifted bands, theoretical and experimental absorption bands exhibit good agreement.

<table>
<thead>
<tr>
<th>ES</th>
<th>E(eV)</th>
<th>λ (nm)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>3.21</td>
<td>386</td>
<td>0.0572</td>
</tr>
<tr>
<td>S4</td>
<td>3.95</td>
<td>314</td>
<td>0.2288</td>
</tr>
<tr>
<td>S10</td>
<td>4.46</td>
<td>278</td>
<td>0.2537</td>
</tr>
<tr>
<td>S12</td>
<td>4.48</td>
<td>277</td>
<td>0.1844</td>
</tr>
<tr>
<td>S17</td>
<td>4.96</td>
<td>250</td>
<td>0.6643</td>
</tr>
<tr>
<td>S1</td>
<td>3.20</td>
<td>387</td>
<td>0.0994</td>
</tr>
<tr>
<td>S4</td>
<td>3.84</td>
<td>323</td>
<td>0.0245</td>
</tr>
<tr>
<td>S5</td>
<td>3.94</td>
<td>311</td>
<td>0.0935</td>
</tr>
<tr>
<td>S7</td>
<td>4.04</td>
<td>307</td>
<td>0.1892</td>
</tr>
<tr>
<td>S9</td>
<td>4.21</td>
<td>294</td>
<td>0.1030</td>
</tr>
<tr>
<td>S17</td>
<td>4.57</td>
<td>271</td>
<td>0.5491</td>
</tr>
<tr>
<td>S1</td>
<td>3.66</td>
<td>338</td>
<td>0.0337</td>
</tr>
<tr>
<td>S3</td>
<td>4.11</td>
<td>302</td>
<td>0.2272</td>
</tr>
<tr>
<td>S9</td>
<td>4.46</td>
<td>278</td>
<td>0.2415</td>
</tr>
<tr>
<td>S10</td>
<td>4.67</td>
<td>266</td>
<td>0.1366</td>
</tr>
<tr>
<td>S30</td>
<td>5.59</td>
<td>222</td>
<td>0.0261</td>
</tr>
<tr>
<td>S1</td>
<td>3.32</td>
<td>373</td>
<td>0.0637</td>
</tr>
<tr>
<td>S6</td>
<td>4.27</td>
<td>290</td>
<td>0.2120</td>
</tr>
<tr>
<td>S9</td>
<td>4.50</td>
<td>276</td>
<td>0.1226</td>
</tr>
<tr>
<td>S11</td>
<td>4.62</td>
<td>268</td>
<td>0.2607</td>
</tr>
<tr>
<td>S12</td>
<td>4.68</td>
<td>265</td>
<td>0.2209</td>
</tr>
<tr>
<td>S20</td>
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<td>237</td>
<td>0.3644</td>
</tr>
<tr>
<td>S1</td>
<td>3.73</td>
<td>332</td>
<td>0.0333</td>
</tr>
<tr>
<td>S2</td>
<td>3.91</td>
<td>321</td>
<td>0.0087</td>
</tr>
</tbody>
</table>
With the intention of understanding the nature and the origin of the electronic transitions, MO analysis was carried out (Figure 7.9). This identifies the bands above 300 nm are associated with metal-to-ligand charge transfer character ($^1$MLCT), involving $d_{xz}$ and $d_{yz}$ orbitals. According to the analysis, the HOMO level is mainly located in the azole ring and the platinum metal centre, where the six-membered azine ring shares no electron density. In contrast, the distribution of electron density in the LUMO is restricted to the six-membered azine ring as in the case of free ligands. The absorption bands below 300 nm exhibit both intra ligand and sometimes $^1$MLCT transitions. Within each azole series, the metal complexes exhibit similar absorption profiles (Figure 7.8 (d-h)), indicating the complexes which are not simulated may also share the similar characteristics in MO arrangement. This can be confirmed with the MO analysis of the 1,2,3-triazole series above.

PL spectra of the dilute solutions ($10^{-6}$ mol dm$^{-3}$) were obtained only for the pyridyl series and for some complexes in the pyrimidyl series, as the rest of the complexes displayed very weak emission profiles (Figure 7.10). All the complexes that gave detectable photoluminescence exhibit emissions around 400 nm: (Pt[2pyaz(1,2)]$_2$ - 402 nm,
Pt[2pyaz(1,2)], $S_0 \rightarrow S_1$ Charge transfer from Pt, pyrazolate to pyridine

Pt[2pyaz(1,2)], $S_0 \rightarrow S_2$ Charge transfer from Pt, pyrazolate to pyridine

