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Variation in solvato-, AIE- and mechano-fluorochromic behavior for furanyl and thiophenyl-substituted anthranyl π-conjugates: role of tiny flanking donor groups

Madhuparna Chakraborty and Manab Chakravarty*

Only a few reports on thiophene or furan-linked typical tetraphenylethene or difluoroboron systems are known as aggregation-induced emission-active fluorogens (AIEgens) with a substantial difference in solvato and mechano-fluorochromic (MFC) features. With a pressing demand on finding a smart strategy to offer MFC-active materials, we herein report unsymmetrically substituted anthracene-vinyl-phenothiazine π-conjugates (TAPTZ and FAPTZ) linked with furan or thiophene as a tiny flanking donor group. Both the compounds are easily synthesized using an economic path by avoiding metal catalysts and harsh reaction conditions. In solvatofluorochromic studies, the varying polarity of solvents from hexane to acetonitrile, bathochromic shifts of 118 nm (3082 cm⁻¹ Stokes shift) for TAPTZ and 112 nm (2840 cm⁻¹ Stokes shift) for FAPTZ are noticed. Such electron-rich but conformationally twisted molecules create a twisted intramolecular charge transfer (TICT) state responsible for the solvatofluorochromic feature. A relatively more significant change in the excited state dipole moment for TAPTZ causes the difference. Both of these molecules exhibit blue-shifted AIE features (faint orange to intense yellow), where TAPTZ has appeared to be relatively better AIEgen with a 65 nm average particle size. Interestingly, FAPTZ has emerged as a stronger emitter than TAPTZ in the solid state. Grinding in a mortar and pestle or by quick pressing (in an infrared pellet maker: 20 MPa), TAPTZ and FAPTZ display reversible MFC features with a 15 nm and 22 nm redshift, respectively. Single crystal study discloses the difference in the molecular twisting and packing in the solid-state for these analogs. A relatively large number of intramolecular interactions (dominated by S···S and C···S) make the crystal packing stronger for TAPTZ and make such difference in the sensitivity. Thus, we find a decent impact of the flanking donor groups thiophene/furan in terms of the emission behavior under different environments. The observed fact is further supported by powder X-ray diffraction and lifetime measurement studies. Also, the intermolecular interactions are quantified by Hirshfeld-surface analyses to validate the empirical facts further. Finally, FAPTZ is documented as a favorable platform for rewritable optical-recording/security-based applications.

Introduction

Urge on the design and synthesis of stimuli-responsive small molecules offers ample demand in the academics and research on security display, sensor, and memory-based applications. Amongst them, mechano-fluorochromic properties (MFC) have gained substantial attention due to the generation of admirable multiple colorations just by grinding or rubbing the compound without performing cumbersome synthetic modifications. There are multiple small organic molecular systems discovered with stimuli-responsive properties. One of the essential needs for a MFC-active solid-state fluorophores is to attain twisted conformation offering numerous intermolecular interactions. In such a context, small heterocycles like furan and thiophene exhibited a wide difference in the MFC and electronic properties. Nevertheless, thiophene and furan are generally considered weak electron-donors and are explored commonly in the donor-π-acceptor like systems. Mostly, thiophene has been established as a promising donor in semiconductor/transistor-based applications. In contrast, the related investigations with furan are inadequate. However, recent studies revealed that the furan is also a favorable building block for generating semiconductors and better charge carrier mobility. The greater extent of biodegradation, smaller size, high planarity makes the choice of furan more favorable despite having relatively inferior aromaticity and polarizability features compared to thiophene. In particular, a household AIE-framework tetraphenylethene (TPE)-linked furan TPE-F (Figure 1) was found to be superior in exhibiting chromic behavior than that of analogous TPE-T under external stimuli. Additionally, the furan/thiophene-linked β-diketo building blocks were incorporated with the TPE system (TDK/FDK) and identified a variation in solvatofluorochromism, AIEE-behaviour, and (non)reversible MFC properties. Apart from the TPE system, the other difluoroboron β-diketonate was attached to thiophene or furan (TBD and FBD) and recognized as reversible stimuli-responsive materials with subtle
differences between thiophene and furan analogs. The extent of molecular planarity, intermolecular interactions, and the crystal packing density was found to play the role behind the variation in the emission color.\textsuperscript{11-13}

