Synthesis and Photophysical Properties of Cu(I) Complexes

M.Sc. Research Thesis

By

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Synthesis and Photophysical Properties of Cu(I) Complexes

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

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CANDIDATE'S DECLARATION

I hereby certify that the work being presented in the thesis entitled **"Synthesis and Photophysical Properties of Cu(I) Complexes"** in the partial fulfillment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted to the **Department of Chemistry, Indian Institute of Technology Indore**, is an authentic record of my work carried out during the period from July 2023 to May 2024 under the supervision of **Dr. Abhinav Raghuvanshi**, Assistant Professor, Department of Chemistry, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.



Trivedi Samarth Himanshu

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.



Trivedi Samarth Himanshu has successfully given his M.Sc. Oral Examination held on 09/05/2024.

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DEDICATE TO MY FAMILY

ABSTRACT

This project aims to synthesise and characterise N-donor ligands, along with their Cu(I) coordination polymers and complexes, and to investigate their potential applications. Cu(I) complexes are luminescent in the UV-visible range upon excitation, and this makes them suitable for use as emitters in optoelectronic devices. Along with their structural diversity, they have other applications such as sensing, separation, adsorption and photocatalysis. In this study, N-donor ligands based on triphenylamine (TPA) moiety and triazole-TPA-based ligands were synthesised (L1 and L2). Owing to the structural properties of TPA, L1 and L2 were emissive at room temperature and demonstrated solvatochromism. acidochromism mechanochromism. and Additionally, the influence of free phenyl on TPA was examined. Further, a new ligand, L3, was synthesised with structural modifications on the TPA backbone. L3 had two pyridyl rings with a free phenyl ring over nitrogen, similar to TPA. All synthesised ligands were characterised by mass spectrometry, ¹H NMR spectroscopy and $^{13}C{^{1}H}$. NMR spectroscopy. Additionally, L1 and L2 were also characterised by SCXRD. These ligands were then reacted with CuI with different stoichiometry in various solvents. Reactions of L3 with CuI gave crystalline, orange luminescent coordination polymer (CP3). CP3 was characterised by SCXRD. CP3 formed a 2D network of Cu₄I₄ SBU and was insoluble in most of the organic solvents, which showed emission at 614 nm in the solid state. Interestingly, it was found that **CP3** could be a potential optical dimethylformamide (DMF) sensor. A significant shift in emissions from orange to cyan-green emission was observed with DMF. It was also observed that CP3 loses crystallinity upon drying. PXRD patterns show an increase in crystallinity with the addition of ACN thereby. Further, to gain insights into the effects of the free phenyl ring, the reaction of L3 and DPyA with Cu-Ipr carbene and PPh₃ was conducted, resulting in the formation of a complex. Carbene complexes formed were of off-white colour under ambient light and green luminescence on UV excitation. Due to instability in solvent, further characterisation was not possible for carbene. However, complexes formed with PPh₃ were characterised by ¹H and ¹³C{¹H} NMR. C4 exhibited mechanochromism, which C3 did not show due to the absence of the free phenyl group.

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NOMENCLATURE

π	pi
δ	Chemical shift
cm	Centimetre
nm	Nanometre
K	Kelvin
mmol	Millimole
mL	Millilitre
rt	Room temperature

ACRONYMS

CDCl ₃	Chloroform-D
ACN	Acetonitrile
MeOH	Methanol
EA	Ethyl acetate
LCMS	Liquid Chromatography Mass Spectrometry
NMR	Nuclear Magnetic Resonance
UV-Vis	Ultraviolet-Visible
Μ	Molar
Ppm	Parts per million
DPyA	di(pyridin-4-yl)amine
DMF	Dimethylformamide
MSR	Multi stimuli responsive
ТРА	Triphenylamine

Chapter 1: INTRODUCTION

1.1 Ligands

Researchers are currently focusing on developing smart emissive materials that can undergo reversible alterations in emission when exposed to different external stimuli like mechanical stress, heat, light, gas, pH, and solvent. These materials find diverse uses in data storage tools, sensors, solar cells, LEDs, electrochromic devices, cell bioimaging and security papers.^{1–5} The origin of reversible emission changes upon exposure to external stimuli is attributed to structural alterations in weak interactions, such as H-bonding, π - π interactions, and C-H- π interactions with various functional groups within the molecule.^{6,7} Lately, there's been a growing interest in crafting multistimuli responsive (MSR) materials, where a single molecule exhibits sensitivity to various chemical or physical changes.^{8–13} To synthesize reversible stimuli-responsive materials, various rigid polycyclic hydrocarbons, such as tetraphenylethene, triphenylamine, pyrene, and thiophene, along with their derivatives, have been utilized as the central structural component.¹⁴



Figure 1: TPA-based MSR active compounds $(a, b)^{15,16}$ and used as ligands $(b, c)^{16,17}$

Particularly, triphenylamine (TPA) is receiving more attention compared to other chromophores due to its propeller-shaped, noncoplanar configuration, making it particularly interesting for its sensitivity to changes such as mechanical force and environmental conditions¹⁴ (Figure. 1). TPA-based compounds have demonstrated a variety of fascinating characteristics, including mechanochromic luminescence, reversible fluorescence switching, solvatochromism, and acidochromism.¹⁸ Molecules with mechanochromism, acidochromism, and solvatochromism are generally termed multi-stimuli-responsive (MSR) materials¹⁹.

Based on these observations, I focused on synthesising MSR materials by incorporating triazole units on the TPA core. Stimuli-responsive properties of both ligands were studied, and the effect of the free phenyl ring was investigated. **L1**, with its free phenyl ring, was more sensitive to external stimuli than **L2**, where all phenyl rings were incorporated with triazoles. Similar compounds based on Schiff bases have also been found to be helpful in biological systems.²⁰ Thus, the prepared ligands could also have biological applications. Given the emission properties of the TPA core, further, a new ligand was synthesised with structural variations directly on the TPA core itself, selecting DPyA for this purpose. DPyA, with its two nitrogen atoms far apart, has many reports which have shown the formation of coordination polymers (CPs) with various metallic ions. Consequently, another ligand was synthesised, and a phenyl ring was substituted over DPyA.

1.2 Copper(I) Coordination compounds:

Luminescent metal complexes and coordination polymers are gaining popularity due to their potential applications in intelligent, responsive luminescence devices.^{21–23} However, most of these compounds rely on noble metal salts, which come with drawbacks in terms of cost and cause severe environmental impacts in extracting them in metallurgical processes, which often outweigh their benefits. Long-term usage of noble metal complexes like Pt(II), Ir(III), Ru (II), and Au(I) is not sustainable due to these challenges.^{24,25} For these reasons, Industries and

scientists are trying to address these issues by turning to cheaper metalbased complexes.



Figure 2: Types of NCs of Cu_nI_n (taken from reference number 26)

Copper-based metallic complexes are of more interest, particularly because copper is more abundant, economical, and less toxic than other heavy metals, presenting a promising alternative as a constituent in coordination compounds. Copper(I) complex compounds are explored across various fields, showing their significance and technological importance.²⁶

Copper with d¹⁰ configuration forms polynuclear metal clusters, which exhibit metallophilic (Cuprophilic) properties. These are very interesting properties as metal-metal interaction can respond to various external stimuli by showing changes in photoluminescent properties. Cuprophilic interaction is observed when Cu···Cu distances are less than 2.8 Å.²⁷ Attributed to such properties of Cu(I), researchers are drawn to luminescent Cu(I) complexes for their relatively low toxicity, diverse structures, and vibrant emission properties, making them increasingly desirable in applications like light-emitting diodes (OLEDs)²⁸ Photovoltaics like Dye-Sensitized Solar Cells (DSSC)²⁹ and Light-emitting electrochemical cells (LEECs).³⁰

Copper(I)-based complexes, particularly those based on Cu(I)-iodide complexes, have gathered attention for their remarkable emissive characteristics and the ability to form various types of metal clusters with the same ligands under minor changes in the environment like solvent and stoichiometry, resulting in altogether different geometries. These metal clusters have a general formula [Cu_xI_x]. Among these, $[Cu_2I_2]$, followed by $[Cu_4I_4]$, are one of the most common types of metal clusters, comprising over three-fourths of the total reported literature on [Cu_xI_x] clusters. Subsequently, clusters like [Cu₃I₃], [Cu₆I₆] and other variations are reported (Figure. 2). CuI-based metal clusters, often referred to as nanoclusters (NC) for 0D Cu(I) compounds, possess many attractive molecular properties on their own. However, constructing systems of NCs that are connected by the coordination of organic ligands is still a significant challenge, yet it is a promising strategy. This approach can construct unique materials with even more intelligent photochemical and physicochemical properties. This chemistry of linking NCs to form extended networks, such as in the case of coordination polymers (CPs)/metal-organic frameworks (MOFs), is now known as reticular chemistry. While reticular chemistry is more related to the 3D network of NCs, similar principles can be applied to CPs, which are 1D or 2D networks of NCs. This leads to the development of the concept of a secondary building unit (SBU). CuIbased NCs can be regarded as useful SBUs, where Cu(I) CPs are known to respond to various stimuli. This occurs mainly attributed to distinct changes in structural arrangements.²⁶



Figure 3: Applications of Cu(I) complexes

These SBUs exhibit properties of both ligands and NCs, as ligand acts as a bridge for NCs. For this reason, there are numerous Cu(I) based CP and MOFs that are porous and semiconductor. As a result, Cu(I) compounds have applications in Sensors for small organic molecules³¹, Bioimaging³², Gas storage³³, Artificial photosynthesis, Organic catalysis³⁴, Energy storage³⁵, Memory devices and many more (Figure. 3). Thus, Cu(I) CPs have a wide range of applications, from addressing global challenges like climate change to detecting early health issues in biological systems.³⁶



Figure 4: (a) N-donor Cu(I) coordination polymer (b) S-donor MSR Cu(I)with TPA moiety as a ligand (Image taken from reference numbers and 16 and 17)

Our lab has reported Cu(I) complexes and CPs that have applications in electrochromic devices³⁷, energy storage³⁵ and sensors for small organic compounds.³¹ There is a limited number of publications on Cu(I) CPs with TPA-based ligands. Among those, our group reported on how CPs on TPA (Figure 4b) based ligands can display stimuli-responsive behaviour, which showed mechanochromism and solvatochromism.¹⁶ While there are multiple reports on CuI with DPyA-based ligands.³⁸⁻⁴² Some reports show the formation of emissive CPs, while others demonstrate relatively lesser emissive CPs. However, DPyA-based ligands used in previous reports were tetradentate³⁸⁻⁴¹; the only bidentate example is with DPyA itself.⁴² Other reports are based on substituted phenyl rings over amine, while in the remaining reports, the amine is attached to aliphatic carbon, which has no TPA backbone (Figure. 5). It was anticipated that different structural interactions would occur with free phenyl rings in our ligands. Thus, the effect of free phenyl was investigated among L1 and L2 and of the Complexes formed of C3 and C4 with DPyA and L3.



