Journal Name

COMMUNICATION

Fluorescence responsive conjugated poly(tetraphenylethene) and its morphological transition from micelle to vesicle†

Lipeng He, Xiaoning Liu, Jianjun Liang, Yong Cong, Zhenyu Weng and Weifeng Bu*

A crown ether-functionalized poly(tetraphenylethene) (AP-TPE) is synthesized and the rotation of the TPE group is successfully restricted *via* the complexation of crown ether and organic ammonium salts, leading to stepwise enhanced fluorescence accompanied with a morphological transition from micellar to vesicular.

Owing to high quantum yield, excellent photophysical stability and facile surface modification, conjugated polymers (CPs) have drawn wide attention in the fields of optoelectronics and biology in recent years.[1] However, the conventional CPs often show weak or quenched fluorescence in their concentrated solutions and aggregate states because of aggregation-caused quenching effect, which have limited their real applications such as for light-emitting diodes (LEDs) and bio-imaging/sensors.[2,3] Recently, aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) have been demonstrated as promising methods to tackle the defect.[4] In the AIE/AIEE systems, luminogens are non-emissive or weakly emissive in the dilute solution but significantly emissive in their concentrated solutions and/or aggregated states. Therefore, incorporation of AIE luminogens (AIEgens) into CPs is a significant attempt to avoid fluorescence quenching.[3] In AIEgen-containing CPs, the steric effect of the rigid chain suppresses intra-molecular motions of AIEgens and thus their emission is remarkably enhanced.[3]

On the other hand, supramolecular polymers (SPs) have also emerged in the optoelectronic and biological fields for their multiple responsiveness, superb self-healing and degradability.[5] Combining non-covalent interactions with conjugated molecules, we[6] and other[7] have developed various fluorescence responsive SPs, many of which exhibit fluorescence quenching or weakening upon non-covalent interactions. We therefore ask whether such studies are extended to the AIE and AIEE systems. Up to now, several non-covalent interactions have been used to activate the AIE/AIEE feature successfully.[8] However, these systems doesn't reveal significant fluorescence responsiveness to external stimuli. In this communication, we synthesized an AIEgen-containing conjugated polymer (AP-TPE) (Scheme 1). Upon treating the solution of AP-TPE

successively with acid and base, the fluorescence intensity was remarkably enhanced and decreased, respectively, together with a morphological transition from micellar to vesicular.
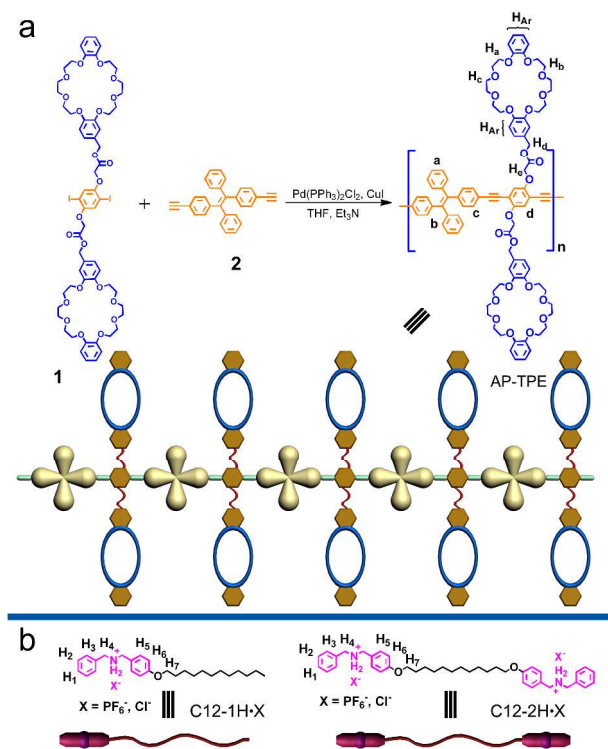
Scheme 1 (a) Synthetic approach of AP-TPE; (b) Chemical structures of the guest molecules, C12-1H·X and C12-2H·X, X = Cl, PF$_6$.