![Figure 1: Known furan/thiophene substituted MFC-active compounds.](image)

Thiophene or furan resides almost in the molecular plane with a slight twisting angle in all the reports above. However, the impact in emission color variation from the furan/thiophene analogs upon solvent or external pressure stimuli looks highly promising. Nevertheless, few molecules are only reported on the comparative solid-state and solvatofluorochromic features between furan and thiophene-conjugated analogs. In our current research on unsymmetrically substituted anthracene-based π-conjugated fluorophores, we noticed that a highly planar anthracene system could avoid disc-like molecular packing in the presence of flanking aryl/heteroaryl mainly due to the conformational variation (twisted at different torsion angles) and resulting in the formation of AIEgens.\textsuperscript{14} The van der Waals interaction between the anthracenyl peripheral H’s with these groups creates such twisted stable conformation. In such a system, thiophene analogs appeared to be better AIEgens than furan.\textsuperscript{15} However, solvato- and mechano-fluorochromic features were not promising for those molecules. Based on our interest in creating multi-stimuli-responsive materials,\textsuperscript{16} we herein focus on introducing anthracene-π-phenothiazine conjugates linked with furan or thiophene as flanking donor group (Figure 2).

![Figure 2: Thiophene/furan-flanked anthracene-π-phenothiazine molecules](image)

The electron-rich and bulky phenothiazine unit is chosen due to its capability in forming weak C-H...S/S...π-C-H...π-π-conjugated interactions and the nonplanar structure of such a core would favor exhibiting AIE-features by avoiding the cofacial π...π stacking. Moreover, highly electron-rich phenothiazine can create a variation in the electronic distribution within the system where anthracenyl part would be relatively electron-poor. Thus, the system would display the solvatofluorochromic properties. The impact of flaking small heterocycle into this system would draw special attention. AIEgens can emit in the solid-state, and the possible conformational changes under mechanical force can offer MFC-feature. We find dissimilarity in terms of the emission behavior in the solution and aggregated and solid-state due to such a tiny difference in molecular structure (thiophene/furan). Thus, the variation in electronic feature, size factor and aromaticity between thiophene and furan can govern such a subtle disparity in stimuli-responsive emission feature for these unsymmetrically substituted π-conjugates. Besides, the difference in intermolecular interactions also has created a contrast in the solid-state emission features. All the observed properties are deliberated with the help of molecular structure analyses, powder X-ray diffractions (PXRD), and fluorescence lifetime studies.

**Results and discussion**

**Synthesis and characterization**

The established synthetic procedure finds a broad scope to tune the substitution effect; the planned molecules FAPTZ (furan-flanked) and TAPTZ (thiophene-flanked) are conveniently synthesized in a decent yield by simple, inexpensive, and efficient Horner-Wadsworth-Emmons (HWE) reactions at room temperature (i.e., energetically economic) from easily accessible phosphonates (Scheme S1) and phenothiazine-carbaldehyde (Scheme 1).

![Scheme 1 Synthesis of FAPTZ and TAPTZ](image)

An expensive metal/ligand combination with high-temperature requirement is escaped to access such molecules where thiophene/furan units are introduced via Friedel-Crafts arylation reaction.\textsuperscript{17} The reaction can be scaled up on a gm scale, indicating easy access to these materials for real-world applications. These compounds are soluble in most organic polar/nonpolar solvents and well-characterized by IR, NMR (\textsuperscript{1}H/\textsuperscript{13}C), and mass-spectroscopic studies. Finally, the molecules are crystallized at room-temperature crystallization method, and the molecular structure with (E)-configuration is explicitly established by single-crystal X-ray diffraction studies (SCXRD, details are discussed later). The phenothiazine unit’s presence raises the thermal stability of the π-conjugates that shows the stability up to 400 °C and beyond as confirmed by thermogravimetric analysis (TGA, Figure S1).

