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Self-reversible thermofluorochromism of D-A-D triphenylamine derivatives and effect of molecular conformation and packing

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Triphenylamine (TPA) based donor-acceptor-donor (D-A-D) compounds were synthesized that showed aggregation enhanced emission (AEE) and molecular conformation and packing dependent rare self-reversible thermofluorochromism in the solid state. **1**, TPA substituted with phenylenediacetonitrile at both end displayed twisted molecular conformation whereas OCH_3 substitution at *ortho* position of TPA (3-MTPA, **2**) resulted in twisted conformation at one end and coplanar conformation at other end. 4-methoxytriphenylamine (4-MTPA) attached acceptor (**3**) displayed coplanar conformation on both end of the acceptor. Highly twisted conformation in **1** lead to strong fluorescence (16.8 %) and coplanar conformation in **3** resulted in weak fluorescence (1.6 %) in the solid state. **2** showed moderate fluorescence (8.4 %) in the solid state. Importantly, **1** and **2** exhibited self-reversible thermofluorochromism with heating and cooling whereas **3** did not show any fluorescence switching with temperature. Computational studies indicate that the molecular conformation and OCH_3substitution influences on the HOMO-LUMO energy level of TPA derivatives.

Introduction

Molecular conformation, packing and supramolecular interactions of π-conjugated organic molecule in the solid state plays significant role on their electrical as well as optical properties.[1] In particular, smart fluorescent organic materials that exhibit reversible fluorescence switching to the different external stimuli such as light, heat and pressure depends on the ability of the molecule to display varied conformation, packing and intermolecular interactions in the solid state.[2] For example, strongly fluorescent π-conjugated organic molecule in solution often converted weak/non-fluorescent in the solid state due to aggregation caused fluorescent quenching (ACQ). To overcome the ACQ, different strategies such as utilization of non-planar fluorophore, supramolecular fluorescent host-guest systems, excited state intramolecular proton transfer systems, substituting with bulky groups and controlling intermolecular interactions have been explored for developing solid state fluorescent materials.[3] Particularly, the discovery of aggregation enhanced emission (AEE) phenomenon in the last decade, an opposite effect of ACQ in which weak or non-fluorescent molecules in solution exhibited strong fluorescence in the solid state via intermolecular interactions induced fluorophore rigidification and restriction of intramolecular rotation (RIR), has offered new methods and tools for constructing solid state fluorescent materials.[4] Numerous organic solid state fluorescent materials have been emerged based on the AEE strategy using diverse core structures such as including tetraphenylethenes, siloles, fulvenes, boron derivatives and conjugated polymers.[5,6] Some of the AEE materials exhibited reversible fluorescence switching upon external stimuli mostly applying mechanical pressure followed by heating or solvent vapor exposure.[7] Ping Lu group reported a unique piezochromic fluorescent organic crystals that showed pressure dependent reversible off-on fluorescence switching.[8] Fluorescence-phosphorescence dual mechanoluminescence at room temperature was observed with terphenyl-dioxaborolane derivative.[9] 3-aryl-2-cyano acrylamide derivatives showed stacking mode dependent mechanofluorochromism in the solid state.[10] However, AEE materials that exhibit temperature induced reversible fluorescence are rarely reported.[11]

Triphenylamine (TPA), a propeller shaped nonplanar optoelectronic molecule, has been extensively used for developing organic solar cell dyes, field effect transistor, sensors, solid state fluorescent and smart fluorescent materials.[12] The conformationally robust, twisted propeller core aryl structure that prevent close stacking produced AEE in the solid state with mechanofluorochromism.[13] The structure of the acceptor, substituent position and halochromic functionality has been exploited to demonstrate self-reversible, reversible mechanofluorochromism, polymorphism induced tunable fluorescence and self-erasable and rewritable platoforms.[14] In this manuscript, we report the synthesis of triphenylamine based donor-acceptor-donor (D-A-D) molecules and investigation of methoxy substituent effect on the molecular conformation and packing as well as self-

