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Solvent assisted fluorescence modulation of a C_3-symmetric organogelator†

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The synthesis and self-assembling properties of C_3 symmetric donor–acceptor molecules containing 1,3,4-oxadiazole and bisthiophene moieties in the core functionalized with octyl (**BTOX8**) and dodecyl (**BTOX12**) substituted phenyl acetylene units at the periphery are reported. **BTOX8** was found to form gels only in aliphatic solvents, whereas **BTOX12** formed gels in both aliphatic and aromatic solvents. Photophysical analysis of **BTOX12** solutions showed a striking effect of the solvent on the nature of the self-assembled aggregate formed. Our studies indicate that in aliphatic solvents such as *n*-decane the solvent molecules interact mainly with the alkyl regions of **BTOX12**. As a result the π–π interaction between the neighbouring molecules becomes feasible resulting in strong excitonic coupling between the neighbouring molecules leading to excimer type emission. In aromatic solvents the solvent molecules interact mainly with the chromophoric part of **BTOX12** resulting in reduced π-stacking between the molecules in the aggregate leading to monomer type emission. Films prepared from aliphatic and aromatic solvents exhibited photophysical properties significantly similar to those observed in the respective solvents. Photophysical studies of the films indicated that the films prepared from *n*-decane exhibited an H-type molecular arrangement whereas the films prepared from toluene exhibited a slipped stack J-type arrangement.

Introduction

The increasing interest in π-conjugated materials, driven mainly by their potential for application in devices such as light-emitting diodes, photovoltaic devices, and field effect transistors, has led researchers to design polymers and small molecules possessing novel architectures and study their supramolecular organization in the bulk state with the intention of optimizing their optical and electronic properties.[1] In spite of these efforts, fine control of the supramolecular organization of these molecules which are dependent on various weak non-covalent interactions remains a major challenge.[2] Depending upon the nature of the application, preferential organization of the molecules can vary, such as for example the formation of H-aggregates formed by face-to-face arrangements of molecules which facilitates better charge transport is desirable for OFETs and solar cells, whereas formation of J-aggregates formed by head-to-tail arrangements is desirable for the formation of highly luminescent materials.[3] Hence by creating a difference in the mode of aggregation it would be possible to control the optical properties of the bulk materials formed from the same set of molecules. Although there are several reports in the literature on controlling the preferential formation of a particular type of aggregate in solution using ionic liquids,[4] host–guest interactions,[5] ultrasound,[6] hydrogen bonding interactions[7] or by making subtle changes in the molecular structure,[8] only a restricted number of reports discuss the role of solvents in such processes.[9] Moreover the control of aggregation using solvents does not normally translate into control of organization in the bulk materials or films drawn from them.

We have been interested in the optical and self-assembling properties of multi-arm oxadiazole based donor–acceptor systems.[10] There is a significant amount of growing interest in developing this class of materials since they can help to increase the dimensionality of conjugation compared to conventional one dimensional polymers and oligomers.[11] The ability of such molecules to self-organize in a columnar fashion can result in materials wherein anisotropic conduction of excitons, charges and ions is possible. In this work we describe the synthesis, self-assembly and optical properties of a class of three arm molecules (**BTOX8** and **BTOX12**) incorporating a bisthiophene moiety between the oxadiazole and alkoxy substituted phenyl acetylene chromophore of the π-conjugated arm (Chart 1). Among the various heterocyclic building blocks thiophene chromophores have been most widely used for the generation of

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† Electronic supplementary information (ESI) available: Experimental details, syntheses, characterization details, dynamic light scattering spectra, preliminary photophysical data in different solvents, excitation, emission, fluorescence lifetime decay curves and data of **BTOX12** in the gel state in toluene and *n*-decane. See DOI: 10.1039/c4tc01008f

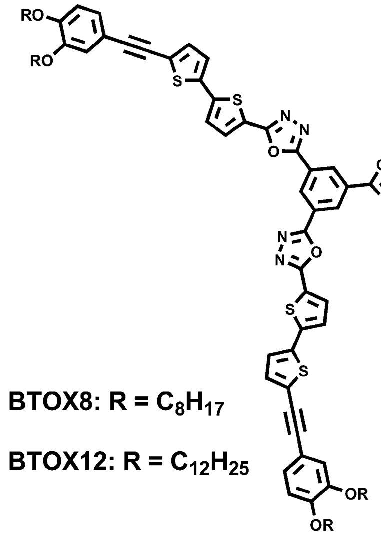


Chart 1 Molecular structure of BTOX derivatives.

conducting materials since they can impart favourable charge transport and redox properties.[12] Here, we report on the photophysical properties of the gels and thin films of these molecules formed from solutions in aliphatic and aromatic solvents. It was observed that **BTOX8** could gelate only aliphatic solvents whereas **BTOX12** formed stable gels in both aliphatic as well as aromatic solvents. Moreover, the luminescent properties of the **BTOX12** organogels were observed to be very sensitive to the nature of the solvent used, which could be attributed to the differences in the nature of the aggregates formed. Thin films drawn from these solvents also exhibited similar differences in their luminescence behavior. The nature of the different aggregates formed and their impact on the luminescence behavior are discussed.