**Solvatofluorochromic studies**

Primarily, the photophysical behaviors in the solution state were examined for these π-conjugates by changing the nature of the solvent with different polarities. A sharp maximum absorption at \(\lambda_{\text{abs}}\approx 405-410\) nm was detected for both the analogs in absorption spectroscopy (Figure S2: For all the absorption and emission spectra) due to π-π* transition, and there was no impressive shift observed by changing the polarity...
of the solvent, indicating an unaffected ground state. A slightly higher \( \lambda_{\text{abs}} \) than that of thiophene. The emission spectra reveal a cleaner discernible coloration for TAPTZ than FAPTZ in most of the solvents of different polarities (Figure 3). The emission at relatively longer \( \lambda_{\text{max}} \) for furan (FAPTZ) has further supported a more planar molecular structure for furan analog. By varying \( E_r(30) \) (a measure of microscopic solvent polarity) of different solvents, a promising positive solvatophoric effect (redshift) is noticed with both the compounds. The solvatophoric range between hexane (nonpolar) and MeCN (polar) is marginally better with 118 nm redshift (3082 cm\(^{-1}\)) for TAPTZ than FAPTZ displaying 112 nm redshift (2840 cm\(^{-1}\)) Stokes shift. All the photophysical parameters, including the solvatophoric shifts for both the compounds, are listed in Table 1.

Figure 3: Normalized emission spectra of (a) TAPTZ (b) FAPTZ, in a different solvent. Concentration of the probe: 10 \( \mu \text{M} \), \( \lambda_{\text{ex}} = 405 \text{ nm} \). The image is taken under 365 nm UV light.

Table 1: Photophysical parameters of the probes at different solvents

| Solvent  | Abs \( \lambda_{\text{abs}} \) (nm) | Emi \( \lambda_{\text{max}} \) (nm) | Stokes Shift | Quantum Yield (\%) | Dipole Moment | \( E_r(30) \) |
|----------|-----------------|-----------------|--------------|-------------------|--------------|-------------|
| Hexane   | 402/404         | 529/538         | 5972/6165    | 14/13             | 0.08         | 31.0        |
| CCl4     | 409/413         | 541/553         | 5966/613     | 8.8/13            | 0            | 32.5        |
| Toluene  | 406/421         | 560/566         | 6774/6604    | 10/10             | 0.43         | 33.9        |
| 1,4-Dioxane | 407/412       | 571/579         | 7057/7001    | 8.9/7.2           | 1.3          | 36.0        |
| THF      | 407/413         | 602/605         | 7959/7684    | 5.7/19            | 1.75         | 37.4        |
| CHCl3    | 408/412         | 590/595         | 7561/7465    | 5.7/22            | 1.15         | 39.1        |
| CH2Cl2   | 408/412         | 615/618         | 8190/8091    | 3.2/7.5           | 1.60         | 40.7        |
| Acetonitrile | 408/410      | 647/650         | 9054/9005    | 0.32/6.4          | 3.45         | 45.6        |

\( \Delta \lambda = \lambda_{\text{abs}} - \lambda_{\text{em}} \) (cm\(^{-1}\)): The wavenumber difference between absorbance and fluorescence. Relative quantum yields are measured using quinine sulfate as standard (See experimental section).

