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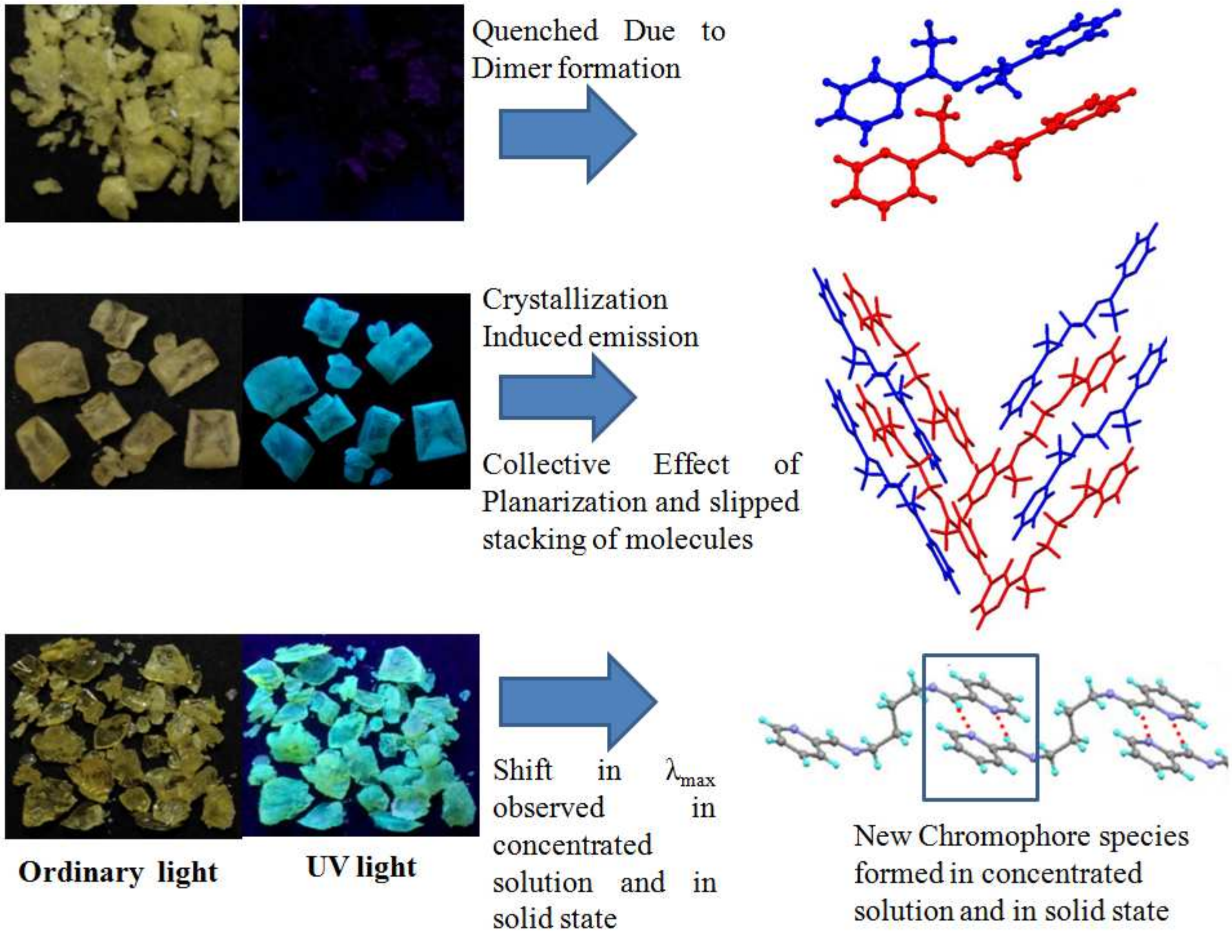
Effects of Non Covalent Interactions in Light Emitting Properties of *bis*-pyridyl-alkyl-*di*-imines

Abstract:

The non covalent interactions (C-H•••N; aromatic π•••π) lead to efficient packing of the crystals of all the three compounds. Crystallization induced emission (CIE) is observed for *bis*-pyridyl-ethyl-di-imine and *bis*-pyridyl-butyl-di-imine. The enhanced emission in the solid state is attributed to the collective effects of planarization and specific arrangement of molecules, which restricts excimer formation. In case of *bis*-pyridyl-di-imines, with no alkyl spacer, the luminescence is absent even in the solid state.



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ARTICLE TYPE

Effects of Non Covalent Interactions in Light Emitting Properties of *bis*-pyridyl-alkyl-*di*-imines

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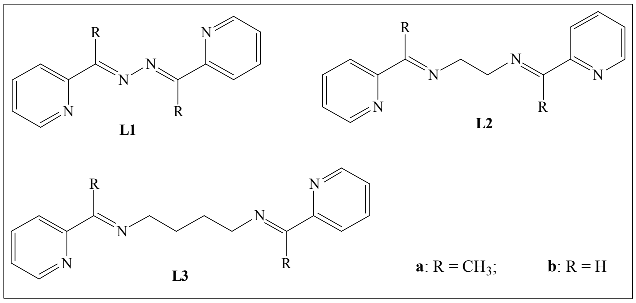
The crystal structure of three *bis*-pyridyl-alkyl-di-imines are studied. The non covalent interactions lead to the packing of the crystals of the compounds in such a way that crystallization induced emission (CIE) is observed for *bis*-pyridyl-ethyl-di-imine and *bis*-pyridyl-butyl-di-imine, while for *bis*-pyridyl-di-imines, with no alkyl spacer, the luminescence is absent in the solid state. The enhanced emission in the solid state is attributed to the collective effects of planarization and specific arrangement of molecules.

Introduction

The light-emitting molecular solids and their potential utility in optical devices such as organic light-emitting diodes (OLEDs)[1], sensors[2a-2d], photovoltaic cells[2e] and biological imaging[2f,2g] has emerged as one of the most promising area of research in the past few years. The optical devices should be able to function in solid state. Therefore, in principle an ideal luminescent material must possess high luminescence efficiency in the solid state. There has been an enormous increase in research study on the luminescence in aggregated state. In 2001, Tang and coworkers first noticed the aggregation based emission (AIE) and explored new kinds of luminescent materials.[3] The AIE property in luminescent materials involves the enhancement in fluorescence intensities, when the molecules form aggregates/clusters. Tang and coworkers reported a series of tetraphenylethene derivatives, where a double bond is surrounded by phenyl groups. The restriction in intramolecular rotation accounts for making it AIE luminogen.[4] Tian and co workers reported a group of triaryl-amine derivatives, which exhibit AIE.[5] Park and co-workers have reported several material systems with AIE properties.[6] Different mechanisms have been suggested to explain the AIE behavior, some of which include Restriction of Intramolecular Rotation, formation of J-aggregates and intramolecular planarization.[7]

The light-emitting property of a compound in solid state is dictated by the arrangement of the entire array of molecules rather than by an individual molecule. Studying crystal structures of the compounds provides essential information on how molecules are arranged with respect to their neighbors, what are the non covalent interactions binding them together and what are their conformational preferences are required to correlate the structure-property relationship. The knowledge of relating various properties with the supramolecular arrangement of the molecules in the solid state, the sensitivity of these properties with respect to the packing in the solids could lead to derive new strategies to tailor made the compounds according to our requirement. Supramolecular synthesis, which involves non covalent interaction has emerged as an efficient route to synthesize a wide range of solid forms. It is also a versatile approach to tune solid-state luminescence by controlling the molecular organization *via* intermolecular interactions. Draper and co workers have observed that the solid state luminescence of 2-cyano-3(4-(diphenylamino)phenyl)acrylic acid can be tuned by co-crystallization with substituted pyridines and amines, which results in effective control in the non covalent interactions.[8] Recently, Varghese have highlighted the reports on non-covalent methods and their utility in attaining switchable solid state emitting molecular materials.[9]

In order to obtain structural correlations to solid state optoelectronic properties of molecular materials, it is necessary to obtain and analyze the crystal structure along with the spectroscopic results. In the present work, we have studied the solid state luminescence of Schiff base molecules and correlate the observed behavior with the crystal structure analysis. The solid state luminescence of a series of Schiff bases (Salen) involving alkyl chains was reported by Kawasaki *et al.* They have observed influence of alkyl chain length on their photo physical properties.[10] The Schiff bases selected in the current work is shown in scheme 1.[11-17] The features selected for the Schiff bases include two pyridyl moities, an alkyl bridge and H or CH_3 groups on the methinine carbon.