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[d] *Electronic Supplementary Information (ESI) available: [Synthesis, NMR data, absorption spectra, crystallographic table for PyBAP and PyBAP-PA, crystal structures, PXRD pattern, excitation spectra. CCDC: 1534730 and 1534731]. See DOI: 10.1039/x0xx00000x*

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reversible thermofluorochromism in the solid state. Triphenylamine attached phenylenediacetonitrile (**1**) showed highly twisted molecular conformation whereas coplanar conformation was observed with 4-methoxytriphenylamine attached acceptor (**3**). 3-methoxytriphenylamine attached phenylenediacetonitrile (**2**) displayed twisted conformation as well as coplanar conformation. In **1**, CN groups showed *cis* conformation whereas *trans* conformation was observed in **2** and **3**. All three molecules showed AEE in the solid state. The formation of highly twisted conformation in **1** resulted in strong fluorescence (quantum yield (Φ_f) = 16.8) whereas **2** that has both twisted as well as planar conformation showed moderate fluorescence (Φ_f = 8.4). **3** showed only weak fluorescence (Φ_f = 1.6). Importantly, **1** and **2** exhibited self-reversible fluorescence switching with heating and cooling. But **3** did not show any fluorescence change with temperature. Computational studies have also been performed to get the insight on the energy level modulation upon changing of the molecular conformation.

Experimental Section

Triphenylamine (TPA), 4-methoxy triphenylamine (4-MTPA), 3-methoxy triphenylamine (3MTPA), dimethylformamide (DMF, HPLC grade), phosphorous oxychloride and 1, 4-phenylenediacetonitrile was purchased from Sigma-Aldrich and used without further purification. The solvents and NaOH were obtained from Merck India. Aldehyde functional group was introduced into TPA/4-MTPA/3-MTPA by following a reported procedure.[14a,b]

General procedure for synthesizing 1, 2 and 3

1,4-phenylenediacetonitrile and aldehyde functionalized triphenylamine compound (1:2 molar ratio) was dissolved in ethanol (10 mL) and stirred at room temperature. To this reaction mixture, ethanol solution (5 mL) of NaOH (0.5eq.) was added drop-wise and stirred for another 2 h at room temperature. The formed precipitate was filtered, washed with cold ethanol and dried under vacuum.

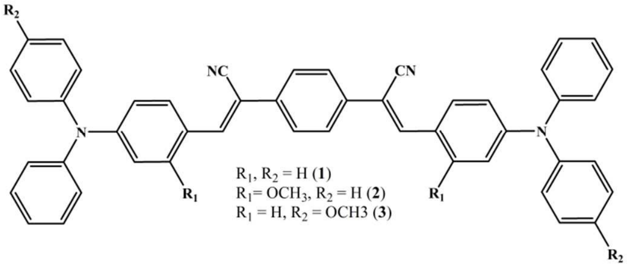
1: Yield = 85%. M.p = 245°C. ^{1}*H NMR* (300 MHz, $CDCl_3$, ppm) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.69 (s, 1H), 7.48-7.45 (m, 1H), 7.35-7.28 (m, 3H), 7.13-7.07 (m, 1H), 7.06-7.03 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm) δ 150.2, 146.5, 141.8, 135.1, 131.2, 130.8, 129.6, 126.1, 126.1, 125.8, 124.5, 120.7, 118.5, 106.6.

2: Yield = 86%. M.p = 267°C. ^{1}*H NMR* (300 MHz, $CDCl_3$, ppm) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 1H), 7.69 (s, 1H), 7.35-7.24 (m, 5H), 7.16-7.09 (m, 6H), 6.66-6.61 (m, 1H), 6.54-6.49 (m, 1H), 3.67 (s, 3H). ^{13}*C NMR* ($CDCl_3$, ppm) δ 159.1, 151.7, 146.6, 136.4, 135.3, 129.5, 128.9, 126.1, 125.9, 124.5, 118.9, 115.9, 113.6, 106.4, 103.1, 55.6.

