

Highly fluorescent supramolecular gels with chirality transcription through hydrogen bonding†

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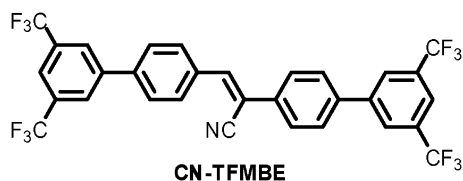
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A highly fluorescent organogel with transparency was formed through a hydrogen (H)-bonding interaction between a non-fluorescent and achiral 2-(3',5'-bis-trifluoromethyl-biphenyl-4-yl)-3-(4-pyridin-4-yl-phenyl)-acrylonitrile (CN-TFMBPPE) monomer and chiral sergeant L-tartaric acid (TA) (or D-TA), with gel formation being accompanied by a drastic fluorescence enhancement as well as chirality induction.

Recently, chiral supramolecular assemblies have attracted considerable attention as candidate materials for use in biological and electro-optical applications since the recognition and transcription of chirality in the self-assembly process has a key role in mimicking the development of biological helical structures with specific function as well as in controlling unique optoelectronic device applications.¹ The first chiral helical supramolecular polymer was prepared by Lehn and co-workers *via* molecular-recognition-directed self-assembly from complementary chiral components.² Subsequently, this design strategy has been used to construct chiral supramolecules from achiral monomers and has been applied to a variety of self-assembled systems including thin films, oligomers, liquid crystals and organogels.³



Previously, we reported a special class of aromatic organogelator (CN-TFMBE) that formed highly fluorescent organogels with aggregation-induced enhanced emission (AIEE).⁴ A unique characteristic of this class of AIEE dye is that it is virtually non-fluorescent in the molecular state in solution but becomes highly fluorescent upon self-assembly into supramolecular fibers. This means that the self-assembly process of CN-TFMBE can be monitored in real time by looking for 'fluorescence turn-on' with the naked eye. The strong self-assembly capability of CN-TFMBE was attributed to cooperative intermolecular interactions induced by the four CF₃ units in addition to the strong π - π interaction of the planarized aromatic segments, which are twisted in isolated molecules in solution.^{4b}

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In the present study, we sought to add specific functional properties to CN-TFMBE, particularly the hydrogen (H)-bonding, optical chirality, and gel transparency. To achieve this, we modified the chemical structure of CN-TFMBE to the pyridine-containing trifluoromethyl-based cyanostilbene (CN-TFMBPPE, see the structure in Fig. 1), which was unlikely to have sufficient self-assembling capability (with only two CF₃ units) and so needed prior complex formation with 3,5-bistrifluoromethyl benzoic acid to attain the proper self-assembling ability for the formation of supramolecular fibers and gels. Moreover, we sought to prepare a transparent organogel from CN-TFMBPPE *via* H-bonding with L-tartaric acid (TA)^{2a,3a,d} as a chiral component, in order to demonstrate chirality transcription in a supramolecular system with concomitant fluorescence turn-on.

CN-TFMBPPE, 2-(3',5'-bis-trifluoromethyl-biphenyl-4-yl)-3-(4-pyridin-4-yl-phenyl)-acrylonitrile, was synthesized in three steps as shown in Scheme S1 (see ESI†).‡ As expected, CN-TFMBPPE was soluble in common organic solvents such as 1,2-dichloroethane (DCE) and did not form a gel. To examine the effect of complementary H-bonding, an equimolar amount of 3,5-bistrifluoromethyl benzoic acid was added to a 1 wt% solution of CN-TFMBPPE in DCE; initially, the CN-TFMBPPE was soluble in DCE and showed no visible color or fluorescence. As the H-bonded complex was generated and thus self-assembly proceeded, a translucent partial gel with a characteristic absorption color and AIEE fluorescence slowly formed over several hours (see Fig. 1). In the FT-IR spectrum of the dried gel (see ESI†), the intermolecular H-bonding of the complex was evidenced by the appearance of broad peaks at *ca.* 2420 cm⁻¹ and 1920 cm⁻¹.^{1g,3e,5} In addition, a SEM image of the dried gel revealed a typical network structure of entangled and fibrillar aggregates. Similar to CN-TFMBE, the gel forming capability of the