AP-TPE was synthesized by a sonogashira cross-coupling reaction of dibenzo-24-crown-8 (DB24C8)-substituted 1,4-diiodobenzene (**1**) and 1,2-Bis(4-ethynylphenyl)-1,2-diphenylethene (**2**) as shown in Scheme 1a. ^{1}H NMR (Fig. S4-S5), gel permeation chromatography methods (Fig. S6) and infrared spectra (Fig. S7) confirmed the

successful polymerization reaction and the formation of AP-TPE. UV-vis absorption spectra of **2** and AP-TPE in their THF solutions (10 µM) were depicted in Fig. S20. In comparison with **2**, the absorption band of AP-TPE showed a large red-shift from 329 to 378 nm, agreeing well with the high conjugation of AP-TPE.[1b,3b] Excited at 375 nm, AP-TPE in pure THF exhibited a weak fluorescence, which was similar with the reported TPE-based polymer.[3] Considering the AIE feature of AP-TPE, an amount of water was added to the THF solution of AP-TPE. As shown in Fig. 1, with the increase of water fraction, the fluorescence intensity of AP-TPE started to rise and reached its maximum value at 70% water content, which was 4.6 times higher than that in pure THF solution. However, when the water content increased to 90%, the fluorescence intensity dropped to some extent. This was because the precipitation of the large-sized aggregates decreased the effective AP-TPE concentration in the solution.[9] Besides this, amorphous aggregates abruptly formed at 90% water content could trap the solvent molecules inside. In these loose aggregates, the intramolecular motions of TPE groups had not restricted completely, which also decreased the emission.[9] From the inner photographs, we could catch sight of the weak emission in THF solution but strong emission in the mixed solvent of 90% water content.
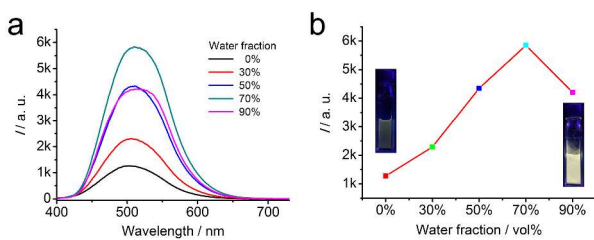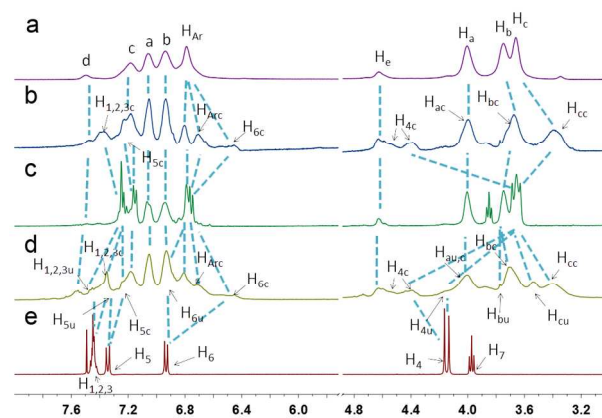

Fig. 2 Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2) of (a) 0.5 mM AP-TPE, (b) 0.5 mM AP-TPE (monomer concentration) and 1.0 equivalent of C12-2 H·PF_6 (DBA/DB24C8 1:1 molar ratio), (c) obtained by adding 2.0 equivalents of P$_1$-tBu to (b), (d) obtained by adding 2.0 equivalents of CF_3COOH to (c), and (e) guest C12-2H·PF_6 ($CDCl_3$/CD_3CN, 1/1). Here "u" and "c" denote uncomplexed and complexed moieties, respectively.

Fig. 1 (a) Fluorescence spectra excited at 375 nm and (b) plot of fluorescence intensity of AP-TPE (10 µm) in THF/water mixture solvents with different water fractions. The inner photographs showed AP-TPE in the mixed THF/water solvent at 0% and 90% water content under UV irradiation. The concentration referred to the monomer concentration.

