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Synthesis, characterization and photophysical studies of zinc(II) complexes derived from a hydralazine hydrazone

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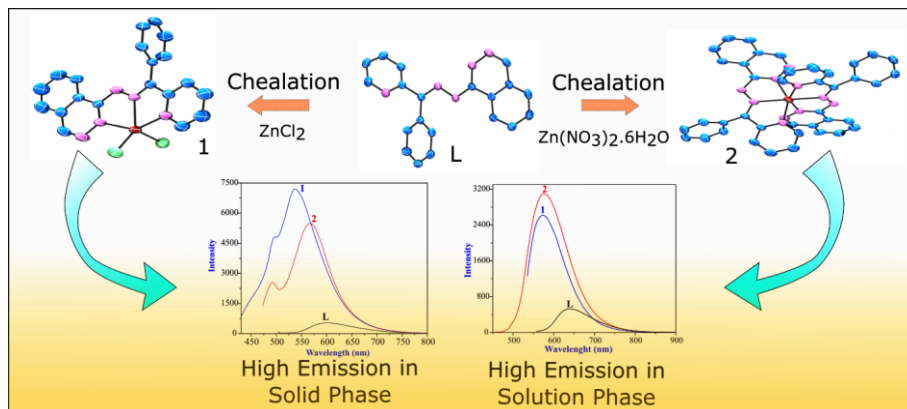
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Graphical abstract



Highlights:

- Two new zinc complexes with different geometry are synthesised using the zinc salts and a hydrazone ligand.
- Photophysical properties in solution phase and solid phase are carried out to have a comparative study.
- Fluorescence quenching in solid phase is accounted for the presence of hydrogen bonding and π – stacking interactions.

ABSTRACT

In the present study, we report two novel mononuclear zinc(II) complexes (**1** and **2**) obtained by reacting (E)-1-(phenyl(pyridin-2-yl)methylene)-2-(phthalazin-1-yl)hydrazine (**L**) with $ZnCl_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ respectively. Photophysical properties of the compounds were studied in both solution and solid phase. The fluorescence absolute quantum yield of the complexes in solution varies in the order **1** (0.01) < **2** (0.030), on the other hand in the solid state it varies in the order **2**(0.034) < **1**(0.69). Quenching of fluorescent intensity of **2** in the solid-state has been attributed to intense and extensive non-covalent interactions present in

the crystal structure. Theoretical calculations, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were also performed to support the experimental findings.

Keywords: Mononuclear zinc(II) complexes; Photophysical properties; Quenching; Non-covalent interactions; Computational studies

1. Introduction

Metal-coordinated organic compounds with luminescent properties have received much attention as potential electroluminescent components [1-2]. The first discovery of a bright and stable emissive material, tris-(8-hydroxyquinolato)aluminum(III) has led to an extensive investigation of luminescent materials based on coordination compounds [3]. Fluorescent metal complexes have many advantages such as the combination of emitting and electron transferring roles, higher environmental stability, and a better extent of diversity that is achievable through tuning of electronic properties by virtue of structural and metal-center variability [4]. Photophysical properties of luminescent complexes of earth-abundant, biologically important, essential and cheaper metals such as zinc(II) are gaining much importance in recent years as an alternative to luminescent platinum group metal complexes [5-6]. In the recent past, much attention is given to the study of a variety of non-covalent interactions [7-10]. It is now well documented that non-covalent interactions like hydrogen bonding and π – stacking interactions form the backbone of the molecular aggregates [11-13]. These interactions can significantly influence the structural motif and consequently several photophysical properties of the systems [14-16]. Several reports have established that the photoluminescence properties of organic compounds are not only associated with the composition of the materials, but also depend on the non-covalent interactions [17]. The hydrogen bonding interactions and interaction between fluorophores found in the X-ray crystal structures have been proven to be an effective means to explain the solid-state

emission quenching and red-shift [18, 19]. Very recently a couple of papers have reported the relationship between luminescence property and supramolecular structures of coordination compounds of zinc and cadmium [20, 21].

Interest in the hydralazine hydrazones is increasing because of their ligational aspects and applications of their metal associates in various fields [22 - 24]. Hydralazine hydrazones are used as chemosensors for first-row transition metal ions but their solid state photophysical properties are not yet studied [25, 26]. In the present work, we have synthesized a hydralazine hydrazone (Scheme 1) by the condensation of hydralazine hydrochloride with benzoyl pyridine [27] and its mononuclear zinc(II) complexes of varied geometries by using zinc(II) salts of different anions (Cl^- and NO_3^-) (Scheme 2). The effect of non-covalent interactions on fluorescence quantum yield has been studied using single crystal X-ray diffraction studies.

