An aggregation-induced blue shift of emission and the self-assembly of nanoparticles from a novel amphiphilic oligofluorene†

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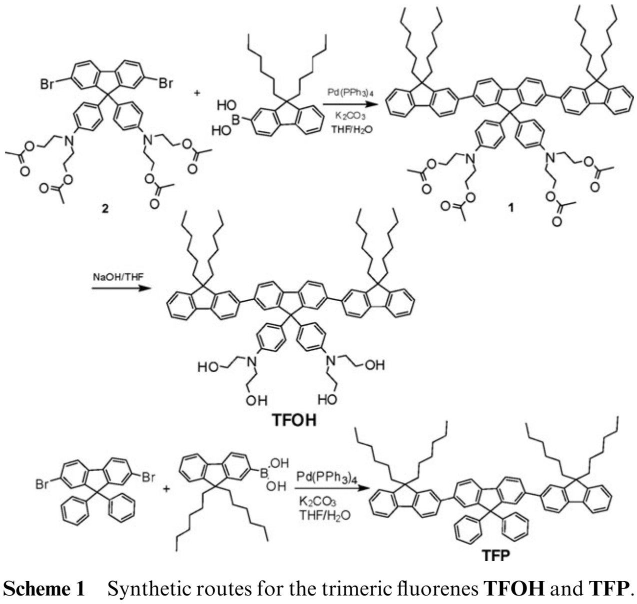
An aggregation-induced blue shift of emission was observed for the first time from a novel amphiphilic trifluorene, TFOH, and tentatively attributed to a similar TICT mechanism; the optical properties and self-assembly behaviors of TFOH, along with their relationships, are presented.

Polyfluorenes and oligofluorenes have emerged as a very important class of optoelectronic materials in virtue of their high luminescent efficiency, good charge-carrier mobility and convenient color tunability.[1] Water-soluble polyfluorenes with cationic side chains have been reported for the detection of biomacromolecules.[2] By modifying them with hydrophilic groups, oligofluorenes/polyfluorenes tend to assemble into nanoparticles of various morphologies, with the formed structures showing characteristic optical properties.[3–5] For example, rod–coil graft copolymers containing oligofluorene/polyfluorene backbones and poly(ethylene oxide) side chains can form fluorescent micellar structures in aqueous solution;[4] amphiphilic trifluorenes with *n*-hexyl and hydroxyethoxymethyl side chains can form self-condensed nanoparticles in THF/H_2O.[5] In both cases, aggregation arising from self-assembly results in excimer formation, and consequently causes a red shift of their fluorescence emission.

In this Communication, we report a novel amphiphilic trifluorene, **TFOH**, having *n*-hexyl and *para*-*N*,*N*-bis-(2-hydroxyethyl)aminophenyl side chains, as well as its hydrophobic analogue, **TFP**, with *n*-hexyl and phenyl pendant groups, for comparison. Interestingly, the ‘‘pure’’ fluorene derivative, **TFOH**, shows a clear green emission in single solvent THF; moreover, its emission spectrum shows an obvious blue shift in the THF/H_2O system or in the film state. This represents the first observation of an aggregation-induced blue shift of emission for oligofluorenes. The optical properties and self-assembly behaviours of **TFOH**, along with their relationships, will be discussed herein.

TFOH and **TFP** were synthesized by a Suzuki coupling reaction, as shown in Scheme 1, and structurally characterized by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy, elemental analysis and mass spectroscopy (see ESI†). We initially investigated the optical properties of **TFOH** and **TFP** in THF solution and in the film state. As shown in Fig. 1, the UV-vis absorption spectra of **TFOH** and **TFP** in THF solution are quite similar, with absorption peaks at 349 and 352 nm, respectively. In addition, the absorption spectra of TFOH and TFP exhibit little change with solvent polarity. However, their fluorescence spectra in THF solution and in the film state show a remarkable difference. **TFP** exhibits an emission maximum of 398 nm in THF solution and 421 nm in the film state, which resembles those of oleophilic oligofluorenes and polyfluorenes. Unexpectedly, **TFOH** exhibits an emission maximum of 494 nm in THF, which is red-shifted by about 70 nm compared to that of **TFP**. In addition, the emission maximum shows almost no shift with THF solution concentration varying from 1.0 × 10^{-7} to 5.0 × 10^{-4} mol L^{-1}, suggesting no aggregation in THF solution. Moreover, the film emission of **TFOH** is blue-shifted by about 60 nm relative to its THF solution, and thus the possibility of long wavelength emission originating from aggregation can be excluded. On the contrary, it seems that aggregation induces a blue shift of the emission in this situation.