The overall difference of 242 cm\(^{-1}\) between TAPTZ and FAPTZ in the Stokes shift (between hexane and MeCN) and the considerable color variation are noteworthy (Figure 3 and Table 1). The redshift may be attributed to the presence of TICT (twisted intramolecular charge transfer state), where the phenothiazine unit can be noted as an electron donor and anthracene as an electron acceptor. The role of significant twisting arises from the flanking thiophene and furan groups. The electronic structure is confirmed by performing a DFT study (Density Functional Theory) on these molecules. Ground-state optimization using DFT at CAMB3LYP-6-31G(d,p) level identifies that the electron clouds in the highest occupied molecular orbital (HOMO) level is majorly located on phenothiazine core (owing to the presence of two heteroatoms), while the lowest unoccupied molecular orbital (LUMO) level is predominantly placed over the anthracene ring with a slight contribution by flanking and phenothiazine groups (Figure 4). Such electronic distribution can also support the ICT feature in the molecules. It is also consistent with the observed solvatofluorochromic properties.

Moreover, a largely twisted conformational structure can create a more polar and energetically stabilized TICT state in the polar solvent, resulting in poor quantum yield with a high redshift.\(^{18b}\) The plot of \( E_r(30) \) vs. Stokes shift and emission \( \lambda_{\text{max}} \) (Figures S4-S5) also supports the possible formation of the TICT state. The TICT state is typically more convincing in the typical D-A system, but the generation of TICT state from such electron-rich and conformationally twisted systems is possible where phenothiazine acts as the donor and anthracene as an acceptor.\(^{19}\) Moreover, anthracene and phenothiazine cores are coupled together through a trans-vinylidene spacer. Twisted conformation arises from the interactions between peripheral H-atoms of vinylidene and anthracenyl systems. However, the fluorescence (FL) intensity enhancement upon increasing the viscosity of the solvent medium (glycerol in methanol, Fig S6) indicates a substantial twisting in the
molecular structures with such bulky rotors and creates the formation of a TICT state. The TICT state formation can also be favored due to the reversible first oxidation potential of phenothiazine upon photoexcitation and subsequent intramolecular rotation. The Lippert-Mataga plot [Stokes shift against orientation polarizability, (Δf)] reveals a quick rise in the Stokes shift with a polar solvent. It also confirms the enhanced dipole moment in the excited state. Although the conventional Lippert-Mataga equation might be inappropriate to apply for such molecular shape; we have examined the Lippert-Mataga plot [Figure S7, Table S1] that reveals a quick linear rise in the Stokes shift with a polar solvent. It also confirms the enhanced excited state dipole moments, showing 14.37 D for TAPTZ and 13.91 for FAPTZ. This marginal change in dipole moment for FAPTZ validates a slightly better redshift for the thiophene analog.

### AIE-properties

The AIE properties are the most exciting photophysical behavior that has widened the application scope of the fluorophores in the solid/aggregated state and gained attention in the last two decades. Acetonitrile was preferred as a good and water-miscible solvent for these studies due to the weakest emission. The AIE properties were examined by measuring absorption (Figure S8) and emission spectra (Figure 5) for each compound in 10 µM acetonitrile solution upon slow addition of water fraction [a bad solvent (v/v%)]. The reduction of FL intensity was observed initially due to the polarity effect till f_w=40%-50% (Figures 5b and 5d) for both cases. There was a sudden upturn in the FL intensity for TAPTZ from f_w = 40%, and the intensity was maximum at f_w = 90% with a 73 nm blue-shift (yellow emission at λ_max 574 nm). For FAPTZ, the FL enhancement started at f_w = 50% and reached maximum till f_w = 70% with 81 nm blue-shift (yellow emission at λ_max 569 nm). Thus, both these compounds exhibit similar AEE-effect (Aggregation-enhanced emission) in terms of the emission color but more pronounced for TAPTZ (14 times enhancement) in comparison to FAPTZ (only five times enhancement). The ups and down in the FL Intensity at higher f_w for FAPTZ was observed earlier due to the formation of nanoparticle suspension with both crystalline and amorphous characters that control the emission intensity in the solution.