Figure 5: (a) Cu(I) CP based on bidentate DPyA-based ligands (b) Cu(I) CP based on tetradentate DPyA-based ligands (Image taken from reference number 39 and 42)

Similarly, L3 was synthesised to investigate the potential effect of the free phenyl ring. Various reactions were carried out with CuI with L1, L2, and L3 and tried to characterise the complex formed. Out of this, CuI-L3 (CP3) was successfully characterised. CP3 was a 2D sheet of Cu₄I₄ SBU. The presence of the free phenyl ring resulted in multiple interactions in CP3, leading to an uncommon structure. This interaction resulted in the parallel stacking of 2D sheets over one another, along with the interpenetration of 2D sheets from the voids of the primary sheet. Further reactions were carried out using PPh₃, and the influence of the free phenyl ring (C3 and C4) was investigated, ultimately leading to mechanochromism in C4.

1.2.1 Overcoming instability of Cu(I) complexes

Although some Cu(I) CPs have demonstrated strong luminescence similar to well-known emissive Ir(III) phosphors, their stability is generally lower due to the reduced ligand field and inner d^{10} electronic configuration compared to noble metal complexes.⁴³ d^{10} electronic configuration of copper(I) results in a flexible pseudo tetrahedral geometry in the complex because of an even distribution of electron density around the copper centre. In the excited state, the copper(I) ion is oxidised to copper(II), which has a d⁹ electronic configuration.



Figure 6: Pseudo-JTD distortion (Image taken from reference number 34)

This leads to the complex undergoing pseudo-Jahn-Teller distortion, which causes the flattening of the tetrahedral geometry of the complex (Figure. 6). This flattened structure is sensitive to interact with coordinating solvent molecules. This leads to the formation of stable excimer species, which quenches the luminescence of the complex. ISC and the flattening distortion occur on a femtosecond to early picosecond timeframe. When the excited state complex is relaxed, it releases energy via nonradiative or radiative transition. Since the radiative transition from the triplet state to the singlet ground state is spin-forbidden, it occurs more slowly than the singlet excited state. Higher non-radiative transitions cause more loss in energy. To avoid this loss of energy, an alternative to tetrahedral complexes is linear complexes, which can effectively avoid pseudo-JTD. Stabilising two-coordinate copper(I) complexes poses a considerable challenge. With copper(I) oxidation state and only two coordination bonds, these complexes are sensitive to atmospheric oxygen or dissolved oxygen of solvents. The most notable characteristic of two-coordinated complexes is their lower nonradiative deactivation rate from the excited state, allowing them to achieve luminescence quantum yields close to unity. Opposite to four-coordinate copper(I) complexes, which rarely achieve luminescence quantum yield of unity, this difference is attributed to the crystal field splitting of the d¹⁰ configuration of the copper centre in both geometries. In twocoordinate copper(I) complexes, the linear geometry prevents the higher-lying d orbital from being degenerate, thereby avoiding the pseudo-Jahn-Teller distortion. This distortion stabilises the excited state in pseudo-tetrahedral geometry, increasing the nonradiative transition to the ground state.³⁴

1.3 Properties of Copper(I) coordination Polymers:

1.3.1 Solvatochromism in Copper(I) coordination polymers

Recently, Cu(I) based CP and MOFs have appeared as promising candidates that can exhibit solvatochromism. In general, Cu(I) complexes have two energy bands (M+X)LCT (HE) and CC (LE), making them sensitive to solvents by interactions with ligands or disrupting Cu···Cu interactions. Cu(I) CPs and MOFs have empty spaces or cages that can trap solvents; sometimes, the size of cages increases in such a way that a solvent can be accommodated. Yunfang Zhao et al. reported that for {[Cu₃I₃(TPSA)] }_n, the solvent molecules get trapped in the cages in which they are synthesised. In DEF, (M+X)LCT is very weak, while CC is very strong, and only a single peak at around 620 nm is observed (figure. 7a).⁴⁴



Figure 7: (a) Structural changes in DEF and DMF (b) Emission spectra with DEF (b) Emission spectra with DEF (Image taken from reference number 44)

However, when this reaction was carried out in DMF, a very different effect was observed. In the luminescence band, the contribution of (M+X)LCT increases to such an extent that it dominates CC, and as a consequence, white emission is observed. The reason for this effect was that in DEF, the cage is bigger and has space for C-H bond vibrations. This led to an increase in thermal vibration from ligand-centred transition, while this effect was not seen with DMF (figure. 7b).

Another example is described by Andrey Yu. Baranov, initially synthesized complexes are highly luminescent because of the solvent molecule. On grinding, this sample solvent is detached, and the dry sample of the complexes has a quantum yield (QY) of 10% - 15% with yellow emission. When this complex is solvated by DCM, ACN or PhCN, emission shifts to cyan luminescence and a 10-fold increase in QY to 100% was observed (Figure 8). This increment in QY is due to increased Franck–Condon factors between the lower energy vibrational modes of the excited state and the higher energy modes of the electronic ground state as experienced in the distorted situation.⁴⁵



Figure 8: (a) Visual images of solvated complexes (b) emission of solvated complexes (c) effect of solvent (Image taken from reference number 45).

1.3.2 Thermochromism in Copper(I) coordination polymers

Several reports of thermochromism in Cu(I) Coordination polymers and complexes exist. Thermochromism can be divided into two types; in the

first case, there is a change in intensity. With decreasing temperature, vibronic oscillations decrease, leading to a decrease in non-radiative transition, which leads to higher quantum yield. For instance [CuI(Brpyrazine)], a red shift from 549 nm to 589 nm is observed on lowering the temperature to 180 K; from here, two peaks around 575 nm are observed. However, the intensity of a band near 450 nm also increases during this temperature range. This emission is due to (M+X)LCT. Nevertheless, with Cu-Cu shorter than the sum of Van der Waals radii, cuprophilic interactions of metal-cluster-centred play a major role in the change in emission behaviour. More remarkably, a monotonous increment of emission of as high as 90 times was observed with decreasing temperature to 7 K (Figure 9). Cu₂--I₂ bonds are flexible and behave like spring. This distance decreases at low temperatures, resulting in a loss of flexibility and increasing the system's rigidity. This rigidity decreases non-radiative transition, and, as a result, an increase in intensity is observed at low temperatures. Thus, a combination of (M+X)LCT and CC is responsible for emission in these cases, but CC dominates for the complete temperature range.⁴⁶



Figure 9: (a) Increase in intensity at low temperature (b) changes in emission wavelength at low temperature (c) Visual changes on lowering temperature under UV lamp (Image taken from reference number 46)

However, there is no significant change in emission wavelength because no other band is observed, and the strength of the other band remains weak compared to the band which dominates at room temperature. Another type of thermochromism involves an increase in intensity along with a shift in emission wavelength.



Figure 10: (a) Thermochromism in [CuIPPh₃.CHCl₃]₄ (b) thermochromism in the grounded sample (c) [CuIPPh₃.CHCl₃]₄ and grounded in ambient light, UV irradiation, and at low temperature (Image taken from reference number 47)

On the contrary, [CuIPPh₃.CHCl₃]₄ and a grounded sample of the same in which the initial cubane isomer (1) is converted to an open chain isomer (1G), which results in a decrease in Cu···Cu interaction and a change in emission is observed. However, with decreasing temperature, the contribution of different bands increases, resulting in Complete shifting of peaks. For 1, blue emission shifts to green with the shifting of the complete band, and no new band has emerged. For 1G, a completely different effect was observed, and at low temperature, a new band at 420 nm was observed while the intensity of the initial yellow band decreased (Figure 10). As a result, a complete shifting of yellow emission to blue was observed in the case of 1G at low temperature

1.3.3 Mechanochromism in Cu(I) coordination complexes

One common factor in the previous two properties was how grinding influences luminescence in Cu(I) complexes. In the previous examples, mechanochromism was observed due to a change in the cluster structure, while in another example, mechanochromism was observed due to the loss of solvent molecules. Another common reason for the observation of mechanochromism is π - π interactions. Grinding the sample removes these π - π interactions, resulting in a shift in emission. For instance, Ping Yu reported that the emission initially appears blue but turns yellow upon grinding. However, the yellow emission reverts to blue upon exposure to various solvents. Upon examination of the crystal structure, multiple π - π interactions were found between pyridine and phenyl. These interactions were absent in the ground samples as observed in the SCXRD structure of the grounded sample. Such complexes exhibiting reversible stimuli-responsive behaviour can find application in coating electronic devices. For example, the grounded compound was coated on an LED, which showed a yellow emission, while fuming with acetone made the LED emit a blue emission. Similarly, such sensitive compounds can be utilised in security papers. In ambient light, the paper appears completely white, but under UV radiation, "Cu" can be read on the paper in the yellow luminescence. Furthermore, this yellow luminescence is converted to blue luminescence when exposed to acetone.⁴⁸ (Figure 11)



Figure 11: (I) Mechanochromic activity of the complex (II) Possible application of reversible properties(Image taken from reference number 48)
Chapter 2: EXPERIMENTAL SECTION

2.1 Material and Instrumentation

Unless otherwise specified, chemicals were used exactly as received. TLC was used to monitor reaction progress using a Merck 60 F254 precoated silica gel plate (0.25 mm thickness), and the products were judged in a UV chamber. All ¹H{¹H} and ¹³C{¹H} and ³¹P{¹H} NMR spectra were collected using a Bruker 400/500 spectrometer in CDCl₃ and DMSO-d₆ at 400/500 MHz for ¹H and ¹³C{¹H} NMR. Data for proton NMR chemical shifts are shown in ppm downfield from tetramethyl silane and are mentioned in delta (δ) units. CDCl₃ is used as an internal standard, which shows a peak at 7.26 ppm. The ¹H NMR splitting patterns are singlet (s), doublet (d), triplet (t), and multiplet (m), and the NMR data was processed by Mestre Nova.

