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PII: S0022-2860(18)30608-2

DOI: 10.1016/j.molstruc.2018.05.042

Reference: MOLSTR 25215

To appear in: Journal of Molecular Structure

Received Date: 6 March 2018

Revised Date: 11 May 2018

Accepted Date: 11 May 2018

Please cite this article as: A. Kundu, S. Karthikeyan, D. Moon, S.P. Anthony, Excited state intramolecular proton transfer induced fluorescence in triphenylamine molecule: Role of structural conformation and reversible mechanofluorochromism, *Journal of Molecular Structure* (2018), doi: 10.1016/j.molstruc.2018.05.042.

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**Graphical Abstract** 

# Excited State Intramolecular Proton Transfer Induced Fluorescence in Triphenylamine Molecule: Role of Structural Conformation and Reversible Mechanofluorochromism

Triphenylamine based Schiff base molecules showed structure and conformation dependent ESIPT induced fluorescence and mechanofluorochromism.



 Excited State Intramolecular Proton Transfer Induced Fluorescence in Triphenylamine Molecule: Role of Structural Conformation and Reversible Mechanofluorochromism
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#### Abstract

Triphenylamine (TPA) based Schiff base molecules (1-4) were synthesized and role of molecular structure and conformation on excited state intramolecular proton transfer (ESIPT) induced fluorescence in both solution as well as solid state has been explored. 1 and 2, which are not hydrogen bonding donor to form intramolecular H-bonding, basis for ESIPT, are non-fluorescent in solution as well as solid. The incorporation of hydroxyl group in 3 and 4 promoted intramolecular H-bonding that could facilitate ESIPT. Interestingly, 3 showed strong fluorescence in solution ( $\lambda_{max} = 489 - 540$  nm,  $\Phi_f = 0.337 - 0.018$  compared to standard fluorescein) as well as solid state ( $\lambda_{max} = 553$  nm,  $\Phi_f = 4.84\%$  (absolute quantum yield) whereas structurally similar 4 did not show fluorescence. Further 3 also showed reversible mechanofluorochromism (MFC) due to the incorporation of non-planar TPA. Solid state structural analysis confirmed intramolecular H-bonding in 3 and 4 but 3 showed coplanar conformation between TPA phenyl and imine group whereas one of the molecules in the asymmetric unit of 4 revealed slightly twisted conformation. Powder X-ray diffraction studies of 3 and 4 provided insight on the ESIPT properties of 3.

#### **1. Introduction**

Organic molecules that can exhibit photoinduced excited state intramolecular proton transfer (ESIPT) from enol (E<sup>\*</sup>) to keto (K<sup>\*</sup>) tautomers, corresponding to proton migration within an intramolecular hydrogen bonding site, have attracted considerable attention because of their potential applications in optical and optoelectronic devices [1]. The enol-keto photocycle (E-E\*-K\*-K-E) offers a distinct four-level laser scheme to achieve population inversion; therefore, ESIPT fluorophores are useful as laser dyes [2]. The formation of intramolecular H-bonding between proton donor and acceptor within the molecule is pre-requisite for ESIPT [3]. The drastic electronic and structural changes through ESIPT often produced strong fluorescence in the solid state with a large Stokes shifts without self-absorption [4]. On the other hand, the majority of the  $\pi$ -conjugated organic molecules that showed strong fluorescence in solution becomes weak or non-fluorescence in the solid state due to aggregation caused quenching. Special approaches such as aggregation enhanced emission (AEE) and supramolecular interactions have often employed to generate strong solid state fluorescent materials [5]. Further, the intramolecular H-bonding and fluorescence of ESIPT fluorophores are strongly influenced by surrounding factors such as pH, solvent polarity and ions that could result in dual fluorescence from ESIPT  $K^*$  and non-ESIPT  $E^*$  tautomers [6]. The subtle conformational and molecular structure change has produced tunable solid state fluorescence [7]. The green emission of ESIPT microcrystal laser was tuned to red by introducing intermolecular H-bonding functional group [8]. Anthracene showed strong fluorescence in solution but weak/non fluorescence in the solid, however, strong solid state fluorescent materials based on anthracene derivatives were synthesized by attaching ESIPT unit [9]. The dual and tunable fluorescence and metal chelating functionality of ESIPT molecules further used for fluorescent sensing and to realize white light emission using single fluorophore [10,11]. External stimuli-responsive reversible fluorescence switching has also been demonstrated by make use of halochromic functionality and incorporation of AEE unit in the ESIPT compounds [12].