The complexation between AP-TPE and guest groups was initially investigated by ^{1}H NMR spectroscopy as shown in Fig. S22 and Fig. 2. Upon treating AP-TPE (0.5 mM) with 1.0 equivalent of C12-2H·PF_6, the resonance signals of DB24C8 moieties and dibenzylammonium salts (DBAs) shifted significantly and became more broadened (Fig. 2a and b). Among these signals, the benzyl protons H_4 of C12-2H·PF_6 shifted downfield from δ = 4.15 to 4.50 ppm, while the others shifted upfield. No uncomplexed signal was detected, indicating the crown ether moieties were completely threaded by the DBA groups and thus the network complex formed as shown in Fig. S21. Subsequent *in-situ* addition of 2.0 equivalents of *N-tert*-butyl-*N′, N′, N″, N″, N‴, N‴*-hexamethyl-phosphorimidic triamide (P$_1$-tBu) caused the deprotonation of C12-2H·PF_6 and the complexed resonances consequently disappeared. The resulting ^{1}H NMR spectrum originated from the combined signals of AP-TPE and neutral C12-2 (Fig. 2c). And then, 2.0 equivalents of CF_3COOH were successively added, leading to the presence of the complexed ^{1}H NMR signals again, but together with small amounts of uncomplexed DB24C8 and DBA resonances (Fig. 2d), which was slightly different from that in Fig. 2b. Similarly, addition of C12-1H·PF_6 to AP-TPE also gave rise to comparable ^{1}H NMR spectral changes as described above (Fig. S22).
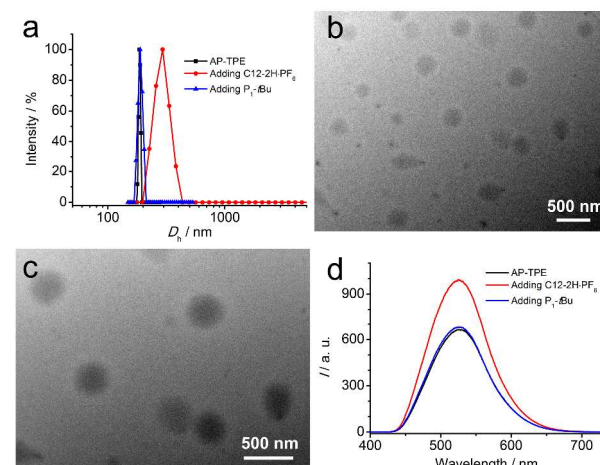

Fig. 3 (a) DLS plot of AP-TPE, (b, c) TEM images of aggregates of AP-TPE and (d) Fluorescence responsiveness of AP-TPE upon successive treatment with C12-2H·PF_6 and P$_1$-tBu (CH_2Cl_2, 0.5 mM).

Next, we examined the sizes of the above-mentioned host-guest complexes through dynamic light scattering (DLS) and transmission electron microscope (TEM) measurements. The results of DLS experiments were shown in Fig. S23a and 3a. In the DLS plot, AP-TPE exhibited a narrow band centred at a hydrodynamic diameter (D_h) of 185 nm, which was much larger than the length of polymer (ca. 39 nm based on DP = 20), probably due to aggregation of AP-TPE under this solvent condition. After the complexation with C12-2H·PF_6, the D_h of the network complexes increased to 294 nm together with a much broader signal. Correspondingly, TEM images revealed that irregular aggregates (Fig. S24) evolved to spherical nanostructures with diameters of 250~400 nm (Fig. 3b and c). Upon adding 2.0 equivalents of P$_1$-tBu to the complexes, D_h returned back to the original location. However, almost no change in D_hs was detected during the self-assembly of AP-TPE and C12-1H·PF_6 (Fig. S23a).

Interestingly, we therefore asked whether the aggregation could activate the AIEE nature of AP-TPE. Upon addition of C12-2H·PF_6, the fluorescence band of AP-TPE (0.5 mM) centred at 525 nm