3: Yield = 85%. ^{1}*H NMR* (300 MHz, $CDCl_3$, ppm) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 2H), 7.45 (s, 1H), 7.34-7.24 (m, 2H), 7.17-7.10 (m, 5H), 7.05-6.94 (m, 2H), 6.90-6.84 (m, 2H), 3.83 (s, 3H). ^{13}*C NMR* ($CDCl_3$, ppm) δ 157.2, 150.5, 146.5, 142.0, 139.2, 135.1, 130.9, 129.5, 128.2, 126.0, 125.4, 125.2, 124.1, 119.4, 118.7, 115.1, 106.0, 55.5.

Spectroscopy and structural characterization

Absorption and fluorescence spectra were measured using Perking Elmer Lambda 1050 and Jasco fluorescence spectrometer-FP-8300 instruments. Solid state fluorescence spectra were recorded by exciting at 370 nm with 5 nm slit width in the detection window. Fluorescence quantum yields (Φ_f) of solid samples were measured using a Jasco (FP-8300) spectrofluorimeter with integrating sphere. The HOMO, LUMO and band gap of all structures are studied using B3PW91/6-31+G(d,p) level theory (Gaussian 09 package). The powder X-ray diffraction (PXRD) patterns were measured using a XRD- Bruker D8 Advance XRD with Cu Kα radiation (λ = 1.54050 Å) operated in the 2θ range from 10^o to 50^o. Single crystals were coated with paratone-N oil and the diffraction data measured at 100K with synchrotron radiation (λ = 0.62998 Å) on a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. CCDC Nos. – 1450595 (**1**), 1570578 (**2**) and 1570577 (**3**) contains the supplementary crystallographic data for this paper.



Scheme 1. Molecular structure of TPA based D-A-D molecules.

Results and Discussion

Aldehyde functionality into TPA, 3-MTPA and 4-MTPA was introduced using Vilsmeier–Haack formylation reaction using $POCl_3$ and DMF. Triphenylamine based donor-acceptor-donor π-conjugated organic molecules (**1-3**) were synthesized by condensing aldehyde functionalized TPA donor molecules with 1,4-phenylenediacetonitrile acceptor (Scheme 1). All three products were formed as orange-red precipitates. The absorption spectra of **1-3** showed λ_{max} around 450 nm and OCH_3 substitution did not exhibit significant influence on the absorption in CH_3CN (Fig. S1). All three donor-acceptor-donor compounds (**1-3**) did not show any fluorescence in solution state.

Interestingly, **1** and **2** showed strong fluorescence in the solid state whereas **3** showed weak but enhanced fluorescence compare to solution state (Fig. 1a). This phenomenon suggests the aggregation enhanced emissive (AEE) behaviour of these compounds.[4-7] Further, the AEE phenomenon was confirmed by slow evaporation of **1** and **2** on a filter paper that exhibited formation of orange-red emitting solids with slow evaporation of CH_3CN solvent (Fig. 1b). **1** showed broad fluorescence between 545 nm to 590 nm with λ_{max} at 563 nm. **2** and **3** showed slightly red shifted fluorescence λ_{max} at 576 nm. It is noted that the fluorescence spectra of **3** was comparatively

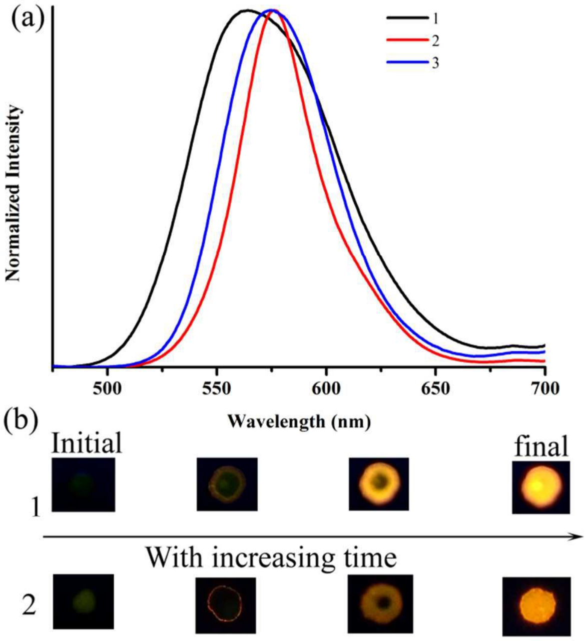


Fig. 1. (a) Fluorescence spectra of **1**-**3** and (b) AEE behaviour of **1** and **2** in CH$_3$CN drops (λ_{exc} = 370 nm (spectra), 365 nm (digital images)).

broad than **2** but sharper than **1**. Absolute quantum yield measurement also confirmed strong fluorescence of **1** (16.8 %) and 2 (8.4 %). **3** showed very weak fluorescence (1.6 %).