Results and discussion

Syntheses

BTOX8 and **BTOX12** were synthesized *via* multistep reactions as shown in Scheme S1.† The final step involved conversion of the corresponding tetrazole derivatives into oxadiazoles by a reaction involving the Huisgen mechanism.[13] The tetrazole derivatives (**8a** and **b**) were synthesized by reacting sodium azide with the corresponding 5′-((3,4-bis(alkoxy)phenyl)ethynyl)-2,2′-bithiophene-5-carbonitrile (**7a** and **b**) which were prepared by performing the Sonogashira coupling reaction between the 5-iodo-2,2′-bithiophene-5-carbonitrile (**6**) and 1,2-bis(alkoxy)-4-ethynylbenzene (**4a** and **b**). All the intermediates as well as the final products were isolated in good yields using chromatographic techniques and were characterized using ^{1}H, ^{13}C NMR, IR spectroscopy and MALDI-TOF analysis.

Gelation properties

The gelation behavior of **BTOX8** and **BTOX12** was investigated in aliphatic solvents such as *n*-decane, hexadecane and aromatic solvents such as benzene and toluene. The gels were prepared by dissolving small amounts of the gelator molecules in the respective solvents at higher temperatures and allowing the solution to cool to room temperature in a closed vial. Gel formation was confirmed by the failure of soft mass to flow on inverting the glass vial.[14] It was found that **BTOX8** could form gels only in aliphatic solvents such as *n*-decane and hexadecane whereas **BTOX12** formed gels in all solvents mentioned above.

The thermal stability of the gels was measured using a "dropping ball" method.[15] The critical gelation concentrations and T_{gel} values for both derivatives in different solvents were estimated and are summarized in Table 1. It may be noted that both **BTOX8** and **BTOX12** do not possess any specific hydrogen bonding moieties and the strong self-assembly leading to gel formation could be mainly through the synergistic effect of π–π stacking, dipole–dipole interactions and hydrophobic interactions between the long alkyl chains in these donor–acceptor molecules. Since **BTOX12** formed gels in both aliphatic as well as aromatic solvents, the aggregation behavior and photophysical properties of this molecule were studied in detail. Dynamic light scattering measurements of 2×10^{-4} M solutions of **BTOX12** revealed the presence of ~0.5 and 1 micrometre sized aggregates in toluene and *n*-decane, respectively (Fig. S1†).

The structures of the aggregates formed in these solutions were investigated using microscopic techniques. Fig. 1 shows the AFM and TEM images observed for **BTOX12** (2×10^{-4} M) in *n*-decane and toluene which indicated an interlocked network structure of fibres. In order to elucidate the molecular arrangements in the fibres we have carried out small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) measurements on the xerogels obtained by drying 5 wt% (3×10^{-2} M) of *n*-decane and toluene gels. Both the xerogels showed only one peak in the small angle region and a broad halo in the wide angle region. For the *n*-decane xerogel a SAXS peak at $2\theta = 1.29°$ and for the toluene xerogel a peak at $2\theta = 1.38°$ corresponding to *d*-spacing values of 67.97 Å and 63.90 Å, respectively (Fig. 2a), were observed. This is indicative of one dimensional columnar arrangement in fibres.[16] The absence of higher order reflections in the SAXS pattern suggests that long range inter-columnar structural ordering is absent in these systems. In the wide angle region only a broad halo was observed corresponding to 4.45 Å ($2\theta = 19.94°$) for the toluene xerogel indicative of liquid like arrangements of the peripheral alkyl chains (Fig. 2b).[17] For the fibres observed in the *n*-decane xerogel, in addition to the reflection peak corresponding to

Table 1 Critical gelation concentrations (CGCs) and T_{gel} values of BTOX12 and BTOX8 in different solvents

	BTOX8		**BTOX12**	
Solvent	CGC	T_{gel}	CGC	T_{gel}
n-Decane	16.2 mM	78 °C	17.6 mM	51 °C
Hexadecane	12.1 mM	87 °C	14.3 mM	56 °C
Benzene	Soluble	—	18.6 mM	65 °C
Toluene	Soluble	—	21.5 mM	68 °C