showed a clear increase in intensity (Fig. 3d), which agreed well with the increase in D_h as described above. Instead of treatment with extra host and/or guest molecules as demonstrated in previous pillar arene-based AIEE system[8], the facile addition of P$_1$-tBu restored completely the enhanced emission to the original level. Of difference was that only less fluorescence enhancement was observed in the case of C12-1H·PF$_6$ and AP-TPE, consistent with the slight increase in D_h (Fig. S23). Corresponding with previous theoretical[4] and experimental[6d] studies, the threading structure based on DB24C8 and DBA groups restricts the intramolecular rotation of TPE moieties at the molecular level and the non-radiative pathway is blocked, leading to visible fluorescence enhancement. Comparatively, in the case of the network complex formed by C12-2H·PF$_6$ and AP-TPE, both the intra- and intermolecular rotations were restricted due to the cross-linked topological structure and thus the fluorescence was significantly enhanced. When the base was added, the intra- and intermolecular motions weren't suppressed any more and the fluorescence was thus recovered. These facts highlighted that the aggregation benefiting from the host-guest interaction of DB24C8 and DBA groups can activate the AIEE feature to a great extent in the present case.
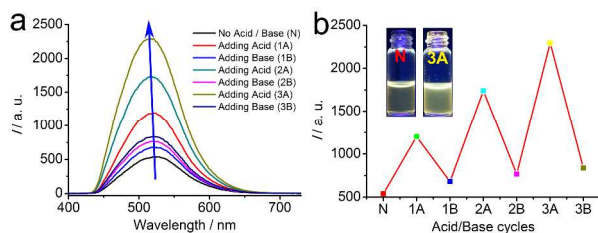

Fig. 4 (a) Fluorescence spectra and (b) plot of fluorescence intensity of AP-TPE/C12-2 in THF treated with HCl and NaOH, repeatedly. The concentrations of AP-TPE and C12-2 were 0.5 mM. The concentrations of HCl and NaOH were 1.0 M in H$_2$O. Here, N, A and B denote the neutral solution and its acid and base treatments, respectively. 1, 2 and 3 denote the sequence of the acid/base cycle.

These results confirmed our attempt available. However, the present fluorescence enhancement was rather less than that of TPE-based CPs in the mixed THF/water solvents (Fig. 1).[3] As reported previously, DB24C8 can bind DBA with chloride counter anion *via* the N-H···O hydrogen bonding in a face-to-face manner, and form a more compact and ordered matrix.[10] Upon successive treatment of HCl and NaOH, we therefore monitored fluorescence changes of the THF solution containing AP-TPE and C12-1/C12-2. The experimental data were depicted in Fig. S25 and 4. When 2.0 equivalents of HCl were added to the neutral solution of AP-TPE/C12-2, the solution became turbid immediately (Fig. S26). Meanwhile, the fluorescence spectra revealed an amazing fact that there was a 2.2 times increase in the fluorescence intensity (Fig. 4a and b). Subsequent addition of 2.0 equivalents of NaOH led to a transparent solution accompanied with a decreased fluorescence. Afterwards, the solution was treated with the acid/base cycles twice and the fluorescence became stronger step by step (Fig. 4a and b). The fluorescence intensity increased nearly 4.3 times after the third acidification. Furthermore, we carried out several control experiments to explain the phenomenon (Fig. S27) and found that the interaction between DB24C8 and DBA and salting-out effect played a leading role in such stepwise enhanced fluorescence. According to the previous works[11], when the TPE moiety took a tighter packing in crystals or highly ordered structures, the intra-

molecular motion was restricted more completely, thus leading to stronger and blue-shifted emissions. In our system, the blue-shift of the emission peak from 523 to 514 nm had certified more and more compact packing of AP-TPE molecules. No significant change was detected in the fluorescence intensity when the THF solution of AP-TPE and C12-1 was treated with the same acid-base cycles (Fig. S25).
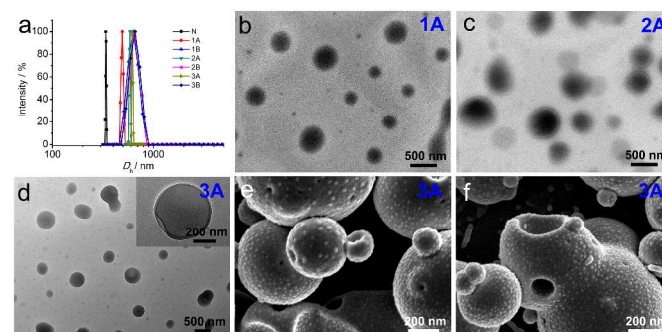

Fig. 5 (a) DLS plot of AP-TPE and C12-2 in THF treated with HCl and NaOH repeatedly. (b-d) TEM images of AP-TPE and C12-2 after the first, second and third acidification. (e-f) SEM images of AP-TPE and C12-2 after the third acidification.