Pt[2pyaz(1,2)], $S_0 \rightarrow S_3$ Charge transfer from Pt to pyridine

Pt[2pyaz(1,2)], $S_0 \rightarrow S_4$ Charge transfer from pyrazolate to pyridine

Pt[2pyaz(1,3)], $S_0 \rightarrow S_1$ Charge transfer from Pt, imidazolate to pyridine

Pt[2pyaz(1,3)], $S_0 \rightarrow S_4$ Charge transfer from Pt $d-\pi$, imidazolate to Pt $d-\sigma$
Pt[2pyaz(1,3)]2 \text{ S}_0 \rightarrow \text{ S}_1, \text{ Charge transfer from pyrazolate to pyridine}

Pt[2pyaz(1,3)]2 \text{ S}_0 \rightarrow \text{ S}_0, \text{ Charge transfer from Pt, pyrazolate to pyridine}

Pt[2pyaz(1,3)]2 \text{ S}_0 \rightarrow \text{ S}_0, \text{ Charge transfer from Pt and pyrazolate to pyridine}

Pt[2pyaz(1,2,3)]2 \text{ S}_0 \rightarrow \text{ S}_1, \text{ Charge transfer from Pt, triazolate to pyridine}

Pt[2pyaz(1,2,3)]2 \text{ S}_0 \rightarrow \text{ S}_1, \text{ Charge transfer from Pt, triazolate to pyridine}

Pt[2pyaz(1,2,4)]2 \text{ S}_0 \rightarrow \text{ S}_1, \text{ Charge transfer from Pt, triazolate to pyridine}
Pt[2pyaz(1,2,4)], $S_0 \rightarrow S_1$, Charge transfer from Pt to pyridine

Pt[2pyaz(1,2,4)], $S_0 \rightarrow S_1$, Charge transfer from Pt, triazolate to pyridine

Pt[2pyaz(1,2,4)], $S_0 \rightarrow S_{10}$, Charge transfer from Pt to pyridine

Pt[2pyaz(1,2,4)], $S_0 \rightarrow S_{10}$, Charge transfer from triazolate to pyridine

Pt[4pyaz], $S_0 \rightarrow S_1$, Charge transfer from Pt, tetrazolate to pyridine

Pt[4pyaz], $S_0 \rightarrow S_1$, Charge transfer from Pt to pyridine

Pt[4pyaz], $S_0 \rightarrow S_1$, Charge transfer from Pt to pyridine
$\text{Pt[4pyaz]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt, tetrazolate and pyridine to pyridine

$\text{Pt[4pyaz]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt, tetrazolate to Pt

$\text{Pt[4pyaz]}_2$, $S_0 \rightarrow S_1$, excitation localised in pyridine

$\text{Pt[3pmaz(1,2,3)]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt, triazolate to pyrimidine

$\text{Pt[3pmaz(1,2,3)]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt to pyrimidine

$\text{Pt[3pmaz(1,2,3)]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt, triazolate to pyrimidine

$\text{Pt[3pmaz(1,2,3)]}_2$, $S_0 \rightarrow S_1$, charge transfer from Pt, triazolate to pyrimidine
Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{15}$ Charge transfer from Pt, triazolate to pyridine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{15}$ Charge transfer from Pt, triazolate to pyridine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{22}$ Charge transfer from Pt, triazolate to pyridine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{15}$ Charge transfer from Pt, triazolate to pyridine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{15}$ Charge transfer from Pt, triazolate to pyridine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_4$ Charge transfer from Pt, triazolate to pyrazine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_4$ Charge transfer from triazolate and pyrazine to pyrazine

