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Introduction

The desirable chemical, optical, electrical and biological properties of donor-acceptor (D-A) conjugated organic molecules provide an attractive platform for the design and fabrication of newer functional materials.¹ Their molecular structures guided by weak intermolecular interactions provide structural tunability enabling them to be utilized as functional building blocks for the construction of self-assembled molecular micro or nanostructures.^{2,3} Among many π -conjugated systems, the cyanostilbene scaffold with terminal substituents on the phenyl group has been developed for multiple organic electronic or biological applications.⁴⁻⁶ The cyano substitution on the double bond yields fluorophores exhibiting unique emission termed aggregation-induced emission (AIE) driven by their 'twist elasticity' characteristics. These fluorophores with good solubility in organic solvents show weak emission but exhibit remarkable emission in aqueous media owing to the formation of aggregates⁷ and self-assemblies.^{4,8} Tapping into these remarkable properties, we extended our earlier work on the cyanostilbenes by introducing a CF3 group on the aromatic ring containing the styrylpyrene unit. Pyrene is a

Photophysical studies of pyrenyl cyanostyrenes: effect of trifluoromethyl substitution on gelation[†]

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 α -Cyanostyrenes bearing a planar pyrene unit and electron withdrawing trifluoromethyl units were designed and synthesized. The conformational restriction due to the presence of the cyano group on the double bond favors aggregation induced emission in aqueous media. The styrylpyrenes aggregate to form microstructures influenced by π - π stacking, cyano and CF₃ substituent interactions. Importantly confluence of the pyrene ring and simple trifluoromethyl (CF₃) unit allows the formation of a stable organogel with bathochromic shifts in emission. The formation of aggregates and the gel was substantiated using ¹H NMR spectroscopy and scanning electron microscopy. The stability of the gels was assessed using rheology investigations and rationalized by single crystal X-ray data.

classic molecule with excellent absorption and emission properties that is widely utilized for various optical and biological applications.⁹⁻¹² We anticipated that introduction of the flat pyrene moiety, capable of forming excimers, may aid in the formation of ordered structures. The polar -CN group strengthens the electrostatic interactions among the neighboring molecules and restricts the intramolecular rotations. The CF₃ end groups help in intermolecular interactions due to its associated hydrophobic character apart from the interactions associated with the strong electronegative F group. Furthermore, the incorporation of CF₃ substituents also helps in the gelation properties of suitable organic molecular scaffolds.13-15 Previously known organogels with pyrene or other molecular structures typically contain long alkyl chain or steroidal substituents¹⁶⁻¹⁹ and show tremendous promise as functional materials for optical and biological applications.²⁰⁻²⁵ The elongated aryl moieties and CF₃ groups lead to increased intermolecular interactions through strong π - π and hydrophobic interactions enhancing the gelation through a self-assembling process.^{26–28} It is known that the larger hydrophobic area achieved by longer or bulkier aryl moieties also aids in the construction of nanostructures.^{29,30} On this basis, we have designed cyanostyrene derivatives with pyrene and trifluoromethyl substitutions (Fig. 1). The results are detailed in the following sections.

Materials and methods

All the chemicals and reagents required for the synthesis of the pyrene derivatives and spectroscopic studies were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics and S. D. Fine-Chem and were used as such. All the synthesized samples were



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Fig. 1 Pyrene derivatives designed and synthesized.