TPA based donor-acceptor molecules are known to exhibit mechanofluorochromism.[13,14] In contrast, all three compounds did not show any fluorescence switching or intensity modulation upon strong grounding of the solids. However, compound **1** and **2** exhibited rare self-reversible temperature induced fluorescence switching (Fig. 2a). **1** showed broad fluorescence with a λ_{max} at 563 nm and solids exhibited orange fluorescence. Interestingly, orange fluorescence of **1** was converted to yellow fluorescent solids with increasing heat (Fig. 2b). The yellow fluorescence was converted to orange upon cooling. Fluorescence spectra of **1** showed only small blue shift in the λ_{max} (560 nm) and clear reduction of broadening. **2** showed quenching of fluorescence with increase of heating and self-recovered the fluorescence upon cooling. As observed with **1**, fluorescence spectra of **2** also exhibited only slight change after heating. In contrast to the spectra, both **1** and **2** showed visible color change of solids (orange to yellow (**1**) and orange to non-fluorescent (**2**)) in the solids upon heating and cooling. This could be due to the change of temperature in the sample before performing the spectral measurement. But the digital images of solids were taken while samples were on the hot surface. Heating and cooling cycle measurements demonstrate clear fluorescence change for both **1** and **2** up to five cycles (Fig. S2). The excitation of spectra of **1** and **2** at room temperature and hot condition also exhibited small change (Fig. S3). In contrast, **3** did not show either fluorescent switching or fluorescence quenching upon heating.

To get the insights on the solid state fluorescence change, single crystals of **1**-**3** were attempted to grow from different solvents (ethyl acetate, toluene, CH$_3$Cl, CH$_2$Cl$_2$, CH$_3$CN, CH$_3$OH, DMF and DMSO). We were able to grow quality single crystals of **1** from ethyl acetate and DCM-diethyl ether, **2** from toluene only and **3** from DMSO. The other solvents did not produce suitable single crystals for structural analysis. The single crystals of **1** obtained from ethyl acetate and DCM-diethyl ether showed a similar structure with the reported literature.[15] Triphenylamine in all compounds displayed propeller conformation (Fig. 3, Table 1). Interestingly, both the CN groups of acceptor in **1** displayed *cis* conformation whereas **2** and **3**, in which methoxy donor attached at different position of phenyl in TPA, exhibited *trans* conformation (Fig. 3a). TPA phenyl groups attached to phenylenediacetonitrile adopted twisted conformation (Fig. 3b, torsion angle ($\tau_{1\ (C1\text{-}C2\text{-}C3\text{-}C4)}$) = 24.90° and $\tau_{2\ (C5\text{-}C6\text{-}C7\text{-}C8)}$ = -21.38°). **2**, methoxy (OCH$_3$) group attached to *ortho* position of TPA, displayed highly twisted conformation on one end and coplanar conformation on the other end of the phenylenediacetonitrile (τ_1 = 33.06° and τ_2 = 1.90°). In contrast, **3** showed coplanar conformation on both sides of the TPA phenyl groups (Fig. 3c), one side of the phenyl twisted up (τ_1 = 16.17°) and other side of the phenyl twisted down (τ_2 = 16.17°).