2. Experimental Section

2.1. Materials and methods

Hydralazine hydrochloride and 2-benzoylpyridine were obtained from Sigma Aldrich and used as received. Zinc nitrate hexahydrate and zinc chloride were purchased from SDFCL. Solvents were of reagent grade and used without additional purification. Elemental (C, H, N) analysis was performed on Elementar Analysensysteme GmbH. IR spectra were recorded on a Perkin-Elmer L-0100 spectrophotometer. ^1H NMR spectra were measured in DMSO- d_6 on Bruker FT 400 MHz spectrometer with TMS as the internal standard. ESI-MS spectra were obtained in methanol on Quattro Micro Mass spectrometer. The UV-Vis absorption spectra and emission spectra were recorded on JASCO UV-Vis NIR Spectrophotometer (Model V-670). The absolute quantum yield was measured using Jasco FP8300 fluorescence spectrometer equipped with a 450W xenon lamp, using a 100 mm integrating sphere attachment. The DFT and TD-DFT studies were made using Gaussian-09 software package.

2.2. Synthesis of [(1E,2E)-1-(phenyl(pyridin-2-yl)methylene)-2-(phthalazin-1(2H)-ylidene)hydrazine] (**L**) [Scheme 1]

A clear dark solution was obtained on stirring hydralazine hydrochloride (0.98 g, 5 mmol) and 2-benzoylpyridine (0.91 g, 5 mmol), in methanol (50 mL) at 60 °C for 8 hours. The solvent was removed under reduced pressure. The dark red solid obtained, was filtered, washed with water, and recrystallized from a minimum amount of methanol which yielded yellow crystalline solid. The crystals suitable for the X-ray diffraction study were obtained by slow evaporation of the methanolic solution. Yield 1.45g (90%). Anal. Calcd. (%) for C₂₀H₁₅N₅: C, 73.83; H, 4.67; N, 21.52. Found: C, 73.58; H, 4.88; N, 21.72. ¹H NMR (DMSO-*d*₆, 400 MHz,) δ (ppm): 13.64 (s, 1H), 8.93 (d, J = 5.2 Hz, 1H), 8.48 – 8.43 (m, 2H), 8.01 (d, J = 7.6 Hz, 1H), 7.96 (t, J=6.4, 6.8 Hz, 1H), 7.92 - 7.80 (m, 2H), 7.78 – 7.72 (m, 1H), 7.64 (d, J = 8 Hz, 1H), 7.61 to 7.51 (m, 5H). FT-IR ν(cm⁻¹): 3294, 1606, 1585, 1524, 1462, 1427. MS: m/z 325 (M)⁺.

2.3. Synthesis of complexes [Scheme 2]

To a hot methanolic solution of **L** (0.5 g, 1.5 mmol in 30 mL), appropriate zinc(II) salt (1.5 mmol), i.e., ZnCl₂ / Zn(NO₃)₂·6H₂O dissolved in minimum amount of methanol was added and refluxed for 3 – 6 hours. The clear solution obtained was concentrated to ~10 mL under reduced pressure and diethyl ether (40 mL) was added. The precipitate obtained was filtered, washed with small volumes of methanol and diethyl ether and dried under vacuum. The crystals suitable for X-ray diffraction were obtained by vapour diffusion method (methanol/ diethyl ether).

2.3.1 [Zn(L)Cl₂] (**1**)

Yield 0.42 g (60%). Anal. Calcd. (%) for C₂₀H₁₅N₅Cl₂Zn: C, 52.03; H, 3.27; N, 15.17. Found: C, 51.82; H, 3.34; N, 15.43. ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.11 (s, 1H), 8.89 (s, 1H),

8.45 – 8.30 (m, 1H), 8.03 (d, J=8 Hz, 1H), 7.88 – 7.69 (m, 6H), 7.56 – 7.73 (m, 4H). FT-IR bands (KBr, ν/cm^{-1}): 3444(br), 1629(sh), 1589 (vs), 1515(m), 1466 (w), 1376 (m). MS: m/z [M-Cl]⁺ 426.