Schiff base organic molecules are very interesting because of their structural versatility, simple synthetic method and easy tailorability, good biological activities, strong photophysical properties and coordination ability with metal ions [13]. Moreover, hydroxyl functional group incorporated Schiff base derivatives can exhibit strong intramolecular H-bonding and offered opportunity to investigate ESIPT [14]. Nevertheless, only some of the Schiff base molecules

exhibited fluorescence and most of the Schiff bases are non-fluorescent. For example, ESIPT coupled AEE in poly(aryl ether) dendron based Schiff base exhibited tunable blue-green-whiteyellow emission by controlling aggregate [15]. Polymorph structure dependent yellow and orange AEE was observed with (E)-4-chloro-2-(((4-(dimethylamino)phenyl)imino)methyl) phenol [16]. Coumarin-based AEE Schiff base derivatives displayed multiple colours depend on the substitution [17]. Recently, we have reported stimuli-responsive high-contrast reversible fluorescence switching and nanofabrication induced white light emission via ESIPT in simple aryl-ether based Schiff bases [18]. However, still it is not clear why only some of the Schiff base molecules showed fluorescence via ESIPT and others are non-fluorescent. Herein, we have attempted to derive some understanding by synthesizing new triphenylamine based Schiff base molecules (1-4) and exploring molecular structure dependent ESIPT induced fluorescence both in solution and solid state [Scheme 1]. 1 and 2 are non-fluorescence due to unavailability of intramolecular H-bonding facilitating hydroxyl functional group in the structure. However, the introduction of hydroxyl functionality in 3 facilitated intramolecular H-bonding and ESIPT that lead to strong solution as well as solid state fluorescence. Absorption studies of 3 in different solvent did not show solvatochromism but exhibited drastic modulation of fluorescence wavelength and intensity. Further the temperature dependent fluorescence reduction and metal ions induced quenching supported the role of ESIPT on the fluorescence of 3. Solid state structural studies also unambiguously confirmed the formation of strong intramolecular Hbonding. Structural studies of 4 also revealed strong intramolecular H-bonding but slightly twisted non-coplanar conformation in the crystal lattice. But structurally similar 4 did not show any fluorescence that might be due to photoinduced electron transfer effect of imino nitrogen/aminophenyl. Interestingly, 3 showed stimuli-responsive reversible fluorescence switching upon strong crushing and heating. PXRD studies revealed the conversion crystalline to amorphous state upon crushing and reversing amorphous to crystalline by heating. Computational studies of 3 and 4 have also been performed to gain insight on the ESIPT properties of 3. Thus the present studies provide structural insight for developing Schiff base based ESIPT fluorescent materials.

#### 2. Experimental section

Triphenylamine, 3-methoxy-N,N-diphenylaniline, dimethylformamide (DMF, HPLC grade), and phosphorous oxychloride were purchased from Sigma-Aldrich and used without further

purification. Solvents were obtained from Merck India. Hydrazine hydrate (99-100%), phenyl hydrazine was obtained from fisher scientific. The metal ion solutions used for the colorimetric sensor experiments were prepared in Mill-Q water. Aldehyde functional group into triphenylamine and 3-methoxy triphenylamine was introduced by following reported procedure [19]. 4-(diphenylamino)-2-hydroxybenzaldehyde was synthesized by converting OCH<sub>3</sub> group of corresponding aldehyde to OH by stirring with BBr<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> following the reported procedure [20].

# General procedure for 1-3 (Scheme S1)

Triphenylamine aldehyde (1.0 mmol) was dissolved in ethanol and stirred at room temperature for 10 min. Then hydrazine hydrate (0.5 mmol, 99-100%) was added drop-wise under vigorous stirring. The solution mixture was stirred at room temperature for 3 h and the resulting precipitate was filtered, washed by cold ethanol and dried under vacuum.