Scheme 1: *Bis*-pyridyl-alkyl-*di*-imines with alkyl spacers of different lengths

The compounds **L1**-**L3** are reported to form wide range of coordination complexes of varied structural features and interesting properties. The compound **L1a** is explored extensively to prepare bimetallic and trimetallic coordination complexes of Cu(II), Cd(II), Ni(II), Ag(I) etc.[11b-11g] and coordination polymers[11h-111] of diverse geometry and properties. The compound **L1b** has also shown to form coordination complexes with wide range of metals.[12,13] The compounds **L2a** and **L2b** were shown to form mainly coordination complexes[14, 15]; while Hor and coworkers have reported a coordination polymer of **L2b**[15p]. Few coordination complexes of **L3a** and **L3b** are reported in the literature.[16,17] Mitra and co workers have reported a heterometallic coordination complex of **L3a** involving Fe(II) and Cu(II) centers.[16b] Chandra and co workers have reported a coordination polymer of **L3b** with Mn(II)[17e], while rest of the reports of **L3b** involves coordination complexes of one or two metal centers.[17]

Although there are numerous reports on coordination complexes, the studies on the compounds **L1**-**L3** itself, are very few. The solid state structure of **L1a**, **L1b** and **L2a** are reported by various research groups. The crystal structure of compound **L1a** is reported by Qing-Jin and co workers.[11a] while the structure of **L1b** is reported by Rudolph and co workers[12e] & also by Forman and coworkers[12f]. Buyukgungor and coworkers[14g] have reported the crystal structure of **L2a** whereas no structural reports are there for the compounds **L2b**, **L3a** and **L3b**. The present work deals with the analysis of the structural features of the compounds **L1a**, **L2a** and **L3b** and correlating their photophysical properties observed in the solid state with that of their crystal structure. The photophysical properties of these compounds in solution is analyzed and compared with that obtained in the solid state.

Experimental Section

General

Infra-red spectrum was recorded in FTIR ABB Bomen MB-3000. UV-Vis absorption spectra were recorded in Shimadzu Spectrophotometer with model UV-2450. Fluorescence spectra were recorded in Shimadzu Spectrofluorophotometer with model RF-5301PC. Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were measured on a 400 MHz NMR spectrometer (Bruker).

2,5-bis(2-pyridyl)-3,4-diaza-2,4-hexadiene (L1a): L1a was prepared according to the literature procedure.[11a] 0.25mL (5 mmol) of hydrazine hydrate was added dropwise to a solution of 2-acetyl pyridine (1.12ml, 10mmol) in ethanol (20ml). The mixture was refluxed at 80°C over night., the solvent was removed under vacuum and the product was recrystallised with hexane. Yield: 39%, Melting point: 52°C. IR(cm^{-1} KBr pellet): 3055(m), 3009(w), 2924(w), 1612(m), 1566(vs), 1466(vs), 1435(vs), 1358(vs), 1304(s), 1242(s), 1149(w), 1095(s), 1041(s), 987(s) (Figure S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.63 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 2H), 8.22 (dt, *J* = 8.0, 1.0 Hz, 2H), 7.74 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 2H), 7.30 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 2H), 2.36 (s, 6H) (Figure S2). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 157.42, 155.58, 148.64, 136.20, 124.03, 121.14, 13.87 (Figure S3); Elemental analysis (Found %): C 70.63, H 5.89, N 23.48; Calculated: C, 70.57; H, 5.92; N, 23.51 (Figure S4).

1,4-bis(2Pyridyl)-2,3diaza-1,3-butadiene (L1b): L1b[12e,12f] was prepared by taking 2-pyridine carboxaldehyde and hydrazine hydrate. Yield: 45%., Melting point: 148°C. IR(cm^{-1} KBr pellet): IR: 3047(w), 3001(w), 2955(w), 1628(vs), 1582(vs), 1466(vs), 1427(vs), 1288(w), 1250(w), 1219(s), 1142(w), 1080(w), 957(s), 864(s), 779(vs), 687(vs), 617(vs), 494(vs) (figure S5). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.70 (ddd, J = 4.8, 1.7, 0.9 Hz, 2H), 8.67 (s, 2H), 8.10 (dt, J = 7.9, 1.0 Hz, 2H), 7.78 (td, J = 7.7, 1.6 Hz, 2H), 7.34 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H) (Figure S6). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 162.14, 152.74, 149.94, 136.54, 125.09, 122.49 (Figure S7). Elemental analysis (Found %): C 68.64, H 4.75,N 26.61;Calculated: C, 68.56; H, 4.79; N, 26.65 (Figure S8).

2,7-bis(2-pyridyl)-3,6-diaza-2,6-octadiene (L2a): L2a was prepared according to the literature procedure.[14a] **L2a** was obtained by taking 0.33ml (5mmol) of ethylene diamine and 2-acetyl pyridine (1.12mL, 10mmol) in ethanol (20ml). Yield: 45%, Melting point: 103 to 106°C. IR(cm^{-1} KBr pellet): 3055(w), 3009(w), 2893(s), 2831(m), 1636(vs), 1558(vs), 1466(vs), 1435(vs), 1358(s), 1281(s), 1242(s), 1180(w), 1103(w), 1041(s), 987(s) (Figure S9). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.58 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.06 (dt, *J* = 8.0, 1.0 Hz, 2H), 7.71 – 7.66 (m, 2H), 7.26 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 2H), 3.96 (s, 4H), 2.42 (s, 6H) (Figure S10). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 167.50, 157.68, 148.21, 136.26, 124.03, 120.86, 53.49, 14.39 (Figure S11); Elemental analysis (Found %): C 72.23, H 6.79, N 20.98;Calculated: C, 72.15; H, 6.81; N, 21.04 (Figure S12).

1,6-bis(2-pyridyl)-2,5-diaza-1,5-hexadiene (L2b): L2b[15] was prepared by taking 2-pyridine carboxaldehyde and ethylene diamine. Yield: 42%, Melting point: 66°C. IR(cm^{-1} KBr pellet): 3047(s), 3009(w), 2916(s), 2885(vs), 2831(s), 1643(vs), 1566(vs), 1466(vs), 1427(vs), 1335(vs), 1296(s), 1219(s), 1041(vs), 972(vs), 918(vs), 864(vs), 771(vs) (Figure S13). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.60 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 2H), 8.40 (s, 2H), 7.96 (dt, *J* = 7.9, 1.0 Hz, 2H), 7.73 – 7.68 (m, 2H), 7.28 (ddd, *J* = 6.3, 4.2, 1.0 Hz, 2H), 4.04 (s, 4H) (Figure S14). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 163.37, 154.27, 149.33, 136.49, 124.71, 121.29, 61.26 (Figure S15); Elemental analysis (Found %): C 70.62, H 5.90, N 23.48;Calculated: C, 70.57; H, 5.92; N, 23.51 (Figure S16).

1,8-bis(2- pyridyl)-2,7-diaza-1,7-octadiene (L3b): L3b was prepared according to the literature procedure.[17a] **L3b** was obtained by taking 0.5 mL (5mmol) of 1,4 diamino butane and 2-pyridine carboxaldehyde (0.95 mL, 10mmol) in ethanol (20ml). Yield: 43%., Melting point: 73.5°C. IR(cm^{-1} KBr pellet): 3055(w), 3009(w), 2916(s), 2839(s), 1636(vs), 1566(s), 1466(vs), 1435(vs), 1366(m), 1335(s), 1288(w), 1211(w), 1188(w), 1142(w), 1088(w), 1041(s), 987(vs) (Figure S21). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.61 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 2H), 8.36 (s, 2H), 7.95 (dt, *J* = 7.9, 1.0 Hz, 2H), 7.73 – 7.69 (m, 2H), 7.28 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 2H), 3.71 (td, *J* = 5.2, 1.4 Hz, 4H), 1.83 – 1.78 (m, 4H) (Figure S22). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 161.88, 154.46, 149.35, 136.47, 124.58, 121.18, 77.32, 77.00, 76.68, 61.18, 28.38 (Figure S23); Elemental analysis (Found %): C 72.21, H 6.78, N 21.01;Calculated: C, 72.15; H, 6.81; N, 21.04 (Figure S24).