2.3.2. [ZnL₂](NO₃)₂ (**2**)

Yield 0.45 g (70%). Anal. calcd. (%) for C₄₀H₃₀N₁₂O₆Zn: C, 57.18; H, 3.60; N, 20.01. Found: C, 57.40; H, 3.36; N, 20.30. ¹H NMR (400 MHz, DMSO-d₆) δ 12.29 (s, 1H), 8.72 – 8.63 (m, 1H), 8.26 – 8.08 (m, 2H), 7.98 – 7.91 (m, 1H), 7.79 – 7.60 (m, 5H), 7.55 – 7.32 (m, 5H). FT-IR bands (KBr, ν/cm^{-1}): 3444(br), 1629(sh), 1589 (vs), 1515(m), 1466 (w), 1376 (m). MS: m/z [M]⁺ 714.

2.4. Crystallographic studies

The X-ray intensity data of single crystals of compound **L**, **1** and **2** were collected on Bruker SMART APEX CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by direct methods and refined by Full-matrix least squares on F^2 using WINGX software which utilizes SHELXL-97 program [28]. All of the non-hydrogen atoms were refined with anisotropic temperature factors. Molecular structures were drawn using ORTEP [29] and all the intermolecular interactions were visualized using Mercury version 3.7 [30] software. Hydrogen bond distances and angles were calculated using PARST [30, 31] and normalized [32, 33].

2.5. Computational Studies

All computations on **L**, **1** and **2** were performed using the Gaussian 09 software. The CIF data of **L**, **1** and **2** were used as an input geometry for optimization by employing the density functional theory (DFT) with the Becke's three-parameter hybrid exchange and the Lee-Yang-Parr non-local correlation functionals (B3LYP) [32]. In the calculation, split valence basis set 6-31G(d-p) augmented with diffuse and polarization functions was assigned

to all elements with the exception of zinc for which the Los Alamos effective core potentials plus the Double Zeta (LanL2DZ) [33] basis set were used.

3. Results and discussion

3.1 Crystallographic study of **L**, **1** and **2**:

The crystal data of **L**, **1** and **2** are compiled in Table 1 and their ORTEP diagrams are displayed in Fig. 1. The selected bond lengths and bond angles of **L**, **1** and **2** are given in Table S3. The torsion angle 148.39° across C(9)-C(16) [N(4)-C(9)-C(16)-N(5)] in **L** reveals that N(4) and N(5) are *trans* to each other. On complexation, a conformational change could be observed, where in N(4) and N(5) have become *cis* to each other. On the other hand, the torsion angles for N(4)-C(9)-C(16)-N(5) in **1** and **2** are 1.58° , and 14.74° respectively. The plane of the phthalazine ring in **L** makes an angle of 48.90° with the plane of the pyridine ring whereas, in **1** and **2**, the corresponding angles are 8.26° and 6.89° respectively. These angles illustrate that phthalazine ring and pyridine ring in **L** are not lying in the same plane, whereas upon complexation, both the rings have become coplanar, which facilitate the chelation via N(2), N(4) and N(5). The complex **1** exist as two crystallographically independent molecules in an asymmetric unit cell. The geometry around Zn(II) in **1** is distorted trigonal bipyramidal geometry with a distortion parameter $\tau = 0.68$. The equatorial positions are occupied by azomethine nitrogen (N4) and two chlorides (Cl1 and Cl2) and axial positions are occupied by phthalazine nitrogen (N2) and pyridine (N5). The complex **2** consists of two equivalent units having distorted octahedral geometry around Zn(II). In an equivalent unit, N(4) atom is in axial position, while N(2) and N(5) atoms lie in basal plane.

3.2. Photophysical properties of compounds **L**, **1** and **2**

The photophysical properties of the compounds are investigated both in solution (10^{-5} M acetonitrile) and in solid phase and the results are compiled in Table 2. All the compounds

show two absorption maxima around 350 and 480 nm in solution phase (Fig. S1). On the other hand a single emission maximum (Fig. 2) is observed at 640, 572 and 575 nm for the compounds **L**, **1** and **2** respectively. In the solid phase, the absorption peaks are found around 380 and 490 nm (Fig. S2) and the emission peaks at 600, 540 and 567 nm for compounds **L**, **1** and **2** respectively (Fig. 3). The hydrazone **L** has low emission both in solution and solid phase ($\Phi = 0.002$ and 0.016 respectively) due to the predominant decay process of the excited state caused by $>C=N$ isomerization. However, the emission intensity increased upon chelation in **1** and **2** as chelation restricts $>C=N$ isomerization [34 -36] and provide structural rigidity. In solution phase, **2** has shown better quantum yield ($\Phi = 0.030$) compared to **1** ($\Phi = 0.01$) where as in solid phase, **2** has shown low quantum yield ($\Phi=0.034$) and red-shift compared to **1** ($\Phi= 0.69$). The time-resolved decay profiles of the compounds **L**, **1** and **2** have been investigated in solution as well as in solid phase. Fig. S3 show a comparison of fluorescence decay dynamics of **L**, **1** and **2** in solution and solid phase at 300K ($\lambda_{exc}= 275$ nm) and the fluorescence lifetimes are given in Table 2. A general increase in the lifetime upon complexation is observed for both solution and solid phase on complexation.