1: Yield = 77%. M.pt = 229 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.58 (s, 1H (imine)), 7.65 (td, *J* = 2.2, 8.7 Hz, 2H), 7.33-7.27 (m, 4H), 7.16-7.11 (m, 4H), 7.09-7.03 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  160.9, 150.4, 146.9, 129.5, 129.4, 127.3, 125.4, 123.9, 121.7. C<sub>38</sub>H<sub>30</sub>N<sub>4</sub> (542.67): calcd. C 84.10, H 5.57, N 10.32; found C 84.16, H 5.66, N 10.12.

**2**: Yield = 75%. M.pt = 254 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (s, 1H (imine)), 7.92 (d, *J* = 8.4 Hz, 1H ), 7.33-7.26 (m, 4H), 7.16-7.13 (m, 4H), 7.11-7.06 (m, 2H), 6.62 (dd, *J* = 2.1, 8.5 Hz, 1H ), 6.54 (d, *J* = 2.1 Hz, 1H), 3.67 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  159.9, 156.5, 151.6, 147.0, 129.4, 127.9, 125.4, 123.9, 116.6, 114.7, 104.6, 55.5. C<sub>40</sub>H<sub>34</sub>N<sub>4</sub>O<sub>2</sub> (602.72): calcd. C 79.71, H 5.69, N 9.30; found C 79.56, H 5.72, N 9.22.

**3**: Yield = 80 %. M.pt = 304 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  11.65 (s, 1H (OH)), 8.52 (s, 1H (imine)), 7.34-7.29 (m, 4H), 7.17 (dd, *J* = 1.2, 8.5 Hz, 4H), 7.13-7.11 (m, 2H), 7.08 (s,1H), 6.55 (s, 1H), 6.51 (d, *J* = 2.4 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  162.0, 160.8, 152.2, 146.4, 132.8, 129.5, 126.3, 124.6, 112.3, 111.1, 107.4. C<sub>38</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub> (574.67): calcd. C 79.42, H 5.26, N 9.75; found C 79.24, H 5.50, N 9.84.

#### Synthesis of 4

Aldehyde (1.0 mmol) was dissolved in ethanol and stirred at room temperature for 10 min. Then phenyl hydrazine (1.0 mmol) was added drop-wise under vigorous stirring. The solution mixture was stirred at room temperature for 3 h. The resulting precipitate was filtered, washed by cold ethanol and dried under vacuum.

**4:** Yield = 85 %. M.pt = 150 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  10.90 (s, 1H (OH)), 7.81 (s, 1H (imine)), 7.35-7.25 (m, 7H), 7.16-7.05 (m, 6H), 6.98-6.87 (m, 4H), 6.63 (d, *J* = 2.1 Hz, 1H), 6.54 (dd, *J* = 8.1, 8.4 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 149.7, 147.0, 143.7, 141.5, 129.9, 129.5, 129.3, 125.5, 123.8, 120.5, 113.4, 112.6, 112.5, 109.2. C<sub>25</sub>H<sub>21</sub>N<sub>3</sub>O (379.45): calcd. C 79.13, H 5.58, N 11.07; found C 79.32, H 5.38, N 11.22.

#### Characterization

NMR spectra were measured on a Bruker 300 MHz AVANCE-II. Absorption spectra were recorded using Perking Elmer Lambda 1050. Fluorescence spectra and quantum yield were recorded on Jasco fluorescence spectrometer FP-8300 instruments equipped with integrating sphere and calibrated light source. Powder X-ray diffraction (PXRD) patterns were obtained using an XRD-Bruker D8 Advance XRD with Cu K $\alpha$  radiation ( $\lambda = 1.54050$  Å) operated in the 2 $\theta$  range from 10° to 50°. Single crystals of **3** and **4** coated with paratone-N oil and diffraction data was measured at 100 K with synchrotron radiation ( $\lambda = 0.62998$  Å) on an ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. CCDC Nos. – 1818752 (**3**) and 1818753 (**4**) contain the supplementary crystallographic data for this paper. The HOMO, LUMO and band gap of **3** and **4** are studied using B3PW91/6-31+G(d,p) level theory (Gaussian 09 package).