Pt[3pzaz(1,2,3)] : $S_0 \rightarrow S_{10}$ Charge transfer from Pt to pyrazine
Pt[2pyaz(1,3)]$_2$ – 438 nm, Pt[3pyaz(1,2,3)]$_2$ – 400 nm, Pt[3pyaz(1,2,4)]$_2$ – 384 nm, Pt[4pyaz]$_2$ – 389 nm, Pt[2pmaz(1,2)]$_2$ – 362 nm, Pt[2pmaz(1,3)]$_2$ – 368 nm, Pt[2pmaz(1,2,3)]$_2$ – 362 nm), suggesting the similar behaviour of the monomeric emission, as observed earlier with the triazole series. Analysis of the pyridyl series shows a range of 54 nm emission tunability, relative to the high energy emission band (around 400 nm region). Compared to this, in Chapter 5, the triazole series exhibited only a 13 nm emission range. This suggests the changes in the HOMO level (by changing the azole ring); introduce more tunability aspect compared to the changes in the LUMO level. Also, the high energy emission bands blue-shift with increasing number of nitrogen atoms in the azole ring, following the similar trend observed with the absorptions of the complexes, and the calculated HOMO-LUMO gaps for the ligands. The only exception is with the 1,2,4 triazole, in which the emission is blue-shifted than expected. In the pyrimidyl series, the high energy emission bands are more tightened compared to the pyridyl series. The emission bands indicate a good spectral overlap with the absorption bands, suggesting the possibility of having fluorescence emission. Another feature in the emission profiles is that, most of them show red-shifted low energy emission peaks along with the high energy emission bands (Pt[(2pyaz(1,3)]$_2$ – 498 nm, Pt[3pyaz(1,2,4)]$_2$ – 590 / 620 nm (shoulder), Pt[4pyaz]$_2$ – 479 nm, Pt[3pmaz(1,2)]$_2$ –
534 nm, [Pt(3pmaz(1,3)]_2 – 567 nm, Pt[3pmaz(1,2,3)]_2 – 541 nm). This suggests the presence of excimer emission/dimer emission even at diluted concentrations. This observation also leads to the fact that the stacking of the complexes is dependent on the characteristics of the ligand.

In order to understand the experimental results, TDDFT calculations were performed for the monomer complexes using PBE0/BS1 (BS1 = 6-31G*_{C,H,N}/SDD_{Pt}). To analyse the

| Table 7.8 - Calculated emission properties of monomer complexes. Excited states ES, vertical emission energies E [eV], wavelengths λ [nm] and oscillator strength f computed with TDDFT/PBE0/6-31G*&SDD in ethanol. |
|----------------------------------------|--------|--------|--------|
| ES | E     | λ     | f      |
| Pt[2pyaz(1,2)]_2 | S_1   | 2.83  | 438    | 0.0958 |
|       | T_1   | 2.48  | 499    |        |
|       |       |       |        |        |
| Pt[2pyaz(1,3)]_2 | S_1   | 2.81  | 441    | 0.1252 |
|       | T_1   | 2.12  | 584    |        |
|       | T_2   | 2.63  | 470    |        |
|       |       |       |        |        |
| Pt[3pyaz(1,2,3)]_2 | S_1  | 3.31  | 375    | 0.0616 |
|       | T_1   | 2.62  | 473    |        |
|       | T_2   | 2.68  | 462    |        |
|       |       |       |        |        |
| Pt[3pyaz(1,2,4)]_2 | S_1  | 2.93  | 423    | 0.1082 |
|       | T_1   | 2.44  | 509    |        |
|       | T_2   | 2.62  | 472    |        |
|       |       |       |        |        |
| Pt[4pyaz]_2   | S_1   | 3.35  | 370    | 0.0671 |
|       | S_2   | 3.68  | 336    | 0.0256 |
|       | T_1   | 2.71  | 458    |        |
|       | T_2   | 2.82  | 440    |        |
|       |       |       |        |        |
| Pt[3pmaz(1,2,3)]_2 | S_1 | 3.23  | 384    | 0.0519 |
|       | S_2   | 3.66  | 339    | 0.0248 |
|       | S_3   | 3.82  | 325    | 0.3222 |
|       | T_1   | 2.65  | 468    |        |
|       |       |       |        |        |
| Pt[3pzaz(1,2,3)]_2 | S_1 | 2.97  | 427    | 0.0397 |
|       | S_2   | 3.37  | 367    | 0.0201 |
|       | T_1   | 2.35  | 528    |        |
|       | T_2   | 2.41  | 513    |        |
trend along a series, singlet and triplet excited states of the pyridyl series were simulated,
whereas to analyse the trend down a group, the (1,2,3)-triazole series was simulated (Table 7.8). The simulated $S_1 \to S_0$ transitions indicate a good compatibility with the experimental data (high energy emission band). In contrast, the predicted phosphorescence emissions are considerably lower in energy. Therefore, the high energy emissions are reasonably assigned as fluorescence in character. Analysis of the leading MO orbitals (Figure 7.11) follows the same trend observed for absorption.