2,9-bis(2- pyridyl)-3,8-diaza-2,8-decadiene (L3a): L3a[16] was prepared by taking 2-acetyl pyridine and 1,4 diamino butane. Yield: 38%, Melting point: 74°C IR(cm^{-1} KBr pellet):3047(w), 3009(w), 2932(vs), 2878(vs), 1628(vs), 1566(vs), 1466(vs), 1435(vs), 1358(vs), 1304(s), 1227(w), 1103(s), 1072(w), 1041(w), 987(w), 787(vs), 741(s) (Figure S17). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 8.57 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H), 8.07 (dt, *J* = 8.0, 1.0 Hz, 2H), 7.68 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 2H), 7.26 (ddd, *J* = 7.5, 5.0, 1.2 Hz, 2H), 3.59 (dd, *J* = 6.3, 5.6 Hz, 4H), 2.36 (s, 6H), 1.93 – 1.89 (m, 4H) (Figure S18). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 166.35, 157.83, 148.16, 136.22, 123.93, 120.82, 77.32, 77.00, 76.68, 52.33, 28.93, 13.96 (Figure S19); Elemental analysis (Found %): C 73.50, H 7.50, N 19.00;Calculated: C, 73.44; H, 7.53; N, 19.03 (Figure S20).

Single-Crystal X-ray Diffraction: The single crystal data were collected on a Xcalibur, Sapphire 3 X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å) by the ω-scan method.[18] The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.[19] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. The crystal data and structure refinements of **L1a**, **L2a** and **L3b** are summarized in Table 1. (CCDC 963345, 962823 and 930055). The ORTEP of **L1a**, **L2a** and **L3b** are shown in figure S25, S26 and S27, respectively.

Results and Discussion

The structural descriptions of the compounds are studied to analyze its relation with the photophysical properties of the compounds.

Structural Description of L1a: The crystal structure analysis of the compound **L1a** shows that it has crystallized in $P2_1$ and has three molecules in the asymmetric unit. The three molecules (Molecule I, II and III) differ in the orientation of the pyridyl and imine moieties (Figure 1a). On further analyzing the structure, it can be observed that the Molecule I and Molecule II are arranged in parallel manner; such that pyridyl rings and C=N moieties of the two molecules are overlapping over one another. The distance between the C=N of the two molecules are 3.906 and 3.943 Å, while the centroid-to-centroid distance between the two pyridyl rings are 3.888Å and 4.009Å.

Aromatic π•••π interactions are present between the Molecule I and Molecule II. The non covalent interactions present in Molecule III are rather significant. There are C-H•••N and aromatic π•••π interactions present between Molecule III & Molecule I and Molecule III & Molecule II (Figure 1b). In fact, Molecule III is sewing the Molecule I and Molecule II in a way such that they form dimers (Figure 1c and 1d).

The crystal structure of a polymorph of **L1a** was reported by Qing-Jin and co workers where it has crystallized in $P2_1/c$ space group. In that structure, there are three molecules in the asymmetric unit and the molecules adopt transoid geometry. In the present structure, the **L1a** molecules are crystallized in non centrosymmetric space group.

Structural Description of L2a: The crystal structure analysis of **L2a** shows that it has crystallizes in orthorhombic *P*cab space group with two molecules present in the asymmetric unit (Figure 2a).

The two molecules differ in the orientations of the pyridyl and imine groups. The ethyl spacer of **L2a** is arranged in *anti* conformation, which gives it a linear geometry; flexible ethyl spacer, the arrangement of the molecules in the solid state give it a "rigid" planar-like geometry. The molecules are further assembled *via* aromatic interactions to form zigzag layers which are stacked further in 3D (Figure 2b and 2c).

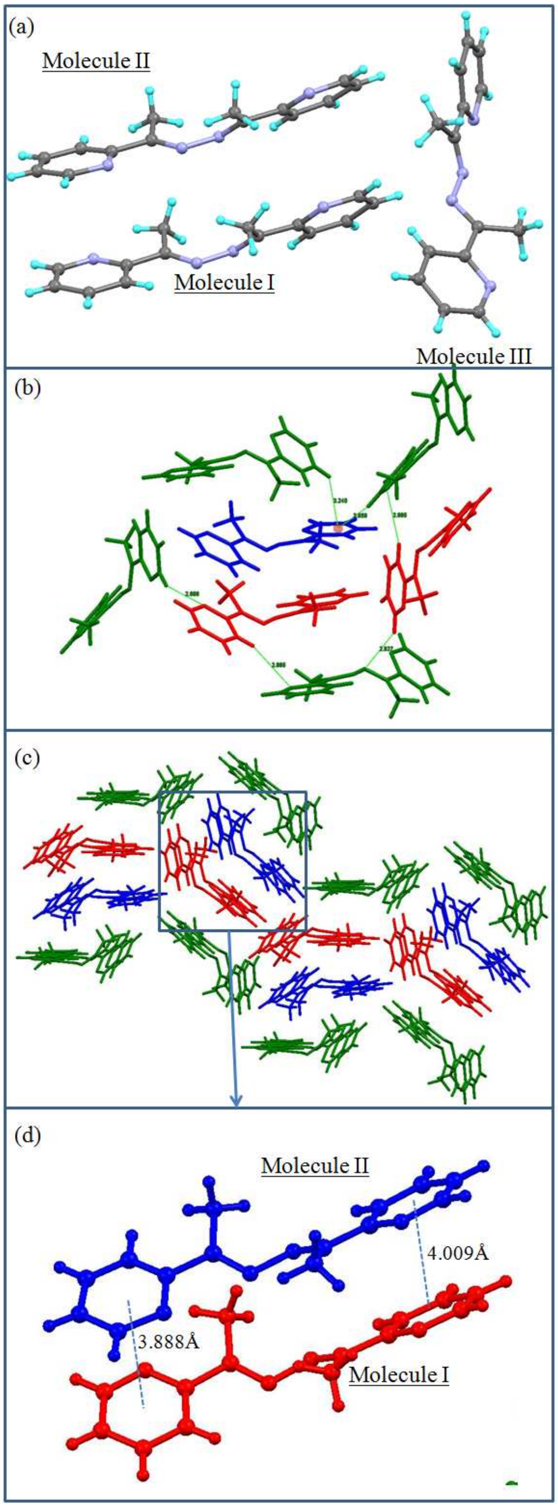


Figure 1: Illustration of the crystal structure of **L1a**: (a) Asymmetric unit. The three molecules are labeled as Molecule I, II & III; (b) Non covalent interaction between the molecules; (c) Packing of the molecules; (d) Parallel arrangement of Molecule I & II

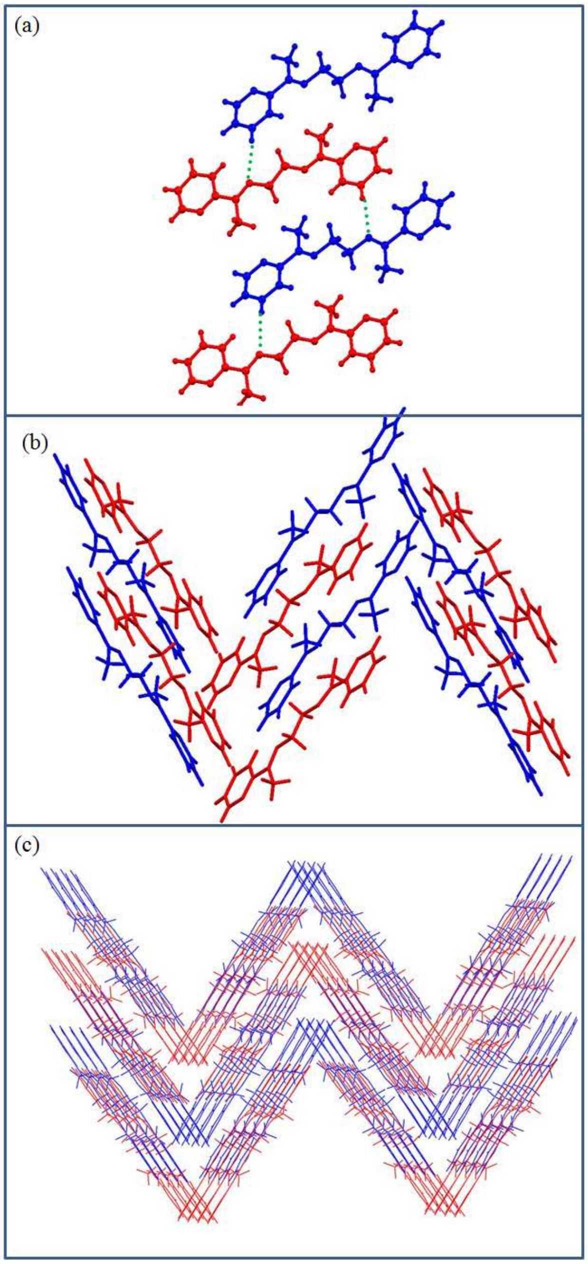


Figure 2: Illustration of the crystal structure of **L2a**: (a) Asymmetric unit contains two molecules; The two types of molecules are shown in different colors; (b) Aromatic interactions leading to zigzag layers; (c) Packing of the zigzag layers

Structural Description of L3b: The compound **L3b** crystallizes in monoclinic $P2_1$/c space group with half of the molecule present in the asymmetric unit (Figure 3a). The molecules are held together by CH•••N hydrogen bond interactions (2.781 Å; 3.709 Å; 176.02°) (Figure 3b); which has resulted as the methyl group on the methinine carbon is replaced by hydrogen. The butyl chain in the spacer of **L3b** adopts *gauche-anti-gauche* conformation, which give "S"-shaped geometry to the molecule. The "S"-shaped molecules of **L3b** are further assembled *via* CH•••N hydrogen bond to form corrugated layers. The corrugated layers are packed in an offset manner (Figure 3c). The aromatic CH•••π interactions are holding the layers together to pack them in 3D (Figure 3d).