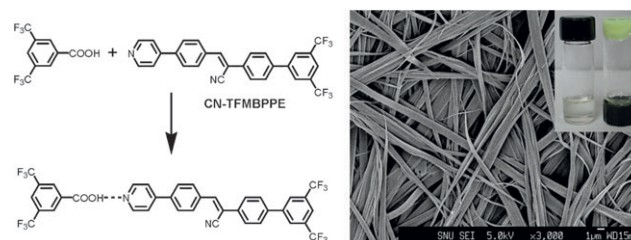
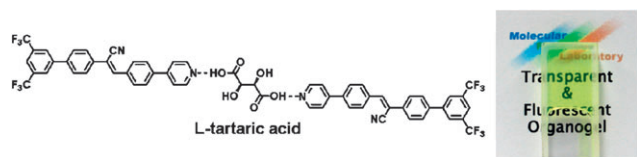


Fig. 1 (a) Schematic representation of the hydrogen (H)-bonded complex between CN-TFMBPPE and 3,5-bistrifluoromethyl benzoic acid (BA). (b) SEM image of a dried gel (partial) formed from the H-bonded complex between CN-TFMBPPE (1 wt%, 1 equiv.) and BA (1 equiv.) in DCE. Inset displays photo images of the corresponding CN-TFMBPPE solution (left) and H-bonded complex gel (right) state. (under daylight).



Scheme 1 H-bonded complex between CN-TFMBPPE and L-TA, and photo image of its transparent gel (L-TA complex gel (1 wt%)) from CN-TFMBPPE (1 wt%, 1 equiv.) and L-TA (0.5 equiv.) in DCE–THF (10 : 1).

CN-TFMBPPE–3,5-bistrifluoromethyl benzoic acid complex is attributed to the presence of CF_3 units at the four peripheral positions. The present results thus support the hypothesis that the self-assembly of these entities relies on cooperative intermolecular interactions induced by four peripheral CF_3 units in addition to the strong π – π interaction of the planarized aromatic segment.

To improve the gel stability as well as to induce chiral organization in this system, L-TA was employed as a chiral H bond donor to CN-TFMBPPE. Surprisingly, a transparent and highly fluorescent organogel promptly formed when 2 equiv. of CN-TFMBPPE (1 wt%, in 500 μl of DCE) was mixed with 1 equiv. of L-TA (in 50 μl of tetrahydrofuran), as shown in Scheme 1. The formation of this gelation was accompanied by the characteristic appearance of a bright yellow color with AIEE fluorescence turn-on. As for the CN-TFMBPPE–3,5-bistrifluoromethyl benzoic acid interaction, broad peaks indicative of H-bonding between the pyridine of CN-TFMBPPE and the carboxylic acid group of L-TA were observed at *ca.* 2500 cm^{-1} and 1920 cm^{-1} in the FT-IR spectrum (see ESI†).^{1g,3e,5} In addition, the presence of strong peaks at 3430 cm^{-1} and 1730 cm^{-1} indicative of H-bonded OH and C=O stretching, respectively, suggested that intermolecular H-bonding⁶ between adjacent molecules of the CN-TFMBE–L-TA trimer complex was additionally contributing to the supramolecular self-assembly. This was indirectly supported by the observation that gelation did not occur when succinic acid which lacks an OH unit, was used instead of L-TA. Furthermore, the intercomplex H-bonding between the neighbouring TA's is so specific as to bring about supramolecular self-assembly and resultant gel formation purely between homo chiral TA units. Neither the gelation nor the remarkable fluorescence enhancement happened in the case of racemic TA mixtures. The CN-TFMBPPE–L-TA complex gel showed a sponge-like morphology (see Fig. 2a) most likely as a result of the release of entrapped solvent during drying.⁷ The different morphology of L-TA–CN-TFMBPPE complex compared to the CN-TFMBPPE–3,5-bistrifluoromethyl benzoic acid gel can be attributed to the additional H-bonding feature of the former system. Closer inspection of the L-TA–CN-TFMBPPE complex gel reveals that the sponge-like film consists of stacked nano-fibrillar aggregates with rather obscure boundaries (see Fig. 2b), giving only a single broad peak in the small angle region of XRD (see ESI†). The excellent optical transparency of the gel must arise from this specific morphological feature. Considering that the molecular length of the trimer complex is considered to be ~ 50 Å, the peak at 16.8 Å in the XRD pattern is most likely to originate from J-type stacking by inclination of trimer complex, of whose optical property (J-aggregate absorption and enhanced fluorescence) is consistent with that typical of J-type

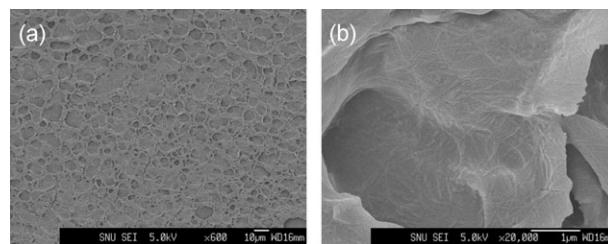


Fig. 2 (a) SEM Image of a dried L-TA complex gel (1.0 wt%) (prepared in Scheme 1) and (b) Its magnified image.

aggregation (*vide infra*). In the wide angle, the peak at 4.6 Å is regarded to represent the intercomplex distance.