In the more concentrated solutions ($10^{-4}$ M) and the thin films of the complexes, new red-shifted emission bands appear exhibiting increased emission tunability (Figure 7.12 and
Table 7.9 – Emission wavelengths of the complexes in more concentrated solutions (10^{-4} M) and in thin films

<table>
<thead>
<tr>
<th>Complex</th>
<th>Concentrated solution emission</th>
<th>Thin film emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt[(2pyaz(1,2)]_2</td>
<td>541 nm</td>
<td>545 nm</td>
</tr>
<tr>
<td>Pt[2pyaz(1,3)]_2</td>
<td>498 nm</td>
<td>578 nm</td>
</tr>
<tr>
<td>Pt[3pyaz(1,2,3)]_2</td>
<td>545 nm</td>
<td>541 nm</td>
</tr>
<tr>
<td>Pt[2pyaz(1,2,4)]_2</td>
<td>582 nm</td>
<td>589 nm</td>
</tr>
<tr>
<td>Pt[4pyaz]_2</td>
<td>486 nm</td>
<td>486 nm</td>
</tr>
<tr>
<td>Pt[2pmaz(1,2)]_2</td>
<td>537 nm</td>
<td>538 nm</td>
</tr>
<tr>
<td>[Pt(2pmaz(1,3)]_2</td>
<td>563 nm</td>
<td>564 nm</td>
</tr>
<tr>
<td>Pt[3pmaz(1,2,3)]_2</td>
<td>541 nm</td>
<td>536 nm</td>
</tr>
<tr>
<td>Pt[3pmaz(1,2,4)]_2</td>
<td>dark/ non-emissive</td>
<td>dark/ non-emissive</td>
</tr>
<tr>
<td>Pt[4pmaz]_2</td>
<td>583 nm</td>
<td>604 nm</td>
</tr>
<tr>
<td>Pt[(2pzaz(1,2)]_2</td>
<td>723 nm</td>
<td>752 nm</td>
</tr>
<tr>
<td>Pt[2pzaz(1,3)]_2</td>
<td>716 nm</td>
<td>636 nm/710 nm</td>
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<tr>
<td>Pt[3pzaz(1,2,3)]_2</td>
<td>598 nm</td>
<td>610 nm</td>
</tr>
<tr>
<td>Pt[2pzaz(1,2,4)]_2</td>
<td>651 nm</td>
<td>652 nm</td>
</tr>
<tr>
<td>Pt[4pzaz]_2</td>
<td>579 nm</td>
<td>577 nm</td>
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</table>

Table 7.9). The Analysis of the emission maxima in the thin films of the complexes show, for pyridine – 103 nm tunability range, for pyrimidine – 68 nm tunability range and for pyrazine – 174 nm tunability range, giving overall 264 nm tunability for the emission. On comparison, a clear trend cannot be identified that is common to all the series. Pt[2pyaz(1,2)]_2 and Pt[2pmaz(1,2)]_2 exhibit blue-shifted emission compared to the Pt[2pyaz(1,3)]_2 and Pt[2pmaz(1,3)]_2. In contrast, Pt[2pzaz(1,2)]_2 is red-shifted by 40 nm compared to the Pt[2pzaz(1,3)]_2. Both Pt[4pyaz]_2 and Pt[4pzaz]_2 show the most blue-shifted emissions in the respective series. In contrary, Pt[4pmaz]_2 exhibit the highest red-shifted emission in the pyrimidyl series. Pyrimidyl complexes exhibit almost no tunability compared to the pyridyl complexes except in the case of Pt[4pmaz]_2, despite the change in the azine ring. In contrast, the change of pyridine into pyrazine shows almost 100 nm of red-shift in the emission values. All these observations suggest that the co-planar Pt---Pt stacking is not the only factor that governs the emission in these complexes i.e fluorescence/phosphorescence, different stacking behaviour etc.
If we assume the same scenario as in Chapter 5, $(d_{z^2} - d_{z^2})^*$ orbital raising in energy becoming the HOMO level (as a result of Pt--Pt stacking) would remove the effects of the azole based HOMO level and the tunability would be further decreased. As the tunability is enhanced, this can be due to:

i. The nature of emission being either fluorescence or phosphorescence depending on the structure of the complexes.

ii. The Pt--Pt distance, therefore, the energy of the $(d_{z^2} - d_{z^2})^*$ orbital is dependent on the structure of the azole ring controlling the HOMO level being either azole based or metal based/ $(d_{z^2} - d_{z^2})^*$.

The simulation of the Pt[2pyaz(1,2)]$_2$--Pt[2pyaz(1,2)]$_2$ dimer showed fluorescence is at 439 nm (same as monomer) and phosphorescence is at 555 nm which is more closer to the experimental value (545 nm). In contrast, Pt[3pyaz(1,2,3)]$_2$ emission was identified as fluorescence emission. This indicates the possibility of having different origins for the emission.