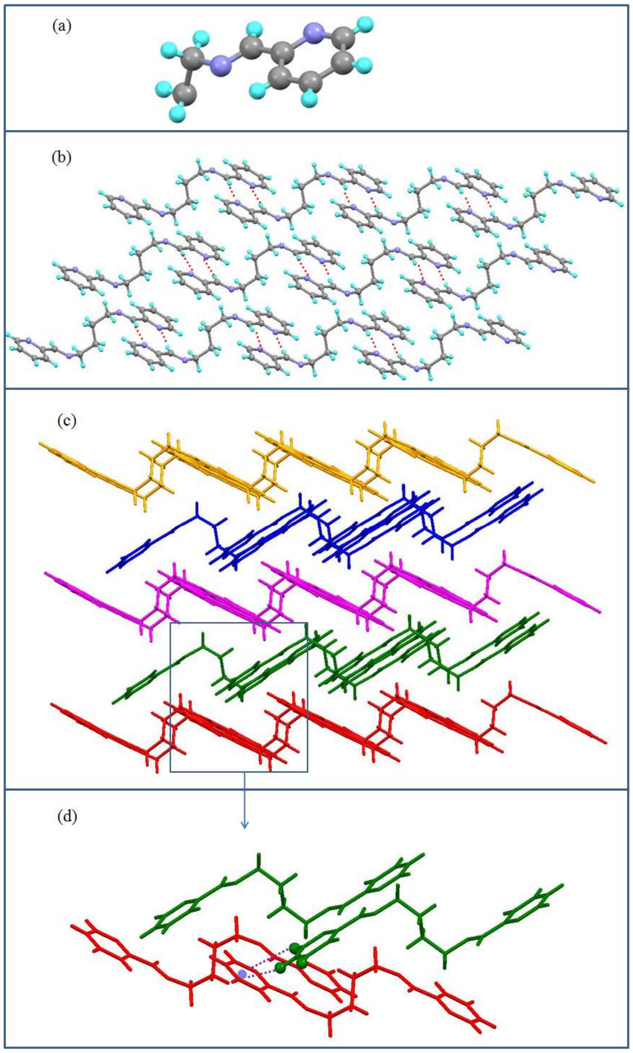


Figure 3: Illustration of the crystal structure of **L3b**: (a) Asymmetric Unit: Half molecule of **L3b**; (b) CH•••N interactions leading to the formation of corrugated 2D layers; Notice the *gauche-anti-gauche* conformation of butyl spacer of **L3b**; (c) Offset packing of corrugated layers; (d) Aromatic CH•••π interactions between the **L3b** molecules of two adjacent layers

Powder XRD Spectra of L1a, L2a and L3b: The powder XRD were taken for **L1a**, **L2a** and **L3b** (Figure 4). The calculated PXRD of the three compounds were compared with that of the experimentally measured one in order to verify the phase purity of the compounds.

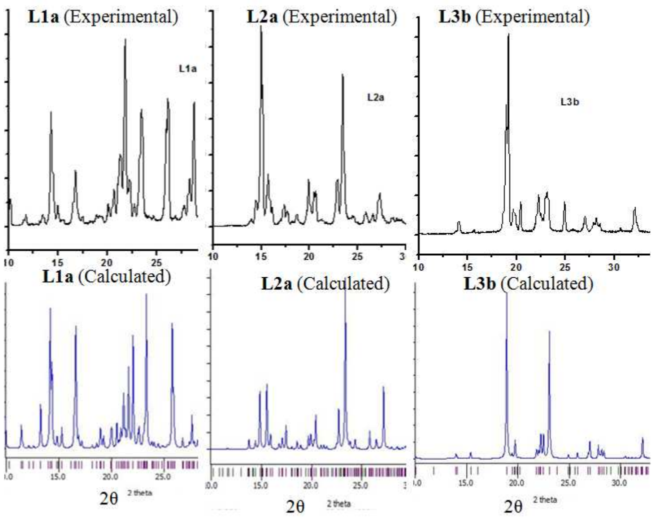


Figure 4: Experimentally measured and Simulated Powder XRD of **L1a**, **L2a** and **L3b**

UV-Vis Absorption Spectra of the compounds: The UV absorption spectra were measured in $CHCl_3$ for **L1-L3**. The compound **L1a** showed λ_{max} at 286 nm and a hump at 259 nm; while for compound **L1b**, peak maxima were observed at 300 with a hump at 262 nm.

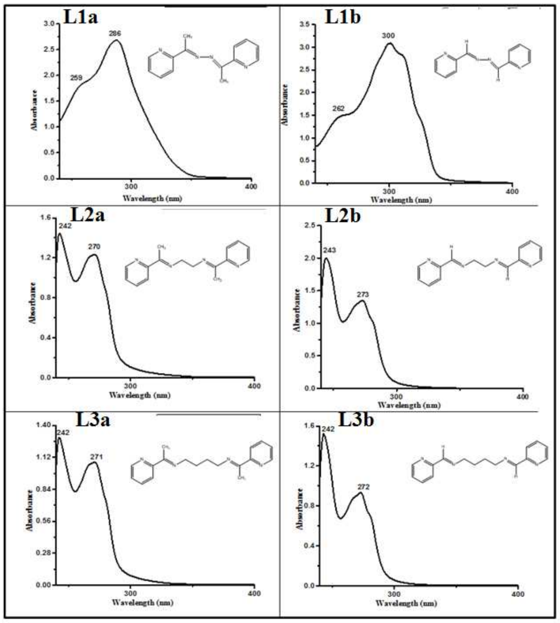
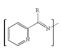


Figure 5: The UV Absorption spectra of the compounds in $CHCl_3$ (conc. of the compounds taken was 1×10^{-4} M)

The compounds **L2a**, **L2b**, **L3a** and **L3b** showed some similarity in the absorption spectra. All the four compounds showed two peaks at 240-241 and 270-273 nm, which may be attributed to π→π* and n→π* transitions, respectively (Figure 5). The solid state UV-Vis spectra of **L1a**, **L2a** and **L3b** are shown in figure S28, S29 and S30.

The chromophore  is responsible for both the transitions in compounds **L2a**, **L2b**, **L3a** and **L3b**, while in **L1a** and **L1b**, the extended conjugation throughout the molecule shifts the peak to longer wavelength.

Excitation Spectra and Photoluminiscence Spectra of L1a and L1b: The excitation and photoluminescence spectra were measured for **L1a** in $CHCl_3$. At 10^{-5}M concentration, **L1a** showed excitation maxima at 315 nm, when the emission wavelength was kept at 365 nm (Figure 6).

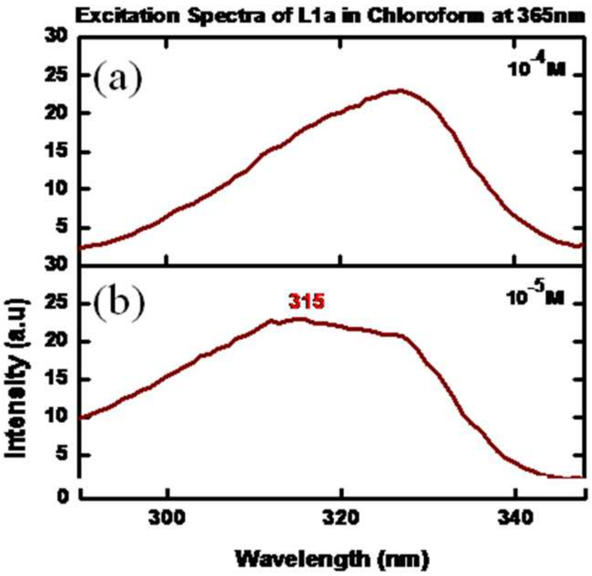


Figure 6: Excitation Spectra of **L1a** in $CHCl_3$ in different concentrations: (a) 10^{-4}M, (b) 10^{-5}M

The photoluminescence spectra at a concentration of 10^{-6}M showed a peak at 365 nm, when an excitation wavelength of 315 nm was used. Quenching of photoluminescence was observed as the concentration was increased (Figure 7). The solid state photoluminescence was negligible (peak at λ = 535nm) with a very low quantum yield (Figure 8). The excitation and PL spectra of **L1b** also show similar behavior (Figure S31 and S32).