The AIEE effect has been shown to originate from the combined planarization and J-type aggregation of CN-TFMBE molecules during supramolecular assembly.^{4a} Absorption and photoluminescence excitation (PLE) spectra of a CN-TFMBPPE (2 equiv., 0.25 wt%)–L-TA (1 equiv.) complex gel as well as the dried gel are shown in Fig. 3a. It is clearly shown that the absorption spectra of the gel consists of two main bands centered at 342 nm and 431 nm (see the deconvolution result in the inset), which are attributed to the monomer and J-aggregate absorption bands, respectively. It must be noted that the 431 nm J-aggregate band is observed in the spectrum of the complex gel and becomes more pronounced in the dried gel, whereas the 342 nm monomer band exactly matches the absorption band of the monomer (CN-TFMBPPE, see ESI†). In Fig. 3a, the PLE spectrum of CN-TFMBPPE–L-TA complex is shown to be comprised of a J-aggregation band with only a weak monomer band, indicating that the strong AIEE fluorescence in the gel state is caused mainly by J-type aggregation. In the dried gel state, monomer band made practically no contribution to the PLE spectrum, indicating the importance of J-stacking to the enhanced fluorescence in the gel state.⁸ Before gel formation, the CN-TFMBPPE solution was very weakly fluorescent with an emission maximum of 430 nm. Upon gelation, however, strong green emission at 514 nm with an intensity of 240 times that of the solution prior to gelation, appeared immediately, as shown in Fig. 3b. This strong and red-shifted AIEE fluorescence in the gel state is attributed to the H-bonding mediated transformation from the twisted conformation in the sol state (which leads to non-radiative decay) to a CN-TFMBPPE–L-TA complex assembly with a planar conformation and J-type aggregation.^{4,8} As a result of this AIEE effect, a very high solid-state fluorescence quantum yield of 57% ($\pm 3\%$) was obtained from a dried gel of the CN-TFMBPPE–L-TA complex.

To investigate the possible chirality transcription in the self-assembling AIEE system, we recorded circular dichroism (CD) spectra of the CN-TFMBPPE complexes with L-TA or D-TA. (see Fig. 3c). In the region of the J-aggregate band, the CD spectra exhibited strong signals with opposite signs (positive for L-TA complex gel, and negative for D-TA complex gel), which is presumably due to the formation of chiral aggregates when the achiral molecule CN-TFMBPPE interacts with the chiral TA.^{3f}

In summary, a highly fluorescent chiral organogel with transparency was prepared *via* the H-bonding mediated supramolecular assembly of non-fluorescent and achiral CN-TFMBPPE and chiral L-TA (or D-TA). Due to the AIEE effect, the supramolecular assembly process could be monitored in the real time by fluorescence turn on.