Analysing the ground state geometry of the Pt[2pyaz(1,2)]$_2$--Pt[2pyaz(1,2)]$_2$ dimer, reveals that it does not exhibit co-planar Pt-Pt stacking, but the two Pt ions are horizontally displaced with respect to each other. In contrast, the Pt[3pyaz(1,2,3)]$_2$--Pt[3pyaz(1,2,3)]$_2$ and
Pt[4pyaz]$_2$---Pt[4pyaz]$_2$ show planar Pt---Pt stacking in the ground state. Also, the ground state Pt---Pt distance decreases with the increasing number of nitrogen atoms in the azole ring. This unwraps a whole new scenario, where the stacking geometry changes depending on the azole ring. The excited state geometries of the dimers were optimized for Pt[2pyaz(1,2)]$_2$---Pt[2pyaz(1,2)]$_2$ and Pt[3pyaz(1,2,3)]$_2$---Pt[3pyaz(1,2,3)]$_2$ (Table 7.8 and Figure 7.15). These indicate the excited state geometries are similar to the ground state geometry. In contrast, to the decreasing Pt---Pt distance in the excited state of the Pt[3pyaz(1,2,3)]$_2$---

Table 7.10 - Calculated emission properties of Pt[2pyaz(1,2)]$_2$---Pt[2pyaz(1,2)]$_2$. Excited states ES, vertical emission energies E [eV], wavelengths $\lambda$ [nm] and oscillator strength $f$ computed with TDDFT/PBE0/6-31G* & SDD in ethanol.

<table>
<thead>
<tr>
<th>ES</th>
<th>E</th>
<th>$\lambda$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.83</td>
<td>439</td>
<td>0.0886</td>
</tr>
<tr>
<td>S2</td>
<td>3.18</td>
<td>390</td>
<td>0.0815</td>
</tr>
<tr>
<td>T1</td>
<td>2.33</td>
<td>555</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 7.15 – Leading molecular orbitals involved in the lowest energy transitions for the complexes. Donating (left) and accepting (right) molecular orbitals

Pt[3pyaz(1,2,3)]$_2$ (Chapter 5). Pt[2pyaz(1,2)]$_2$---Pt[2pyaz(1,2)]$_2$ does not show such an effect
(4.64 Å (S₁ - geometry), 4.66 Å (T₁ - geometry)), indicating lack of excimerisation. The
analysis of the leading MOs of the Pt[2pyaz(1,2)]₂--Pt[2pyaz(1,2)]₂, at S₁ and T₁ excited
states indicate, no involvement of the (d₂z² − dₓ²)\(^*\) orbital, but MOs resembling monomer
MO of the Pt[2pyaz(1,2)]₂. This again shows lack of aggregation/ stacking related effects.
This effect has promoted phosphorescence over fluorescence. On the completion of the
theoretical studies on all the dimer complexes, would give insights into the stacking
properties of the complexes, thereby establishing a structure–property relationship.

**Summary**

In this chapter, the photo-physical properties of the library of ligands and their
platinum metal complexes were discussed. The absorption and emission data of the ligands
indicated that an increasing number of ring nitrogen atoms in the azole and azine rings
stabilizes the HOMO and LUMO levels of the ligands, thereby displaying tunability in the
photo-physical properties. Also, the data indicated that the respective positions of the
nitrogen atoms in the ring are also important in governing the arrangement of the energy
levels. The theoretical and experimental data also indicated a good agreement.

Platinum metal complexes also indicated a good tunability of the emission colour
(around 264 nm tunability) as a function of the content and position of the ring nitrogen
atoms in the ligands. However, with the current experimental and theoretical work, a general
trend to elaborate the photo-physical properties of the complexes could not be established. It
was found that the hetero-atomic effect of the ligands influence different stacking patterns of
the complexes and also the nature of the emission (fluorescence and phosphorescence), which
cumulatively affect the emission properties of the complexes. The completion of the
theoretical studies and the emission lifetime measurements will provide insights into the
behaviour of the complexes, and will help to identify a general trend that describes the
properties of the complexes. Finally, this work shows the importance of the molecular level
changes in a material that can deliver highly tunable photo-physical properties at the
macroscopic level.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

This project was started with the intention of analysing the importance of molecular level design in optoelectronic materials and to investigate the importance of the structure-property relationship between the azole-azine ligand based homoleptic platinum complexes and the related photo-physical properties. Hitherto in the literature, a generalised overview on the structure-property relationship of the azole-azine ligand class or the related platinum complexes is yet to be established.