3.3. Correlation between solid-state fluorescence properties and X- ray crystal structure

The interaction between fluorophores [39, 40], hydrogen bonding [41] and anion - π interactions present in the X-ray crystal structures of the compounds are often used to explain the solid state fluorescence properties [42, 43]. It is well established that face to face $\pi - \pi$ stacking between the fluorophores will cause fluorescence quenching. In complex **2**, there is emission quenching and red shift, which can be accounted for the presence of strong intermolecular π stacking in the crystal structure between phthalazine fluorophores. The shortest centroid distance is between phthalazine fluorophores with centroid distance 3.761 \AA (Fig. 4) in **2**. Whereas in **1**, coordinated chloride ions have prevented the $\pi - \pi$ overlapping between phthalazine fluorophores resulting in weak π -stacking interaction with greater

centroid distance of 4.510 Å (Fig. 5) [19]. The presence of nitrate anions in **2** have involved in extensive of N-H...O and C-H...O interactions (Fig. S4 & Table S1), where as in **1**, N-H...Cl-M, C-H...Cl-M, and C-H...N type interactions are present which are relatively weak and less in number (Fig. S5 & Table S2). From the above discussion it is clear that, π – stacking and hydrogen bonding interactions are weak in **1**, whereas in **2** these intermolecular interactions are stronger which are responsible for fluorescence quenching in solid state. However in solution these interactions become weak and the inherent fluorescence is expressed and **2** has shown bright fluorescence intensity compared to **1**.

3.4. Computational Studies

All the molecular calculations were performed in the gas phase as well as solution phase using Gaussian 09 package [44]. The geometrically optimised bond lengths and bond angles differ from corresponding experimental values (Table S3). This might be due to the presence of intermolecular interactions and packing forces in the solid phase, which are absent in isolated molecule in gas phase used for theoretical calculations [45]. The HOMO-LUMO energy gap in the **L**, **1** and **2** is 3.493, 2.974 and 3.204 eV respectively (Table S4). In complexes **1** and **2**, the contribution from d-orbitals has reduced HOMO-LUMO energy gap. In **1** the HOMO electron density is dominated by metal d-orbitals (~98%) with insignificant contribution from ligand p-orbitals. On the other hand, the LUMO electron density of **1** is significantly localised over the ligand suggesting remarkable MLCT transitions (Fig. S6). Where as in **2**, HOMO and LUMO are spread over the ligand molecules with small metal centered HOMO suggest the transitions are partly MLCT and ILCT. TD-DFT calculations were performed to calculate the nature and energy of the lowest energy transitions. The TD-DFT results (Table 2) reveal a close similarity with the experimental absorption maxima (Fig. S7). The longer wavelength absorption in **1** is attributed to almost pure MLCT transitions and the high energy absorption for **2** is mainly due to ILCT [46].

4. Conclusions

(E)-1-(phenyl(pyridin-2-yl)methylene)-2-(phthalazin-1-yl)hydrazine and its Zn(II) complexes **1** and **2** were synthesized and thoroughly characterized. A comparative study of photophysical properties of complexes was made both in solution and solid state. Complex **1** has shown high absolute quantum yield compared **2**, which can be accounted for the presence of weak intermolecular interactions. In **1**, the coordinated chloride ligands intervene phthalazine fluorophore interaction and contribute to greater centroid distance between the fluorophores (4.510 Å). Where as in **2**, the non-coordinating anions present outside coordination entity will cause extensive hydrogen bonding interactions and also close stacking interaction present between phthalazine fluorophores (3.761 Å) resulting in emission quenching in the solid state. However in solution, the effect of these non-covalent interactions become weak and **2** has shown bright fluorescence intensity compared to **1**. Computational studies of **L**, **1** and **2** show that the HOMO–LUMO band gaps is decreased in complexes compared to free ligand and **1** has mainly MLCT transition and **2** has partly MLCT and ILCT transitions. The present study demonstrates that emission properties of zinc complexes can be modulated using coordinating and non-coordinating anions. The non-coordinating anions will a cause decrease in fluorescence intensity through non-covalent interactions in the solid state.

