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1	Organogel Composed of Trifluoromethyl Anthryl Cyanostyrenes: Enhanced
2	Emission and Self-Assemblies
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## 9 Abstract

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A series of  $\alpha$ -cyanostyrenes bearing anthracene and electron withdrawing trifluoromethyl 10 units were designed and synthesized. The  $\alpha$ -cyanostyrene skeleton favors the aggregation 11 induced enhanced emission behavior due to the restriction of intramolecular rotations. 12 Remarkably, the anthryl cyanostyrenes bearing simple trifluoromethyl ( $CF_3$ ) substituents 13 form stable organogels with enhanced fluorescence emission compared to its solution 14 state. In water, the  $CF_3$  substituted anthrylstyrenes self-assembles to an entangled fibrous 15 nano/ microstructures through intermolecular H- bonding,  $\pi - \pi$  stacking and cyano 16 substituent interactions. The morphological features of the aggregates and the gels were 17 substantiated using scanning electron microscopy, TEM, Powder XRD measurements. 18 The stability of the gels was assessed using rheology investigations. 19

#### 20 Introduction

 $\pi$ -Conjugated organic fluorophores have attracted much attention for their use as materials 21 for optoelectronic and biological applications<sup>1-8</sup>. The synthetic feasibility through the 22 incorporation of suitable push-pull substituents, their desired optical properties such as the 23 24 absorption, emission in the solution and the solid state, tunable redox properties, photochemical interconversions complement their use for several optical and biological 25 applications<sup>9-11</sup>. In particular, conjugated substrates bearing diarylethylene scaffold have 26 attracted a sustained interest for their use as switches, photochromic materials, and cellular 27 imaging<sup>12-17</sup>. Among materials with this ethylene scaffold, cyanostilbene derivatives, have 28

attracted great attention towards the development of novel functional materials particularly due 1 to their characteristic unique emission, termed Aggregation Induced Enhanced Emission 2 (AIEE), in aqueous media<sup>18-22</sup>. Incorporation of suitable push-pull substituents in the 3 cyanostilbene architecture allowed construction of various luminogens with characteristic 4 emission and morphological features<sup>21, 23</sup>. These fluorophores exhibit remarkable 5 enhanced emission in an aggregated state in contrast to the weaker emission in the 6 solution state. This emission behavior is attributed to the restriction of intramolecular 7 rotation (RIR), the formation of H- or J-type aggregates, charge transfer and other excited 8 state processes<sup>24, 25</sup>. Apart from their unique emission and morphological behavior, the 9 lower molecular weight  $\pi$ -conjugated organic molecules also self-assemble to micro 10 structures<sup>26</sup>. Such self-assembly of functional organic materials bearing suitable 11 substituents such as steroidal or alkyl chains, triggered by a combination of non-covalent 12 interactions like H-bonding,  $\pi$ - $\pi$  stacking, van der Waals forces, can result in an organogel 13 formation<sup>8, 27-30</sup>. The organogel systems derived of  $\pi$ -conjugated molecular systems have 14 fascinating applications as white light emitting materials, sensing and imaging<sup>31-34</sup>. In this 15 16 work, we designed and developed  $\pi$ -conjugated substrates bearing an anthracene moiety linked to α-cyanostyrene scaffold containing trifluoromethyl (CF<sub>3</sub>) substituents. Previous 17 literature reports suggest that introduction of CF<sub>3</sub> groups endows excellent gelation (low 18 molecular weight organogels: LMOG) properties to the molecular systems and also results 19 in an enhanced emission<sup>26, 35-39</sup>. We thought the introduction of fused planar ring systems 20 such as anthracene could direct more ordered packing in the gels through their  $\pi$ - $\pi$ 21 interactions<sup>40, 41</sup>. Structural modifications to the  $\pi$ - scaffold are also known to influence 22 the architecture and its electronic properties. Considering these observations, we designed 23 styrylanthracene fluorophores, anticipating the favorable properties of anthracene and CF<sub>3</sub> 24 groups [Fig-1], and investigated their absorption, emission, and gelation properties. We 25 observed the formation of fibrous aggregates with enhanced emission and good gelation 26 stability. The self-assemblies and the organogels were characterized by scanning electron 27 microscopy (SEM), transmission electron microscopy (TEM), fluorescent microscopy and 28 rheology studies. The results are detailed in the following sections. 29