characterized using ¹H NMR and ¹³C NMR in CDCl₃ and with tetramethylsilane (TMS) as an internal standard using a Bruker AvanceIII-500 MHz NMR spectrometer. Mass spectral data were obtained using an ESI-QToF Waters-Synapt G2S high-resolution mass spectrometer. UV-vis absorption spectra were recorded using an Analytik Jena Specord 210 plus and the fluorescence emission studies were performed using a Horiba-Jobin Yvon Fluolorog-3 spectrofluorimeter. Typically the excitation wavelengths were set at the absorption maxima (λ_{abs}) of the compounds under investigation. All the fluorescence spectra were recorded in a 10 mm path length quartz cuvette with a slit width of 2 nm. Fluorescence quantum yields of compounds were estimated using quinine sulphate ($\phi = 0.546$ in 0.5 M H₂SO₄) as a reference standard. For the fluorescence measurements, $\sim 10 \mu M$ concentrations of chromophores were used. Single crystal X-ray studies were performed using a CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. Scanning electron microscopy (SEM) analysis was carried out using a field emission SEM (JSM 7600F JEOL). For this purpose, one drop of the sample [$\sim 10^{-6}$ M solution in water] was deposited on a Si-wafer mounted on an aluminum stub with the help of double-sided adhesive carbon tape. The samples were dried to ensure complete removal of any residual water and coated with platinum before being analyzed. The rheological properties of the gels were analyzed using an Anton Paar MCR 302 rheometer. A typical cone and plate geometry with a cone diameter of 25 mm and truncation angle of 2° with a gap of 0.105 mm at a constant temperature of 20 $^{\circ}$ C was used and the following rheological measurements were performed: small amplitude oscillatory frequency sweep and large amplitude oscillatory sweep measurements. Powder XRD analysis was carried out using a Bruker D8 Discover, with Cu K-alpha operating at 40 kV and 30 mA. The scan speed for the analysis was 0.3 s per step with a single step size of 0.01.

The desired compounds were prepared as per the synthetic methodology given in Scheme 1. In a typical procedure, a commercially available CF_3 substituted phenylacetonitrile (0.01 mol) derivative was taken in 25 mL methanol. To the alcoholic solution, KOH (0.01 mol) was added and vigorously stirred for 15 min. To this, pyrene-1-carboxaldehyde (0.01 mol) in 25 mL of methanol was added slowly, and the contents were stirred for 10–15 min at room temperature. The shining yellow crystals obtained were washed with excess methanol and recrystallized from absolute ethanol.



Scheme 1 Synthesis of styrylpyrene derivatives

Results and discussion

The synthesized styrylpyrenes are shown in Fig. 1. (*Z*)-2-Phenyl-3-(pyren-3-yl)acrylonitrile (1) has no trifluoromethyl substitution, (*Z*)-2-(4-(trifluoromethyl)phenyl)-3-(pyren-3-yl)acrylonitrile (2) has one trifluoromethyl substitution on the aromatic ring and (*Z*)-2-(3,5-bis(trifluoromethyl)phenyl)-3-(pyren-3-yl)acrylonitrile (3) has two trifluoromethyl substituents on the *meta* positions of the aromatic ring. All the styrylpyrenes have a cyano group in the double bond. Molecule (1), devoid of any CF₃ groups, shows absorption bands at ~ 380 nm with a shoulder at ~ 396 nm and another band at ~ 300 nm (Fig. S1a, ESI†).

Substituting a CF_3 group in (2) results in smaller absorption maxima shifts (+2 to +3 nm) and increasing the number of CF_3 substituents (3) does not yield any significant absorption maxima changes (Fig. 2 and Fig. S1b, ESI⁺). Solvent polarity



Fig. 2 Absorption spectra of (a) (2) in different organic solvents and (b) (1), (2) and (3) in acetonitrile at a concentration of 10 μ M.