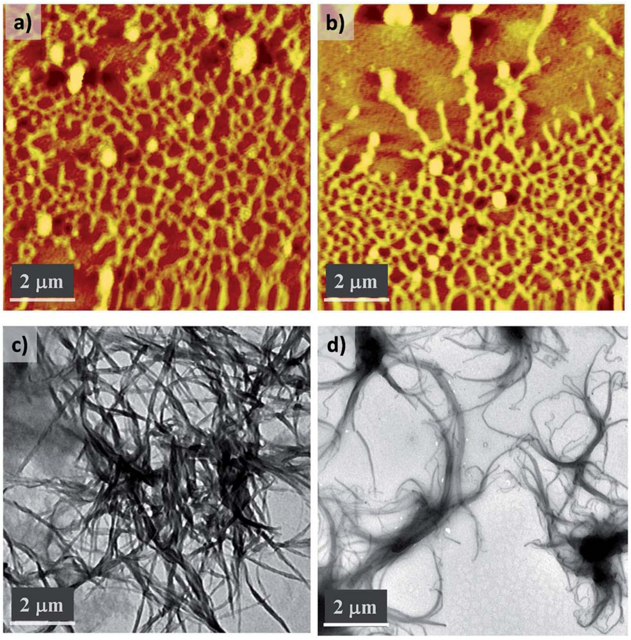


Fig. 1 AFM and TEM images of 2 × 10^{-4} M solution of **BTOX12** in (a and c) toluene and (b and d) *n*-decane.

4.5 Å, a peak corresponding to 3.7 Å indicative of the π–π interaction was also observed. This indicates more ordered packing of the molecules in the nano-fibres formed in *n*-decane compared to that formed in toluene. The differences in molecular ordering of the gels in the two solvents may be attributed to the aliphatic solvent interacting more strongly with the alkyl chains of the gelator molecule without hindering the π–π interaction between the molecules, and the aromatic solvent interacting with the aromatic part of the gelator molecule which would minimize the effective π–π interaction between the gelator molecules.

Photophysical properties

The photophysical properties of the **BTOX12** derivative in different solvents under dilute conditions were measured (Fig. S2 and Table S1†). A minimal shift in the absorption maxima with solvent polarity (Fig. S2a†) indicated that the dipole moment values for both ground and Franck–Condon (FC) excited states are the same, whereas a bathochromic shift with increasing polarity (Fig. S2b†) indicated that luminescence occurred from a non-Franck–Condon polar intramolecular charge-transfer (ICT) state.[18] Since the X-ray measurements indicated clear differences in the nature of the self-assembly of **BTOX12** molecules in the xerogels formed from *n*-decane and toluene detailed photophysical properties of the aggregates formed in these solvents were compared.

Aggregation behavior in *n*-decane

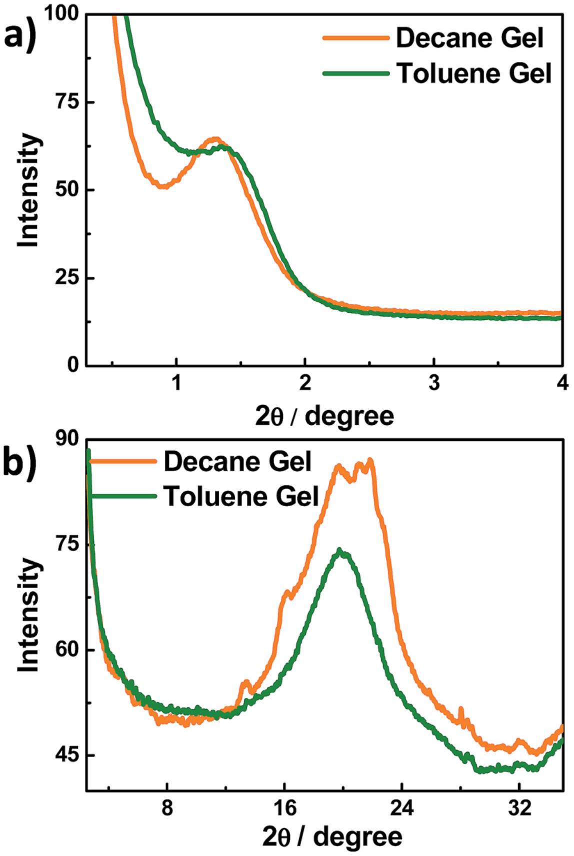


Fig. 2 (a) SAXS and (b) WAXS patterns of the **BTOX12** xerogel in *n*-decane and toluene.

Fig. 3a shows the normalized absorption and emission spectra of **BTOX12** in a dilute (1 × 10^{-7} M) solution containing solvated molecules and in 2 × 10^{-4} M solution containing the aggregates. Except for a slight broadening the absorption spectrum of the aggregate is very similar to that of the monomer. In contrast the emission spectra of the monomer and the aggregated forms were significantly different. In comparison to the structured monomer emission in the 450–600 nm region the aggregates formed in *n*-decane exhibited a broad, structureless and highly red shifted emission spectrum (Stokes shift ~ 200 nm) with a maximum centered at 610 nm. The presence of aggregates was confirmed by studying the effect of temperature on the absorption spectrum (Fig. 3b). With decrease in temperature, formation of aggregates is indicated by the hypochromism and slight broadening of the absorption spectrum. Such changes in the absorption spectrum on formation of aggregates are normally attributed to the formation of H-type aggregates.[19] Fig. 4a shows the excitation spectrum measured in 1 × 10^{-7} M and 2 × 10^{-4} M solutions of **BTOX12** in *n*-decane. In the dilute solution, **BTOX12** exhibited a narrow excitation spectrum with a maximum centered at 402 nm which could be attributed to the solvated molecules. The excitation spectrum measured in aggregated solutions however showed considerable broadening with a slight blue shift in the excitation maximum (389 nm) suggesting the presence of exciton coupled aggregates. Fluorescence lifetimes of the excited species formed in the 1 × 10^{-7} M and 2 × 10^{-4} M solutions were measured by monitoring at their emission maxima (500 nm for dilute solution and 610 nm for the concentrated solution; Fig. 4b). The