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Fig. 1 Structures of compounds synthesized

#### 3 Experimental

Materials All the chemicals, reagents required for the synthesis of the anthracene 4 derivatives were purchased from Sigma-Aldrich, Alfa Aesar, Acros and S. D. Fine. 5 Solvents used for absorption and fluorescence investigations were dried and distilled 6 before use. All the synthesized samples were characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR 7 in CDCl<sub>3</sub> with Tetramethylsilane (TMS) as an internal standard using Bruker AvanceIII-8 9 500 MHz NMR spectrometer. Mass spectral data were obtained using ESI-QToF Waters-Synapt G2S high-resolution mass spectrometer. UV-Vis absorption spectra were recorded 10 using Analytik Jena specord 210 plus and the fluorescence emission studies were 11 performed using Horiba-Jobin-Yvon Fluolorog-3 spectrofluorometer. Typically the 12 excitation wavelengths were set at the absorption maxima ( $\lambda_a$ ) of the compounds under 13 investigation. All the fluorescence spectra were recorded in a 10mm path length quartz 14 15 cuvette with a slit width of 1nm. Fluorescence quantum yields of compounds were estimated using quinine sulfate ( $\Phi = 0.546$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>) as a reference standard. For 16 the fluorescence measurements  $\sim 10 \mu M$  concentrations of chromophores were used. 17 Scanning electron microscopy (SEM) analysis was carried out using field emission SEM 18 (JSM 7600F JEOL). For this purpose, one drop of the sample [ $\sim 10^{-6}$  M solution in water] 19 20 was deposited on a Si-wafer mounted on an Aluminum stub with the help of a doublesided adhesive carbon tape. The samples were heat-dried at 35°C for 12 h and vacuum 21 dried for 30 min to ensure complete removal of any residual water and coated with 22 platinum before being analyzed. Fluorescence microscopic images of gels were taken 23 24 using Nikon Ci-S. The rheological properties of gels are analyzed using strain and stress controlled Anton Paar MCR 302 rheometer. A typical cone and plate geometry with a 25

cone diameter 25 mm and truncation angle of 2° with a gap of 0.105 mm at a constant 1 temperature of 20°C is used, and the small amplitude oscillatory frequency sweep and 2 large amplitude oscillatory sweep rheological measurements are performed TEM 3 measurements were carried out using JEOL JEM1011 with an accelerating voltage of 100 4 kV. Samples were prepared by drop casting of gel (2) on to carbon-coated copper grids at 5 the required concentrations at ambient conditions. The solvent was removed under 6 vacuum. Powder XRD patterns were obtained by X-ray diffraction (XRD) with Bruker D8 7 Discover diffractometer using Cu K $\alpha$  in the Bragg angle range of 5–60°. 8

#### 9 Synthetic Methods

The desired compounds were synthesized as per the methodology given in Scheme-1. In a typical procedure, CF<sub>3</sub> substituted phenyl acetonitrile (0.01mol) was taken in 25 mL methanol. To the alcoholic solution, KOH (0.01mol) was added and stirred vigorously for 15min. To this stirred mixture, a solution of aryl aldehyde (0.01mol) in 25mL of methanol was added slowly and stirred for 10-15 min at room temperature. Shining yellow crystals obtained were washed with excess methanol and recrystallized from absolute ethanol.