As the first step of the project, 2-pyridyl-1H-1,2,3-triazole based ligand systems were synthesised. In a number of studies, it has been shown that the photo-physical property tunability of the complexes was hard to achieve by the substitution on the nitrogen of the triazole ring. Therefore in this project, instead of substituting the triazole ring, the substitution was carried out on the 5th position of the pyridyl ring with electronically diverse donor-acceptor groups (–N(CH₃)₂, -H, -CHO, -CHC(CN)₂). The intention of this approach was to directly affect the LUMO levels of the complexes thus their emission parameters. Also by leaving the acidic N-H proton on the triazole ring would facilitate strong field ligation to the metal/platinum centre which helps to prevent deleterious d-d transitions that quench emission, especially in platinum related complexes. In Chapter 3 the experimental procedures involved in the synthesis of diversely substituted pyridyl triazole ligands and their homoleptic platinum complexes were explained. Also a general introduction of the techniques used for the structural and photo-physical characterisation of the ligands was noted. Out of the four ligands, three were synthesised as novel ligands (3pyaz(1,2,3) – N(CH₃)₂, 3pyaz(1,2,3) – CHO, 3pyaz(1,2,3) – CHC(CN)₂) and all the four complexes were obtained as novel platinum complexes. In Chapter 3.3, the synthesis of a library of different combinations of azole-azine based ligands and their homoleptic platinum complexes was reported. The intention of the synthesis of this library of ligands was to analyse the effect of the content and relative position of the nitrogen/heteroatoms in heterocyclic rings, towards the photo-physical properties the complexes. Azole ring was represented by pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole and tetrazole rings whereas the azine ring was represented by pyridine, pyrimidine and pyrazine rings resulting in 15 different combinations of ligands.
In Chapter 4, the structural characterisation of the four pyridyl triazole ligands and the intermediates involved in the synthetic process (16 compounds) was discussed. All the ligands and intermediates were characterised by $^1$H and $^{13}$C NMR, Mass spectrometry, IR spectroscopy etc. Also the reaction mechanisms involved in the synthesis (Sonogashira carbon-carbon coupling, 1,3–dipolar cycloaddition/ click chemistry protocols) and importance of certain synthetic conditions and reactants were discussed accordingly. Characterisation of the homooleptic platinum complexes of the pyridyl-triazole ligands were discussed at the final section of Chapter 4. Metal complexes were characterised by Mass spectrometry and whenever the solubility allows HRMS was used. Due to poor solubility of the compounds only $^1$H NMR were obtained. Poor solubility which arises from strong stacking of the platinum complexes hindered the growth of single crystals for X-ray analysis.

Chapter 5 was dedicated to the analysis of photo-physical properties of the pyridyl-triazole ligands and their homooleptic platinum complexes. Absorption and emission spectra of the free ligands indicated a clear dependence of the photo-physical properties on the substituents attached to the pyridyl ring. Indeed, the lowest energy absorption band of the ligands, red-shifts with increasing acceptor power over a range of 104 nm. The photoluminescence spectra of the free-ligands exhibit tunability over a range of 69 nm, which also correspond to the donor-acceptor strengths of the substituents. Moreover, the analysis of the molecular orbitals indicated the charge-transfer character of these transitions involving mainly a triazole based HOMO level and a pyridyl based LUMO level. Despite the tunability effects observed in the free ligands, the diluted solutions of the homooleptic platinum complexes indicated lack of tunability in the absorption and emission spectra restricted to a range of few nanometers (20 nm in absorption and 9 nm in emission). TDDFT calculations identify the emission at the molecular level as fluorescence from $^1$MLCT state. In addition, the emission lifetime also confirm the emission to be fluorescent in nature. Key to our findings, however is, the “turning-on” of the substituent effects with increasing concentration of the complexes. A coarse tunability of nearly 140 nm was observed in the thin films spanning across a large portion of the visible spectrum emitting blue (486 nm - 4a), green (540 nm – 4b), orange (602 nm – 4c) and red (625 nm – 4d). A linear relationship between the emission energy and the donor-acceptor strength ($\sigma_p$) of the substituents was established with an R$^2$ value of 0.97 ($\rho = –0.4$) for the thin film results suggesting that the tunability is directly related to the substituents.
In order to understand the restored substituent effects at higher concentration, theoretical calculations were performed. The results indicate that upon excitation, increased metallophilic interaction resulting from the decrease in the Pt--Pt distance in the excited state. This directs to excimer formation as a result of sigma type overlap between the $d_{x^2}$ atomic orbitals of the two Pt centers. Indeed, at higher concentration $\frac{1}{3}$MLCT emitting states of the monomers are replaced by excimer states with metal-to-metal-to-ligand charge-transfer character ($\frac{1}{3}$MMLCT) and the emission is associated with transitions from ligand-centered molecular orbitals to metal-centered molecular orbitals. Lifetime measurements indicate the involvement of fluorescence based process and a phosphorescence or delayed fluorescence processes.