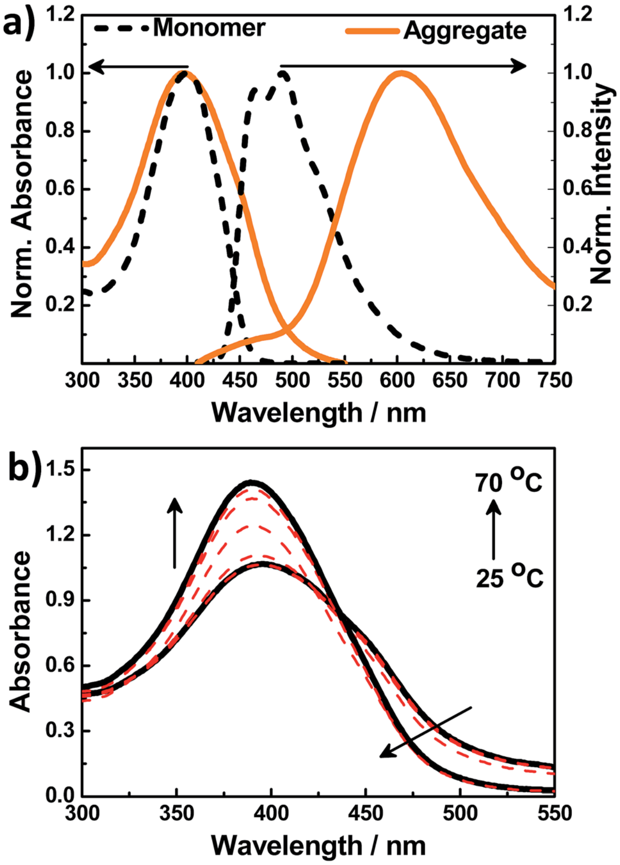


Fig. 3 (a) Absorption and emission spectrum (λ_{ex} = 400 nm) of **BTOX12** in dilute ($C = 1 \times 10^{-7}$ M; black dashed line) and aggregated solutions ($C = 2 \times 10^{-4}$ M; orange line) in *n*-decane and (b) temperature dependent changes in the absorption spectrum of 2×10^{-4} M solution of **BTOX12** in *n*-decane.

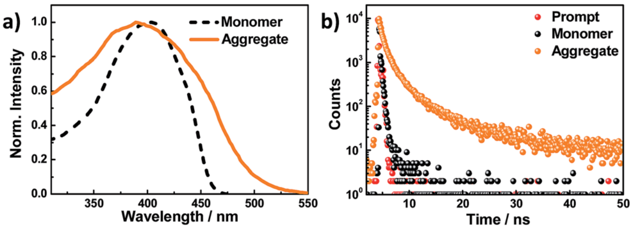


Fig. 4 (a) Excitation spectrum (monitored at emission maximum) and (b) fluorescence lifetime decay profile of **BTOX12** in 1×10^{-7} M (black) and 2×10^{-4} M (orange) solution in *n*-decane.

fluorescence lifetime decay profile for the 1×10^{-7} M solution exhibited a mono-exponential decay with a lifetime value of 0.3 ns attributable to the solvated monomer species present under these conditions. For the concentrated solution a triexponential decay was observed with all the species having higher lifetimes [$T_1 = 0.5$ ns (36%), $T_2 = 1.8$ ns (47%), $T_3 = 7.4$ ns (17%)].

The broadening of the absorption spectrum coupled with the red-shifted emission spectrum and long lifetimes confirm the formation of H-type aggregates in the concentrated solutions. Although such types of aggregates are usually reported to be non-emissive or weakly emissive due to rapid intraband relaxation processes there are a few reports in the literature describing luminescent H-aggregates where the observed emission was ascribed to the formation of either excimer type species or due to slight rotation of the two exciton coupled molecules in the excited state.[20] The photophysical properties of the gel formed in *n*-decane were very similar to those observed in the concentrated solution (Fig. S3 and Table S2†).