- 17 Scheme 1. Synthesis of anthracene-based cyanostyrenes.
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### 19 Characterization Data

20 (*Z*)-3-(anthracen-9-yl)-2-phenylacrylonitrile (1): UV (dioxane,  $\lambda_{abs}$ :388 nm,  $\epsilon$ =9005 M<sup>-1</sup> 21 cm<sup>-1</sup>) <sup>1</sup>H NMR (500Hz, CDCl<sub>3</sub>): 8.57(s, 1H), 8.47(s,1H), 8.10(d,4H, *J*=7Hz), 7.93(d, 2H,

22 J=7.5Hz), 7.54-7.61(m,7H); 13C NMR(125 Hz): 140.14, 133.34, 131.3, 129.84, 129.30,

23 129.12, 128.99, 127.85, 126.67, 126.17, 125.53, 125.04, 121.33, 116.50, 96.16, HRMS

24 (ESI-MS) *m/z* calculated: 305.1204; found 305.1207

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(Z)-3-(anthracen-9-yl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile
 (2): UV (dioxane,
 λ<sub>abs</sub>:391 nm, ε=6605 M<sup>-1</sup>cm<sup>-1</sup>) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.59 (s, 2H), 8.08 (d, J = 8
 Hz, 2H), 8.00-8.03 (m, 4H), 7.81 (d, J = 8.5 Hz, 2H), 7.52-7.57 (m, 4H). <sup>13</sup>C NMR (125
 MHz, CDCl<sub>3</sub>) δ 116.02, 120.03, 124.75, 125.63, 126.34, 126.53, 126.96, 127.09, 129.24,
 129.37, 129.53, 131.26, 131.62, 131.88, 136.66, 142.53; HRMS (ESI-MS) *m/z*: calcd for
 [M]<sup>+</sup> 373.1078 found 373.1059.

(Z)-3-(anthracen-9-yl)-2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile (3): UV (dioxane,
λ<sub>abs</sub>:404 nm ε=8505 M<sup>-1</sup>cm<sup>-1</sup>) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.62 (s, 1H), 8.58 (s, 1H),
8.31 (s, 2H), 8.09 (d, J=8, Hz, 2H), 8.02 (d, J=7.5, 2H), 7.99 (s, 1H), 7.53-7.59 (m, 4H).
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.93, 135.54, 133.20, 132.93, 131.22, 130.01, 129.33,
127.20, 126.38, 126.13, 125.70, 124.54, 123.31, 118.70, 115.46, 96.13. HRMS (ESI-MS) *m/z*: calcd for [M]<sup>+</sup> 441.0952, found 441.0958.

#### 14 Results and Discussions

#### 15 Absorption and Emission Studies

Trifluoromethyl substituted phenyl acetonitrile derivatives bearing anthracene were 16 17 synthesized and examined for their absorption and emission behavior in the solution and solid state. Compound (1) has no trifluoromethyl (CF<sub>3</sub>) group, (2) has one CF<sub>3</sub> group 18 19 substituted at the *para*- position of the phenyl ring and (3) bears two CF<sub>3</sub> groups substituted at the *meta*- position on the aromatic ring. Through this arrangement, we 20 21 sought to examine the effect of trifluoromethyl and the anthracene substitution on the aggregation-induced emission properties. The absorption shows no significant changes 22 post introduction of the CF<sub>3</sub> groups [Fig 2a] with absorption maxima in the range of 386 -23 411 nm [Fig S1 and Fig 2b] in various solvents. Substitution by strong electron 24 withdrawing CF<sub>3</sub> group and solvent polarity has only a meager effect on the absorption 25 maxima. However, in water broader bands with a slight red-shift of the absorption maxima 26 are noted for both (2) and (3) but not for (1). 27



Fig. 2 Absorption spectra of a) (1-3) in ACN, b) (2) in different organic solvents

3 Compound (1) emits at  $\sim$ 430 nm in heptane. With the increase in solvent polarity, solvatochromic emission shifts (+ 59 nm) were noted. Likewise (2) emits at ~435nm in 4 5 heptane and shows similar solvatochromic shifts (+ 56nm) with peaks at 474-490 nm in solvents of higher polarity. Compound (3) also shows comparable emission shifts (+ 6 7 57nm), 440nm in heptane to 471-497 nm in solvents of higher polarity. Despite its electron withdrawing strength  $CF_3$  has no role play in improving the solvatochromic 8 properties [Fig 3a]. This is possible as there is no resonance effect due to lack of orbitals 9 or electron pairs that can overlap with those of the aromatic ring. In water, however, we 10 observed considerable emission (+16-23 nm) shifts with emission bands at 505nm for (1), 11 513nm for (2) and 520nm for (3) [Fig S2, Fig. 3b and 3c]. This unique emission behavior 12 in aqueous media is attributed to the exquisite phenomenon known as aggregation induced 13 enhanced emission or in short AIEE and is a result of restriction of intramolecular rotation 14 that blocks the non-radiative decay pathway. 15

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**1 Table-1**: Absorption and emission of compounds (1-3) in organic solvents and water.