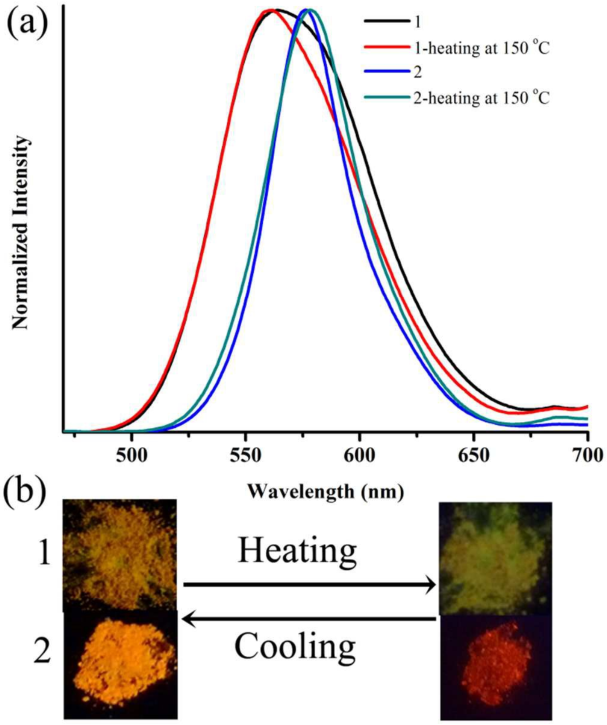


Fig. 2. Thermofluorochromism of **1** and **2** (a) fluorescence spectra and (b) digital images (λ_{exc} = 370 nm (spectra), 365 nm (digital images)).

The twisted molecular conformation prevented any close packing of molecules in the crystal lattice. **1** showed only C-N…π intermolecular interaction (3.240 Å) that leads to the

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Table 1. Crystallographic data of **2** and **3**.

Compound	**2** (1570578)	**3** (1570577)
chemical formula	$C_{107}H_{84}N_8O_4$	$C_{54}H_{50}N_4O_4S_2$
formula mass	1545.82	883.10
crystal system	monoclinic	Triclinic
space group	P21/c	P-1
a (Å)	9.7430(19)	6.9670(14)
b (Å)	8.5910(17)	10.922(2)
c (Å)	48.988(10)	15.965(3)
α, β, γ (deg)	90, 93.39(3), 90	89.68(3), 87.94(3), 78.03(3)
unit cell volume($Å^3$)	4093.2(14)	1187.6(4)
temp (K)	100	243
Z	2	1
abs coeff (μ/mm^{-1})	0.060	0.111
no.reflns measured	38285	12323
no. independent reflns	10950	6197
R_{int}	0.0425	0.0373
final R_1 values ($I > 2\sigma(I)$)	0.0482	0.0550
final $R_2(F^2)$ values ($I > 2\sigma(I)$)	0.1334	0.1352
final R_1 values (all data)	0.0602	0.1209
final $R_2(F^2)$ values (all data)	0.1415	0.1586
GOF on F^2	1.073	0.854

formation of dimer with slipped face to face arrangement (Fig. 4a). The assembly of next dimer produced a ladder like structure in the crystal lattice. The molecular packing suggested well separation of molecules along *a* and *c* axis (Fig. 4b). **2** showed dimer formation through multiple weak intermolecular interactions, C-H…π ((3.321 Å), π…π (between cyano carbon and phenyl (3.370 Å) and C-H…O hydrogen bonding between methyl C-H and methoxy oxygen (3.362 Å). These dimers are further linked along *b* axis through cyano-phenyl π…π interactions (Fig. 5a). The molecular arrangement along *b* axis showed ABAB pattern (Fig. S4). The molecular packing of **2** further revealed the inclusion of toluene solvent molecule in the crystal lattice (Fig. 5b). The toluene was stabilized in the crystal lattice by hydrogen bonding between cyano nitrogen and phenyl hydrogen, methoxy oxygen and methyl hydrogen of methyl and C-H…π interactions (Fig. S5). **3** also exhibited dimer arrangement in the crystal lattice without any intermolecular interactions (Fig. 6a). It included DMSO solvent molecules in the crystal lattice. These DMSO molecules forms intermolecular hydrogen bonding with **3** and connect the molecules along *a* axis (Fig. 6b). PXRD patterns of **1-3** perfectly matched with the simulated pattern using single crystal structure that confirmed the phase purity of the sample (Fig. S6).