2.2 Synthesis of TPA-based ligands

2.2.1 Synthesis of 4-((E)-((4H-1,2,4-triazol-4yl)imino)methyl)-N-(4-((E)-((4H-1,2,4-triazol-4yl)imino)methyl)phenyl)-N-phenylaniline (L1)

In a two-neck round bottom flask, d-TPA (3.3 mmol, 1000 mg) was dissolved in 10 mL of toluene. To this solution, 4-amino-1,2,4-triazole (7.2 mmol, 612.2 mg) was added with 1 mL of acetic acid. The reaction mixture was stirred for 12 hours under reflux. Upon completion of the reaction period, a yellow product was formed. The mixture was cooled, and the resulting mixture was then washed with dichloromethane (5 mL) two to three times and once with ethanol (5 mL), then dried in a vacuum. The yellow solid was recrystallized in ethanol to get the pure product. (Yield: 1.186g, ~80%). IR: 1580 cm⁻¹ (n C=N), 1167 cm⁻¹, 1267 cm⁻¹, 1319 cm⁻¹ (n C–N), 3080 cm⁻¹ (n C–H). ¹H NMR (500 MHz, DMSO-d₆) δ 9.11 (s, 4H), 9.01 (s, 2H), 7.80 (d, J = 8.7 Hz, 4H), 7.45 (t, J = 7.9 Hz, 2H), 7.27 (t, J = 7.5 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 8.5 Hz, 4H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ (ppm) 157.28, 149.79, 145.46, 138.93, 130.23, 130.00, 126.51, 126.40, 125.73, 122.90.

HRMS m/z was calculated for $C_{24}H_{19}N_9Na$ [M+Na]⁺, 456.1656 and found 456.1643.



Scheme 1: Synthesis of L1

2.2.2 Synthesis of tris(4-((E)-((4H-1,2,4-triazol-4-yl)imino)methyl)phenyl)amine (L2)

Similarly, **L2** was synthesized where t-TPA (3 mmol, 1000mg) was mixed in 10 mL of toluene with 4-amino-1,2,4-triazole (9.6 mmol, 820 mg), followed by the addition of 1 mL of acetic acid. The reaction mixture was stirred for 12 hours under reflux. Further, washing with dichloromethane (5 mL) two to three times and once with ethanol (5 mL) and recrystallization in ethanol gave the desired product. **L2** was obtained as a light-yellow powder (Yield: 1.36g, ~75%). ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): δ 9.13 (ppm) (s, 6H), 9.06 (s, 3H), 7.85 (d, J = 8.5 Hz, 6H), 7.27 (d, J = 8.7 Hz, 6H) ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ (ppm): δ 157.19, 149.15, 138.98, 130.18, 127.70, 124.51. HRMS m/z calculated for C₂₇H₂₁N₁₃Na [M+Na]⁺, 550.1935, found 550.1959.



Scheme 2: Synthesis of L2

2.3 Synthesis of di(pyridin-4-yl)amine based ligand

2.3.1 Synthesis of di(pyridin-4-yl)amine

DPyA was synthesized by following the procedure reported by Filip Bures et al.⁴⁹ Briefly, in 2 neck r.b. 2 g 4-aminopyridine was added in 4 mL PCl₃, followed by 4 mL pyridine. The reaction mixture was stirred for 5 hours at 420 K. An orange cake type was formed in r.b. This was vacuum-dried to remove unreacted pyridine and PCl₃. Later, 2 mL EtOH, 2 mL HCl and 10 mL DI water were added and stirred for 1 hour at 373K. The liquid was immediately filtered, and the residue was washed with a 20% HCl solution of 30 mL 3 times. The filtrate was kept in an ice batch, and the NaOH solution was slowly poured to neutralise the acid. After a while, white ppts have started to form. On complete neutralization, the ppts were filtered, dissolved in EtOH, and recrystallized (Yield 1.8 g, 3 %). **LCMS** m/z calculated for $C_{10}H_9N_3$, [M+Na]⁺, 172.0967, found 172.0869.



Scheme 3: Synthesis of DPyA

2.3.2 Synthesis of *N-phenyl-N-(pyridin-4-yl)pyridin-4-amine* (L3)

In a two-neck r.b. DPyA (2000 mg, 11.6 mmol) was added in 2 neck rb. Containing CuSO₄ (360 mg, 2.2 mmol), 18-crown-6 (120 mg, 0.5 mmol) in diphenyl ether (15 mL), later potassium carbonate (3200mg, 23.4 mmol) was added with bromobenzene (3 mL). The reaction temperature was maintained at 450K for two days in N₂. 2 days later, 200 mL of DCM and 200 mL of MeOH were added to the reaction mixture and passed through the celite-pad. Then, this mixture was dried. However, the mixture was not completely dried because of the diphenyl ether. The mixture was purified by column chromatography, and a pure product was obtained in EA. (Yield:2200 mg, ~70%). ¹H NMR (500 MHz,

DMSO-d₆) δ 8.41 (s, 4H), 7.50 (t, J = 7.7 Hz, 2H), 7.37 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 4.7 Hz, 4H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 150.99, 150.16, 143.03, 129.92, 127.17, 126.52, 115.52. LCMS (ESI) *m*/*z* calculated for C₁₆H₁₃N₃ [M+H]⁺ 248.1182, found 248.1201.



Scheme 4: Synthesis of L3

2.4 Synthesis of coordination polymers (CPs):

2.4.1 Synthesis of CP1

Into a Schenk tube under N_2 condition, CuI (176 mg, 0.92 mmol) dissolved in acetonitrile was added, to which L1 (100 mg, 0.23 mmol) dissolved in MeOH was added. Instant yellow precipitates were observed. This reaction mixture was stirred for 12 hours, after which the precipitates were filtered and washed with ACN and MeOH to remove unreacted CuI and ligands. These precipitates were then dissolved in different solvents to get crystals. Layering, autoclave synthesis, and slow evaporation were conducted to obtain crystals of the same; however, no crystals were observed in all cases.



Scheme 5: Synthesis of CP1

2.4.2 Synthesis of CP2

Into a Schenk tube under N_2 condition, CuI (216 mg, 1.13 mmol) dissolved in acetonitrile was added, to which L2 (100 mg, 0.19 mmol) dissolved in MeOH was added. Instant yellow precipitates were observed. This reaction mixture was stirred for 12 hours, after which the precipitates were filtered and washed with ACN and MeOH to remove unreacted CuI and ligands. These precipitates were then dissolved in different solvents to get crystals. Layering, autoclave synthesis and slow evaporation were conducted to obtain crystals of the same; however, no crystals were observed in all cases.



Scheme 6: Synthesis of CP2

2.4.3 Synthesis of CP3

Into a Schenk tube under N₂ condition, **L3** (100 mg, 0.8 mmol) was dissolved in DCM, to which CuI (153 mg, 1.6 mmol) dissolved in ACN was added instant white precipitates of orange luminescence were observed. The reaction was stirred for 12 hours, after which the compound was dried and washed with ACN. Yield 200 mg (79%) Crystals were obtained by slow diffusion of CuI dissolved in ACN over ligand dissolved in DCM.



Scheme 7: Synthesis of CP3

2.5 Synthesis of complexes

2.5.1 Synthesis of C1

In a 50 mL Schlenk tube, IPr-Cu-Cl was added (100 mg, 0.2 mmol) and dissolved in dichloromethane. DPyA (35.3 mg, 0.3 mmol) was added to this solution. Then, the reaction mixture was stirred for 12h. After 12h, green precipitates were observed. KPF₆ (57 mg, 0.3 mmol) was mixed and stirred for 2 hours. This reaction mixture was then filtered and concentrated. Hexane was added to precipitate out the compound. A white-coloured, green emissive compound was obtained. The formation of the complex was confirmed by LCMS. However, **C1** was unstable in the solution phase, and further studies could not be conducted. (ESI) m/z calculated for [**C**₃₇H₄₅N₅CuPF₆], [M-PF₆⁻]⁺ 622.2965, found 622.2966.



Scheme 8: Synthesis of C1

2.5.2 Synthesis of C2

In a 50 mL Schlenk tube, under N₂ flow, IPr-Cu-Cl was added (100 mg, 0.2 mmol) and dissolved in dichloromethane. To this solution **L3** (51 mg, 0.2 mmol) was added. Then, the reaction mixture was mixed and stirred for 12h. After 12h, green precipitates were observed. KPF₆ (57 mg, 0.3 mmol) was stirred for 2 hours. This reaction mixture was then filtered and concentrated. Hexane was added to precipitate out the compound. The white-coloured green emissive compound was obtained. The formation of the complex was confirmed by LCMS. However, **C2** was unstable in the solution phase, and further studies could not be conducted. (ESI) m/z calculated for [C₄₃H₄₉N₅CuPF₆], [M-PF₆⁻]⁺ 698.3278, found 698.2605.