Considering the structural differences between **TFP** and **TFOH**, an analogue of a twisted intramolecular charge-transfer state (TICT) is proposed as a possible explanation for these observations.[6] For **TFOH**, the electron-donating bis-(2-hydroxyethyl) amino group is able to internally rotate with respect to the benzene ring. In the low polarity medium of toluene, the emission spectrum of **TFOH** is structured and behaves like a locally excited (LE) state (Fig. 1); in the polar solvent THF, the emission spectrum is remarkably red-shifted and becomes structureless, which indicates a large dipole



Scheme 1 Synthetic routes for the trimeric fluorenes **TFOH** and **TFP**.

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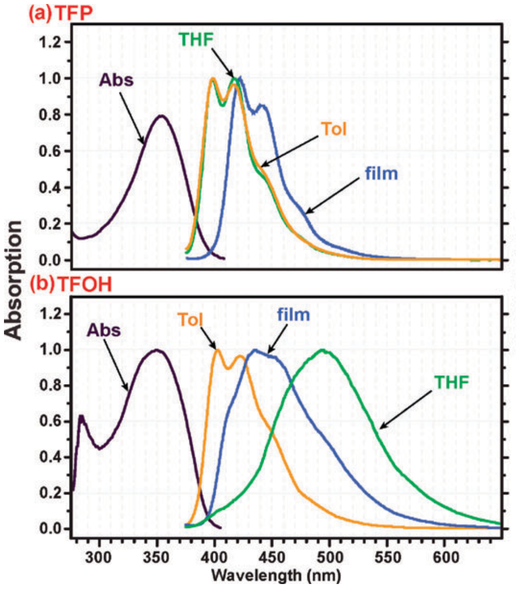

Fig. 1 UV-vis absorption and fluorescence spectra of (a) **TFP** (5.0 μM) and (b) **TFOH** (5.0 μM) in THF, toluene and in the film state. The excitation wavelengths for **TFP** and **TFOH** are 360 and 350 nm, respectively.

moment of the emitting state that could be assigned to a phenomenon similar to TICT emission.[7] In contrast, **TFP** does not exhibit dual fluorescence and red-shifts as the solvent polarity increases from toluene to THF, obviously owing to the absence of amino substitution on the pendant benzene ring. In addition, the quantum yield of **TFOH** is remarkably increased by 86.1% in toluene from 10.2% in THF, while the quantum yield of **TFP** shows a relative small variation, from 77.9% in THF to 93.9% in toluene.

To further prove our assumption, we measured the fluorescence spectra of **TFOH** in THF in the temperature range of 77–300 K (Fig. 2). A clear critical temperature was observed at 157 K, which is close to the freezing point of THF (165 K). Above 157 K, the maximum emission was red-shifted with decreasing temperature, possibly due to increasing solution polarity when the temperature dropped.[8] Below 157 K, the maximum emission shifted to higher energies with decreasing temperature, from about 530 nm at 157 K to 420 nm at 77 K. This may be attributed to the restricted rotation of bis-(2-hydroxyethyl) amino groups with respect to the benzene ring in rigid glass below the freezing point of THF.[9] In addition, the emission dependence on the viscosity also provides evidence for the TICT analogue mechanism. Similarly, when glycerol was added to the solution of **TFOH** in methanol, a significant blue shift of the emission was observed due to the suppression of rotation of the amino groups.

Finally, we investigated the self-assembly behavior of amphiphilic **TFOH** in the THF/H_2O system by FE-SEM and TEM images, and the corresponding optical properties. As shown in Fig. 3, with increasing water fraction, the maximum emission wavelength first shows a slight red shift, then a prominent blue shift. Most likely, when the THF/H_2O ratio is higher than 6 : 4, the increasing water fraction enhances the polarity of the system, consequently bringing about the red shift in emission. By the time water dominates in the system, micellization may occur, with the formed nanoparticles restricting the rotation of the bis-(2-hydroxyethyl)amino group with respect to the benzene ring, as in the rigid glass or film state, consequently resulting in a blue shift of the emission. As for **TFP**, the emission spectrum showed a slightly red shift when the THF/H_2O ratio was changed from 5 : 5 to 4 : 6, while no blue shift occurred, even when the THF/H_2O ratio reached 1 : 99 (see ESI†).