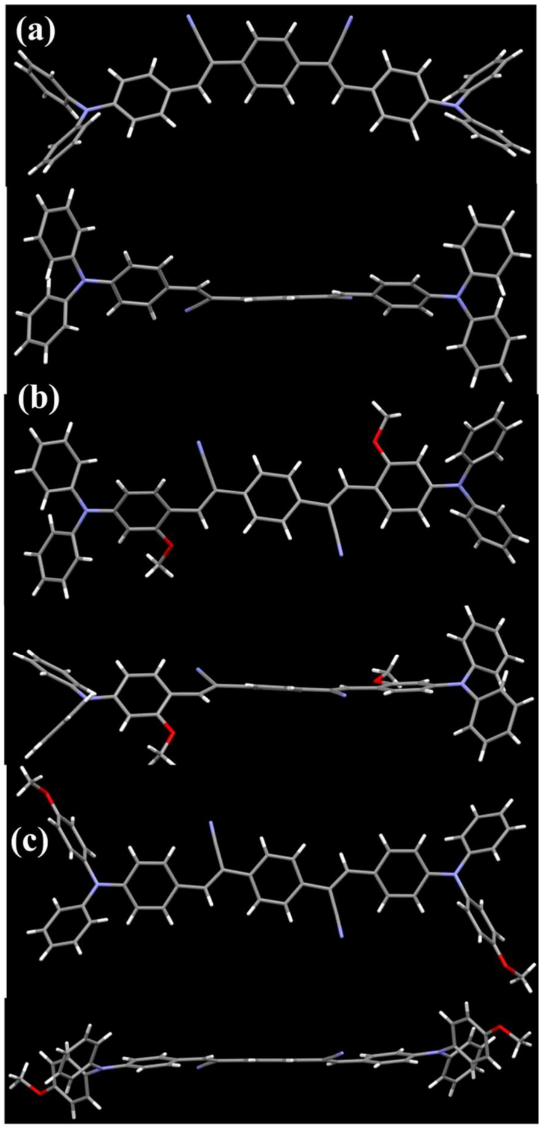

Fig.3. Molecular conformation of (a) **1**, (b) **2** and (c) **3** in the crystal lattice. C (grey), N (blue), O (red), H (white).

The different weak intermolecular interactions observed in the crystal lattice of **1-3** rigidified the fluorophore in the solid state and lead to the AEE.[4-7] **1-3** solid state fluorescence intensity differences and thermofluorochromism could be explained based on the molecular conformation in the crystal structure. Highly twisted molecular conformation of **1** at both ends lead to the strong enhancement of fluorescence (16.8 %) whereas one end twisted conformation in **2** exhibited moderate fluorescence (8.4 %) and coplanar conformation in **3** resulted in weak fluorescence (1.6 %). The inclusion of DMSO solvent in the crystal lattice of **3** might have also contributed for weak fluorescence. The slight red shift of fluorescence λ_{max} for **2** and **3** compared to **1** might be due to the coplanar

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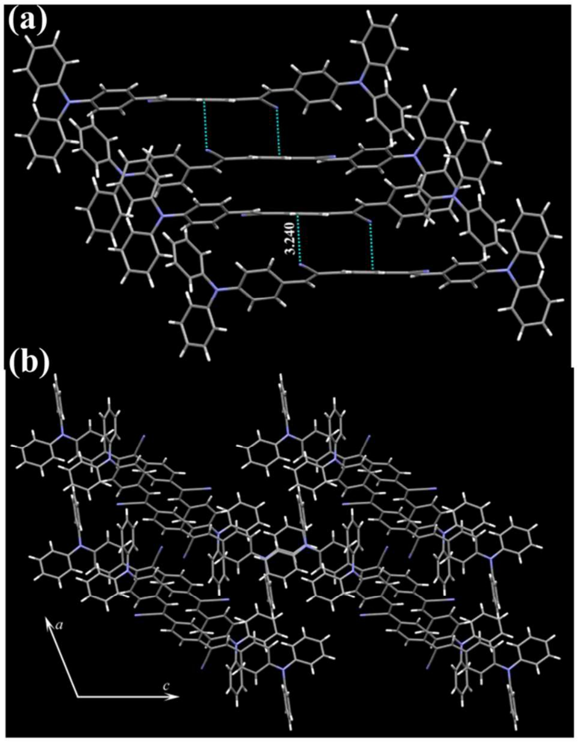

Fig. 4. (a) Ladder like arrangement and (b) molecular packing in the crystal lattice of **1**. C (grey), N (blue), O (red), H (white). C-N…π interactions (broken line) distances are marked in Å.