# **3. Results and Discussion**

Compound 1-4 was synthesized by simple condensation reaction between different triphenylamine aldehyde and hydrazine hydrate/phenyl hydrazine [Scheme 1 and S1]. Absorption spectra of 1 in DMF showed  $\lambda_{max}$  at 406 nm that could be assigned for n- $\pi^*$  transition [Figure S1]. Introducing electron donor methoxy group at *ortho* position (2) slightly red shift the absorption to 418 nm whereas hydroxyl attached 3 exhibited further red shift of absorption ( $\lambda_{max} = 425$  nm). In contrast, phenyl hydrazine based 4 showed blue shifted absorption ( $\lambda_{max} = 380$  nm). Interestingly, 1 and 2 showed very weak fluorescence in DMF whereas 3 exhibited highly enhanced emission [Figure S2]. The strong fluorescence of 3 compared to 1 and 2 could be attributed to the ESIPT since structure of 3 can form intramolecular H-bonding between phenyl hydroxyl donor and imine acceptor but 1 and 2 could not form such intramolecular H-bonding due to non-availability of hydroxyl functional group. Absorption studies of 3 in different solvent did not show solvatochromism ( $\lambda_{max} = 424$  to 431 nm, Table 1) and suggest that there might not be any change in the dipole moment of molecular

ground and excited states [21, Figure 1a]. However, fluorescence  $\lambda_{max}$  and intensity of **3** was strongly influenced by solvent polarity [Figure 1b, Table 1]. 3 in toluene showed strong fluorescence at 489 nm ( $\Phi_f = 0.107$  compared to standard fluorescein) whereas red shifted very weak fluorescence at 540 nm ( $\Phi_f = 0.018$ ) was observed in CH<sub>3</sub>OH. The strongest fluorescence for **3** was obtained from CH<sub>2</sub>Cl<sub>2</sub> ( $\Phi_f = 0.337$ ). In non-polar environment, intramolecular Hbonding of 3 might be intact whereas polar solvents could form intermolecular H-bonding between solvent and hydroxyl group of 3 and compete with intramolecular H-bonding that lead to reduction of fluorescence intensity [14b]. Further, temperature dependent fluorescence change also supported the role of intramolecular H-bonding on the fluorescence via restricting C=N isomerization [Figure S3]. At 0 °C, 3 in CH<sub>3</sub>CN showed strong fluorescence at 523 nm, however, increase of temperature to 80 °C lead to three times reduction in the fluorescence intensity with slight blue shift of  $\lambda_{max}$  (513 nm). Similarly, **3** dissolved in CH<sub>3</sub>CN and injected into water also exhibited decrease of fluorescence intensity with temperature [Figure S4]. The increase of temperature could reduce the molecular rigidity and might weaken the intramolecular H-bonding. In contrast, 4 in which phenyl group was attached with other end of the hydrazine amine did not show fluorescence in any solvent, probably because of the photoinduced electron transfer (PET) from imino nitrogen or aminophenyl nitrogen [22]. The strong solution fluorescence coupled with metal chelating functional group prompted us to explore metal induced fluorescence changes since that can also support the role of ESIPT on the fluorescence of 3 [Figure 2]. Interestingly, addition of  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  metal ions quenched the fluorescence of 3 whereas other ions did not show significant change. 3 showed absorption  $\lambda_{max}$ at 427 nm in DMF. Addition of Co<sup>2+</sup> showed disappearance absorption at 427 nm and appearance of weak featureless broad absorption from 350 to 550 nm [Figure 2a]. On the other hand, Ni<sup>2+</sup> addition exhibited decrease of absorption intensity with slight blue shift of  $\lambda_{max}$  to 408 nm whereas  $Cu^{2+}$  addition showed decrease of intensity with broadening of absorption without changing  $\lambda_{max}$ . Fluorescence spectra of **3** with Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> showed complete disappearance of peak at 516 nm whereas other metals did not show any significant change in the fluorescence [Figure 2b]. The coordination of **3** with  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  metal ions might lead to loss of intramolecular H-bonding and ESIPT and hence the fluorescence was quenched. These studies clearly indicated that ESIPT played important role in the fluorescence of **3**.