Aggregation behavior in toluene

Fig. 5a shows the normalized absorption and emission spectra of **BTOX12** in 1×10^{-7} M and 2×10^{-4} M solutions in toluene. Unlike in *n*-decane the absorption and emission spectra were nearly the same for the two solutions, although dynamic light scattering measurements of the concentrated solution had revealed the presence of aggregates with an average size of ~0.5 micrometer (Fig. S1b†). The absence of significant spectral changes suggests that the excitonic coupling between the neighboring molecules is very weak in these aggregates. Temperature dependent absorption changes however indicated the break-up of the aggregates with increasing temperature (Fig. 5b). Except for a slight broadening, the excitation spectra of the aggregates were very similar to those of the monomers

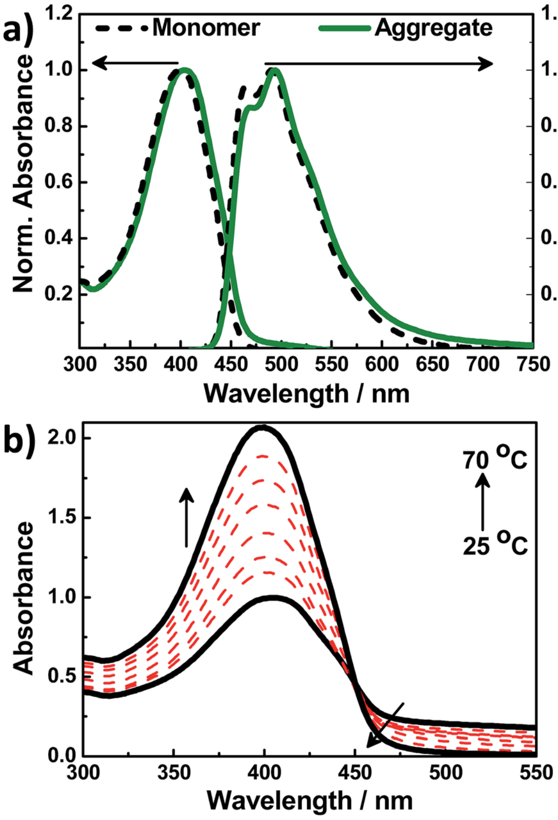


Fig. 5 (a) Normalized absorption and emission spectra (λ_{ex} = 400 nm) of **BTOX12** in dilute ($C = 10^{-7}$ M; black short dashed line) and aggregated solutions ($C = 2 \times 10^{-4}$ M; green line) in toluene and (b) temperature dependent changes in the absorption spectrum of 2×10^{-4} M solution of **BTOX12** in toluene.

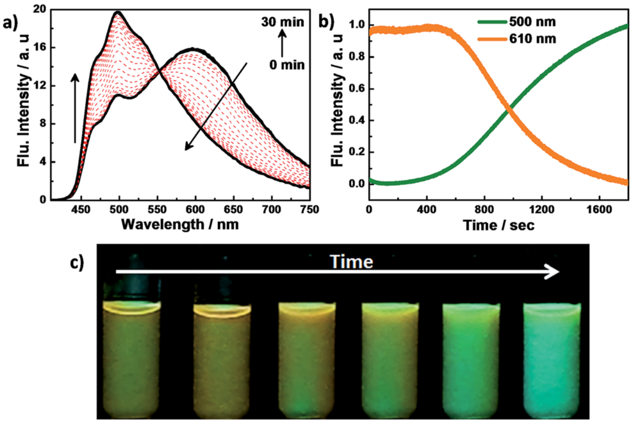


Fig. 7 (a) Time dependent changes in the emission spectrum (λ_{ex} = 400 nm; 1 mm cuvette) of 1×10^{-3} M solutions of BTOX12 in toluene and (b) secondary plot showing the changes in the intensity at 610 nm and 500 nm with time and (c) photographs showing the time dependent changes in fluorescence colour of 1×10^{-3} M solution of BTOX12 in toluene under 365 nm UV light.

(Fig. 6a). Fluorescence lifetime measurements of the aggregated solution exhibited a triexponential decay with the majority component (83%) exhibiting a lifetime (0.4 ns) very similar to that observed for the monomer (0.3 ns) (Fig. 6b). These results confirm that although the molecules are aggregated, the excitonic coupling between the molecules within the aggregates formed in toluene is significantly weaker than that observed in *n*-decane. The photophysical properties of the toluene gel were nearly similar to those observed in the concentrated toluene solution (Fig. S4 and Table S2†).

An interesting observation was made while preparing solutions of higher concentration ($\geq 10^{-3}$ M) and gels of **BTOX12** in toluene. **BTOX12** solutions of concentrations $\geq 10^{-3}$ M were prepared by dissolving appropriate amounts of the compound at high temperature and subsequently allowing the solution to cool to room temperature. Initially the emission spectra of these solutions were very similar to those observed in *n*-decane, with the emission maximum centered at 610 nm. Over a period of time (~30 minutes) the intensity of the 610 nm emission band decreased and a concomitant increase in the intensity of an emission band centered at 500 nm was observed (Fig. 7a). The change in the fluorescence intensities at the two wavelengths (500 nm and 610 nm) plotted as a function of time showed that the initial fluorescence spectrum was stable for up to 8 minutes following which transformation of one band to the other took place over a period of ~30 minutes (Fig. 7b). This change could be visually perceived as a change in the color of emission from orange to green (Fig. 7c).