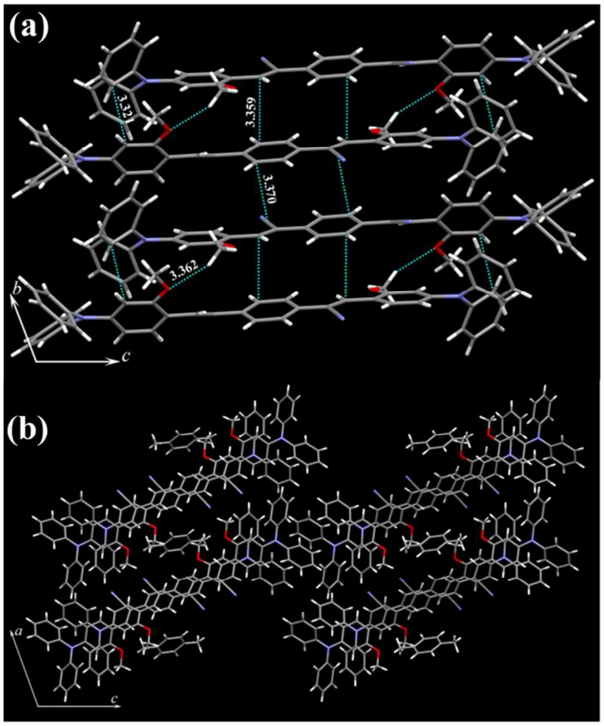

Fig. 5. (a) Different intermolecular interactions and (b) molecular packing in the crystal lattice of **2**. C (grey), N (blue), O (red), H (white). H-bonding, C-H…π and π…π interactions (broken line) distances are marked in Å.

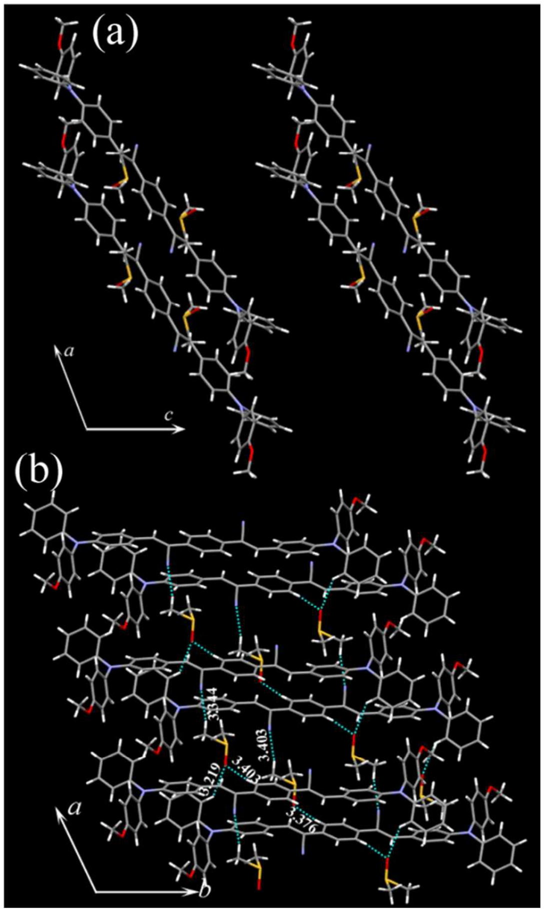

Fig. 6. (a) Dimer structure and (b) H-bonding interactions in the crystal lattice of **3**. C (grey), N (blue), O (red), S (yellow) H (white). H-bonding interactions (broken line) distances are marked in Å.