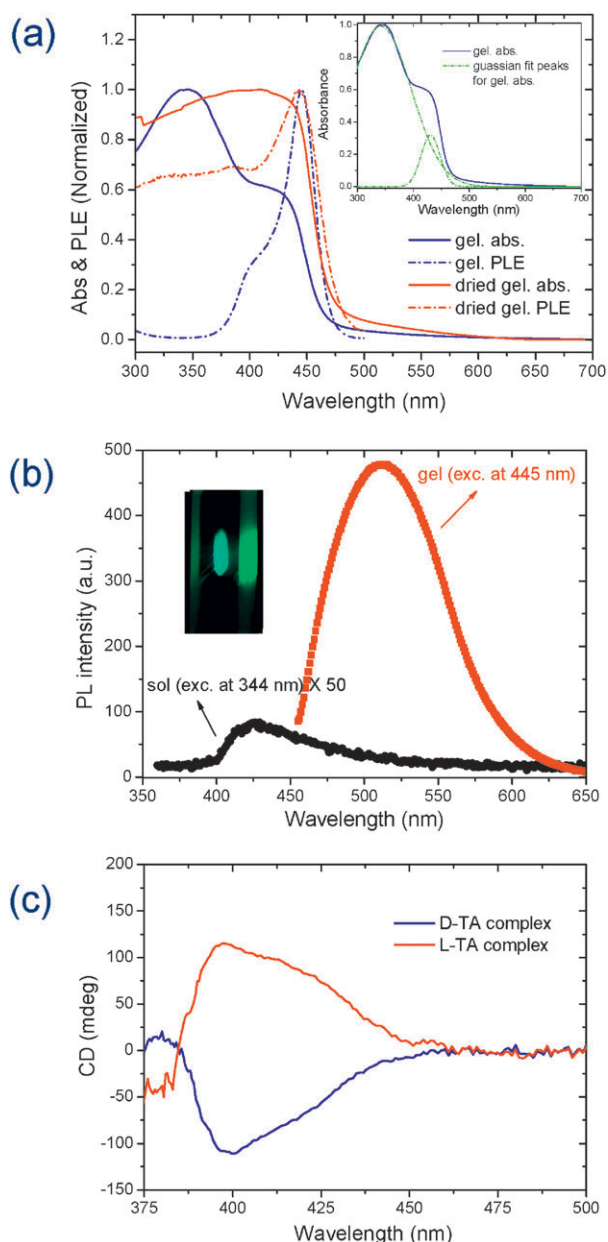


Fig. 3 (a) UV-vis. Absorption (solid) and PLE (dash-dot) spectra of an L-TA complex gel (0.25 wt%) and the corresponding dried gel. PLE was probed at 530 nm. Inset displays two Gaussian-fit peaks for absorption spectrum of gel. (b) PL spectra of CN-TFMBPPE (0.25 wt%, 1 equiv.) in DCE before (black, sol) and after (red, gel) adding L-TA (0.5 equiv.) in THF. Inset shows a fluorescence photo image of the gel. (c) CD spectra of L-TA and D-TA complex gels (0.25 wt%).

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Notes and references

† **General experimental:** UV-vis absorption, circular dichroism (CD) and fluorescence spectra were recorded on a HP 8452-A, Jasco J-715 and Shimadzu RF-500 spectrofluorophotometer, respectively. FE-SEM images were acquired on a JSM-6330F (JEOL). FT-IR spectra were measured on MIDAC corp. FT-IR PRS spectrometer. X-Ray

diffraction patterns were carried out on Bruker GADDS instrument. The QY of the solid film was measured using IESP-150B (Sumitomo Heavy Industries Advanced Machinery Co. Ltd.) including a 15 cm integrating sphere equipped with a Xe-lamp (CW500W) and CCD attached to a monochromator. The details of the analytical procedure used to obtain the QY for the solid films are described elsewhere.⁹

Synthesis of 2-(3',5'-bis-trifluoromethyl-biphenyl-4-yl)-3-(4-pyridin-4-yl-phenyl)-acrylonitrile (CN-TFMBPPE): To the mixture of 4-(pyridin-4-yl)benzaldehyde (0.30 g, 1.64 mmol) and 2-(3',5'-bis(trifluoromethyl)biphenyl-4-yl)acetonitrile (0.54 g, 1.64 mmol) in *tert*-butyl alcohol (30 mL) and THF (2 drops), tetrabutylammonium hydroxide (TBAH) (1M solution in methanol) (0.16 mL) was slowly dropped. After stirring at 50 °C for 2 h, the reaction mixture was poured into water. The precipitate was collected by filtration and was dried. The crude product was purified by column chromatography (dichloromethane) and precipitated in methanol to afford a pale-yellow solid (0.50 g, yield = 62%); mp = 280 °C; ¹H NMR (300 MHz, CDCl₃) δ[ppm]: 8.72 (d, 2H, pyridine-H), 8.06 (m, 4H, Ar-H), 7.90 (s, 1H, Ar-H), 7.86 (d, 2H, Ar-H), 7.78 (d, 2H, Ar-H), 7.72 (d, 2H, Ar-H), 7.67 (s, 1H, vinyl), 7.56 (d, 2H, Ar-H); MS (FAB+) (*m/z*): calcd for C₂₈H₁₆F₆N₂: 494, found: 495; anal. calcd for C₂₈H₁₆F₆N₂: C, 68.02; H, 3.26; N, 5.67, found: C, 67.89; H, 3.00; N, 5.46.

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- The isolated CN-TFMBPPE monomer showed virtually no fluorescence (fluorescence QY = 0.002 in solution compared to 9,10-DPA as reference) because of its energetically-stable twisted conformation, which suppresses radiative decay in the isolated state, as explained in the previous works. See ref. 4 and ESI†.
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