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The intramolecular H-bonding facilitated ESIPT in 3 also lead to good solid state fluorescence [Figure 3,  $\Phi_f = 4.84\%$  (absolute quantum yield)]. AEE property of **3** has also been demonstrated by increasing water fraction in methanol solution. Addition of water into  $\mathbf{3}$ dissolved in methanol leads to decrease of fluorescence intensity initially before exhibiting a new peak at 537 nm [Fig. S5a]. The green fluorescence of DCM droplet of 3 was converted to yellowish green upon solvent evaporation [Fig. S5b]. Further addition of water reduced the fluorescence intensity due to precipitation of formed colloidal particles. The non-planar triphenylamine unit coupled with solid state fluorescence of **3** expected to exhibit mechanical stimuli-induced fluorescence switching since triphenylamine based derivatives is known to exhibit AEE and mechanofluorochromism (MFC) [23]. The crystals of 3 showed fluorescence at 553 nm and slight breaking lead to slight blue shift of fluorescence to 540 nm that might be due to the disruption of long range molecular ordering and generating defects [24]. Hard crushed crystals of 3 exhibited complete fluorescence quenching whereas heating lead to turn-on fluorescence  $l\lambda_{max} = 537$  nm). In contrast, structurally similar 4 did not show fluorescence in the solid state as well. PXRD studies of crystals showed clear sharp diffraction peaks that perfectly matched with pattern simulated using single crystals data of 3 [Figure 4, S6]. The perfect matching of experimental and simulated pattern confirmed the phase purity of the compound. The hard crushed solids showed very weak diffraction peaks that indicated the conversion of crystalline to amorphous or partially amorphous phase. However, heated solids showed recovering of clear sharp diffraction peaks that matched with initial diffraction peaks of 3 crystals. The re-appearance of clear diffraction suggested the formation of crystalline phase from amorphous phase and perfect matching with initial crystals peak indicated that there was no structural change. Thus the solid state reversible fluorescence switching of 3 was due to the reversible conversion of crystalline to amorphous and vice-versa by hard crushing followed by heating. FTIR peaks of **3** before and after grinding did not show significant change in the peak position except reduction of intensity after crushing [Fig. S7]. Hard crushing can cause the molecules to have close packing in the powders that could lead to loss of molecular vibrations and peak intensity [25].

Solid state structural analysis has been performed to confirm the presence of intramolecular H-bonding and get the insight on the molecular packing induced solid state fluorescence. Single crystals of **3** were grown by diffusing diethyl ether into  $CH_2Cl_2$  whereas **4** 

were grown from ethanol (EtOH) by slow evaporation, but 1 and 2 did not produce quality crystals. 3 revealed P21/n space group with one molecule in the asymmetric unity [Table S1-4]. As expected, 3 showed strong intramolecular H-bonding between hydroxyl donor and imine acceptor [Figure 5a, Table 2]. Further the symmetric structure showed same intramolecular Hbonding on the both end of the hydrazine. The hydroxyl group attached phenyl ring in both triphenylamine along with hydrazine imine adopted coplanar geometry [Figure 5b, S8, torsion angle ( $\tau$ ) of C<sub>3</sub>-C<sub>4</sub>-C<sub>7</sub>-N<sub>2</sub> = 0.12]. The weak intermolecular interaction between hydroxyl oxygen and phenyl hydrogen and C-H... $\pi$  interactions lead to the formation of ladder like structural arrangement in the crystal lattice of 3 [Figure 5c, Table 2]. The asymmetric unit of 4 contain two molecules that also showed strong intramolecular H-bonding in the crystal lattice but with different H-bonding distances due to conformational differences [Figure 6a,b, Table 2]. Compared to 3, higher torsional angle between hydroxyl phenyl group of triphenylamine and phenyl hydrazine was observed for both molecules in the crystal lattice of 4. One of the molecule showed relatively more coplanar conformation compared to another molecule in the asymmetric unit [Figure S9,  $\tau_1 = 2.38$  and  $\tau_2 = 3.86$ ]. The slightly higher twisted molecule formed dimer via  $\pi$ ... $\pi$  interactions between hydrazine amine and imine carbon and the dimer on both end was connected with more planar molecule through C-H... $\pi$  interactions [Figure 6c, Table 2]. Thus the structural comparison of 3 and 4 suggest that although both exhibit strong intramolecular Hbonding the higher twisting along with PET effect from imine nitrogen/phenyl hydrazine amine in 4 might lead to non-fluorescence in the solid state. However, the role of twisting on the solid state fluorescence of Schiff base ESIPT molecules need further exploration with more examples.