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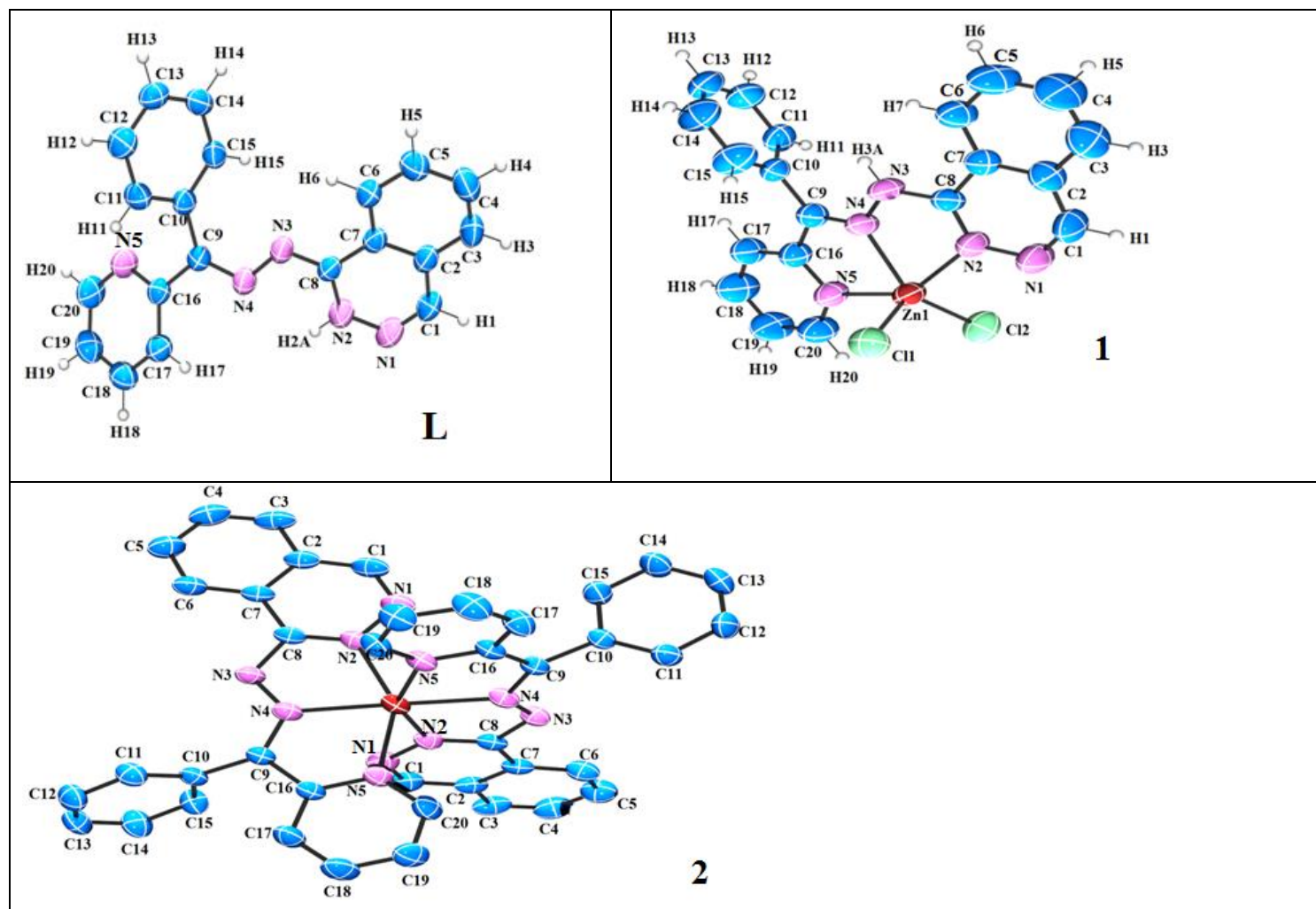


Fig.1 ORTEP diagram of **L**, **1** and **2**. Hydrogen atoms and anions have been omitted for clarity in complex **2**