arrangement of TPA phenyl groups. Further, to get the insight of the molecular conformation and substitution on the HOMO-LUMO energy level change, DFT calculations were performed using single crystal structure of **1, 2** and **3** (Fig. 7, Table S1)). The isodensity surface plot (isodensity contour = 0.02) of the highest occupied molecular orbitals (HOMOs) of **1** indicated that electron density was predominantly localized on the TPA and slightly over the dicyanophenyl acceptor. The electron density in the lowest occupied molecular orbitals (LUMOs) was mainly localized on the dicyanophenyl acceptor (Fig. 7). In contrast, HOMO of **2** was mainly localized on the OCH_3 substituted phenyl and dicyanophenyl acceptor and LUMO was mainly localized on the dicyanophenyl acceptor and coplanar phenyl group. In **3**, HOMO was localized on the dicyanophenyl acceptor and adjacent phenyl groups and LUMO was occupied on the acceptor and slightly on the adjacent phenyl groups with small change of electron density. Comparison of electron density change indicates that **1** and **2** showed higher electron density shift in the HOMO-LUMO compared to **3**. The calculated HOMO level of **1** is -5.336 eV and LUMO level is -2.498 eV. HOMO and LUMO level of **2** and **3** are -5.173 (2), -5.172 (3) and -2.302 (2) and -2.340 eV, respectively. The calculated band gap of **1**, **2** and **3** is 2.838, 2.871 and 2.832 eV,

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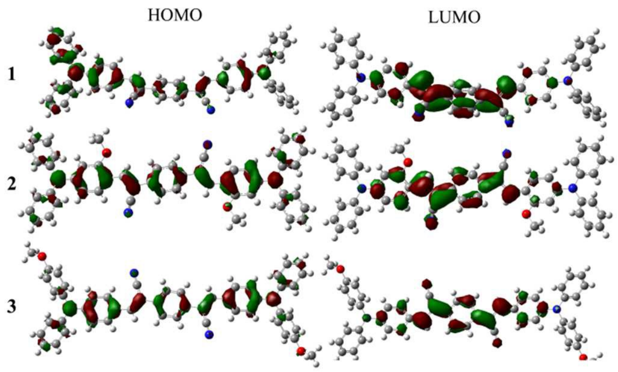

Fig. 7. Molecular orbital plots of the HOMOs and LUMOs of **1**, **2** and **3**.

respectively. Thus the computational studies showed molecular conformation dependent optical band gap and support the solid state fluorescence change of **1**-**3**. The twisted molecular conformation of **1** and **2** could be attributed for their thermofluorochromism. At high temperature, the twisted conformation of **1** and **2** might be adopting more planar conformation that might be responsible for switching of fluorescence. **3** that displayed symmetrical coplanar conformation might not undergo any conformational change with heat. DSC studies of both 1 and 2 exhibited clear phase transition at 116 and 95 °C, respectively (Fig. S7). DSC of **2** also exhibited another phase transition at 121°C that might be due to the loss of toluene from the crystal lattice. PXRD studies confirmed that both 1 and 2 did not undergo any structural change after heating (Fig. S8).

Conclusion

In conclusion, we have synthesized TPA based D-A-D AEE compounds and demonstrated substitution dependent molecular conformation, packing and rare self-reversible thermofluorochromism in the solid state. Highly twisted molecular conformation and same side orientation of cyano group was observed with **1** whereas **2** exhibited opposite side orientation of cyano group and one twisted and one coplanar conformation. In contrast, **3** revealed symmetrical coplanar conformation with opposite side orientation of cyano groups in the crystal lattice. Interestingly, **1** and **2** showed self-reversible fluorescence switching with heating and cooling but **3** did not show any change of fluorescence. PXRD studies confirmed that there is no structural change in **1** and **2** after heating. Computational studies provided insight on the energy level modulation upon altering the molecular conformation by changing the substituent. Thus the present studies indicate that molecule with twisted molecular conformation without strong intermolecular interactions in the crystal lattice could be interesting for generating self-reversible thermofluorochromism.

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Self-reversible thermofluorochromism of D-A-D triphenylamine derivatives and effect of molecular conformation and packing

Triphenylamine based donor-acceptor-donor compounds exhibited conformation and packing dependent solid state fluorescence and self-reversible thermofluorochromism.