The entire set of calculations have been performed using DFT-B3PW91 method with 6-31+G(d,p) basis set using Gaussian 09 program package [26]. Computational studies were performed using the crystal structure of **3** and **4** without optimization to get insight on the fluorescence [27, Figure 7]. The bond length, bond angle of structure **3** and **4** are given in the supporting information [Figure S10, Table S5]. Figure 7 shows the isodensity surface plot (isodensity contour =0.02) of highest occupied molecular orbitals (HOMOs), and lowest unoccupied molecular orbital (LUMO) for structure **3** and **4**. The HOMOs of **3** indicated that electron density was predominantly localized on both TPA donor phenyl group as well as slightly over the hydrazine imine nitrogen. The electron density in the LUMO was mostly localized on the hydrazine imine nitrogen acceptor. HOMO-LUMO calculation for **4** was

performed for both unique molecules observed in the asymmetric unit. Similar to **3**, electron density in the HOMO of **4-I** (less twisted) and **4-II** (more twisted) was mainly occupied on the triphenylamine donor, however, in LUMO electron density was occupied on the imine nitrogen and adjacent phenyl ring. The less twisted **4-I** LUMO was more stabilized compared to **4-II** and lead to lower band gap (3.65 eV). **3** showed the lowest band gap of 3.09 eV. Hence, although both **3** and **4** showed intramolecular H-bonding interactions, the band gap was strongly influenced by molecular conformation and packing.

# 4. Conclusion

In conclusion, we have synthesized new ESIPT fluorophore, 3, based on triphenylamine Schiff base that showed strong fluorescence both in solution as well as solid state due to hydroxyl functionality facilitated intramolecular H-bonding. Structural comparison revealed the lack of intramolecular H-bonding site in 1 and 2 makes them non-fluorescent. Solvent polarity and temperature dependent fluorescence modulation in solution indicated that ESIPT played significant role for the fluorescence of 3. Solid state structural studies also confirmed the formation of strong intramolecular H-bonding between the hydroxyl donor and imine nitrogen acceptor. Incorporating non-planar triphenylamine unit was exploited for demonstrating reversible MFC in the solid state. In contrast, the structurally similar Schiff base 4 that also exhibited strong intramolecular H-bonding in the solid state did not show any fluorescence. This could be attributed to the PET effect of imino nintrogen/aminophenyl and non-coplanar molecular conformation in the solid state. PXRD studies suggested that conversion of crystalline to amorphous and vice versa upon crushing and heating was responsible for fluorescence switching of **3**. Computational studies further provided insight on the ESIPT fluorescence of **3**. Thus the present studies indicate that even though the Schiff base molecule can form strong intramolecular H-bonding, the molecular conformation and presence of other functionality plays significant role on the fluorescence.

#### Acknowledgement

Financial support from the Science and Engineering Research Board (SERB), New Delhi, India (SERB No. EMR/2015/00-1891) is acknowledged with gratitude. "X-ray crystallography at the PLS-II 2D-SMC beamline was supported in part by MSIP and POSTECH.