### MFC-studies

Initially, the solid-state photophysical properties are investigated before and after grinding both the pristine samples to examine the change in emission color. The solid-state UV-Vis spectrum displays a broad and substantial absorption in the region of 440 nm, mainly due to π-π* transition for both the pristine samples. Upon grinding in a mortar and pestle or applying pressure (20 MPa) using an IR-pellet maker, the change in absorption spectrum is slightly blue-shifted (~17 nm) for TAPTZ, but almost no difference for FAPTZ (Figure 6), indicating almost similar behaviour in the ground state. However, the solid-state FL spectrum for TAPTZ is noticeably redshifted from 550 nm to 565 nm (15 nm) after grinding. The absolute quantum yield (ϕ_i, %) for the pristine sample is 9.1, and that was weakened to 6.02 after grinding. Thus, one can visualize the sharp FL switching from light green to yellow emitting solid (15 nm contrast) through the naked eye under a 365 nm UV-light after grinding the solid. On fumigation of the ground sample with hexane, the original green color is returned. Notably, thermal energy could not bring back the actual green color. On the other hand, the furan analog FAPTZ emitted a relatively brighter green light (emission λ_max = 537 nm) with ϕ_i (%) 24 and switched to 559 nm upon grinding.
These two molecules in the solid-state (Figure 7).

Additionally, the excited state’s fluorescence lifetime (ns) was determined for solid TAPTZ and FAPTZ in both the pristine and ground states (Figure S12 and Table S2). All the related parameters are stated in Table 2. More Φf (%) for FAPTZ can be elucidated with a relatively better ratio Kf/Knr. [radiative rate constant (Kf) and non-radiative rate constant (Knr)]. Grinding the compounds resulted in a lessening in the quantum yield and could be deciphered with lower Kf/Knr values (Table 2).

Table 2: Solid-state photophysical parameters for compounds with absorption/emission wavelength λabs/λem in nm, absolute Φf in % (error: ± 2%), an average lifetime (τ) and the ratio of radiative rate constant (Kf) and non-radiative rate constant (Knr). Kf = Φf/τ; Knr = (1-Φf)/τ.

| Samples | States   | λmax abs (nm) | λmax em (nm) | Φf (%) | τ(ns) | Kf/Knr |
|---------|----------|---------------|--------------|--------|-------|--------|
| TAPTZ   | Pristine | 440           | 550          | 9.1    | 0.65  | 0.100  |
|         | Ground   | 423           | 565          | 6.2    | 1.16  | 0.060  |
| FAPTZ   | Pristine | 436           | 537          | 24.0   | 0.57  | 0.323  |
|         | Ground   | 438           | 559          | 10.0   | 0.54  | 0.121  |

SCXRD studies

It is essential to examine the single-crystal X-ray structures for these n-conjugates to meet a molecular-level understanding and investigate the cause for the FL-switching upon grinding. Typically, such FL Switching is regulated by the change in the supramolecular assembly. The crystal structures were easily determined with suitably grown single crystals, obtained from 30% EtOAc in hexane through room-temperature slow evaporation technique. Both the compounds TAPTZ and FAPTZ crystallized in a triclinic system with a P-1 space group [See Table S3 (ESI) for all the crystallographic parameters]. Predominantly, the molecular structures determined from SCXRD have presented the fundamental difference between these two molecules in the solid-state (Figure 7).

Figure 6: Pristine and Ground sample of TAPTZ and FAPTZ along with the corresponding (reversible) emission spectra [λex = 420 nm] The images are taken under a 365nm UV-light.