![Figure 8.1 – Summary of Chapter 4 and 5 ‘turning on substituent effects via Pt--Pt metallophilic stacking’](image)

Chapter 6 involves the structural characterisation of the library of azole-azine ligands and homoleptic platinum complexes. Ligands were characterised by $^1$H and $^{13}$C NMR, Mass spectrometry, IR spectroscopy as in Chapter 4. The reaction mechanisms involved in the synthesis of different azoles were also discussed accordingly. Characterisation of the homoleptic platinum complexes was mostly carried out by Mass spectrometric analysis. In most of the cases, poor solubility of the complexes hindered the NMR analysis.

Chapter 7 was related to the discussion of photo-physical properties of the different azole-azine ligands and their homoleptic platinum complexes. The absorption and emission profiles of the ligands indicated a clear dependence on the content and the position of the nitrogen atoms in the heterocyclic rings. For the ligands, both experimental data and theoretical calculations together show the stabilisation of the HOMO level results on
increasing number of nitrogen atoms in the azole ring; and in the case of having the same number of nitrogen atoms in the azole ring the stabilisation is based on the delocalisation effects that is associated with the position of the nitrogen atoms (when the nitrogen atoms are adjacent to each other the delocalisation is better). The same trend is followed for the stabilisation of the LUMO level of the ligands that is associated with the structure of the azine ring. For the homoleptic complexes, different absorption profiles were observed indicating tunability effects. Also the absorption spectra indicated the possibility of having ground state aggregation. Diluted solution emission of the complexes exhibit lowered tunability compared to the free ligand emissions. In concentrated solutions and thin films, the tunability is enhanced ranging over 250 nm (486 – 750 nm). Theoretical calculations of all the dimers could not be completed due to time restrictions and technical difficulties. From the completed simulations it can be seen with changing nitrogen content in the azole ring, the stacking of the monomers into dimers is changed (co-planar or displaced Pt---Pt stacking), leading to different origins of emission (fluorescence/ phosphorescence).

Figure 8.2 – Library of ligands and complexes studied in the chapter 6 and 7. The thin film emission peaks of the complexes are given alongside each complex. 1 – ligand, 2 – complex: a = 2pyaz(1,2), b = 2pma(2,1), c = 2pzaz(1,2), d = 2pyaz(1,3), e = 2pma(1,3), f = 2pzaz(1,3), g = 3pyaz(1,2,3), h = 3pma(1,2,3), i = 3pzaz(1,2,3), j = 3pyaz(1,2,4), k = 3pma(1,2,4), l = 3pzaz(1,2,4), m = 4pyaz, n = 4ma(1,2,4), o = 4pzaz.
8.2 Future work

The importance of structure-property relationship and molecular level design aspects involved in above mentioned class of complexes was studied and useful phenomena were established. As a continuation of the study related to the library of complexes described in Chapter 7, the relevant computational studies should be completed. In addition, the following measurements need to be carried out; (i) Temperature dependent lifetime measurements to study excited state dynamics, (ii) Quantum efficiency, (iii) Band-gap determination through electrochemistry, and, (iv) Thermo-gravimetric analysis (TGA) for purity verification.

Throughout this study, three positions were identified as potential modifiers of the photo-physical properties of this class of materials i.e. azole ring (HOMO), azine ring (LUMO) and the metal centre to affect metalophilic stacking and spin orbit coupling within the complex. In the case of 2-pyridyl-1H-1,2,3-triazole platinum complexes, as the HOMO levels show hardly any dependence on the triazole ring in the dimer state (therefore in the thin films that is important for application purposes), the substitution on the 4\textsuperscript{th} carbon of the azole ring with different –R groups, can be used to improve the solubility of the complexes which will be useful in future application purposes. The effect of different metal ions can also be studied by changing the metal centre. Preliminary studies indicated that by changing Pt(II) to Pd(II), the emission wavelength red-shifts by around 110 nm compared to the corresponding platinum complex (eg. Pt[3pyaz(1,2,3)]\textsubscript{2} emits at 540 nm whereas Pd[3pyaz(1,2,3)]\textsubscript{2} emits at 648 nm). The study can be expanded over to the metal ions in other groups, such as Iridium and Ruthenium to examine their photo-physical properties. Once the behaviour of homoleptic complexes is understood the photo-physical properties of the

![Diagram](image)

\[ X = C, N \quad M = \text{metal centre} \]

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\[ X = C, N \quad M = \text{metal centre} \]

Figure 8.3 – Three positions at the molecular level to influence the tunability of the final material
heteroleptic complexes that involve different ligand combinations can be explored. This will allow the study of inter-ligand charge transfer properties.