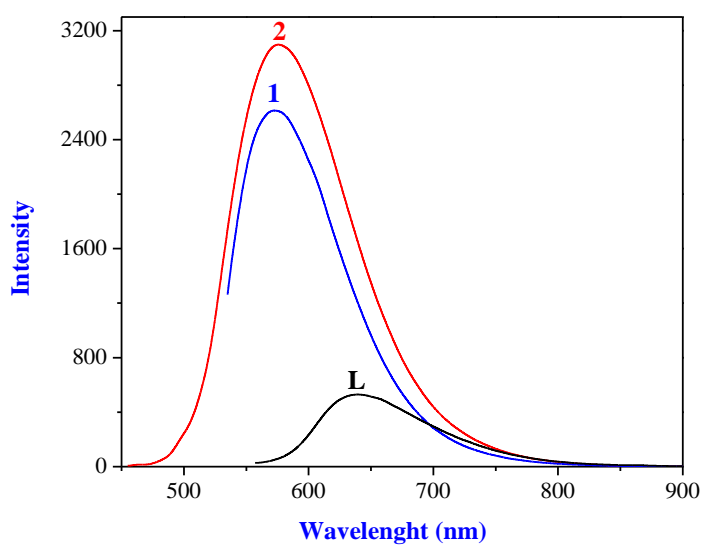


Fig. 2: Fluorescence spectra of **L**, **1** and **2** measured in acetonitrile (10^{-5} M)