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To gain a deeper insight into the above slight variation in MFC-feature, powder X-ray diffraction (PXRD) studies are performed. Both these analogs demonstrate many sharp and intense diffraction signals in the pristine state (Figure 9), specifying a well-ordered crystalline structure. However, TAPTZ has appeared to be relatively more crystalline than FAPTZ as deciphered before. Some of the diffraction planes are designated based on the simulated diffraction patterns for both the compounds, and the diffractions are consistent with the experimentally determined signals. The reversible MFC behavior for both the compounds is supported by the diffractogram for pristine, ground, and fumed samples. The crystal to amorphous state transformation is noticed after grinding because almost no diffraction peaks at the same 2θ are observed (Figure 9). The original intense diffractions recur upon fuming with hexane. It depicts a considerable decrease in the crystallinity (transform towards the amorphous phase) after grinding the solid and restoring the crystallinity after fuming and fuming with hexane assists in rearranging the molecules to reach the original crystalline from the amorphous state. Thus, changes in the PXRD pattern support the difference in displaying MFC features for such a phase transition in these molecules.

Table 3: intermolecular interactions (Å) for both the π-conjugates.

| Compounds     | C···H   | O···H | S···S | S···H | C···S | H···H |
|---------------|--------|------|------|------|------|------|
| TAPTZ (10 interac. | 2.887, | 2.885 | 2.861 | 2.829 | 2.803, | 2.816 |
|               | 2.829, |      |      |      |      |      |
| FAPTZ (8 interac. | 2.833, | 2.818 | 2.898 | 2.747 | 2.865, | 2.816 |
|               | 2.816, |      |      |      |      |      |

The TAPTZ molecules are oriented so that PTZ-PTZ units are closer, whereas PTZ-furan has appeared to be joined for FAPTZ in the crystal lattice (Figure 8). The C···H interactions for both the compounds enforce more flexibility and are more helpful to exhibit MFC behavior. Nevertheless, a relatively more number of interactions for TAPTZ achieve little higher rigidity and higher crystal lattice energy compared to TAPTZ, and thus becomes less sensitive. Notably, both these compounds display MFC-feature under grinding/pressure by improving the degree of planarization in molecular conformation that would elucidate the observed redshift. The penetration of hexane vapor into the distorted crystal packing will permit molecules to develop flexibility and rearrange the molecular conformation to return the pristine crystal packing to induce the authentic emission. This repeatable fluorescence switching using FAPTZ is almost similar (change of ±10 nm wavelength) even after multiple grinding/fuming processes. Thus, the material is supportive of numerous cycles of reversible color change upon solvent exposure.

PXRD analysis

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Figure 8 Crystal packing for (a) TAPTZ and (b) FAPTZ showing a few intermolecular interactions (d/Å).

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The crystal packing showed the contribution of C···H interactions inside the crystal lattice. The quantitative analyses of intermolecular interactions are calculated through the Hirshfeld surface generations for pristine, ground, and fumed state. The crystal packing showed the contribution of C···H interactions inside the crystal lattice. The quantitative analyses of intermolecular interactions are calculated through the Hirshfeld surface generations (Figure S14). A significant amount of C···H type interactions (33.3%) is acting on FAPTZ crystal compared to TAPTZ (30.5%). Notably, there are 4.5% C···C interactions for TAPTZ, whereas FAPTZ shows 3% of such interactions. The higher ratios of C···C interactions for FAPTZ designate good MFC behavior in comparison to TAPTZ. This Hirshfeld analysis is very well aligned with our experimentally observed features and the crystal packing analysis. Thus, the difference in the intermolecular interactions between these two molecules can elucidate the slight difference in MFC-feature for these two analogs.

Application as optical rewritable recorder

Further, such MFC-active materials are also recognised as a platform for rewritable optical recording. Such FL-switching is very much appropriate for real-world applications. An economical filter paper-based rewritable optical recorder is created by dispersing TAPTZ on the filter paper. Thus, the yellow-emitting surface becomes ready for the writing. The letters are suitably printed on this yellow-emitting surface by pressing with a metal spatula. The letters emit orange and are visible in bare eyes under 365 nm UV-torch (Figure 10). The orange emitting part can be further returned into a yellow-emitting surface by fuming with hexane. Thus, this TAPTZ-coated filter paper is documented as encouraging MFC material for repetitive usage in optical recording.
Materials Advances Accepted Manuscript