Tang *et al.* have reported Aggregation Induced Enhanced Emission (AIEE) for Salicylaldehyde Azine derivatives; which has two salicylaldimine moieties connected by rotatable N-N single bond (Scheme 2).[20] They have suggested that intramolecular hydrogen bonds of salicylaldimine moieties and stacking of molecules resulted in AIEE; which resulted due to the inhibition of free intramolecular rotation when changed from solution to aggregate state. Though the skeletal structure of **L1a** and **L1b** is similar to Salicylaldehyde Azines, but in **L1a** and **L1b** quenching of photoluminescence is observed on moving from "free state" to aggregated state. The crystal structure of **L1a** showed some important aspects about the packing of the molecules, which is associated with quenching of fluorescence of **L1a** in solid state. The arrangement of the molecules of **L1a** in a π•••π stacked molecular pairs (dimers) facilitates the two molecules forming an excimer, which explains its non fluorescent behavior in the solid state (Figure 1d).[21]

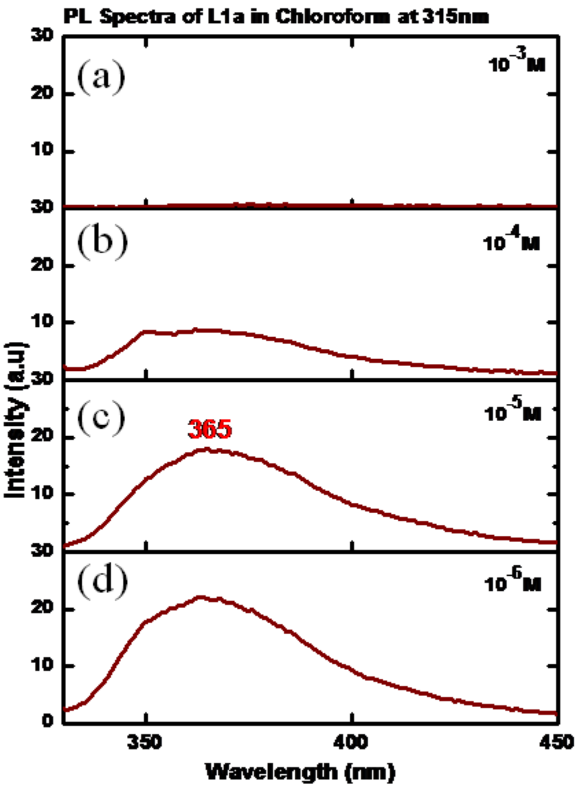
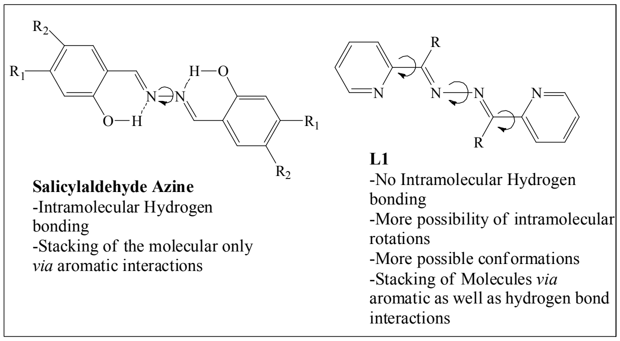


Figure 7: PL Spectra of **L1a** in $CHCl_3$ in different concentrations: (a) 10^{-3}M, (b) 10^{-4}M, (c) 10^{-5}M, (d) 10^{-6}M



Salicylaldehyde Azine

-Intramolecular Hydrogen bonding

-Stacking of the molecular only *via* aromatic interactions

L1

-No Intramolecular Hydrogen bonding

-More possibility of intramolecular rotations

-More possible conformations

-Stacking of Molecules *via* aromatic as well as hydrogen bond interactions

Scheme 2: Comparison of **L1** with Salicyladehede Azines[20]

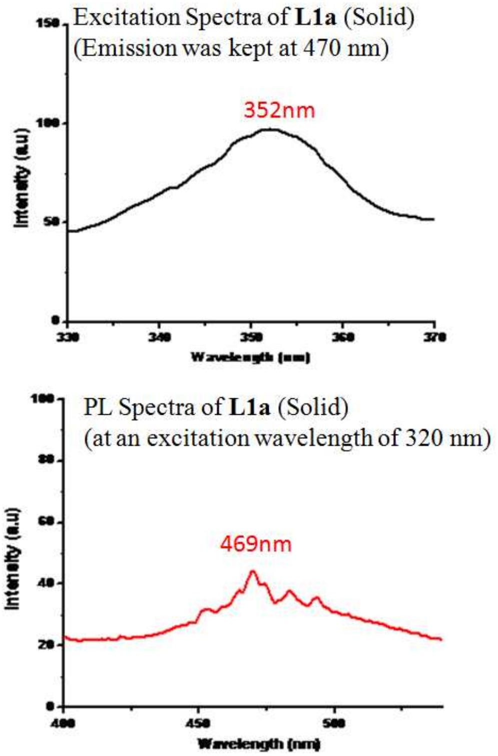


Figure 8: Excitation Spectra and PL Spectra of **L1a** in solid state

Excitation Spectra and Photoluminescence Spectra of L2a and L3a:

The excitation spectra of **L2a** were taken in $CHCl_3$ by varying the concentration. The spectra showed maxima at a wavelength of 370-385nm, when the emission wavelength was kept at 455 nm.

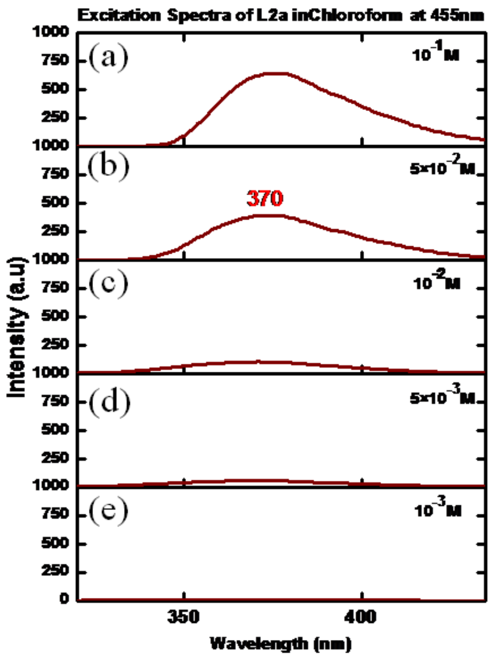


Figure 9: Excitation Spectra of **L2a** in $CHCl_3$ in different concentrations: (a) 10^{-1}M, (b) 5×10^{-2}M (c) 10^{-2}M (d) 5×10^{-3}M, (e) 10^{-3}M

Increasing the concentration of **L2a** resulted in increase in the intensity along with a slight red shift of the peak maxima (Figure 9). The excitation spectra of **L2a** at an emission wavelength of 370 nm are shown in figure S33.

The photoluminescence spectra of **L2a** in CHCl$_3$ showed a weakly intense peak at 455 nm (when an excitation wavelength of 370nm was used) at a concentration of 10^{-3}M. The change in concentration resulted in change in intensity of the peak; slight shift was observed in the peak position (Figure 10). The solid state photoluminescence spectra of **L2a** shows highly intense band at 453 nm (Figure 11). The enhancement of the luminescence intensity along with a red shift of peak positions for the solid **L2a** is related to Crystallization Induced Enhanced Emission.