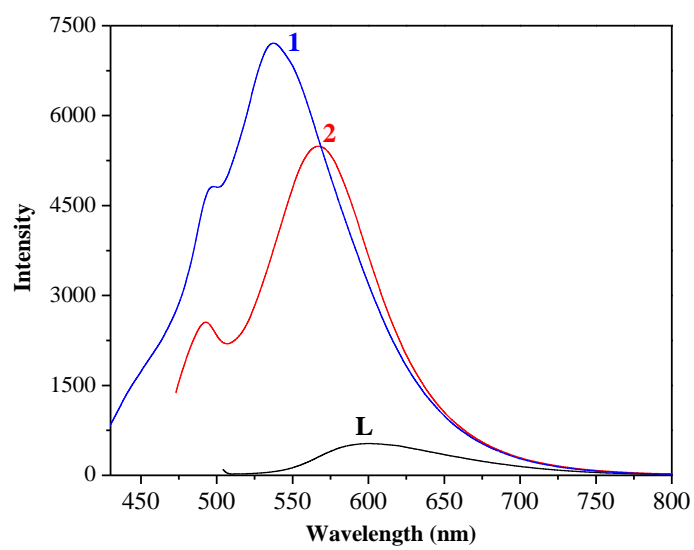


Fig.3: Fluorescence spectra of **L**, **1** and **2** measured in solid phase

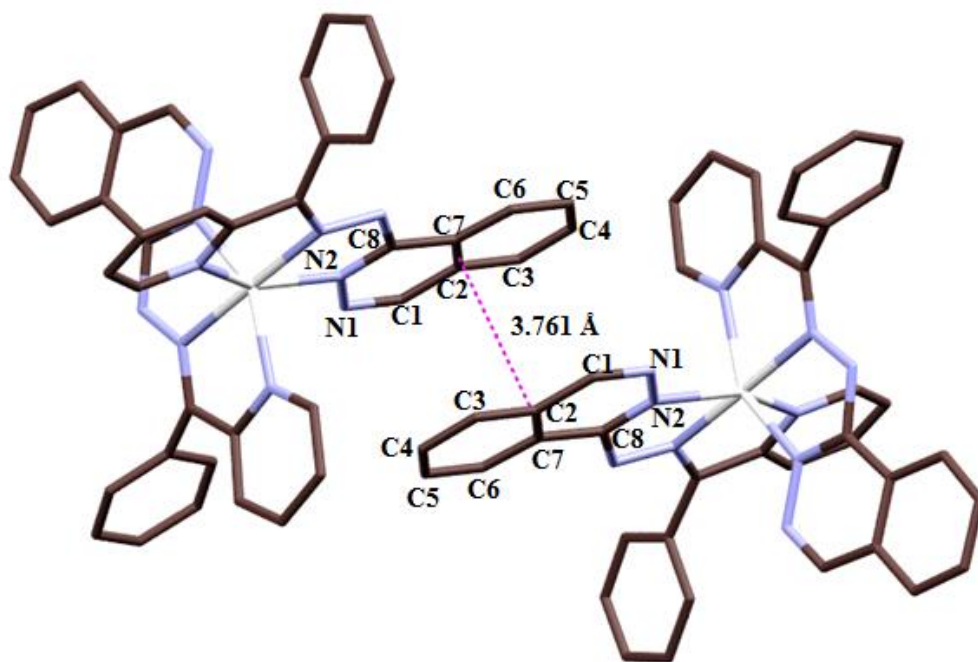


Fig.4 Centroid distance between two phthalazine fluorophores in **2**

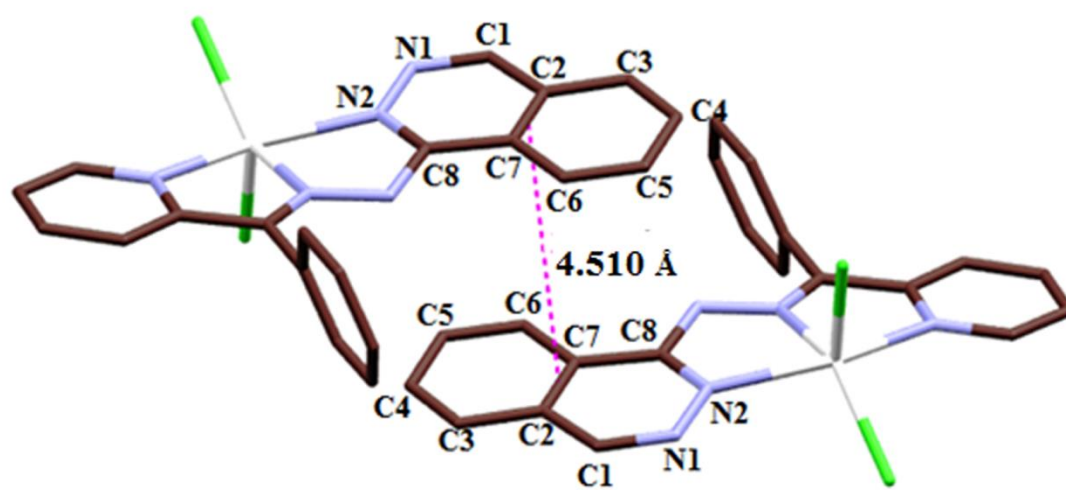
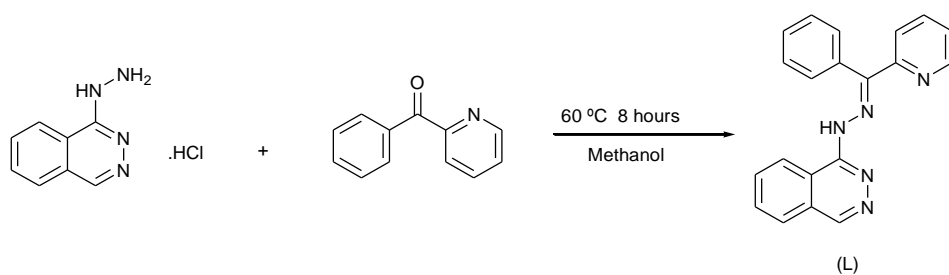
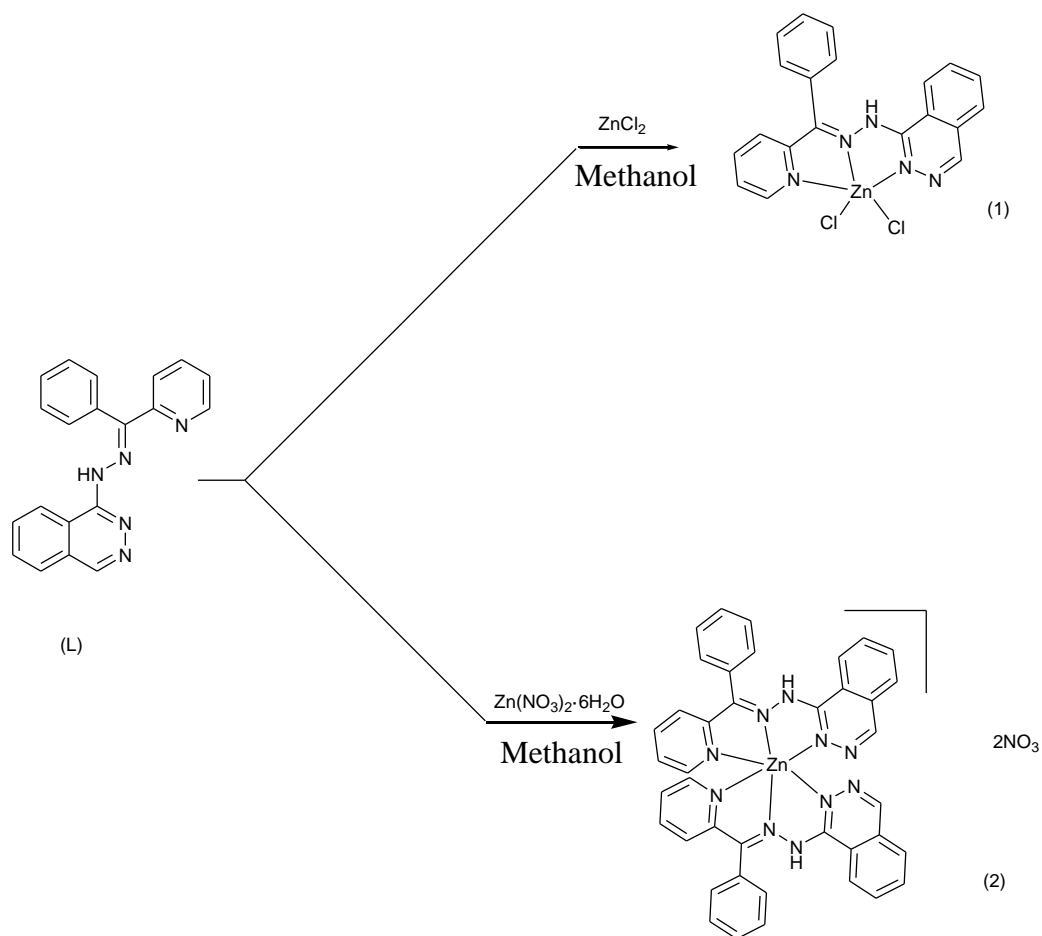