Based on the spectral changes it could be summarized that in the concentrated **BTOX12** solutions in toluene, excitonically coupled π-stacked H-type aggregates are initially formed. Over a period of time, the interaction of toluene with the aromatic part of the **BTOX12** molecules leads to disruption of the π-stacked H-type aggregates yielding aggregates in which excitonic coupling between neighbouring **BTOX12** molecules is weak.

To confirm that the toluene solvent molecules disrupt the formation of exciton coupled aggregates the emission spectra of 1×10^{-3} M solutions of **BTOX12** in toluene–*n*-decane solvent mixtures of varying proportions were studied (Fig. 8) by diluting a concentrated solution of **BTOX12** in *n*-decane. Upon increasing the percentage composition of toluene in the mixture, the intensity of the fluorescence band centered at 610 nm decreased and a concomitant increase in the intensity of the 500 nm emission band was observed. Based on these studies we can conclude that toluene being an aromatic molecule is capable of forming weak complexes with the chromophoric part of **BTOX12** and thereby interferes with the excitonic coupling between the molecules in the aggregates by disrupting the π-stacking between them. Recently, Banerjee and coworkers have reported the involvement of solvent molecules in forming charge transfer complexes with gelator molecules. Using spectroscopic and computational studies, the authors have shown that different aromatic solvents (toluene, xylenes and mesitylene) form CT complexes with a naphthalene diimide based gelator molecule. The strength of the CT complex formed was found to depend on the electron donating ability of the solvent molecule.[21] In order to test the hypothesis that the aromatic solvent molecules could interact with the chromophoric unit of **BTOX12** and prevent the formation of H-stacked

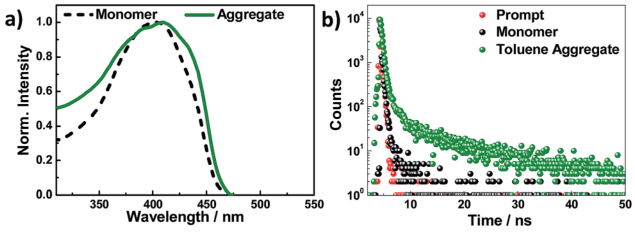


Fig. 6 (a) Excitation spectrum (monitored at emission maximum) and (b) fluorescence lifetime decay profile of BTOX12 in 1×10^{-7} M (black) and 2×10^{-4} M (green) solutions in toluene.

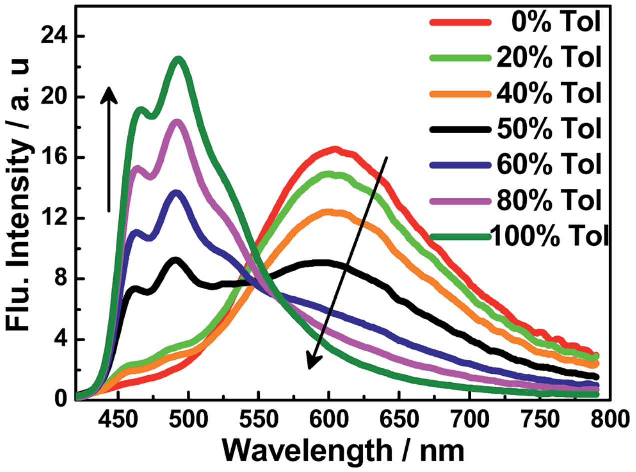


Fig. 8 Changes in the emission spectrum (λ_{ex} = 400 nm; 1 mm cuvette) of 1×10^{-3} M solution of BTOX12 in *n*-decane–toluene solvent mixtures.