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# **Figure Captions**

- Scheme 1. Molecular structure of **1-4**.
- Figure 1. (a) Absorption and (b) fluorescence spectra of 3 in different solvent.  $\lambda_{exc} = 360$  nm.
- Table 1.Absorption and fluorescence data of 3 in different solvents.
- Figure 2. (a) Absorption and (b) fluorescence responses of **3** ( $10^{-3}$  M) to different metal ions ( $10^{-3}$  M).  $\lambda_{exc} = 360$  nm.
- Figure 3. Solid state and mechanofluorochromism of **3**.  $\lambda_{exc} = 360$  nm.
- Figure 4. PXRD pattern of **3**.
- Figure 5. (a) Intramolecular H-bonding, (b) molecular conformation and (c) weak intermolecular interactions in the crystal lattice of 3. C (grey), N (blue), O (red), H (white). H-bonding, C-H...O and π...π interactions (broken line) distances are marked in Å.
- Table 2. Inter and intramolecular H-bonding, C-H... $\pi$  and  $\pi$ ... $\pi$  interactions in the crystal lattice of **3** and **4**.
- Figure 6. Intramolecular H-bonding, (b) molecular conformation and (c) weak intermolecular interactions in the crystal lattice of 4. C (grey), N (blue), O (red), H (white). H-bonding, C-H...π and π...π interactions (broken line) distances are marked in Å.
- Figure 7. Molecular orbital plots of the HOMOs and LUMOs of **3** and **4**.





Figure 1. (a) Absorption and (b) fluorescence spectra of **3** in different solvent.  $\lambda_{exc} = 360$  nm.

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# ACCEPTED MANUSCRIPT

Table 1.

Solvents	Absorption	$c (I mol^{-1} cm^{-1})$	Fluorescence	$\Phi_f$ (compared to				
Solvents	$\lambda_{max}$ (nm)		$\lambda_{max} nm$	fluorescein				
Toluene	432	$1.45 \ge 10^2$	489	0.107				
CH <sub>2</sub> Cl <sub>2</sub>	432	$1.50 \ge 10^2$	507	0.337				
THF	424	$1.41 \text{ x } 10^2$	495	0.105				
EtOAc	424	$1.32 \times 10^2$	495	0.094				
DMF	425	$1.32 \times 10^2$	513	0.088				
CH <sub>3</sub> CN	423	$1.32 \times 10^2$	513	0.176				
DMSO	425	$1.43 \times 10^2$	517	0.057				
EtOH	425	$1.41 \times 10^2$	532	0.050				
МеОН	424	$1.34 \text{ x } 10^2$	540	0.018				
Isopropylalcoho 1	424	$1.39 \ge 10^2$	530	0.060				

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Figure 2. (a) Absorption and (b) fluorescence responses of **3** (10<sup>-3</sup> M) to different metal ions (10<sup>-3</sup> M).  $\lambda_{exc} = 360$  nm.

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Figure 3. Solid state and mechanofluorochromism of 3.  $\lambda_{exc} = 360$  nm.



Figure 4. PXRD pattern of **3**.



Figure 5. (a) Intramolecular H-bonding, (b) molecular conformation and (c) weak intermolecular interactions in the crystal lattice of **3**. C (grey), N (blue), O (red), H (white). H-bonding, C-H...O and  $\pi$ ... $\pi$  interactions (broken line) distances are marked in Å.



Figure 6. Intramolecular H-bonding, (b) molecular conformation and (c) weak intermolecular interactions in the crystal lattice of **4**. C (grey), N (blue), O (red), H (white). H-bonding, C-H... $\pi$  and  $\pi$ ... $\pi$  interactions (broken line) distances are marked in Å.

Table 2.

	Hydrogen bonding			<b></b>	С-Нπ
	D-HA	d(DA) (Å)	<(DHA) (°)	interactions (Å)	interactions (Å)
3	$O_1$ - $H_1$ $N_2$	2.646	146.0	3.272	
5	$C_{19}$ - $H_{19}$ $O_1$	3.484	153.9		
4	$O_{1A}$ - $H_{1A}$ $N_{2A}$	2.664	146.0	3.204	3.493
	O <sub>1B</sub> -H <sub>1B</sub> N <sub>2B</sub>	2.651	142.9		3.502



Figure 7. Molecular orbital plots of the HOMOs and LUMOs of **3** and **4**.

# Highlights

- Schiff base molecules for ESIPT induced fluorescence.
- Molecular structure dependent ESIPT.
- Role of molecular conformation and substituent on the ESIPT fluorescence.
- Stimuli-responsive high contrast off-on fluorescence switching.