Scheme 9: Synthesis of C2

2.5.3 Synthesis of C3

In a 100 mL r.b. CuI (165 mg, 0.87 mmol) was dissolved in ACN; to this solution, PPh₃ (459 mg, 1.75 mmol) was added, and precipitates were formed. These precipitates were dissolved by adding more ACN. Once the complete solution was dissolved, DPyA (50 mg, 0.29 mmol) dissolved in MeOH was added, and instant precipitates were observed. This reaction mixture was stirred for 12 hours. The reaction mixture was filtered, and precipitates were obtained by slow evaporation of complex C3 in ACN, Yield (80%). ¹H NMR (500 MHz, CDCl₃) δ 8.35 (d, *J* = 5.8 Hz, 4H) ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 151.16, 134.15, 133.35, 133.15, 129.78, 128.67, 112.27., 7.37 (t, *J* = 8.9 Hz, 36H), 7.32 (d, *J* = 7.5 Hz, 18H), 7.22 (d, *J* = 7.6 Hz, 36H), 6.96 (s, 4H).



Scheme 10: Synthesis of C3

2.5.4 Synthesis of C4

In a 50 mL Schlenk tube, under N₂ flow, CuI (38.5 mg, 0.2 mmol) was suspended in 4 mL toluene under reflux conditions. To this suspension, PPh₃ (107 mg, 0.4 mmol) was added, and this reaction mixture was stirred for 10 minutes till the solution became transparent. To this mixture, L3 (50 mg, 0.2 mmol) was added, and the reaction mixture was stirred for 12 hours. After the reaction, the mixture was dried, and the solid product was dissolved in a minimum amount of ACN (4 mL). To this solution, 10 mL ether and 30 mL hexane were added. When product is completely precipitated, a few drops of ACN were added to dissolve unreacted CuI, PPh₃ and L3. Precipitates were filtered and washed with ACN and Et₂O, Yield (65%). ¹H NMR (500 MHz, CDCl₃) δ 8.48 – 8.40 (m, 4H), 7.51 (t, J = 9.2 Hz, 6H), 7.43 (t, J = 7.9 Hz, 2H), 7.34 (t, J = 7.6 Hz, 4H), 7.26 (t, J = 7.9 Hz, 6H), 7.14 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 6.4 Hz, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 152.21, 151.30, 143.52, 134.21, 133.41, 133.18, 130.59, 129.75, 128.60, 127.88, 127.62, 116.35.



Scheme 11: Synthesis of C4

Chapter 3: RESULT AND DISCUSSION

3.1 Characterization

3.1.1 Characterization of ligands

3.1.1.1 Characterization of L1

L1 was synthesised according to scheme 2. In the reaction, acetic acid was used as a catalyst and toluene as a solvent. The final product was a yellow solid compound with an 81 % yield. The obtained solid product was characterised by Mass spectrometry (Figure 12) and ¹H and ¹³C{¹H} NMR spectroscopy (Figures 13 and 14). Peaks of triazole hydrogen were observed near nine ppm, thereby confirming that triazole is attached to the TPA core.



Figure 12: Mass spectrogram of L1



Figure 13: ¹H NMR spectra of L1



Figure 14: ¹³C{¹H} NMR spectra of L1

3.1.1.2 Characterization of L2

L1 was synthesised according to scheme 3. In the reaction, acetic acid was used as a catalyst and toluene as a solvent. The final product was a yellow solid compound with 75 % yield. The obtained solid product was characterised by Mass spectrometry (Figure 15) and ¹H and ¹³C{¹H} NMR spectroscopy (Figures 16 and 17). Peaks of triazole hydrogen were observed near nine ppm, thereby confirming that triazole is attached to the TPA core. Also, L2 is more symmetric than L1, which can be easily observed with the number of peaks in ¹H and ¹³C{¹H}. 6 peaks were observed in L1, while only four peaks were observed in L2, thereby confirming the symmetric nature of L2.



Figure 15: Mass spectrogram of L2



Figure 16: ¹H NMR spectra of L2



Figure 17: ${}^{13}C{}^{1}H$ NMR spectra of L2

Both ligands were also characterised by SCXRD techniques (Figure 18). As expected with TPA, all the rings were non-planar and had an angle of almost 60° . Further, triazole rings and phenyl rings were also not in the same plane with varying degrees of angles ranging from 10° to 60° . Additionally, multiple pi-pi interactions were also identified in L1, leading it to show mechanochromism. Although no such interactions were observed with L2.



Figure 18: SCXRD structures of L1 and L2

3.1.1.3 Characterization of L3

L3 was synthesised according to scheme 5. The final product was a yellow solid compound with 70 % yield. The obtained solid product was characterised by Mass spectrometry (Figure 20) and ¹H and ¹³C{¹H} NMR spectroscopy. A broader peak in ¹H NMR was observed of hydrogen of carbon attached to Nitrogen in the pyridyl ring of L3.



Figure 19: Mass spectrogram of L3



Figure 20: ¹H NMR spectra of L3



Figure 21: ${}^{13}C{}^{1}H$ NMR spectra of L3

3.1.2 Characterization of CP3

Slow diffusion of **L3** dissolved in DCM with CuI in ACN yielded fibrous crystals of **CP3**. The phase purity of the compound was confirmed by PXRD.



Figure 22: (a) PXRD patterns of CP3 (b) TGA of CP3

The asymmetric unit has two molecules of ligand **L3**, Cu₂I₂ rhomboid unit and two discrete Cu-I. Iodide was in μ^3 -I bridging mode in the Cu₄I₄ cluster, thereby forming 2D Cu₄I₄ SBU. Cu-Cu distances were between 2.624-2.698 Å, while Cu-I were 2.624-2.748 Å in the [Cu₄I₄(**L3**)₂]_n tetrahedra. While the angle of Cu-I-Cu is mostly around 60°, these values lie within the normal range of the bond distances in other iodocuprates⁵⁰. The Cu–N bond lengths are in the range of 2.023–2.047 Å, which can be compared with the corresponding values of other copper pyridine bond lengths. These clusters were connected by ligands from two pyridyl units, thereby forming a 2D network of clusters.



Figure 23: (a) 2D network of Cu₄I₄ SBU (b) Cu₄I₄ as SBU in **CP3** (c) interpenetrating sheet (d) parallel stacking of sheets

Free phenyl ring over Nitrogen showed multiple interactions leading to the uncommon structural arrangement. Ortho and meta hydrogen of the free phenyl ring resulted in an interpenetrated sheet which emerged from the voids of the sheet. This sheet was at 77.75° to the original sheet (Figure 23 c). Further C-H--I interactions were observed, which led to parallel stacking of sheets (Figure 23 c). These parallel sheets further had interpenetrating sheets, thereby forming a 3D network of Cu₄I₄ units. Over a period of 2-3 months, **CP3** loses its emission and crystallinity. However, this loss in crystallite is most probably due to the loss of solvent molecules (confirmed by TGA). However, this doesn't affect the purity of **CP3**, and PXRD still matches the simulated pattern. Although the PXRD of both samples corresponds to pure compound, **CP3** had lost its crystallinity. This loss in crystallinity can be recovered to some extent by adding a few drops of ACN. This was previously observed by Fan et al ⁵¹. Analysing TGA showed a loss of 1.5%, which

was observed at around 150 °C, most probably attributed to the loss of a solvent molecule of ACN. **CP3** shows high thermal stability till 220 °C, and thus can be used in various applications that require higher operating temperatures till 200 °C.



Figure 24: (a) Loss in crystallinity of **CP3** (b) regaining of crystallinity of **CP3** on adding ACN

3.1.3 Characterization of complexes

3.1.3.1 Characterization of C1

The complex formation of **C1** was confirmed by LCMS (Figure. 25), but this complex was unstable in solvent. The complex was white in colour when synthesised in the solid state. **C1** had good solubility in most of the solvents. However, in a very short span of time, the solution turns green, and precipitates are observed. This might have occurred most probably due to dissolved oxygen in the solvent because of which further studies were not possible for **C1**.



Figure 25: Mass spectrogram of C1

3.1.3.2 Characterization of C2

The complex formation of **C2** was confirmed by LCMS (Figure. 26), but this complex was unstable in solvent. The complex was white in colour when synthesised in the solid state. **C1** had good solubility in most of the solvents. However, in a very short span of time, the solution turns green, and precipitates are observed. This might have occurred most probably due to dissolved oxygen in the solvent, because of which further studies were not possible for **C2**.



Figure 26: Mass spectrogram of C2

3.1.3.3 Characterization of C3

Single crystals of **C3** were grown by slow evaporation of concentrate solution of **C3** in ACN. In the crystal structure, two types of structure were observed. In both structures, copper was in tetrahedral geometry, and iodide did not act as a bridging ligand, thereby forming mononuclear systems. The nitrogen of both pyridyl rings was coordinated on two different copper atoms. Two units of the copper atom were connected to two triphenylphosphine units and one Iodine. Thus, the mononuclear system was observed on both sides. Another structure observed in the crystal structure was in which ACN coordinated to Cu, along with two PPh₃ and one iodide. NMR (Figures. 27, 28 and 29) of the complex showed a 1:6 ratio of the ligand and PPh₃, thereby confirming the crystal structure of the bulk sample.



Figure 27: ¹H NMR spectra of C3



Figure 28: ${}^{13}C{}^{1}H$ NMR spectra of C3



---5.48

3.1.3.4 Characterization of C4

Complex C4 was synthesised according to scheme 5. The final product was a white solid product, which was observed with a 60 % yield. The obtained solid product was characterised by ¹H, ¹³C{¹H} and ³¹P{¹H} NMR (Figures. 30, 31 and 32) spectroscopy. Here, NMR suggests 1:1 ratio of ligand PPh₃. This could either result in the formation of a dimeric complex or a coordination polymer.