changes exert weaker effects on the absorption maxima. In water, however, broad absorption is noted with peaks coinciding with the original absorption at \sim 380 nm and another absorption band at \sim 435 nm. This broad and bathochromic absorption in water could be due to the formation of aggregates. The absorption and emission data are given in Table 1. Compound (1) in heptane shows emission maxima at 439 nm with a shoulder peak at 463 nm. In dioxane, (1) emits at \sim 460 nm and in acetonitrile, the observed emission is at \sim 477 nm. In water, however, the emission shows a significant red-shift with a distinct emission band at \sim 548 nm with a shoulder at ~476 nm [Fig. S2, ESI[†]]. Compound (2) shows moderate solvatochromic emission shifts. In heptane, (2) shows structured emission with an emission peak at 450 nm and in water, the emission is noted at ~ 467 nm with a tail emission in the range of 550 nm to 600 nm. The former peak indicates the monomer emission and the tail emission could be due to the formation of the aggregates [Fig. 3a]. Compound (3) bearing two CF₃ groups also shows comparable emission behavior [Fig. 3b] but with a conspicuous emission band at 565 nm. The lower wavelength peak is attributed to the monomer emission, and the longer wavelength band is attributed to the aggregates.³¹ The CF₃ groups show a strong -I effect because of the presence of electronegative fluorine atoms but exhibit no resonance effect with the aromatic ring. The twisted conformation due to the presence of vinyl substitution may hinder the formation of excimers. The concentration dependent emission investigations in 1,4-dioxane indicates concentration quenching with no new emission bands excluding the possibility of the excimer emission in organic solvents [Fig. S5, ESI⁺]. The optical measurements were performed at concentrations of 10 µM.

Emission in dioxane-water binary mixtures

Increasing the percent water fraction in dioxane results in ~8.5 fold increase (80%) in the emission intensity along with a ~9 nm hypsochromic wavelength shift for (2). Further increase in water percent decreases the emission intensity, but at 100% water, a broad emission band at ~565 nm appears along with the 470 nm band [Fig. 4a]. Compound (1) without any CF₃ group shows aggregation induced emission at 100% water³² (Fig. S4, ESI†). The observations for compound (3), containing two CF₃ substituents are comparable to that observed for (1).³² The 480 nm emission noted in dioxane shows a hypsochromic shift (-20 nm) with an increase in water percentage (60%) along with enhanced intensity (2-fold increase). Further increase in water percentage

yields a ~ 2.7 fold increase in the emission intensity. Interestingly a new emission band begins to appear at ~ 560 nm, but it remains as a broad shoulder. In contrast to (2), a distinct emission band is noted at ~ 558 nm [Fig. 4b]. The bathochromic emission observed for (1–3) in water is attributed to the emission from the aggregates.

However, it is interesting to note that (3) with two CF_3 groups shows a distinct emission band in comparison to (2) where only a shoulder is observed. It is possible that the CF_3 substitution in (2) may be helping in stabilizing the structure through non-covalent forces and restricting the formation of the aggregates. In (3) such stabilization may be hindered due to steric effects of *meta*-substituted CF_3 groups, and in (1), no additional stabilizing forces are present, or the interactions are purely random readily allowing the formation of the aggregates.

For comparison, the emission was also measured in the solid state. Compounds (1) and (3) show comparable emission with emission maxima at ~ 500 nm while compound (2) shows a significant red-shifted emission band at 580 nm [Fig. 4c]. To better understand the morphology of the aggregates, we recorded scanning electron microscopy images at two different water fractions where emission enhancement is maximum (80%) and at 100%.

The SEM images of (2) and (3) show distinct morphological differences (Fig. 5). Compound (2) at 80% water fraction shows irregular pebble like structures that are close together. At 100% water, irregular short dendritic structures are noted. Compound (3) shows different morphologies with sheet like structures (80% water) and square/distorted square like structures (at 100% water) (Fig. 6). SEM dropcast images were recorded using 10 μ M concentration of the compounds.

CF₃ substituted small molecules have been shown to form self-assemblies or organogels due to favorable intermolecular interactions through weak non-covalent interactions that provide both strength and enable reversibility.^{33–36} Fused ring systems such as pyrene aided by trifluoromethyl units (CF₃) can assist in the formation of stable assemblies at higher concentrations. To study the gel formation, compounds (2) & (3) were dissolved in *t*-BuOH (1.8 wt%) in a glass vial, and heated to 70 °C to obtain a clear solution. The hot *t*-BuOH solution was sonicated for 30 minutes at 25–36 °C using a bath sonicator and rapidly cooled in the refrigerator for 5 minutes and allowed to warm up to room temperature. The solution (2) subsequently turns to a viscous gel and shows no gravitational flow even after inversion of the vial (Fig. 7a) indicating the overall stability. The gel so formed was also reversible upon heating (\sim 70 °C) and cooling cycles.