Steady-State Absorption and Fluorescence Measurements:

Methods and measurements

Steady-State Absorption and Fluorescence Measurements.: The solution-state absorption spectra were taken on a UV-vis-NIR spectrophotometer (Hitachi F7000, Japan), and solid-state absorption spectra were recorded on a JASCO-500 spectrophotometer. The solid-state emission spectra were recorded using a fluorimeter (Fluorolog, HORIBA) and solution-state (FP-6300, Jasco) using 10 µM MeOH solution upon incremental addition of FAPTZ samples, i.e., step width 0.2, the scan rate of 2°/min from 5-45° (Cu, Kα radiation λ = 1.54 Å). The IR spectrums were taken using an FTIR spectrometer (FT/IR-4200, Jasco). Solid samples were mixed with KBr to find the spectra.

Time resolve measurement: Time-resolved fluorescence measurements were completed using a time-correlated single-photon counting (TCSPC) unit (Horiba Deltaflex). The pulse diode laser used was 403 nm with a setup target of 10000 counts. The solid powder was made a sandwich in between two quartz slides followed by keeping in a solid-sample holder. The instrument response function was measured before fluorecence lifetime measurements using an aluminum foil. All of the decay curves were fitted using the supplied EZ Time software. All measurements were done at room temperature (298 K). A magic angle (54.7°) configuration was used for all measurements. All fittings were done by keeping the χ² value nearer to 1.

Dynamic light scattering (DLS) measurement

The average particle size in the aggregated state was found using a Malvern particle size analyzer (zeta sizer nano-ZS), keeping a concentration of 10µM.

Thermogravimetric and differential scanning calorimetry analysis

The TGA and DSC thermograms were recorded using Themys One®, Setaram instrument keeping the temperature range 30 °C – 650 °C with 10 °C/min under N₂ atmosphere.

Single crystal X-ray measurement

All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation (λ = 1.54184 Å). The data were collected at a temperature of −173 ± 1 °C to a maximum 20 value of 149.8°. Data were collected and processed using CrysAlisPro (Rigaku Oxford Diffraction). The linear absorption correction coefficient, μ, for Cu-Kα radiation is 18.391 cm⁻¹. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.227 to 0.593. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR2011) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the Olex 2 crystallographic software package except for refinement, which was performed using SHELXL Version 2014/7.
**Density functional theory**

The DFT studies were performed on these molecules using CAM-B3LYP 6-31G(d,p) basis set. The HOMO and LUMO energies were calculated, and corresponding cubes were generated using Gaussian 09 package.

**Hirshfeld Surface Analyses**

Hirshfeld surface analysis and void space calculation is a quantitative tool to understand non-covalent interactions. We have generated Hirshfeld surfaces for TAPTZ and FAPTZ with an iso-value of 0.5 au. The surface is generated, and the interactions are shown in terms of $d_1$ and $d_2$. Where $d_1$ and $d_2$ are distances of an atom external or internal to the generated Hirshfeld surfaces, together, these pair ($d_1$ and $d_2$) generates a 2D fingerprint plot. The different colors on the fingerprint plot represent the frequency of occurrence of interaction.

A red spot represents the direct interaction between two atoms. Ultimately it gives a normalized contact distance ($d_{norm}$). The $d_{norm}$ values are mapped onto the Hirshfeld surface using a red, white, and blue color scheme; red, white, and blue regions correspond to the strong, medium, and weak interactions, respectively. All the Hirshfeld surfaces were generated using Crystal Explorer 3.1 software.