Figure 32: ³¹P{¹H} NMR spectra of C4

3.2 Photoluminescent Studies

3.2.1 Photoluminescence of L1 and L2

3.2.1.1 Solid state emission, Mechanochromism and Single Crystal analysis of L1 and L2

Both the ligands were found to be yellow-green emissive under UV light in the solid state. To investigate the photoluminescent properties, solidstate emission spectra were recorded at room temperature. Broad emission and excitation spectra were observed for both L1 and L2. (Figure. 33)



Figure 33: Excitation and emission spectra of L1 and L2

Excitation spectra of L1 showed two peaks at 365 nm and 450 nm. While L2 showed a broad descending peak at 355 nm. On excitation of 365 nm, the λ_{max} was at 529 nm for L1 and at 499 nm for L2, respectively. On mechanical grinding of L1 on mortar with pestle, the emission changes from yellow-green to green, displaying a blueshift from 529 nm to 505 nm. This is rarely observed, as mechanochromism generally results in redshifts. However, there are many reports on blueshifted mechanochromism as well^{52–54}. Emission maxima red-shifted to 520 nm on fuming with DCM (Figure. 34 (a and b)). Mechanochromism in L2 was not observed. To further know the mechanism SCXRD studies were performed. To understand the mechanochromic behaviour of the L1 and L2 molecular packing, dihedral angle and Van der Waals interactions were checked in crystal structures.



Figure 34: (a) Emission spectra of **L1** and **L2** (b) visual changes in luminescence in **L1** (c) SCXRD of **L1**

In **L1** strong multiple and intra-molecular interactions (CH… π (2.89 Å), π … π (3.33 Å, 3.76 Å), and N…H (2.48 Å, 2.59 Å)), (Figure. 34 (c)) between different H-atoms and π -cloud of the phenyl and triazole rings where observed. On grinding, these multiple C–H… π , π … π interactions could be removed and as a consequence change in emission is observed^{55–57}.

3.2.1.2 Solvatochromism

Both ligands L1 and L2 had different emissions in different solvents, which probably depended on the polarity of the solvent. To further confirm polarity dependence, emission spectra of L1 and L2 were recorded in various solvents. The emissions spectra were recorded at an excitation wavelength of 365 nm in these solvents, each at a concentration of 1 mM. Both compounds showed a shift in the emission spectra. With increasing solvent polarity, a redshift was observed. Emissions in different solvents with their polarities expressed in $E_T(30)$ are provided in Table 1. The highest redshift was observed in MeOH where, emission maxima were found to be at 542 nm and 528 nm for L1 and L2, respectively. Meanwhile, in non-polar solvent (dioxane), both compounds showed maximum emission wavelengths at around 470 nm. The shift of emission From green to cyan in non-polar solvents was easily observable under UV lamps (Figure. 35)

Solvents	Ет(30) /	$\lambda_{abs}/$	$\lambda_{em}/$	λem/
	kcal mol ⁻¹	nm	nm (TPA-	nm (TPA-
	ncui moi		Tz1)	Tz2)
MeOH	55.4	365	542	528
EtOH	51.9	365	528	514
DMSO	45.1	365	513	502
DMF	41.8	365	512	490
DCE	41.3	365	501	481
THF	37.0	365	474	475
Me-THF	36.5	365	472	475
Dioxane	36.0	365	470	471

Table 1. Emission maxima (λ_{em}) for TPA-Tz1 and TPA-Tz2 in different solvents

E_T(**30**) is solvent polarity parameter⁵⁸.



Figure 35: (a) Solvatochromic visuals of L1 under UV-lamp (b) Solvatochromic visuals of L2 under UV-lamp (c) Emission spectra of L1 in different organic solvents (d) Emission spectra of L1 in different organic solvents

It is reported that the energy gap reduces with increasing solvent polarity as polar solvents stabilise the lowest unoccupied molecular orbital (LUMO) in excited more than the highest occupied molecular orbital (HOMO)^{5,59,60}; thus, solvent-dependent shifting is observed in such molecules. However, there are other reasons for such shifting, and to find out possible mechanisms, further study was conducted. TPA-based molecules are known to undergo TICT. To confirm TICT in our



compounds, the THF/Hexane test was conducted on a preliminary basis.

In the test, **L1** showed a blue shift, while such a phenomenon was not observed in **L2**.

Further emission intensity was recorded for L1 with an increasing fraction of hexane. A blue shift of around 20 nm and 23 times increment in intensity was observed (Figure. 36). Similar phenomena are observed in TPA-based molecules that are explained by the participation of a coplanar, high-energy locally excited (LE) state and a low-energy twisted state. Excited luminogen is stabilised in non-polar solvents in planar conformation, directing to the LE state. This LE state is higher in energy, and thus, a blue shift is observed. However, structural rotations are observed in polar solvents, leading to a TICT state⁶¹⁻⁶³. This rotation

speeds up the intramolecular transfer of electrons for solvatochromism in **L1**. Thus, suggesting that **L1** display solvatochromism through a TICT phenomenon.

3.2.1.3 Acidochromism

Change in luminescence in the presence of acid was also observed for both ligands L1 and L2. To record these gradual changes in emission, a 0.25 mM solution in THF was prepared for L1 and L2. A shift from 475 nm to 533 nm and 518 nm was observed for L1 and L2 on the addition of 270 eq and 360 eq of **TFA**, respectively. Along with the redshift, a decrease in intensity was also observed. The reversibility of change in emission was confirmed by the addition of TEA in a similar equivalent. The original emission colour reappeared with the addition of TEA to the THF/TFA solution of compounds. The emission λ_{max} shifted back to 479 and 475 for L1 and L2, respectively, accompanied by an increase in intensity. Similar observations were made in solid-state samples of both ligands. Exposure to TFA leads to a red shift in both L1 and L2, thus resulting in a similar phenomenon to the solution phase. L1 showed shifting from 529 nm to 592 nm, while L2 showed a shift from 499 nm to 543 nm (Figures. 37).



Figure 37: (a) Emission spectra of acidochromism with TFA of L1 (b) Emission spectra of reversible acidochromism with TEA of L1 (c) Emission spectra of acidochromism with TFA of L2 (d) Emission spectra of reversible acidochromism with TEA of L2 (e) solid-state

reversible acidochromism emission spectra of L1 (f) solid-state reversible acidochromism emission spectra of L2.

Both samples show a recovery of emission in the solid state upon exposure to TEA. The wavelength shifted back to 562 nm for L1 and 520 nm for L2. To understand the mechanism, ¹H NMR studies were performed with L1. TFA was added to L1 dissolved in DMSO-d₆. Deshielding of triazolyl protons (H_a) of 1 ppm was observed, while a slight deshielding of .1 ppm for iminic protons (H_b) was observed, as shown in Figure. 38. This suggests the protonation of triazolyl nitrogen in the presence of acids, which forms an ionic species, resulting in the deshielding of more affected protons.



Figure 38: Deshelling of triazolyl hydrogen in the presence of TFA

Such effects on highly conjugated systems have been explained based on DFT, where in interaction with H⁺, both HOMO and LUMO are stabilised due to a deficiency in electrons. However, this decrement in energy is more prominent for LUMO, thereby decreasing the energy gap.^{64,65}

3.2.2 Photoluminescent study Cu (I) CPs 3.2.2.1 Emission of CP1 and CP2

Ligands L1 and L2 were very emissive, but corresponding CP1 and CP2 were very weakly emissive. The only peaks observed here were at 459 nm and 453 nm with CP1 and CP2, respectively. CP1 exhibited

higher emission maxima than **CP2**, similar to **L1** having higher emission maxima than **L2**. This trend was also followed in emission intensity where **CP2**, although lower, exhibited higher emission intensity than **CP1** (Figure. 39).



Figure 39: Emission spectra of CP1 and CP2 with respect to their corresponding ligands

3.2.2.2 Emission of CP3 at room temperature and low temperature

CP3 was of white colour in ambient light; on irradiating with UV, **CP3** showed orange emission. A broader band was observed at around 620 nm. This luminescence is similar to many previous reports with Cu₄I₄ cluster having CC transition, which exhibits emission maxima in the range of 550 nm to 650 nm⁶⁶. Along with this CC, another band of one-third intensity was observed at around 450 nm. (M+X)LCT transition is responsible for emissions in this region. With two bands in emission spectra, it was expected for **CP3** to show thermochromic behaviour by increased intensity of the bands. When kept in liquid nitrogen for a minute, the orange emission of **CP3** was shifted to Cyan emission (Figure 40). This effect could be attributed to the strengthening of the (M+X)LCT band around 470 nm; thus, a shift in maxima of 120 nm will be observed on recording further data.



Figure 40: Thermochromism in CP3

Solvent Dependent emission of CP3

Freshly prepared **CP3** exhibited bright orange luminescence at 614 nm. Over time, **CP3** experienced a decline in luminescence, typically within 3 to 4 months, coinciding with a decrease in its crystalline structure. However, the addition of dichloromethane partially restored its orange emission. This trend persisted with many other solvents as well. A change in luminescence was observed in dimethylformamide (DMF), which displayed a cyan-green emission different from the expected orange. Further investigation into solvent effects on emission spectra revealed shifts in emission wavelength when different solvents were introduced; emission maxima shifts with the broadening of emission spectra in DMF (Figure 40 a and b).



Figure 41: (a) Changes in intensity depending on solvents (b) changes in emission wavelength (c) Sensitivity to DMF of **CP3**

To assess solvent sensitivity, **CP3** was spread and pressed on a black sheet of paper. A drop of some common solvents was added, and initial orange emission persisted for most of the papers except for DMF. DMF showed a completely different emission of cyan-green which was studied from emission spectra (Figure 41 c). Examination of the crystal structure revealed dichloromethane and ACN molecules within the voids, with dichloromethane demonstrating Cl---H-C interactions, while no such interactions were observed with ACN. Owing to interpenetrations of sheets, the size of the void generated could be responsible for such changes.