Table 1 Absorption and emission data of (2) and (3) in organic solvents

Solvent	(0)				(2)			
	$\frac{(2)}{\lambda_a (nm)}$	$\lambda_{\rm f}$ (nm)	Stokes shift (cm ⁻¹)	Quantum yield (Φ)	$\frac{(3)}{\lambda_{a} (nm)}$	$\lambda_{\rm f} ({\rm nm})$	Stokes shift (cm ⁻¹)	Quantum yield (Φ)
Heptane	383, 410	450	3887	0.0302	385, 411	458	4139	0.0632
Dioxane	382, 410	470	4991	0.0110	384, 412	480	5208	0.0611
THF	383, 410	483	5337	0.0112	385, 412	493	5690	0.0051
DMF	382, 410	498	6097	0.0043	384, 412	508	6356	0.0027
CH ₃ CN	380	502an	6395	0.0025	385	510	6366	0.0034
Methanol	382, 409	457	4296	0.0037	381, 409	482	5499	0.0035
Water	419, 425	467, sh 565	2116	0.0073	382, 417	565	8478	0.0070

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Fig. 3 Emission spectra of (a) (2) and (b) (3) in different organic solvents and (λ_{ex}: 380 nm) measured at a concentration of 10 μM.



Fig. 4 Emission spectra of compounds (a) (2) and (b) (3) in dioxane-water binary mixture measured at a concentration of 10 μ M and (c) solid state fluorescence spectra of compounds (1-3).

Examination of the gel emission reveals a bathochromic emission (61 nm) band at 517 nm (Fig. 7b) as compared to the observed emission in *t*-BuOH (456 nm). The compounds (1) and (3) form no gel (Fig. S6, ESI[†]) under the same experimental conditions with emission at \sim 553 nm.

Single crystal analysis

The crystal structures of (2) and (3) were determined by single crystal X-ray diffraction. The single crystals were obtained as

yellow color needles (2) and colorless needles (3). The compound (2) crystallized in the monoclinic crystal system and $P2_1/c$ space group, while the compound (3) crystallized in the orthorhombic system and *Pbca* space group. The crystal structure details of (2) and (3) are deposited into the Cambridge Crystallography Data Center, and their CCDC numbers, respectively are 1858766 and 1858773.† The ORTEP diagrams of the compounds (2) and (3) are illustrated in Fig. 8. The molecular structure of (2) is composed of *trans*-disposition of the pyrenyl ring group to the *p*-trifluorotolyl



Fig. 5 SEM images of compound (2) in (a) 80% water (scale: 100 nm; inset at scale: 1 μ m) and in (b) 100% water (scale: 100 nm) measured at a concentration of 10 μ M.



Fig. 6 SEM images of compound (3) in (a) 80% water and in (b) 100% water (scale: 1 µm) measured at a concentration of 10 µM.

group while the pyrenyl group is in the *cis*-position to the cyano group around the olefin double bond. The C17–C18 double bond distance is 1.3566(16) Å while the C19–N1 triple bond distance is 1.1460(16) Å. There are at least four types of intermolecular non-covalent bond interactions as noted for compound (2): (i) π – π stacking, (ii) F–F interaction,^{37,38} (iii) F–H interaction, and (iv) N–H interaction. The intermolecular π – π stacking arrangements are observed in the crystal structure of the mono-CF₃ compound [Fig. S7, ESI†]. The intermolecular π – π stacking effect can be visualized between the polycyclic pyrene rings as well between the –CF₃ substituted phenyl rings. The π – π interaction is shown in Fig. S8 (ESI†) with ring centroid–centroid G1–G1', G2–G2', G3–G3', G4–G4' and G5–G5' distances of 3.916, 3.873, 3.854, 3.822 and 3.839 Å, respectively.