Fig. 5 Centroid distance between two phthalazine fluorophores in **1**



Scheme 1. Synthesis of **L**



Scheme 2. Synthesis of **1** and **2**

Table 1: Crystal data and structure refinement for **L**, **1** and **2**

	L	1	2
Empirical formula	C ₂₀ H ₁₅ N ₅	C ₂₀ H ₁₅ Cl ₂ N ₅ Zn	C ₄₀ H ₃₀ N ₁₂ O ₆ Zn
Formula weight	325.4	461.64	840.13
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group P 2 ₁ /n	P 2 ₁ /n	P-1	C 2/c
<i>a</i>	8.9276(2)	10.880(5)	17.836(2) Å
<i>b</i>	9.7631(2)	10.957(5)	10.4537(11) Å
<i>c</i>	18.8898(4)	17.075(5)	19.708(2) Å
α	90.000(0)	85.516(5)	90
β	93.231(1)	89.119(5)	93.760
γ	90.000(0)	80.531(5)	90°
<i>V</i> / Å ³	1643.84(1)	2001.7(14)	3666.6(7)
Dc/g cm ⁻³	1.31	1.532	1.522
μ /mm ⁻¹	0.082	1.509	0.738
θ /°	2.2 to 26.00	1.89 to 26.48	2.07 to 26.45
Range <i>h</i>	-11 to 10	-13 to 13	-22 to 21
Range <i>k</i>	-12 to 10	-13 to 13	-12 to 13
Range <i>l</i>	-23 to 21	-21 to 21	-24 to 24
Reflections collected	13836	30215	14394
Unique reflections	3210	8171	3747
Data/restraints/parameters	3210/0/287	8171 / 1 / 625	3747 / 0 / 327
<i>R</i> ₁ , w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0344, 0.0906	0.0483, 0.0917	0.0454, 0.0997
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0443, 0.986	0.1090, 0.1112	0.0797, 0.1132
GOF	1.015	0.983	0.974
CCDC number	1402700	1400558	1400559

Table 2: List of Photophysical properties

Sample	Abs $\lambda_{\text{abs}}/\text{nm}$	Fluor $\lambda_{\text{em}}/\text{nm}$	Exci energy E/eV	Osci strength f	Stokes Shift $\Delta\lambda/\text{nm}$	Quant Yield /%	Lifetime τ/ns
L	^a 373, 472* / ^b 380, 480* / ^c 383, 490	^a 640 / ^b 600	^c 3.234, 2.455	^c 0.1600, 1.0372	^a 168 / ^b 180	^a 0.002 / ^b 0.016	^a 0.367 / ^b 0.519
1	^a 346, 482* / ^b 381, 495* / ^c 357, 495	^a 572 / ^b 540	^c 3.479, 2.428	^c 0.1362, 0.5158	^a 90 / ^b 40	^a 0.01 / ^b 0.69	^a 0.990 / ^b 0.540
2	^a 358, 478* / ^b 394, 511* / ^c 356, 487	^a 575 / ^b 567	^c 3.482, 2.544	^c 0.2404, 0.4939	^a 97 / ^b 56	^a 0.03 / ^b 0.043	^a 1.080 / ^b 0.737

* shoulder peaks

^a experimentally measured at room temperature in acetonitrile (10^{-5} M)

^b experimentally measured in solid phase

^c obtained from TD-DFT studies.