3.2.3 Emission of Cu(I) Complexes

3.2.3.1 Emission of C1 and C2

Both C1 and C2 were of green luminescence; their photophysical studies showed a green emission at 502 nm for C1 and 516 nm for C2 on excitation at 365 nm (Figure 42). With a phenyl ring over L2, C2 was

expected to show higher emission wavelength because of a decrease in the HOMO-LUMO energy gap. **C1** oxidises faster than **C2** and in both cases oxidised complexes did not show emissions.



Figure 42: Emission spectra of (a) C1 and (b) C2

3.2.3.2 Emission of C3

C3 was of white colour under ambient light and showed emission at 459 nm on excitation at 365 nm, thus displaying a blue emission; these emissions are displayed (M+X)LCT. An interesting property observed in this case was that when dissolved in DCM and precipitated with hexane, it displayed green emission. This emission reverted to 480 nm on adding ACN to the green emissive **C3** (Figure 43). The reason for this could be attributed to the fact that when dissolved in DCM, solvated ACN was removed, and DCM had different interactions that led to an increase in emission wavelength.



Figure 43: (a) Spectral changes in emission of **C3**(b) Normalised spectra of emission changes (c) observed visual changes in UV lamp

3.2.3.3 Emission of C4

C4 was of white colour under ambient light and showed emission at 470 nm on excitation of 365 nm, displaying a cyan emission. This emission is displayed by (M+X)LCT. This complex exhibited mechanochromism, and a notable shift of 70 nm was observed on mechanical grinding, which can easily be reverted by any solvent (Figure 44). Another remarkable property of this complex is that not only its emission but also its colour in ambient light is converted to yellowish when mechanical stress is applied. Thus, this can have wider application in security papers.



Figure 44: (a) Changes in emission on mechanical grinding (b) Normalised intensity of C4 (c) visual changes in UV lamp

Chapter 4: CONCLUSION AND FUTURE SCOPE

4.1 CONCLUSION

In summary, I have successfully synthesised and characterised three new ligands. Among these, L1 and L2 were characterised by NMR and SCXRD. Their MSR nature was studied along with probable reasons for those behaviours. Free phenyl ring in L1 led to a more sensitive nature of L1 to external stimuli in comparison to L2, where all rings were incorporated with triazole units. Ligand L3 was also synthesised with a free phenyl ring to investigate the effect of a free phenyl ring. Further, all synthesised ligands were reacted with CuI salt, out of which only CP3 was characterised by SCXRD, and a very different structure from previously reported structures on DPyA was observed. CP3 is a 2D sheet of Cu₄I₄ SBU with orange emission in a UV lamp. CP3 is also a potential candidate for an optical DMF sensor. A further effect of free phenyl was studied by synthesising two Cu(I) complexes with PPh₃ as an ancillary ligand characterised, and the effect of free phenyl was investigated. In the case of the MSR nature of L1 and L2 and C3 and C4, a common effect was observed, which was that free phenyl over amine enhanced the MSR activity of the compound.

4.2 FUTURE SCOPE

Further, we will try to characterise **CP1** and **CP2**. **CP1** and **CP2** with multiple sites of donating can lead to a 2D structure similar to **CP3**. Such CPs can show highly selective sensing and could also have applications in energy storage, like supercapacitors. Thus, both **CP1** and **CP2** will be explored for potential application in gas sensing and energy storage. Additionally, the fluorescence-based sensitivity of **CP3** with DMF will be investigated and compare its selectivity with other organic solvents.

C1 and **C2** oxidise in the solution phase and are highly unstable. But where stable in the solid state, inert conditions will be tried for the characterisation of these complexes. Subsequently, their electrochromic properties will be studied for application in OLED devices. Characterised **C3** and **C4** have shown sensitivity to solvent and mechanical force. Photoluminescent properties of both complexes will be investigated with possibilities of application in the mechanical sensor as both compounds showed similar blue emissions.
References

- Zhang, J.; Li, A.; Zou, H.; Peng, J.; Guo, J.; Wu, W.; Zhang, H.; Zhang, J.; Gu, X.; Xu, W.; Xu, S.; Liu, S. H.; Qin, A.; Lam, J. W. Y.; Tang, B. Z. A "Simple" Donor–Acceptor AIEgen with Multi-Stimuli Responsive Behavior. *Mater. Horiz.* 2020, 7 (1), 135–142. https://doi.org/10.1039/C9MH01041F.
- (2) Kushwaha, A. K.; Kumar, Y.; Kumar, S.; Singh, R. S. Competitive ICT in Asymmetric D–A Scaffolds Showing Visible Solvatochromism, Temperature-Induced Emission Enhancement and AIE Based Acidochromism. J. Lumin. 2022, 250, 119072. https://doi.org/10.1016/j.jlumin.2022.119072.
- (3) Huang, Y.; Ning, L.; Zhang, X.; Zhou, Q.; Gong, Q.; Zhang, Q. Stimuli-Fluorochromic Smart Organic Materials. *Chem. Soc. Rev.* 2024, *53* (3), 1090–1166. https://doi.org/10.1039/D2CS00976E.
- (4) Yan, D.; Wang, Z.; Zhang, Z. Stimuli-Responsive Crystalline Smart Materials: From Rational Design and Fabrication to Applications. Acc. Chem. Res. 2022, 55 (7), 1047–1058. https://doi.org/10.1021/acs.accounts.2c00027.
- (5) Prabakaran, K.; Manivannan, R.; Son, Y.-A. Highly Emissions of TPA-Linear Based Pyrazine Derivatives with Different Mechanochromic Luminosity. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 2023, 285, 121874. https://doi.org/10.1016/j.saa.2022.121874.
- (6) Zhang, M.; Yang, W.; Li, K.; Zhou, W.; Gong, T.; Xue, R. Multi-Branch Effect on Aggregation-Induced Emission Enhancement and Tunable Emission of Triphenylamine Fluorophores. *Mater. Chem. Phys.* 2018, 204, 37–47. https://doi.org/10.1016/j.matchemphys.2017.10.030.
- (7) Raju, T. B.; Gopikrishna, P.; Vaghasiya, J. V.; Soni, S. S.; Iyer, P.K. The Solvatochromism and Aggregation-Induce Enhanced

Emission of Triphenylamine Substituted Styrene Derivatives andIts Application in Dye Sensitized Solar Cells. J. Photochem.Photobiol.Chem.2019,376,12–21.https://doi.org/10.1016/j.jphotochem.2019.02.015.

- (8) Singh, V. D.; Kushwaha, A. K.; Singh, R. S. Achieving Flexibility/Rigidity Balance through Asymmetric Donor–Acceptor Scaffolds in Pursuit of Dual State Emission with Application in Acidochromism. *Dyes Pigments* 2021, *187*, 109117. https://doi.org/10.1016/j.dyepig.2020.109117.
- (9) Gayathri, P.; Pannipara, M.; Al-Sehemi, A. G.; Anthony, S. P. Triphenylamine-Based Stimuli-Responsive Solid State Fluorescent Materials. *New J. Chem.* 2020, 44 (21), 8680–8696. https://doi.org/10.1039/D0NJ00588F.
- (10) Huang, G.; Xia, Q.; Huang, W.; Tian, J.; He, Z.; Li, B. S.; Tang, B. Z. Multiple Anti-Counterfeiting Guarantees from a Simple Tetraphenylethylene Derivative High-Contrasted and Multi-State Mechanochromism and Photochromism. *Angew. Chem.* 2019, 131 (49), 17978–17983. https://doi.org/10.1002/ange.201910530.
- (11) Zhao, Z.; Lam, J. W. Y.; Tang, B. Z. Tetraphenylethene: A Versatile AIE Building Block for the Construction of Efficient Luminescent Materials for Organic Light-Emitting Diodes. *J. Mater. Chem.* 2012, 22 (45), 23726. https://doi.org/10.1039/c2jm31949g.
- (12) Li, J.; Shen, P.; Zhuang, Z.; Wu, J.; Tang, B. Z.; Zhao, Z. In-Situ Electro-Responsive through-Space Coupling Enabling Foldamers as Volatile Memory Elements. *Nat. Commun.* **2023**, *14* (1), 6250. https://doi.org/10.1038/s41467-023-42028-5.
- (13) Feng, X.; Wang, X.; Redshaw, C.; Tang, B. Z. Aggregation Behaviour of Pyrene-Based Luminescent Materials, from Molecular Design and Optical Properties to Application. *Chem. Soc. Rev.* 2023, 52 (19), 6715–6753. https://doi.org/10.1039/D3CS00251A.

- (14) Huang, B.; Jiang, D.; Feng, Y.; Chen, W.-C.; Zhang, Y.; Cao, C.; Shen, D.; Ji, Y.; Wang, C.; Lee, C.-S. Mechanochromic Luminescence and Color-Tunable Light-Emitting Devices of Triphenylamine Functionalized Benzo[d , e]Benzo[4,5]Imidazo[2,1- a]Isoquinolin-7-One. J. Mater. Chem. C 2019, 7 (32), 9808–9812. https://doi.org/10.1039/C9TC02592H.
- (15) Fang, B.; Lai, L.; Chu, M.; Shi, Y.; Yin, M. A Multifunctional Triphenylamine–Benzothiazole Derivative with Blue-Shifted Mechanochromism, Acidochromism and Amplified Spontaneous Emission. *ChemPhotoChem* 2021, 5 (3), 270–274. https://doi.org/10.1002/cptc.202000225.
- (16) Pandey, D.; Singh, G.; Mishra, S.; Viau, L.; Knorr, M.; Raghuvanshi, A. Solvatochromic Behaviour of Cyclic Dithioether-Functionalized Triphenylamine Ligands and Their Mechano-Responsive Cu(I) Coordination Polymers. *Dalton Trans.* 2023, *52* (39), 14151–14159. https://doi.org/10.1039/D3DT02226A.
- (17) Hu, L.-X.; Gao, M.; Wen, T.; Kang, Y.; Chen, S. Synthesis of Halide-Modulated Cuprous(I) Coordination Polymers with Mechanochromic and Photocatalytic Properties. *Inorg. Chem.* 2017, 56 (11), 6507–6511. https://doi.org/10.1021/acs.inorgchem.7b00598.
- (18) Karak, A.; Manna, S. K.; Mahapatra, A. K. Triphenylamine-Based Small-Molecule Fluorescent Probes. *Anal. Methods* 2022, *14* (10), 972–1005. https://doi.org/10.1039/D2AY00134A.
- (19) Shu, J.; Ni, T.; Liu, X.; Xu, B.; Liu, L.; Chu, W.; Zhang, K.; Jiang, W. Mechanochromism, Thermochromism, Protonation Effect and Discrimination of CHCl3 from Organic Solvents in a Et2N-Substituted Salicylaldehyde Schiff Base. *Dyes Pigments* 2021, *195*, 109708. https://doi.org/10.1016/j.dyepig.2021.109708.
- (20) Çakmak, R.; Başaran, E.; Şentürk, M. Synthesis, Characterization, and Biological Evaluation of Some Novel Schiff Bases as Potential Metabolic Enzyme Inhibitors. *Arch. Pharm. (Weinheim)* 2022, *355* (4), 2100430. https://doi.org/10.1002/ardp.202100430.