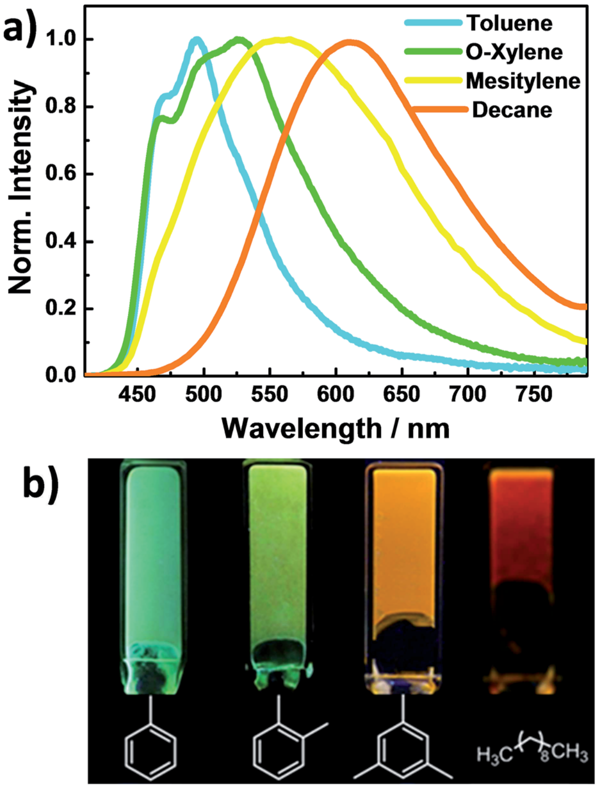
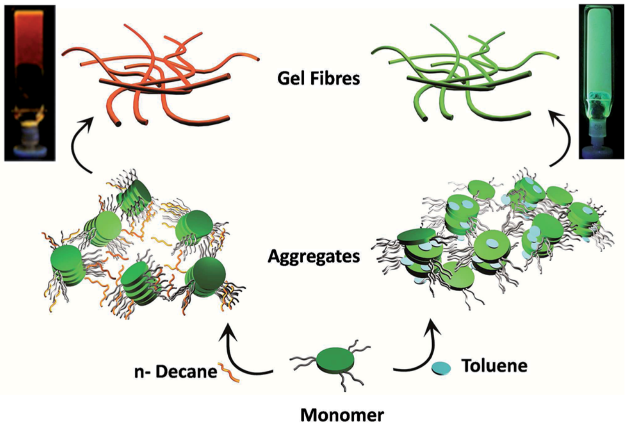


Fig. 9 (a) Emission spectrum of BTOX12 in the gel state in different solvents (λ_{ex} = 400 nm; 1 mm cuvette) and (b) photograph of various gels under 365 nm UV illumination.



Scheme 1 Schematic representation of the aggregate formation of BTOX12 in *n*-decane and toluene.

aggregates, we have investigated the gels formed in different aromatic solvents differing in their bulkiness with respect to toluene (Fig. 9). The emission spectra showed an increasing red-shift (toluene < *o*-xylene < mesitylene) with increasing bulkiness of the solvent. This confirms that the aromatic solvents can disrupt π-stacking between the molecules in the aggregates leading to a reduction in exciton coupling between them. As the bulkiness of the aromatic solvent increases, its ability to interfere with the π-stacking between neighbouring molecules decreases leading to improved exciton coupling between the molecules.

Based on these results a schematic representation of the mode of disruption of the π-stacking within the aggregates is shown in Scheme 1. The alkyl solvent *n*-decane will mainly interact with the alkyl regions of the molecule and hence will not interfere with the excitonic coupling of the aromatic core of the **BTOX12** molecules. It was interesting to note that films cast from toluene and *n*-decane retained to some extent the differences in photophysical characteristics observed in the respective solvents. Fig. 10a shows the emission spectra of films of **BTOX12** prepared by drop casting 5×10^{-3} M solution in *n*-decane and toluene on a quartz plate. Although the fluorescence spectrum of the film drawn from *n*-decane was identical to that observed in solution (Fig. 10a and S6†) the maximum of the fluorescence band of the film drawn from toluene was red shifted by 50 nm compared to that observed in the toluene solution. The excitation spectra of the film from *n*-decane exhibited a broad band centered at 360 nm, whereas the film prepared from toluene exhibited a sharp red shifted peak with the maximum at 480 nm (Fig. 10b). In comparison with the spectra observed in solutions it is clear that in the **BTOX12** films drawn from *n*-decane the molecules are arranged in a face to face arrangement. The red-shifted excitation and emission peaks observed for the films drawn from toluene compared to the respective spectra measured in solution indicate that in the

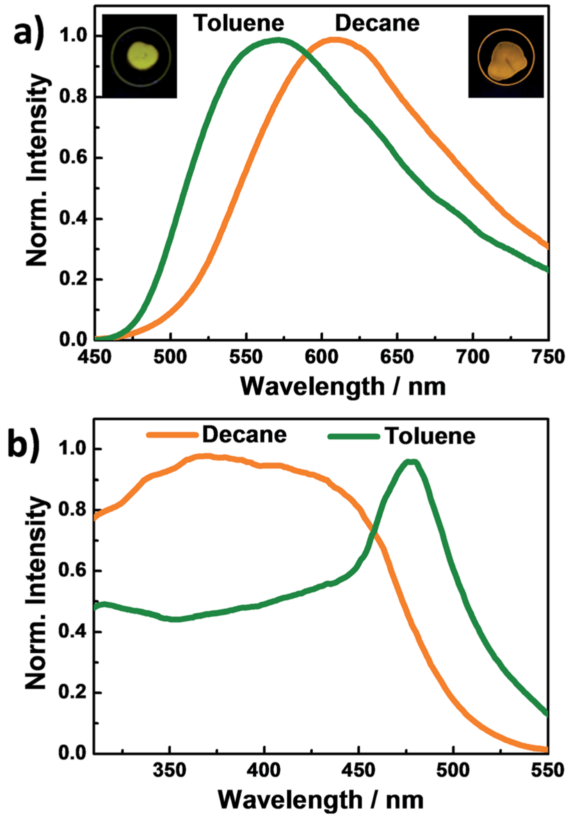


Fig. 10 (a) Emission spectrum (λ_{ex} = 400 nm) and (b) excitation spectrum (emission monitored at λ_{max}) of films of BTOX12 cast from *n*-decane (orange) and toluene (green).