#### 1 Emission in dioxane-water binary mixture

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Compound (1) emits at 461nm in dioxane. As percent water increases in dioxane, 2 significant enhancement in emission was observed. As the water fraction increases from 0 3 to 40%, the fluorescence intensity increases  $\sim$ 4.5 folds along with a blue shift (-32 nm). In 4 water, compound (1) shows incremental emission intensity (1.8 folds) with a red shift of +5 90 nm (Fig S4). These initial emission changes are attributed to the formation of dispersed 6 particles. However, with the further addition of water, the solvatochromism takes over 7 with the greater formation of aggregates. The general insolubility of the compounds in 8 water meant that the existing geometry noted in a solution state (dioxane) changes to a 9 dispersed state in the binary mixture (aqueous dioxane) and aggregated state in water. In 10 dioxane, (2) with one CF<sub>3</sub> group, emits at  $\sim$ 457nm. With added water, the intensity of the 11 12 peaks initially increases and later result in solvatochromic emission shifts as a consequence of polarity increments. At 80% water, the emission maxima show a band at 13 ~502 nm with ~35 fold intensity enhancement [Fig. 4a]. Quenched emission follows this 14 intensity enhancement at 90% and 100% water, but bathochromic emission shifts ( $\lambda_f = 527$ 15 nm) was observed. Similar to (2), compound (3) also shows the highest emission intensity 16 at 80% water [a ~5-fold increase] with a bathochromic shift at 497 nm, with further red-17 shift to 528 nm [Fig. 4b]. These enhanced emissions are due to intra and intermolecular 18 interactions exerted by aggregation of fluorophores caused by stacking of twisted 19 20 cyanostyrenes. The intensity enhanced red-shifted emission of these molecular systems is attributed to the combined effects of aggregation induced planarization and J-aggregate 21 formation. Compounds (2) & (3) have a similar bathochromic emission shifts (44 nm & 42 22 nm), but compound (2) shows dramatic intensity enhancement ( $\sim$ 35 fold) compared to (3) 23 24 (~5 fold) in 80% water. The lower intensity enhancement in (3) could be due to the presence of two CF<sub>3</sub> groups decreasing their packing ability. 25

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Fig. 4 Emission of compounds (2) and (3) in the dioxane-water mixture.

For comparison of the emission with aggregates and solid state, we also recorded emission in the solid state (Fig. 5a). The designed compounds show emission in the lower energy regions [535nm (1), 538nm in (2) and 543nm in (3) ] than that observed in aggregated or dispersed state. These emission shifts are attributed to close packing of the molecules that restrict the dynamic motion. The bathochromic absorption shift and the broadening of the absorption spectra indicate the formation of J- type aggregates (Fig S3a, b & c).



Fig. 5 a) Solid state emission of compounds (1-3) and b) emission of (2 & 3) in *t*-BuOH
and after the formation of the gel.

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#### **1** Morphology of the Aggregates

The SEM images of (1) were recorded at different water fractions (10%, 40%, 80% and 2 100%) of samples using the same set of solutions utilized for fluorescence experiments. At 3 40% water fraction (Fig S5b), images revealed smaller sized aggregates while at 100% 4 water fraction, larger lumps are observed (Fig S5c) and no aggregates were seen in 5 dioxane (Fig S5a). The absorption spectra showed in (Fig S3) reveals bathochromic 6 7 absorption shifts at 80% or more water fractions indicating the possible formation of aggregates. The large emission intensity changes observed at 40% water fractions<sup>4,5</sup> could 8 be due to the presence of differently sized aggregates. For (2 and 3), no aggregates are 9 seen in dioxane, but aggregate-like structures are noted at 80% water. In 100% water rod-10 11 like crystalline structures (Fig. 6 and 7) was observed. The formation of such structures was aided by the presence of lipophilic  $CF_3$  groups and its contribution to the overall 12 packing. 13



Fig.6 SEM images of compound (2) in (a) 100% dioxane (scale: 1µm), (b) 80% water
(scale: 1µm) and in (c) 100% water (scale: 1µm).