To understand the observed phenomena, DLS and TEM measurements were employed to check the D_hs and aggregate structures of the complexes. In the initial solution of AP-TPE and C12-2, the DLS plot exhibited a narrow band centred at 338 nm (Fig. 5a). Upon acid treatment with HCl, the complexation of DB24C8 and DBA moieties occurred, leading to the formation of supramolecular assemblies. Consequently, the value of D_h increased to 492 nm and spherical micelles were observed in TEM images (Fig. 5b). The ordered micellar aggregates resulted in a much stronger fluorescence as shown in Fig. 4. When the solution was subsequently treated with NaOH, the fluorescence intensity dropped remarkably. However, the DLS plot displayed something extraordinary that D_h of the mixture didn't revert back to the original value but increased to 631 nm with a broad distribution (Fig. 5a). We therefore speculated that AP-TPE might form some large but unordered aggregates in the solution after the first acid-base cycle. As expected, the irregular and unordered aggregates were clearly observed in TEM images (Fig. S30), substantiating our speculation. In the latter twice cycles, the DLS plots exhibited a similar trend and the only distinct from the first cycle was the sizes of aggregates grew stepwise with 586 and 622 nm upon acidification, respectively. As shown in Fig. 5c, the self-assembly of AP-TPE with C12-2 formed spherical aggregates with diameters of 400~600 nm after the second acidification. The spherical aggregates showed a clear contrast between the exterior and interior, which was consistent with the typical feature of vesicles. After the third acidification, many more legible vesicles were observed with diameters ranging from *ca*. 500 to 700 nm (Fig. 5d). To confirm the vesicular structure, scanning electron microscopy (SEM) measurement was further performed (Fig. 5e-f). Several collapsed and ruptured vesicles were captured. Furthermore, the inside and outside of ruptured vesicles were observed clearly. Usually, vesicular aggregates originated from the solvophobic self-assembly of molecules in a specific solvent.[12] In our case, DB24C8 bound DBA to form polar groups after the first acidification. As a result of the solvophobic effect, the complex formed micelle and the polar groups were located on the inner of the micelle.

Subsequent acid-base reaction led to the generation of NaCl, which further promoted the aggregation due to the salting-out effect. Until the next acidification, both the interaction between DB24C8 and DBA and salting-out effect modified the solvophilic-solvophobic effect and the system reached a new balance, and thus the highly ordered vesicle was formed. These changes were consistent with the stepwise enhanced fluorescence and blue-shifted emission peaks.[11] To the best of our knowledge, such morphological transition-induced step-by-step enhancement was seldom brought out in the previous AIE/AIEE systems.[3,4,8,11]

In summary, we have confirmed our attempt that the complexation of DB24C8 and DBA groups can suppress the motion of the TPE moiety and thus active the AIEE feature of AP-TPE. Particularly, the reduplicative complexation of AP-TPE and C12-2H·Cl not only enhances the fluorescence remarkably, but also induces a morphological transformation from micellar to vesicular. Moreover, it is emphasized that such acid-base responsive vesicular assembly/disassembly has a potential for encapsulation and release of small molecules such as drugs and dyes.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures and full characterizations of AP-TPE, C12-1, C12-1H·PF₆, C12-2 and C12-2H·PF₆, additional DLS plots and TEM images. See DOI: 10.1039/c000000x/

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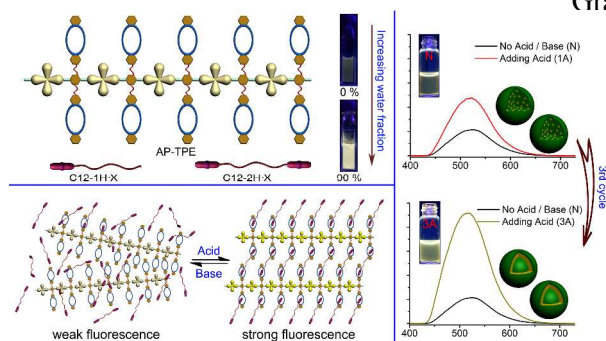
Graphical Abstract

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