Along the *a*-crystallographic axis, the molecules are arranged and stabilized through two types of interactions, π - π stacking due to the pyrene ring and intermolecular fluoride–fluoride interactions.^{39,40} The F1–F1', F1–F3' and F2–F3' fluoride–fluoride non-bonding interaction lengths, respectively are 2.915 Å, 2.875 Å, and 2.841 Å. Along the crystallographic *b*-axis from fluoride to hydrogen of the pyrene ring, the non-bonding interaction can be observed with F1–H11 and F3'–H12 interaction lengths of 2.582 Å and 2.661 Å, respectively [Fig. S8, ESI†]. The nitrogen of the cyano group forms a three-centered interaction with two hydrogens, and H21 and H17 forming an extended array along the *c*-crystallographic axis, N1···H17 = 2.604 Å (with styrene C−H group) and N1···H21 = 2.576 Å (with phenyl C−H group) [Fig. S9, ESI[†]]. The ORTEP diagram of the compound (2) is illustrated in Fig. 8a. The short contact interactions are given in Table S1 (ESI[†]). Similar to (2), the molecular structure of (3) is composed of trans-disposition of the pyrenyl ring group to the *p*-3,5-bis(trifluoromethyl)phenyl group while the pyrenyl group is in the *cis*-position to the cyano group around the olefin double bond. The C17-C18 double bond distance is 1.340(4) Å while the C19-N1 triple bond distance is 1.152(4) Å. The C \equiv N bond lengths for (2) and (3), respectively are 1.1460(16) Å and 1.152(4) Å. The slight elongation in the cyano group bond length may be due to the involvement in the formation of noncovalent intermolecular interactions such as N1...C10 = 3.238 Å, and C19...H3 = 2.863 Å and C19...H7 = 1.861 Å. These intermolecular interactions and orientations of the molecules do not favor the π - π pyrene ring stacking in the molecular packing arrangements.

Also, the following intermolecular interactions, F3···H7 (2.596 Å), F5···C23 (3.095 Å), H13···C7 (2.587 Å) and H13···C4 (2.789 Å) support the three-dimensional crystal structure formation [Fig. S10, ESI†]. Unlike in (2), in (3), the F···F and π - π ring stacking are not observable. These interactions stabilize the



Fig. 7 (a) Photographs of gel (2) in the solution state (70 °C) and in the gel state (25 °C) in *t*-BuOH (1.8 wt%) and (b) emission spectra of the gel formed by (2) in *t*-BuOH.



Fig. 8 ORTEP diagram of compounds (a) (2) and (b) (3). Thermal displacement ellipsoids are drawn at the 50% probability level.

aggregates formed and stronger molecular packing support better gel formation for (2) than in (3). The orientation of both the molecules is given in Fig. S11 (ESI⁺). The substituted phenyl ring plane of compound (2) is oriented with a deviation of 53° with respect to the pyrene ring plane, but in compound (3), this deviation is only minimal around 3° , and the rings are slightly tilted facing each other. For (2), the dihedral angles C2–C1–C17–C18 and C17–C18–C20–C21 are –32.52 and –18.90 degrees, respectively and for compound (3), these corresponding dihedral angles are 40.49 and –37.51 degrees, respectively. The data for the crystals (1) and (2) are given in Tables S1–S12 in the ESI.†

Rheology behavior

The stability and viscoelastic properties of the synthesized organogels were studied by rheological measurements.

The storage modulus (G') and loss modulus (G'') represent solid and liquid-like properties of the material. Time and frequency sweep experiments were conducted at a constant temperature of 20 °C. Before the rheological measurements, the sample was equilibrated for 5 minutes. The organogel formed by (2) in *t*-BuOH was subjected to an angular frequency (ω) of 0.1–100 rad s^{-1} . These experimental conditions ensure that both the storage modulus (G') and loss modulus (G'') were measured in the linear viscoelastic regime. In all cases, the value of G'' was less than the value of G' at all frequencies. Among these different treatment conditions, organogel (2) showed the highest storage modulus (G') in the order of 10^4 Pa as compared to the loss modulus (G''). Low tan δ values $(\tan \delta = G''/G')$ obtained for gel (2) revealed the gel-like nature of the sample with possible cross-linked networks. The G'value for gel (2) was independent of experimental time, and frequency range as shown in Fig. 9 and also indicates that the G' value is in the order of 10^4 Pa, which shows the higher mechanical strength of gel (2). The π - π stacking interactions between pyrenyl segments provide the essential gelation, and strongly support the view that the aromatic units induce rigidity in the structure and help in a linear fashion to form an organogel. The relatively higher strength of the gel can be understood by the existence of CF₃ groups which play a key role in the formation of stronger gel networks by reinforcing non-covalent interactions.^{13,40,41} In the case of (3), the positioning of the CF₃ groups hinders the formation of stable gels although different emission bands were observed at higher concentration (Fig. S12, ESI[†]).