Fig.7 SEM images of compound (3) in (a) 100% dioxane (scale: 100 nm), (b) 80% water
(scale: 1µm) and in (c) 100% water (scale: 1µm).

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#### 1 Gelation and Rheology studies

2 Encouraged by the unique emission in aqueous media and the propensity of  $CF_3$ 3 substituted compounds to form organogels, we investigated the formation of low molecular weight organogelators with compounds (2 & 3) containing trifluoromethyl 4 substituents. To study the gelation properties, (2) and (3) were dissolved in t-butanol (1.8) 5 6 wt%) in a glass vial, heated to 70°C to obtain a clear solution. When the hot solutions of (2)& (3) in t-BuOH were kept in the refrigerator for  $\sim 5$  min and then left at room temperature 7 for 30min, organic fibers/ribbons have formed gradually in the solution by assembling 8 through noncovalent interactions (H-bonding and hydrophobic interactions). The hot t-9 BuOH solution is followed by sonication and subsequently cooled for five minutes in the 10 refrigerator. Warming up the solution to the room temperature results in the formation of 11 a viscous gel [Fig 11]. The gel so obtained has no gravitational flow even after inversion of 12 the vial (Fig. 8a & b) indicating its overall stability. This gelation was also thermo-reversible 13 with heating (~70 °C) and cooling cycles [Fig. 8]. Examination of its emission reveals a 14 bathochromic shift in wavelength with a concomitant increase in emission intensity [Fig. 15 5b] as compared to the solution. The gelation was also successful in toluene and 1, 2-16 dichloroethane but here we report the studies of gels with t-butanol as a solvent. 17 Compound (1) with no  $CF_3$  group shows no gel formation (Fig. S6) due to insufficient 18 intermolecular interactions. 19



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Fig. 8 The thermo-reversible sol-gel transitions of the gels of (2 & 3).

To ascertain the formation of gels and assess the stability and viscoelastic properties of (2) & (3), rheological properties were characterized by the time, frequency and amplitude sweep measurements. The samples were equilibrated for 5 minutes before starting the rheological experiments and further subjected to an oscillatory strain ( $\gamma$ ) = 0.1% and angular frequency ( $\omega$ ) of 100 - 0.1 rad/s. These conditions ensure that the storage

modulus (G') and loss modulus (G") are measured in the linear viscoelastic (LVE) regime. 1 Oscillatory strain sweep measurements probe the non-linear response of the samples in the 2 range of  $\gamma = 0.01$  % - 100 % at a fixed  $\omega$  of 6.28 rad/s. Our data indicate that the storage 3 moduli (G') is quite higher than the loss moduli (G'') indicating low tan  $\delta$  (tan $\delta$ =G''/G') 4 values obtained for both gel samples (2) and (3) which reveal their gel nature. The G' 5 values for both gel (2) and (3) were independent of experimental time and frequency 6 range<sup>42, 43</sup> as shown in Figure 9 and 10. The figures further indicate that the G' obtained 7 for gel (2) is in the order of  $10^3$  Pa, while for gel (3) the obtained G' value is in the order of 8  $10^4$  Pa, which suggests the higher strength of gel (3) as compared to gel (2). Even though, 9 the strong  $\pi - \pi$  stacking interactions between the rigid anthryl segments provide the 10 essential driving force for gelation; the relatively higher strength of gel (3) can be 11 understood by the existence of two  $CF_3$  groups in the gel (3). These  $CF_3$  moieties play a 12 key role in the formation of stronger gel networks by reinforcing non-covalent 13 interactions<sup>26</sup> as opposed to gel (2) that consist of only a single  $CF_3$  group. Figure S7 14 shows that with an increase in strain amplitudes, the gel starts forming liquid by a steep 15 decrease in the values of both moduli and the reversal of the viscoelastic signal (G'' > G'). 16 17 The contribution of  $CF_3$  groups in the formation of gels by non-covalent interactions is widely reported<sup>21, 36, 44</sup> 18



Fig. 9 a) Time sweep measurement b) Frequency sweep measurement of gel (2) in tBuOH.