Fig. 4(a) shows an SEM image of a molecular aggregate of **TFOH** after transferring from a THF/H_2O (1 : 9) solution onto a quartz substrate; nanoparticles of radius of 80–250 nm were clearly observed. The TEM image (Fig. 4(b)) further shows the solid inner structure of the nanoparticles, and the high-resolution TEM image (inset of Fig. 4(b)) clearly shows molecular self-assembly patterns. It is noteworthy that the diameters of the nanoparticles measured by DLS (dynamic light scattering) are correlated with the THF/H_2O ratio.[3c] With the increasing proportion of water, the mean diameter of the nanoparticles decreased (THF/H_2O 4 : 6, 342 nm; 2 : 8, 255 nm; 1 : 9, 170 nm; 1 : 99, 122 nm), which suggests a more compact aggregation. It is also important to note, from the DLS measurements, that the nanoparticles cannot form when the THF/H_2O ratio is higher than 4 : 6. This ratio is close to the ratio (6 : 4) that initially caused the blue shift of the emission.

We note that the aggregation-induced blue shift (AIBS) phenomenon is somewhat homothetic to that of aggregation-induced emission (AIE)[10] because of its rotation restrainability due to low temperature, high viscosity or high aggregation state. However, we have to point out that both mechanisms

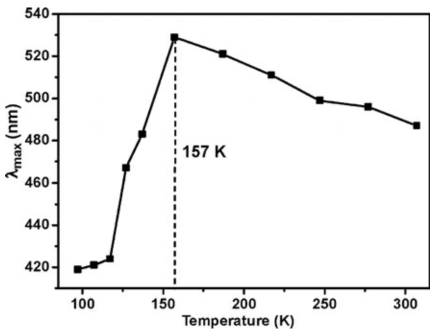

Fig. 2 The maximum emission wavelength of **TFOH** in THF (5.0 μM) at different temperatures. The excitation wavelength was 350 nm.

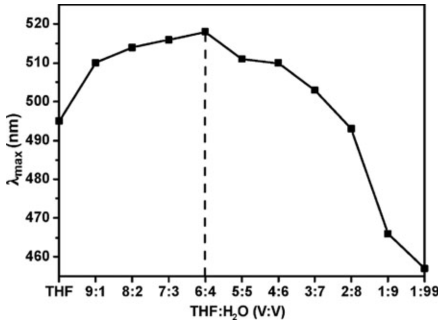

Fig. 3 The maximum emission wavelength of **TFOH** in the THF/H_2O system (5.0 μM) at different solvent ratios. The excitation wavelength was 350 nm.

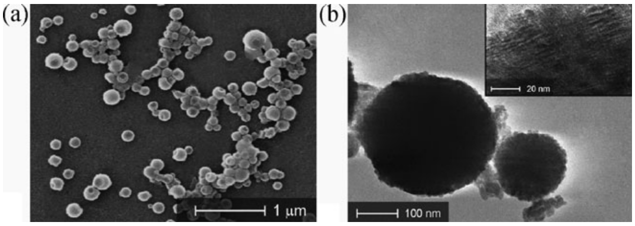

Fig. 4 The (a) SEM image and (b) TEM image of **TFOH** prepared from THF/H_2O, 1 : 9. The inset of (b) shows a high resolution TEM image of an edge of the nanoparticles.

are largely different. In the AIE system, the molecules are out of coplanarity in the single-molecular state (dilute solution), which is weakly emissive. In the aggregated state, intramolecular rotation is restricted, resulting in fluorescence emission enhancement. AIE is usually correlated to the intramolecular rotation of phenyl rings, and no charge-transfer is involved. In contrast, in our case, the rotation of the phenyl rings has no influence on fluorescence, as the comparative analogue, **TFP**, does not show a similar phenomenon to **TFOH**. Instead, the blue shift of the emission originates from the restriction of rotation of the amino groups, and an analogue of twisted intramolecular charge-transfer is involved.

In conclusion, we have presented an unusual aggregation-induced blue shift of emission from a new amphiphilic trifluorene. This phenomenon is tentatively attributed to a similar TICT mechanism. We note that there is only one report about the green emission of oligofluorene attributed to its aggregation behavior in a THF/H_2O system,[5] while this work is the first report that trimeric fluorenes show green emission in a single polar solvent, providing a new way to tune the emission spectra of oligofluorenes. The unique AIBS property may find an application in the detection of micro-environments, especially in biological processes. We are currently investigating the scope and generality of this phenomenon and its applications.

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