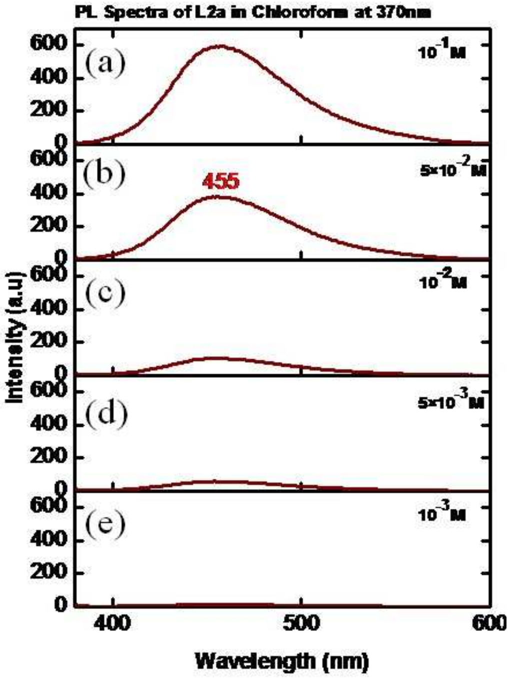
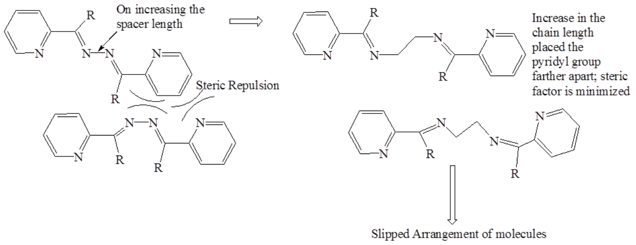


Figure 10: PL Spectra of **L2a** in CHCl$_3$ in different concentrations: (a) 10^{-1}M, (b) 5×10^{-2}M (c) 10^{-2}M (d) 5×10^{-3}M, (e) 10^{-3}M

The crystal structure of **L2a** showed that although the spacer has a flexible ethyl chain, the arrangement of the molecules in the solid state give it a "rigid" planar-like geometry (Figure 2). The enhanced emission in the solid state of **L2a** can be interpreted in terms of simultaneous effects of intra- and intermolecular effects exerted by the aggregation of the molecules. The planar-like geometry of the molecule in the solid state activates the radiation process, while the aggregation morphology resulting due to the supramolecular arrangement of the molecules also influences the emission process. The molecules in **L2a** are arranged in parallel manner but they are arranged in a specific slipped-type pattern, so that the excimer formation is avoided (Figure 2b). The presence of the ethyl spacer in **L2a** made it possible to have a slipped-type arrangement of the molecules. This type of arrangement in **L1** is not possible due to steric reasons and packing of the molecules is mostly *via* aromatic π•••π interactions, which promotes the formation of dimers (Scheme 3).



Scheme 3: Comparison of **L1** and **L2** to understand the effect of spacer length on slipped-type arrangement of the molecules

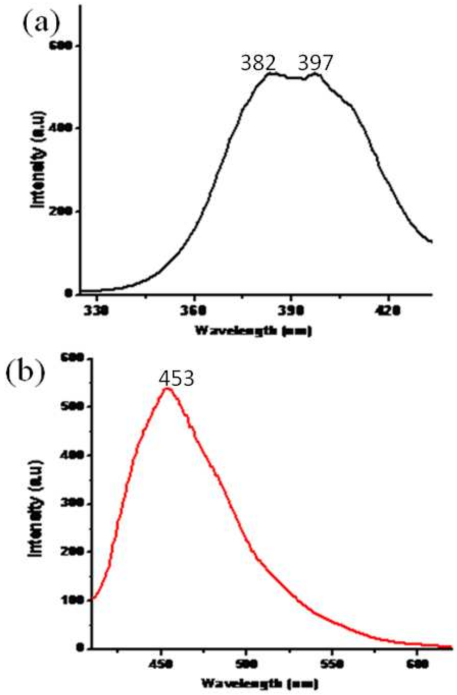
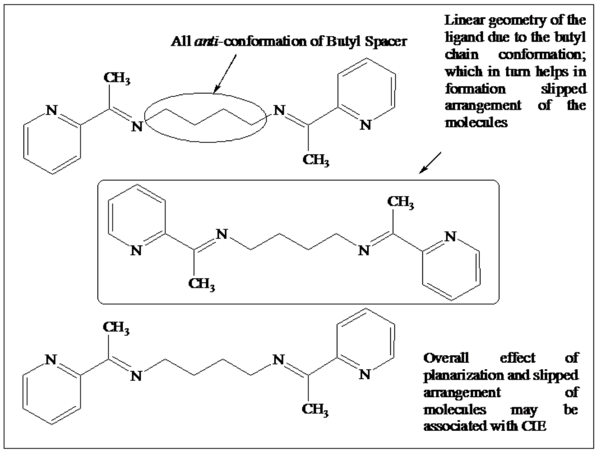


Figure 11: Excitation Spectra (Emission was kept at 455 nm) and PL Spectra (at an excitation wavelength of 400 nm) of **L2a** in solid state

The excitation and the PL spectra were recorded for **L3a**, which showed a similar behavior as **L2a**. At 10^{-3} M concentration, excitation spectra of **L3a** in CHCl$_3$ showed a peak at 370 nm (when the emission wavelength is kept at 460 nm). On increasing the concentration, the slight red shift of peak maxima alongwith increase in the intensity was observed (Figure S34 and S35).

The PL spectra in CHCl$_3$ at an excitation wavelength of 450 nm showed enhancement in the intensity with increase in concentration and a red shift by ~10nm of the peak maxima. The solid state spectra of **L3a** showed a highly intense band at 495 nm (Figure S36). The similarity in excitation and the PL spectra of **L2a** and **L3a** suggests that the packing of the molecules in **L3a** may be similar to **L2a**, where all *anti* conformation of the butyl spacer results in slipped type arrangement of the molecules and diminishes the possibility of forming excimers (Scheme 4). The crystal structure analysis of **L3a** couldn't be done because the good quality crystals of **L3a** couldn't be obtained.



Scheme 4: Suggested structure of **L3a** in the solid state to account for the CIE

Excitation Spectra and Photoluminescence Spectra of L2b and L3b: Interesting photoluminescence spectral properties were observed for **L2b** and **L3b**, where the methyl group on the methinine carbon is replaced by H-atom, so that there will be enough opportunity for the formation of non-covalent interactions. The concentration dependent excitation spectra of **L2b** in $CHCl_3$ showed that at a concentration of 10^{-3}M, the spectra had maxima at 365 and 420 nm (emission wavelength was kept at 460nm). On increasing the concentration, the intensity of the peak at 420nm was increased, while a hump appeared at 365 nm. The peak intensity at 365 nm also increases with concentration (Figure 12).

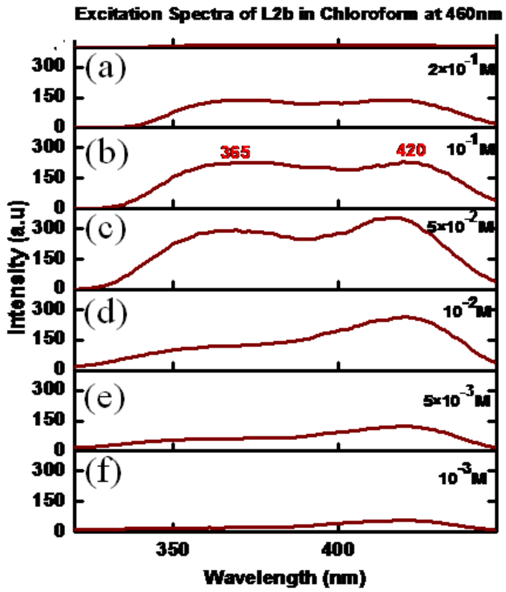


Figure 12: Excitation Spectra of **L2b** in $CHCl_3$ in different concentrations: (a) 2 × 10^{-1}M, (b) 10^{-1}M (c) 5×10^{-2}M (d) 10^{-2}M (e) 5 ×10^{-3}M, (f) 10^{-3}M

The concentration dependent PL spectra of **L2b** in $CHCl_3$ were measured at an excitation wavelength of 420 nm. A peak at 465nm was observed at a concentration of 10^{-3}M, which on further increasing concentration resulted in increase in the peak intensity. But at a concentration of 5×10^{-2}M, a hump appeared at 545nm, which became intense with the concentration increase. Finally, at a concentration of 5×10^{-1}M, the peak at 455 nm disappeared, while an intense peak at 555nm was observed (Figure 13). In the solid state spectra of **L2b**, strong emission peak appeared in the region between 555 nm (Figure 14).