**Synthesis and characterizations**

(E)-pentyl-3-(2-(10-(furan-2-yl)anthracen-9-yl)vinyl)-4a,10a-dihydro-10H-phenothiazine TAPTZ: In a 50 mL round-bottomed flask, diethyl ((10-(thiophen-2-yl)anthracen-9-yl)methyl)phosphonate (0.50 g, 1.218 mmol) was dissolved in 30 ml of dry THF under argon atmosphere at room temperature. BuOK (0.410 g, 3.65 mmol) was added and stirred for 4–5 min. 10-pentyl-10H-phenothiazine-3-carbaldehyde (0.39 g, 1.34mmol) was carefully added to the solution. The reaction was allowed to stir for 12 h of reaction and the reaction was monitored by TLC. The resulting reaction mixture was quenched with water, extracted with ethyl acetate (20 mL x 3), dried over anhydrous sodium sulphate, and concentrated under a rotary evaporator. The compound TAPTZ was purified by column chromatography (100-200 mesh-sized silica gel) using 3% ethyl acetate in petroleum ether.

**FAPTZ:** Yield: 0.48 g, yield 70%, m.p - 165-167 °C. IR (ν cm⁻¹, in KBr): 3066, 2928, 2861, 1704, 1603, 1460, 1334, 1296, 1242, 1126, 1037.

H NMR (400 MHz, CDCl₃) $\delta$ 8.37 (dd, $J = 7.8, 1.3$ Hz, 2H), 7.87 – 7.76 (m, 3H), 7.60 (dd, $J = 5.2, 1.1$ Hz, 1H), 7.50 (d, $J = 2.0$ Hz, 1H), 7.39 – 7.42 (m, 5H), 7.30 (dd, $J = 5.2, 3.4$ Hz, 1H), 7.19 – 7.14 (m, 6H), 6.96 – 6.87 (m, 3H), 6.83 (d, $J = 16.5$ Hz, 1H), 3.92 – 3.86 (m, 2H), 1.92 – 1.80 (m, 2H), 1.49 – 1.31 (m, 4H), 0.92 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 144.9, 136.5, 131.7, 131.7, 129.5, 129.3, 127.5, 127.3, 127.2, 127.0, 126.7, 126.2, 126.0, 125.2, 125.6, 125.4, 125.2, 125.0, 123.1, 122.5, 115.4, 47.6, 29.2, 26.6, 22.4, 14.1 (some signals are merged together). HR-MS for C₃₂H₂₈N₇O₂ calc. 554.1976, found to be 554.1786 [M+H]^+; X-ray structure is done for this sample (CCDC Number: 2100036).

**Conclusions**

In conclusion, two new anthranyl n-conjugates TAPTZ and FAPTZ linked with thiophene or furan as flanking donors, are easily synthesized. Thiophene analogs are found to be superior in displaying solvatochromic features than furan analog, with a slightly better variation in the excited state dipole moment. The emission wavelength in solution dictates a better conjugation in FAPTZ than TAPTZ, and that is interpreted by the DFT-optimized molecular structures, presenting better n-electronic conjugations in FAPTZ from a comparatively lesser torsion angle between furan/anthracene by keeping the rest almost similar. Contrarily, the solid-state emission appears at a lower wavelength for FAPTZ because of the higher torsion angle between anthracene (acceptor)/PTZ (donor). TAPTZ has appeared to be a better blue-shifted AIEGen with relatively smaller particle size. The tilted conformation and a cross-packing enable these molecules to be emissive in solid-state and exhibit reversible redshifted MFC-feature. Relatively lower redshift and sensitivity for TAPTZ are described by more substantial crystal packing with two extra C···S and S···S interactions than FAPTZ. Such a dissimilarity is deduced with SCXRD, PXRD, DSC, and fluorescence lifetime studies. Hirshfeld surface analyses indicate quantitatively more C···H interactions in FAPTZ than TAPTZ. Thus, this work has provided a thought on the effect of a tiny change in a flanking donor that can impact the solvato-, AIE- and MFC-features, which would develop new MFC-active materials. The practical application of reversible security writing demonstrates the efficacy of these n-conjugates.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

We thank DST-SERB (CRG/2018/000456) for financial support. MC thanks BITS-Pilani Hyderabad for NMR/X-ray facilities. We thank Prof Durba Roy for the DFT calculations.
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