- (21) Grätzel, M. Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells. *Inorg. Chem.* 2005, 44 (20), 6841–6851. https://doi.org/10.1021/ic0508371.
- (22) Liu, Y.; Yiu, S.-C.; Ho, C.-L.; Wong, W.-Y. Recent Advances in Copper Complexes for Electrical/Light Energy Conversion. *Coord. Chem. Rev.* 2018, 375, 514–557. https://doi.org/10.1016/j.ccr.2018.05.010.
- (23) Czerwieniec, R.; Leitl, M. J.; Homeier, H. H. H.; Yersin, H. Cu(I) Complexes – Thermally Activated Delayed Fluorescence. Photophysical Approach and Material Design. *Coord. Chem. Rev.* 2016, 325, 2–28. https://doi.org/10.1016/j.ccr.2016.06.016.
- (24) Lu, J.; Pan, Q.; Zhu, S.; Liu, R.; Zhu, H. Ligand-Mediated Photophysics Adjustability in Bis-Tridentate Ir(III) Complexes and Their Application in Efficient Optical Limiting Materials. *Inorg. Chem.* 2021, 60 (17), 12835–12846. https://doi.org/10.1021/acs.inorgchem.1c01142.
- (25) Shen, Y.; Kong, X.; Yang, F.; Bian, H.-D.; Cheng, G.; Cook, T. R.; Zhang, Y. Deep Blue Phosphorescence from Platinum Complexes Featuring Cyclometalated *N* -Pyridyl Carbazole Ligands with Monocarborane Clusters (CB ₁₁ H ₁₂ ⁻). *Inorg. Chem.* 2022, *61* (42), 16707–16717.

https://doi.org/10.1021/acs.inorgchem.2c02467.

- (26) Troyano, J.; Zamora, F.; Delgado, S. Copper(I)–Iodide Cluster Structures as Functional and Processable Platform Materials. *Chem. Soc. Rev.* 2021, 50 (7), 4606–4628. https://doi.org/10.1039/D0CS01470B.
- (27) Cariati, E.; Lucenti, E.; Botta, C.; Giovanella, U.; Marinotto, D.; Righetto, S. Cu(I) Hybrid Inorganic–Organic Materials with Intriguing Stimuli Responsive and Optoelectronic Properties. *Coord. Chem. Rev.* 2016, 306, 566–614. https://doi.org/10.1016/j.ccr.2015.03.004.
- (28) Klein, M.; Rau, N.; Wende, M.; Sundermeyer, J.; Cheng, G.; Che, C.-M.; Schinabeck, A.; Yersin, H. Cu(I) and Ag(I) Complexes with a New Type of Rigid Tridentate N,P,P-Ligand for Thermally

Activated Delayed Fluorescence and OLEDs with High External Quantum Efficiency. *Chem. Mater.* **2020**, *32* (24), 10365–10382. https://doi.org/10.1021/acs.chemmater.0c02683.

- (29) Franchi, D.; Leandri, V.; Pizzichetti, A. R. P.; Xu, B.; Hao, Y.; Zhang, W.; Sloboda, T.; Svanström, S.; Cappel, U. B.; Kloo, L.; Sun, L.; Gardner, J. M. Effect of the Ancillary Ligand on the Performance of Heteroleptic Cu(I) Diimine Complexes as Dyes in Dye-Sensitized Solar Cells. *ACS Appl. Energy Mater.* 2022, *5* (2), 1460–1470. https://doi.org/10.1021/acsaem.1c02778.
- (30) Chen, X.-W.; Yuan, H.-L.; He, L.-H.; Chen, J.-L.; Liu, S.-J.; Wen, H.-R.; Zhou, G.; Wang, J.-Y.; Wong, W.-Y. A Sublimable Dinuclear Cuprous Complex Showing Selective Luminescence Vapochromism in the Crystalline State. *Inorg. Chem.* 2019, 58 (21), 14478–14489.

https://doi.org/10.1021/acs.inorgchem.9b01972.

- (31) Mishra, S.; Patel, C.; Pandey, D.; Mukherjee, S.; Raghuvanshi, A. Semiconducting 2D Copper(I) Iodide Coordination Polymer as a Potential Chemiresistive Sensor for Methanol. *Small* 2024, 2311448. https://doi.org/10.1002/smll.202311448.
- (32) Yin, S.-N.; Liu, Y.; Zhou, C.; Yang, S. Glutathione-Mediated Cu(I)/Cu(II) Complexes: Valence-Dependent Effects on Clearance and In Vivo Imaging Application. *Nanomaterials* **2017**, *7* (6), 132. https://doi.org/10.3390/nano7060132.
- (33) Li, Y.; Wang, Y.; Fan, W.; Sun, D. Flexible Metal–Organic Frameworks for Gas Storage and Separation. *Dalton Trans.* 2022, 51 (12), 4608–4618. https://doi.org/10.1039/D1DT03842G.
- (34) Beaudelot, J.; Oger, S.; Peruško, S.; Phan, T.-A.; Teunens, T.; Moucheron, C.; Evano, G. Photoactive Copper Complexes: Properties and Applications. *Chem. Rev.* 2022, *122* (22), 16365– 16609. https://doi.org/10.1021/acs.chemrev.2c00033.
- (35) Mishra, S.; Singh, M. K.; Pandey, D.; Rai, D. K.; Raghuvanshi, A. A Two-Dimensional Semiconducting Cu(I)-MOF for Binder and Conductive Additive-Free Supercapattery. *J. Mater. Chem. A* 2024, *12* (8), 4534–4543. https://doi.org/10.1039/D3TA04708C.

- (36) Schlachter, A.; Tanner, K.; Harvey, P. D. Copper Halide-Chalcogenoether and -Chalcogenone Networks: Chain and Cluster Motifs, Polymer Dimensionality and Photophysical Properties. *Coord. Chem. Rev.* 2021, 448, 214176. https://doi.org/10.1016/j.ccr.2021.214176.
- (37) Kharabe, L. S.; Ghosh, T.; Pandey, D.; Kumar, R.; Raghuvanshi,
 A. Heteroleptic Cu(I) Complex with Vapochromism and Its Application as Electrochromic Material. *Appl. Organomet. Chem.* 2024, e7451. https://doi.org/10.1002/aoc.7451.
- (38) Fan, G.-Y.; Wang, Y.-L.; Han, S.-D.; Xue, Z.-Z.; Pan, J. Assembly of One-, Two-, and Three-Dimensional Cu(I)-Based Coordination Frameworks for Tunable White Light Emission and Effective Fluorescence Sensing. *Cryst. Growth Des.* 2023, *23* (12), 8735–8744. https://doi.org/10.1021/acs.cgd.3c00881.
- (39) Jeong, A. R.; Shin, H. J.; Jang, Y. J.; Min, K. S. Two-Dimensional Zinc(II) and Copper(I) Coordination Polymers for Photoluminescence. *J. Mol. Struct.* 2022, *1251*, 132031. https://doi.org/10.1016/j.molstruc.2021.132031.
- (40) Tang, Y.-Y.; Ding, C.-X.; Ng, S.-W.; Xie, Y.-S. Syntheses, Structures and Photoluminescence of Zn(Ii), Ag(i), Cu(i) and Co(Ii) Coordination Polymers of a Tetrapyridyl Ligand. *RSC Adv*. 2013, *3* (39), 18134. https://doi.org/10.1039/c3ra43405b.
- (41) Ding, C.; Li, X.; Ding, Y.; Li, X.; Ng, S. W.; Xie, Y. Novel Bis(4,4'-Dipyridylamine) Ligand with a Flexible Butadiyne Linker: Syntheses, Structures, and Photoluminescence of d ¹⁰ Metal Coordination Polymers. *Cryst. Growth Des.* 2012, *12* (7), 3465–3473. https://doi.org/10.1021/cg201655n.
- (42) Cordes, D. B.; Hanton, L. R.; Spicer, M. D. The Use of H-Bonding to Increase the Dimensionality of Coordination Networks of Cu(I) and Cu(II). *J. Mol. Struct.* 2006, 796 (1–3), 146–159. https://doi.org/10.1016/j.molstruc.2006.03.106.
- (43) Tang, R.; Xu, S.; Lam, T.; Cheng, G.; Du, L.; Wan, Q.; Yang, J.;
 Hung, F.; Low, K.; Phillips, D. L.; Che, C. Highly Robust Cu^I TADF Emitters for Vacuum-Deposited OLEDs with Luminance

up to 222 200 Cd m $^{-2}$ and Device Lifetimes (LT $_{90}$) up to 1300 Hours at an Initial Luminance of 1000 Cd m $^{-2}$. *Angew. Chem. Int. Ed.* **2022**, *61* (33), e202203982. https://doi.org/10.1002/anie.202203982.