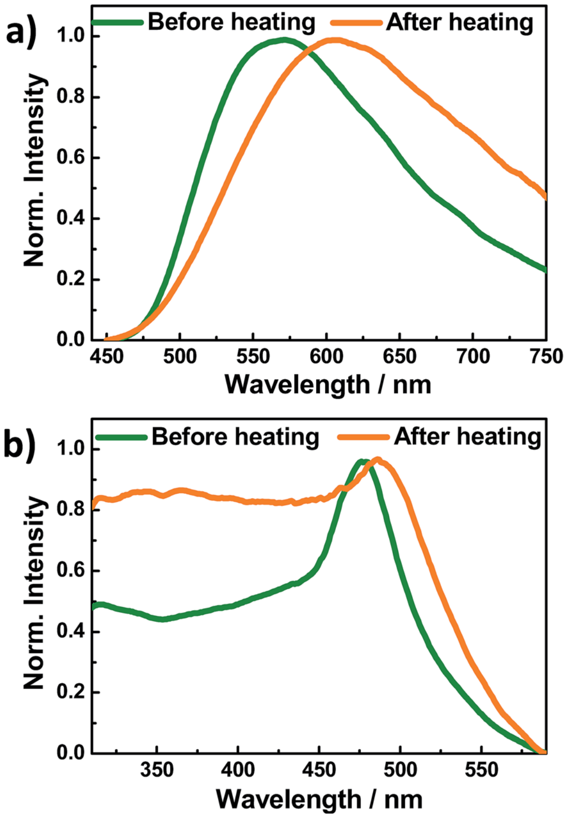


Fig. 11 (a) Emission spectrum (λ_{ex} = 400 nm) and (b) excitation spectrum (λ_{em} monitored at 610 nm) of the toluene film of BTOX12 before and after thermal treatment.

films the molecules are organized in a slip-stacked J-type arrangement.[22]

Removal of the aromatic solvent complexed with the aromatic core of **BTOX12** would lead to improved coupling between the chromophores resulting in the formation of a J-type aggregate. On annealing the **BTOX12** films prepared from toluene by holding it at 120 °C for 20 minutes the emission changed from yellow (~550 nm) to orange red (~610 nm) (Fig. 11a), which can be attributed to the transformation of the J-type aggregate into the H-type aggregate. It is to be noted that there was no phase transition and the compound was stable at this temperature as evidenced from the DSC and TG analyses (Fig. S5†). The excitation spectra also showed a broadening, with increased intensity of emission at lower excitation wavelengths which is in support of the J- to H-type transformation on annealing (Fig. 11b). The films drawn from *n*-decane however did not show any change on similar treatment, confirming that the face-to-face H-type aggregates are the thermodynamically more stable form for this molecule.

Conclusion

The synthesis, self-assembly and gelation behavior of two C_3 symmetric donor–acceptor molecules **BTOX8** and **BTOX12** have been investigated. **BTOX8** was observed to form gels only in aliphatic solvents, whereas **BTOX12** formed gels in both aliphatic and aromatic solvents. Photophysical studies indicated that the nature of the aggregates of **BTOX12** formed in these two types of solvents were remarkably different. Absorption, fluorescence and lifetime analysis of the aggregated and gel states indicated that the aliphatic solvent molecules interact mainly with the alkyl regions of the **BTOX12** molecule, allowing strong π–π interactions to occur between the chromophoric units of the molecules. This led to the formation of strongly excitonic coupled H-aggregates as indicated by the broadening of the absorption spectrum accompanied by highly red shifted excimer type emission with significantly long fluorescence lifetimes. The aromatic solvents on the other hand interact more strongly with the chromophoric part of **BTOX12** resulting in reduced π-stacking between the molecules in the aggregate leading to monomer type emission. It was interesting to note that films prepared from aliphatic and aromatic solvents retained the photophysical characteristics seen in the respective solvent to a significant extent. Films prepared from *n*-decane exhibited an H-type molecular arrangement whereas the films prepared from toluene exhibited a slipped stack J-type arrangement. Such control on the nature of the aggregate formed by changing the type of solvent is highly desirable since it would be possible to control the optoelectronic properties of the bulk materials formed from the same set of molecules using simple techniques.

Acknowledgements

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