¹H NMR studies

The formation of the self-assembled structures and possible interactions can be gauged by ¹H NMR measurements⁴² [Fig. 10]. The experiments were performed in CDCl₃ for (2) at higher concentrations to probe the driving force for the self-assembly process. With increase of concentration from 0.4 wt% to 0.8 wt%, the aromatic ¹H NMR signal (7.7–8.7 ppm) shows a slight upfield shift [H_a (0.019 ppm), H_b (0.035 ppm), H_c (0.026 ppm), and H_d (0.0161 ppm)] indicating the possible role of π - π stacking interactions between the pyrenyl rings. These results support the formation of aggregates through stabilization of π - π interactions in the gel phase and support our view that the interacting pyrene units assist in the formation of the

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Fig. 9 (a) Time sweep measurement and (b) frequency sweep measurement of gel (2) in t-BuOH.

organogel. We could not conduct the ¹H-NMR measurements at higher concentrations as the sample tends to lose the locking ability. The scanning electron microscopy (SEM) of the dried xerogel of (2) indicates the formation of an entangled two-dimensional network consisting of bundles of ribbonlike aggregates [Fig. 11a]. These bundles of self-assembled aggregates are aided by strong hydrophobic and π - π interactions of the aromatic pyrene unit and interactions through CF₃ groups



Fig. 10 1 H NMR spectra of (2) with increasing concentration (0.4–0.8 wt%) in CDCl₃ solution.



Fig. 11 (a) SEM images of the xerogels obtained from *t*-BuOH gelation sols of (2) (scale: 10 μ m) and (b) powder XRD pattern of the xerogel of (2) formed in *t*-BuOH. The powder XRD pattern obtained from single crystals of (2) is given in the ESI.†

(C-F···H-Ar). The CF_3 group plays a key role in improving intermolecular interaction much like the long alkyl chain or steroidal group.

Powder XRD studies

Powder XRD measurements were performed on the xerogels of (2) prepared from *t*-BuOH to obtain further information on the molecular arrangement in their gel state. Well-resolved X-ray diffraction signals of (2) are shown in Fig. 11b. Sharper peaks appear in the gel state indicating structural changes to the morphology, *i.e.*, the formation of micro ribbons/micro crystals. The peak of the powder sample at angle $2\theta = 15.21^{\circ}$ (full-width half maximum = 0.5657) shifts to $2\theta = 15.17^{\circ}$ (FWHM = 0.3479) with intense peaks. The low FWHM indicates greater crystallinity in these xerogels. The data show that the xerogels obtained have higher order packing aided by non-covalent attractions. The single crystal powder XRD of (2) reveals sharp and intense signals that correspond to the dominant crystal-line planes (Fig. S13, ESI⁺).

Conclusions

We have designed pyrene-containing cyanostyrene derivatives bearing simple trifluoromethyl groups and discussed their absorption and emission properties in organic solvents and water. At higher concentrations, the styrylpyrenes efficiently form organogels despite lacking steroidal or long alkyl chain substituents. This unique gelation ability is attributed to the influence of π - π interactions of the planar pyrene moiety assisted by the interactions from the CF₃ units. Such formation of organogels through the introduction of small molecular entities such as CF₃ groups could boost the development of luminescent low molecular weight gelators.

Conflicts of interest

There are no conflicts to declare.

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