- (44) Zhao, Y.; Yu, M.; Liu, C.; Li, S.; Li, Z.; Jiang, F.; Chen, L.; Hong, M. Tunable Dual-Emission Luminescence from Cu(I)-Cluster-Based MOFs for Multi-Stimuli Responsive Materials. *J. Mater. Chem.* C 2021, 9 (8), 2890–2897. https://doi.org/10.1039/D0TC05311B.
- (45) Baranov, A. Yu.; Rakhmanova, M. I.; Hei, X.; Samsonenko, D. G.; Stass, D. V.; Bagryanskaya, I. Yu.; Ryzhikov, M. R.; Fedin, V. P.; Li, J.; Artem'ev, A. V. A New Subclass of Copper(1) Hybrid Emitters Showing TADF with near-Unity Quantum Yields and a Strong Solvatochromic Effect. *Chem. Commun.* 2023, *59* (20), 2923–2926. https://doi.org/10.1039/D3CC00119A.
- (46) Murillo, M.; Álvarez-Conde, J.; Wannemacher, R.; Cabanillas-González, J.; González-Platas, J.; Rodríguez-Mendoza, U. R.; Liang, A.; Turnbull, R.; Errandonea, D.; Martínez, J. I.; Amo-Ochoa, P. A 1D Cu(1)–I-Pyrazine Coordination Polymer with Controlled Pressure-Induced Phase Transition and Opto-Electronic Response Depending on Mechanical Stimuli, Temperature, and CuI Content. *J. Mater. Chem. C* 2022, *10* (47), 18004–18016. https://doi.org/10.1039/D2TC04127H.
- (47) Huitorel, B.; El Moll, H.; Cordier, M.; Fargues, A.; Garcia, A.; Massuyeau, F.; Martineau-Corcos, C.; Gacoin, T.; Perruchas, S. Luminescence Mechanochromism Induced by Cluster Isomerization. *Inorg. Chem.* 2017, *56* (20), 12379–12388. https://doi.org/10.1021/acs.inorgchem.7b01870.
- (48) Yu, P.; Peng, D.; He, L.-H.; Chen, J.-L.; Wang, J.-Y.; Liu, S.-J.; Wen, H.-R. A Mechanochromic and Vapochromic Luminescent Cuprous Complex Based on a Switchable Intramolecular $\Pi \cdots \pi$ Interaction. *Inorg. Chem.* **2022**, *61* (1), 254–264. https://doi.org/10.1021/acs.inorgchem.1c02807.

- (49) Bureš, F.; Cvejn, D.; Melánová, K.; Beneš, L.; Svoboda, J.; Zima, V.; Pytela, O.; Mikysek, T.; Růžičková, Z.; Kityk, I. V.; Wojciechowski, A.; AlZayed, N. Effect of Intercalation and Chromophore Arrangement on the Linear and Nonlinear Optical Properties of Model Aminopyridine Push–Pull Molecules. J. Mater. Chem. C 2016, 4 (3), 468–478. https://doi.org/10.1039/C5TC03499J.
- (50) Raghuvanshi, A.; Strohmann, C.; Tissot, J.; Clément, S.; Mehdi, A.; Richeter, S.; Viau, L.; Knorr, M. Assembly of Coordination Polymers Using Thioether-Functionalized Octasilsesquioxanes: Occurrence of (CuX) n Clusters (X=Br and I) within 3D-POSS Networks. *Chem. Eur. J.* 2017, 23 (65), 16479–16483. https://doi.org/10.1002/chem.201704911.
- (51) Fan, H.-C.; Xia, X.; Zeng, Y.-B.; Wang, Q.-F.; Chen, D.; Qin, S.-C.; Wang, C.-Q.; Cao, Q.-E.; Zheng, L.-Y. Various Dimensional CuI–DPA Coordination Polymers Based on the Same Components for Different Electronic and Photothermal Properties. *Small Struct.* 2022, *3* (7), 2200030. https://doi.org/10.1002/sstr.202200030.
- (52) Feng, F.; Yang, B.; Yan, S.; Ma, H.; Tao, T.; Huang, W. Phenyl/Benzoxazole-Extended Tetraphenylethene Derivatives for Reversible Mechanochromism and Acidichromism. *Dyes Pigments* 2023, 219, 111567. https://doi.org/10.1016/j.dyepig.2023.111567.
- (53) Fang, B.; Lai, L.; Chu, M.; Shi, Y.; Yin, M. A Multifunctional Triphenylamine–Benzothiazole Derivative with Blue-Shifted Mechanochromism, Acidochromism and Amplified Spontaneous Emission. *ChemPhotoChem* 2021, 5 (3), 270–274. https://doi.org/10.1002/cptc.202000225.
- (54) Chen, M.; Chen, R.; Shi, Y.; Wang, J.; Cheng, Y.; Li, Y.; Gao, X.; Yan, Y.; Sun, J. Z.; Qin, A.; Kwok, R. T. K.; Lam, J. W. Y.; Tang, B. Z. Malonitrile-Functionalized Tetraphenylpyrazine: Aggregation-Induced Emission, Ratiometric Detection of Hydrogen Sulfide, and Mechanochromism. *Adv. Funct. Mater.* 2018, 28 (6), 1704689. https://doi.org/10.1002/adfm.201704689.

- (55) Xue, P.; Ding, J.; Chen, P.; Wang, P.; Yao, B.; Sun, J.; Sun, J.; Lu, R. Mechanical Force-Induced Luminescence Enhancement and Chromism of a Nonplanar D–A Phenothiazine Derivative. *J. Mater. Chem. C* 2016, *4* (23), 5275–5280. https://doi.org/10.1039/C6TC01193D.
- (56) Chan, C. Y. K.; Lam, J. W. Y.; Zhao, Z.; Chen, S.; Lu, P.; Sung, H. H. Y.; Kwok, H. S.; Ma, Y.; Williams, I. D.; Tang, B. Z. Aggregation-Induced Emission, Mechanochromism and Blue Electroluminescence of Carbazole and Triphenylamine-Substituted Ethenes. *J Mater Chem C* 2014, *2* (21), 4320–4327. https://doi.org/10.1039/C4TC00097H.
- (57) Sun, Y.; Lei, Z.; Ma, H. Twisted Aggregation-Induced Emission Luminogens (AIEgens) Contribute to Mechanochromism Materials: A Review. J. Mater. Chem. C 2022, 10 (40), 14834– 14867. https://doi.org/10.1039/D2TC02512D.
- (58) Reichardt, C. Solvatochromic Dyes as Solvent Polarity Indicators. *Chem. Rev.* 1994, 94 (8), 2319–2358. https://doi.org/10.1021/cr00032a005.
- (59) Xu, Z.; Luo, Y.; Yang, X.; Ren, Y.; Liu, G.; Zhang, M.-X. Synthesis and Properties of D-π-A Triphenylamine Derivatives with Solvatochromism and Bioimaging Application. J. *Photochem. Photobiol. Chem.* 2023, 444, 115002. https://doi.org/10.1016/j.jphotochem.2023.115002.
- (60) Yu, Y.; Zhao, R.; Liu, H.; Zhang, S.; Zhou, C.; Gao, Y.; Li, W.; Yang, B. Highly Efficient Deep-Blue Light-Emitting Material Based on V-Shaped Donor-Acceptor Triphenylamine-Phenanthro[9,10-d]Imidazole Molecule. *Dyes Pigments* 2020, *180*, 108511. https://doi.org/10.1016/j.dyepig.2020.108511.
- (61) Zhang, Y.; Feng, Y.-Q.; Wang, J.-H.; Han, G.; Li, M.-Y.; Xiao, Y.; Feng, Z.-D. Moiety Effect on the Luminescent Property of Star-Shaped Triphenylamine (TPA) Derivatives as Mechanochromic Materials. *RSC Adv.* 2017, 7 (57), 35672–35680. https://doi.org/10.1039/C7RA03123H.

- (62) Pandey, D.; Singh, G.; Mishra, S.; Viau, L.; Knorr, M.; Raghuvanshi, A. Solvatochromic Behaviour of Cyclic Dithioether-Functionalized Triphenylamine Ligands and Their Mechano-Responsive Cu(1) Coordination Polymers. *Dalton Trans.* 2023, *52* (39), 14151–14159. https://doi.org/10.1039/D3DT02226A.
- (63) Kundu, A.; Karthikeyan, S.; Sagara, Y.; Moon, D.; Anthony, S. P. Temperature-Controlled Locally Excited and Twisted Intramolecular Charge-Transfer State-Dependent Fluorescence Switching in Triphenylamine–Benzothiazole Derivatives. ACS Omega 2019, 4 (3), 5147–5154. https://doi.org/10.1021/acsomega.8b03099.
- (64) Wang, Q.; Liu, J.; Gao, X.; Sui, N.; Zhang, H.; Lu, R.; Zhang, J.; Wang, Y. Conjugated Branch Modulated Optical Characteristics of Multibranched Push–Pull Molecules Composed of Quinoxaline and Triphenylamine Groups: Transition of the Conjugated Branch from Unusual Effects to Usual Effects. *J. Mater. Chem. C* 2022, *10* (35), 12795–12808. https://doi.org/10.1039/D2TC02606F.
- (65) Yang, J.; Liu, X.; Liu, Z.; Wang, L.; Sun, J.; Guo, Z.; Xu, H.; Wang, H.; Zhao, B.; Xie, G. Protonation-Induced Dual Fluorescence of a Blue Fluorescent Material with Twisted A-π-D-π-A Configuration. *J. Mater. Chem. C* 2020, 8 (7), 2442–2450. https://doi.org/10.1039/C9TC06425G.
- (66) Schlachter, A.; Tanner, K.; Scheel, R.; Karsenti, P.-L.; Strohmann, C.; Knorr, M.; Harvey, P. D. A Fused Poly(Truncated Rhombic Dodecahedron)-Containing 3D Coordination Polymer: A Multifunctional Material with Exceptional Properties. *Inorg. Chem.* 2021, 60 (17), 13528–13538. https://doi.org/10.1021/acs.inorgchem.1c01856.