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Fig. 10 a) Time sweep measurement b) Frequency sweep measurement of gel (3) in *t*-BuOH.

For further insight on aggregation morphology of (2) and (3), a dried organogel sample was transferred onto a silicon wafer and subjected to the scanning electron microscopy (SEM) observation. The SEM images in Figure 11 suggest that (2) and (3) form entangled three-dimensional networks consisting of the bundles of fibrous aggregates, which must be responsible for the observed gelation. The corresponding fluorescent microscopy images were shown in Fig S8. The transmission electron microscopy images (TEM) also confirm this observation and reveal entangled bundles of fibers (2), built up from thin fibrils (Fig 12). The TEM image also shows intertwined and entangled microfibers. The image reveal thicker and longer multiple of nanometers in width and micrometers in length) fibers for gel (2) (Fig. 11a). It should be noted that conjunctions emerged for (2) as shown in SEM and TEM images, was in accordance with organogel formation.



Fig. 11 SEM images of the xerogels obtained from t-BuOH gelation sols of (a) (2), (b) (3)
(scale: 10 μm). (inset: shows magnified image of scale: 10 μm showing attachment points)
and

12 These self-assembled structures are aided by non-covalent forces such as hydrophobic forces,  $\pi$ -  $\pi$  interactions of any moieties and intermolecular interactions through the CF<sub>3</sub> 13 14 group (C-F---H-Ar). The polar cyano group on the vinyl bond helps in regulation of growth of the molecular self-assembly by strengthening the electrostatic interactions 15 between two adjacent molecules. For optimum interactions the system becomes 16 planarized, but the repulsion induced from the relatively bulkier CF<sub>3</sub> group lead the 17 18 molecules to slide away along the molecular axis. However, the H-bonding arising from C-F---H-Ar and  $\pi - \pi$  interaction of the neighboring anthryl rings stabilize these repulsive 19 movements resulting in the construction of 1D or 2D microfibril-like structures formed 20 through lengthwise stacking (*i.e.*, head-to-tail J- aggregation). 21



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Fig.12 TEM image of organogel formed by (2): (scale: 1 μm) (inset: shows magnified
 image of scale: 200 nm)

#### **3 Powder XRD studies**

4 Powder XRD measurements were performed on the xerogels of (2) & (3), prepared from t-BuOH, to obtain further information on the molecular arrangement in their gel state 5 6 (Fig.S9a and S9b). Well-resolved X-ray diffraction signals of (2) are shown in Fig S8a. The sharper peaks, formation, and disappearance of the new peaks appear in the gel state 7 indicating structural changes to the morphology, *i.e.* formation of fibers/microcrystals. 8 The peak of powder sample at angle  $2\theta$ =17.13° (Full Width Half Maximum=0.498) shifts 9 to  $20=17.18^{\circ}$  (fwhm=0.457) with intense peaks. The low FWHM indicate greater 10 crystallinity in these xerogels. Similarly, the X-ray diffraction (XRD) pattern of gel (3) 11 also showed new sharper peaks distinct from the powder sample. The data appears that the 12 xerogels obtained have higher order packing aided by non-covalent attractions. 13

#### 14 Conclusion

We have demonstrated the efficient formation of low molecular weight organogels by the self-assembly of simple anthrylcyanostyrenes bearing CF<sub>3</sub> groups into a three-dimensional network of fibrous structures. The gels exhibit a bathochromic emission wavelength shifts accompanied by an enhancement in emission intensity compared to that of the solution. The unique gelation is attributed to the combined intermolecular interactions of the CF<sub>3</sub> group and  $\pi$ - $\pi$ \* interactions of the anthryl moiety and the restrictions offered by the presence of cyano group on the double bond.

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#### 26 Supporting Information

27 Fig S1-S12 including NMR characterization spectra are provided

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CF3 substituted Anthryl cyanostyrenes were synthesized and examined for their self-assembly and organogel formation.

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