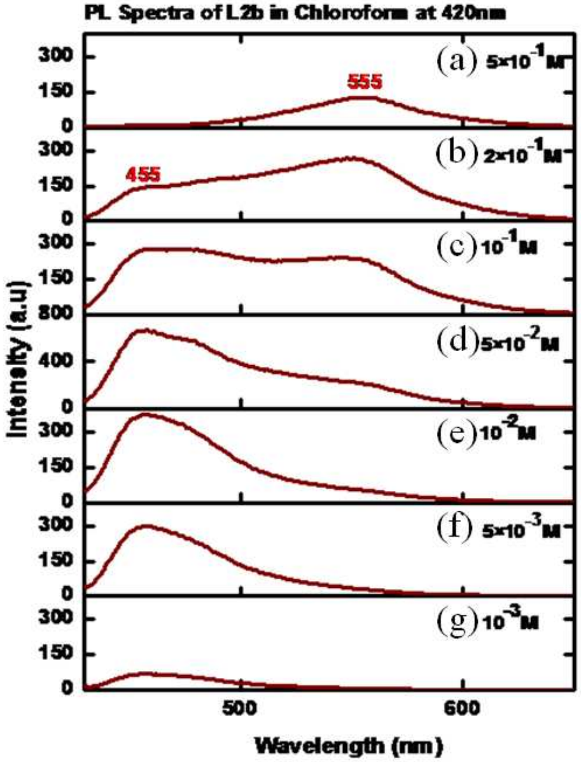


Figure 13: PL Spectra of **L2b** in $CHCl_3$ in different concentrations(a) 5×10^{-1}M; (b) 2×10^{-1}M; (c) 10^{-1}M (d) 5×10^{-2}M ; (e) 10^{-2}M (f) 5 ×10^{-3}M, (g) 10^{-3}M

The excitation and photoluminescence spectra of **L3b** in $CHCl_3$ showed similar behaviour as that of **L2b**. The concentration dependent excitation spectra of **L3b** in $CHCl_3$ showed that at a concentration of 5×10^{-3}M, the spectra had maxima at 365 and 420 nm (emission wavelength was kept at 460nm) (Figure 15).

The PL spectra of **L3b** for a concentration of 5×10^{-3}M showed maxima at 460 nm, when an excitation wavelength of 420nm was used. On increasing the concentration, the increase in the intensity of peak maxima was observed. However, at a concentration of 5×10^{-2}M, a hump appeared at 545nm, intensity of which increases with increase in the concentration. Finally, at a concentration of 5×10^{-1}M, an intense peak was present at 545 nm while the peak at 460 nm disappeared (Figure 16). The solid-state photoluminescence spectra of **L3b** showed strong emission peak appeared in the region between 548 nm (Figure 17).

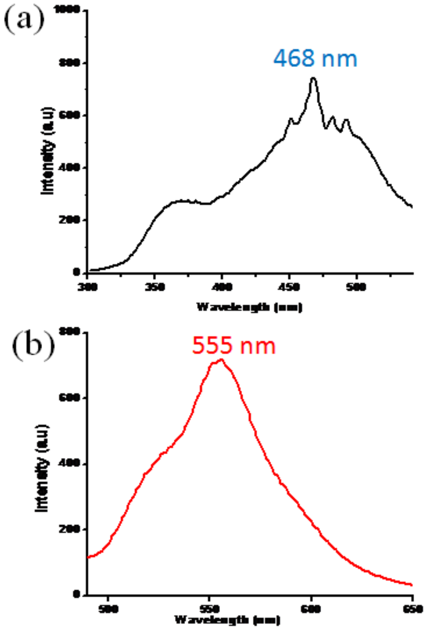


Figure 14: Excitation Spectra (Emission was kept at 555 nm) and PL Spectra (at an excitation wavelength of 470 nm) of **L2b** in solid state

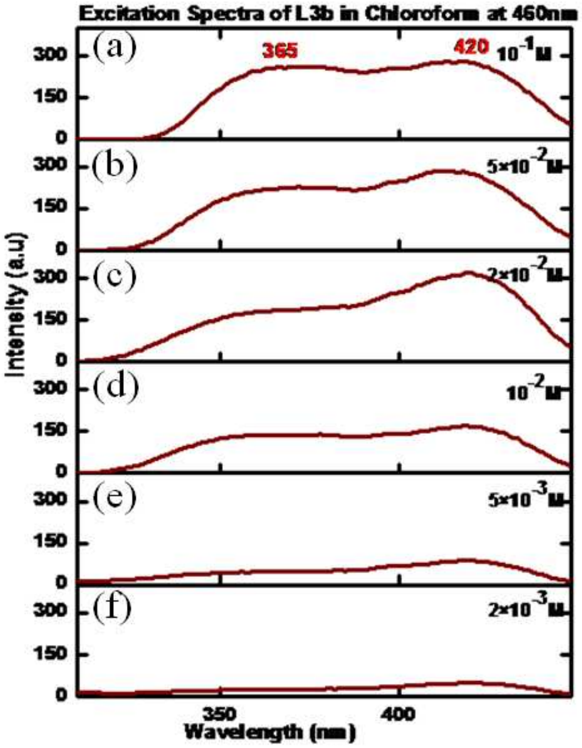


Figure 15: Excitation Spectra of **L3b** in CHCl$_3$ in different concentrations: (a) 10^{-1}M, (b) $5{\times}10^{-2}$M, (c) $2{\times}10^{-2}$M (d) 10^{-2}M (e) $5\ {\times}10^{-3}$M, (f) 10^{-3}M

The appearance of a new peak at a concentration of $5{\times}\ 10^{-1}$ M followed by a red shift of the same peak in case of solid **L2b** and **L3b** suggested the formation of non-covalently bonded "species" of the molecules. The large bathochromic shift of the emission peak suggested the formation of chromophore dimers of **L2b** and **L3b** in the aggregated state (Scheme 5).

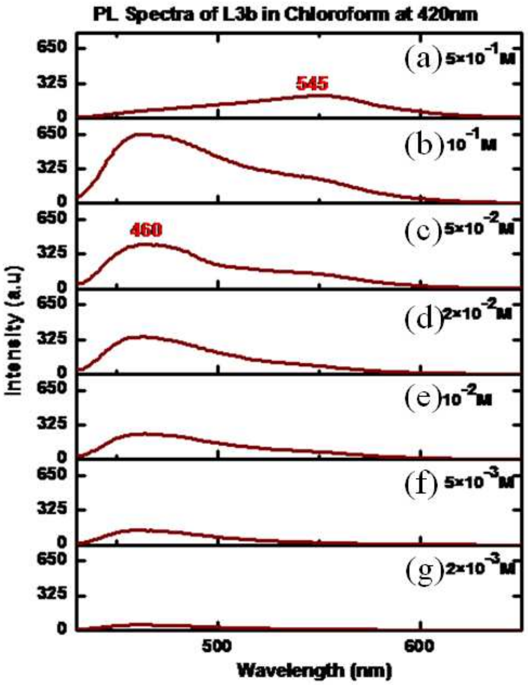


Figure 16: PL Spectra of **L3b** in CHCl$_3$ in different concentrations(a) $5{\times}10^{-1}$M; (b) 10^{-1}M; (c) $5{\times}10^{-2}$M; (d) $2{\times}10^{-2}$M; (e) 10^{-2}M (f) $5{\times}10^{-3}$M ; (g) $2\ {\times}10^{-3}$M

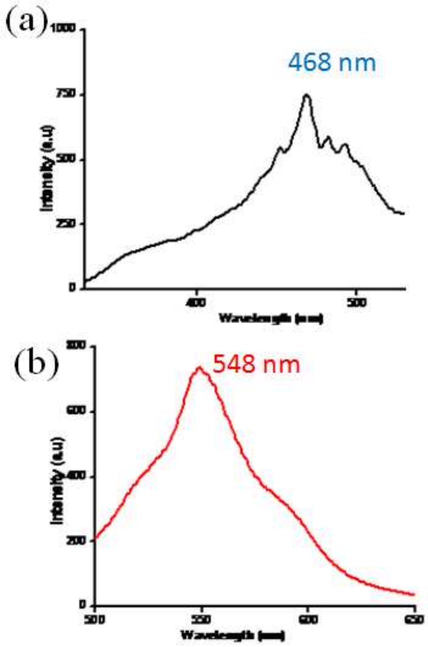
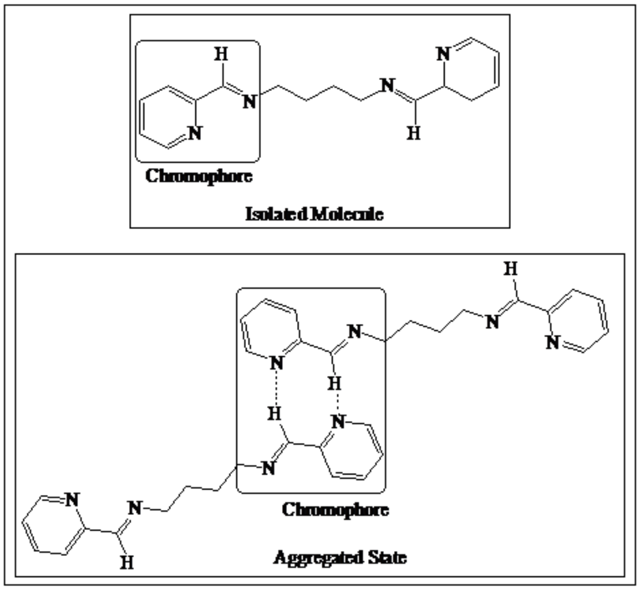