Preliminary microscopic analysis indicated microcrystal formation with the complexes. As discussed previously since the Pt---Pt distance is important in the tunability of emission wavelengths, the materials can be subjected to high pressure studies and to analyse the variation of the emission wavelengths as a function of Pt---Pt distance and pressure. The decrease in the Pt---Pt distance leads to more interaction of the $d_{z^2}$ orbitals, which increases the energy of the $(d_{z^2} - d_{z^2})^*$ orbital in the dimer, leading to reduced HOMO-LUMO energy gaps that can be exploited to discover new IR emitting materials.

![Diagram showing the effect of pressure on Pt-Pt distance and metallophilic interaction](image)

**Figure 8.4 – Design towards IR emitters by applying high-pressure**

Further, lifetime measurements and temperature dependent studies will help the investigation of the origins of the emission in these types of materials. Preliminary studies of Pt[3pyaz(1,2,3)₂] show two radiative decay processes to be involved in the emission at room temperature whereas three radiative decay processes to be involved at 0 K and a change in the emission colour from green to orange. Investigation of this aspect may lead to the discovery of new thermometric materials.

From the perspective of device fabrication, materials emitting different colours can be explored as materials for white OLEDs. Since the molecules are based on the same structural skeleton, these materials would be important to address the issues related to different aging times of the compounds in white light generation. Preliminary OLED fabrication resulted in electroluminescence from these materials, but the efficiencies were low as it was difficult to
achieve uniform films due to poor solubility. Therefore the solubility issue needs to be addressed before deploying the materials in device fabrication.
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Appendix 1

The Jablonski Diagram

![Jablonski Diagram illustrating the possible electronic transitions within a molecule once absorbed energy](image)

The energy absorbed by a molecule causes an electron to be promoted to a higher electronic energy level. Figure shown above indicates the major photo-physical radiative and non-radiative processes exhibit by a molecules in solution. The symbols So, S1, T1, T2, etc., refer to the ground electronic state (So), first excited singlet state (S1), first excited triplet state (T1), and so on. The horizontal lines correspond to the vibrational levels of each electronic state. Straight arrows indicate radiative transitions whereas curly arrows indicate non-radiative transitions. The boxes explain the electronic spins in each orbital, with electrons shown as up and down arrows, to distinguish their spin.
Appendix 2
Absorption and Emission Spectra of the Neutral / Protonated Ligands

Absorption spectra of the free ligands in their neutral/protonated forms ($10^{-5}$ M, in ethanol) 3pyaz(1,2,3)-N(CH$_3$)$_2$ – blue, 3pyaz(1,2,3) – green, 3pyaz(1,2,3)-CHO – orange, 3pyaz(1,2,3)-CHC(CN)$_2$ – red.

PL spectra of the free ligands in their neutral/protonated forms ($10^{-5}$ M, in ethanol) 3pyaz(1,2,3)-N(CH$_3$)$_2$ – blue, 3pyaz(1,2,3) – green, 3pyaz(1,2,3)-CHO – orange, 3pyaz(1,2,3)-CHC(CN)$_2$ – red.
Appendix 2

Absorption Spectra of the Pt[3pyaz(1,2,3)]₂ at Different Concentrations

Absorption Spectra of Pt[3pyaz(1,2,3)]₂ at different concentrations (in ethanol); Blue – 1 X 10⁻⁴ M, Red– 1 X 10⁻⁵ M, Black– 1 X 10⁻⁶ M.
Appendix 3
High Resolution Mass Spectra of the Complexes

Figure a - High Resolution Mass Spectrum of Pt[2pyaz(1,2)]₂

Figure b - High Resolution Mass Spectrum of Pt[2pyaz(1,3)]₂
Figure c - High Resolution Mass Spectrum of Pt[3pyaz(1,2,3)]₂

Figure d - High Resolution Mass Spectrum of Pt[3pyaz(1,2,4)]₂
Figure e - High Resolution Mass Spectrum of Pt[2pmaz(1,2)]$_2$

Figure f - High Resolution Mass Spectrum of Pt[2pmaz(1,3)]$_2$
Figure g - High Resolution Mass Spectrum of Pt[3pma(1,2,3)]2.

Figure h - High Resolution Mass Spectrum of Pt[2pz(1,2)]2.
Figure i - High Resolution Mass Spectrum of Pt[2pzaz(1,3)]₂

Figure j - High Resolution Mass Spectrum of Pt[3pzaz(1,2,3)]₂
Figure k - High Resolution Mass Spectrum of Pt[3pzaz(1,2,4)]$_2$