Figure 17: Excitation Spectra (Emission was kept at 550 nm) and PL Spectra (at an excitation wavelength of 470 nm) of **L3b** in solid state



Scheme 5: Hydrogen bonded dimeric species in the aggregated state of **L2b** and **L3b**; which account for appearance of new peak in high concentrated solutions and a large bathochromic shift in case of solid state PL spectra

NMR Assay for detecting the aggregation in compound L3b: The expected nature of the NMR spectra for non-aggregating compound includes sharp NMR resonance peaks at all concentrations and peak position is independent of the concentration. In case of aggregating compounds, higher concentrations result in self association of the molecules, while dilution will result in free state of the molecules. As a result, the effect of concentration changes will be observed in the NMR spectra. The NMR features that may become concentration dependent for aggregating compounds include chemical shifts, shape and intensity of the peaks.[22]

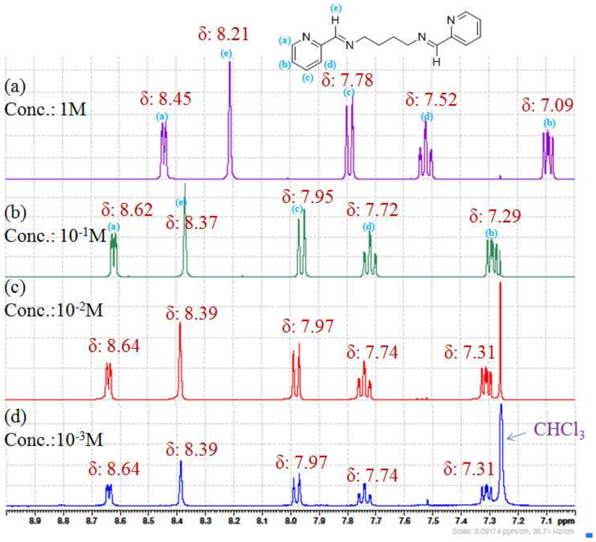


Figure 18: ^{1}H NMR spectra of **L3b** in $CDCl_3$ by changing the concentration of compound; (a) 1 M; (b) 10^{-1} M; (c) 10^{-2} M; (d) 10^{-3} M

The ^{1}H NMR spectra of **L3b** was recorded as a function of compound concentration (Figure 18, Figure S37). The protons in the aromatic region show change in chemical shift when the concentration of **L3b** in $CDCl_3$ was increased from 10^{-2} M to 1 M. The crystal structure of **L3b** shows the packing of the molecules, where the imine proton (H_e in the Figure 18) is in close proximity with pyridyl nitrogen. The protons H_a, H_b and H_c interact with pyridyl ring of another molecule as shown in figure 3d. The aromatic protons and the imine proton are becoming more shielded protons on increasing the concentration of **L3b**.

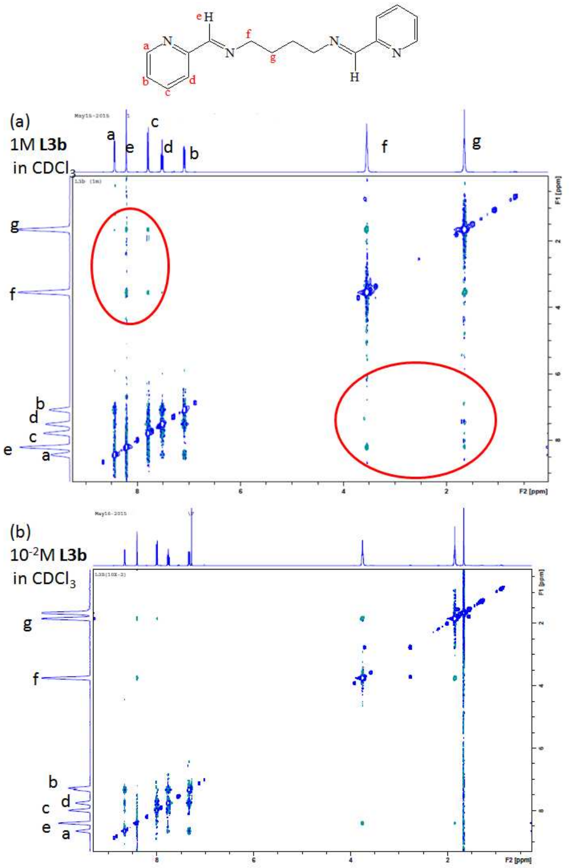


Figure 19: NOESY of **L3b** in $CDCl_3$ at a concentration of (a) 1 M; (b) 10^{-2} M

The NOESY of **L3b** was recorded to further observe the aggregation of the molecules at high concentration (Figure 19, Figure S38, S39). The spectra recorded at a concentration of 1M of **L3b** in $CDCl_3$ shows interaction between the aromatic and the aliphatic protons (Figure 19a), while very less interaction is observed at a concentration of 10^{-2}M. Further, quite intense interaction between the aromatic protons is observed at a higher concentration than that at a lower concentration.

Table 1: Crystal Data and Structure Refinement Parameters of **L1a**, **L2a** and **L3b**

Compound	**L1a**	**L2a**	**L3b**
Formula	$C_{14}H_{14}N_4$	$C_{16}H_{18}N_4$	$C_{16}H_{18}N_4$
Molecular Weight	238.29	266.34	266.34
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1$	*P*cab	$P2_1/c$
a/Å	8.6694(4)	19.379(5)	9.2157(5)
b/Å	17.8009(8)	24.584(5)	8.9944(5)
c/Å	12.8064(6)	12.300(5)	9.3471(5)
α/°	90.00	90.00	90.00
β/°	98.394(4)	90.00	107.344(6)
γ/°	90.00	90.00	90.00
V/Å^3	1955.15(16)	5860(3)	739.55(7)
Z	6	16	2
$D_{calcd.}$/g cm^{-3}	1.214	1.208	1.196
T/K	293(2)	293(2)	293(2)
Theta (°) range for data used	3.51 to 25.99	3.65 to 26.00	3.54 to 26.00
R_{int}	0.0418	0.0690	0.0441
Reflections with I > 2σ(I)	4636	2710	993
No. of Parameters refined	493	366	91
Final R (with I > 2 σ (I))	R_1^a = 0.0637; wR_2^b = 0.1609	R_1^a=0.0813; wR_2^b= 0.1901	R_1^a = 0.0445; wR_2^b =0.1085
GOF on F^2	1.001	1.038	1.042

Conclusions

The study of structure and photophysical property has revealed some important rationale regarding the interplay of molecular geometry and non-covalent interactions in deciding the light emitting properties of compounds. The compounds **L1a** and **L1b** show PL spectra in dilute solution and quenching in PL spectra is observed on increasing concentration. The compounds **L2a**, **L2b**, **L3a** and **L3b**, show enhancement in the PL intensity on increasing the concentration.

Although the molecule **L1a** and **L1b** are rigid, when compared to **L2a**, **L2b**, **L3a** and **L3b**, doesn't show any emission spectra in the solid state, while **L2a**, **L2b**, **L3a** and **L3b** show highly intense PL spectra in the solid state.

The flexible spacer (alkyl bridge) in **L2a, L2b, L3a and L3b**, helped in assembling the molecules in a way which results in enhancement in PL spectra on aggregation. In **L2b** and **L3b**, the presence of Hydrogen atom in place of CH_3-group further enhances the possibility of forming various aggregates/non covalently bonded species which enhances the emission intensity.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Crystallographic data; IR, ^{1}H NMR, ^{13}C NMR, NOESY, UV absorption spectra, Excitation Spectra, Photo Luminiscence Spectra and other supplementary material.]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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