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A self-assembly induced emission system constructed by the host–guest interaction of AIE-active building blocks†

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Dibenzo[24]crown-8 (host) and benzylamine (guest) modified tetraphenylethenes are prepared and used to construct supramolecular polymers, which demonstrate the merits of reversible assembling–disassembling and tunable aggregation-induced emission by acid–base treatments.

Aggregation-induced emission (AIE) has attracted great attention in the research areas including fabrication of chemo- and biosensors, photo-electronic materials, and stimuli-responsive elements.[1] Tetraphenylethene (TPE) is a typical AIE luminogen (AIE-gen). It emits faintly in dilute solution but becomes highly emissive in the aggregate state. TPE has been widely used to construct AIE-active materials due to its good AIE performance and easy preparation.[2] As for the underlying mechanisms, the restriction of intramolecular rotation (RIR), among all the possible theories, is the best acceptable one and has been proven by different methods.[1c,3] The RIR process is briefly described as follows. In solution, the rotations of the phenyl groups of TPE (see the blue moiety in Scheme 1) are active. Regarding kinetics, the rate of the intramolecular rotations is in the femtosecond range, which is faster than the irradiative decay rate of the excited state. As a result, the emission of the excited TPE molecules is quenched. In the aggregate state, the intramolecular rotations are restricted, thus the non-irradiative channels are blocked and the emission can be observed. Based on the RIR mechanism, a series of novel AIE-active compounds have been designed and
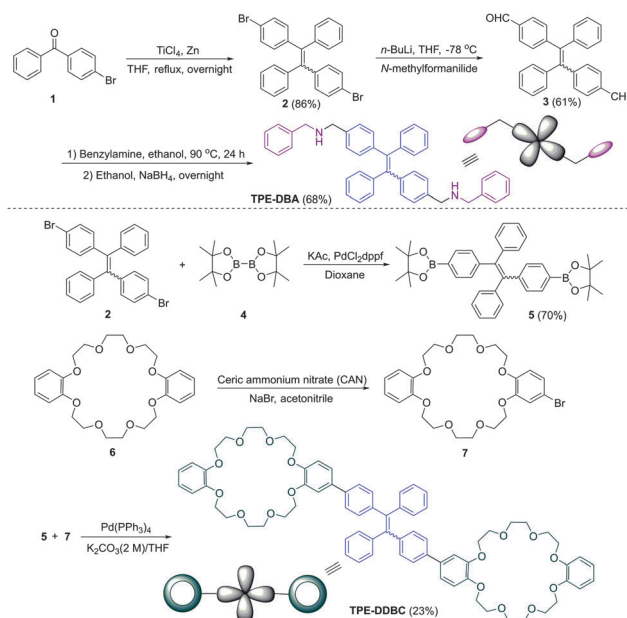
Scheme 1   Synthetic routes to TPE–DBA and TPE–DDBC.

constructed, and their AIE characteristics together with other properties have been studied.[1–3]

To date, developing more AIE-active systems and opening a wider range of application fields have been the main topics of research. During the past few decades, supramolecular chemistry has been one of the hottest research areas. Supramolecular systems are constructed from secondary bonds (*i.e.* hydrogen bonds, coordinating bonds, π–π stacking, host–guest interactions, *etc.*), rather than covalent bonds, among the building blocks. This trait bestows supramolecular systems with unique advantages such as good degradability, stimuli-responsiveness and self-healing properties.[4,5] Among a variety of supramolecular systems, the host–guest recognition of crown-ether to different guest species, ranging from potassium ions to ammonium and paraquat derivatives has received considerable attention.[4] It is noted that all these processes are highly dynamic. Considering that the restriction and emancipation of the intramolecular rotations

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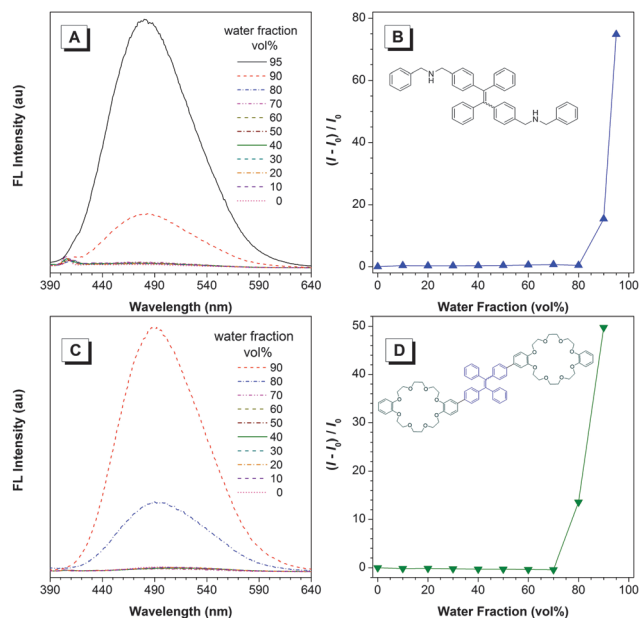
Fig. 1 Fluorescence (FL) spectra of (A) TPE–DBA and (C) TPE–DDBC; and plots of peak FL intensity of (B) TPE–DBA and (D) TPE–DDBC in THF–water mixtures with different water fractions. Concentrations of TPE–DBA and TPE–DDBC: 10^{-5} M, λ_{ex} for TPE–DBA and TPE–DDBC: 360 nm.

Fig. 2 (A) An illustration of the reversible self-assembling and disassembling between TPE–DBA and TPE–DDBC *via* host–guest interaction. (B) FL spectra of TPE–DBA and TPE–DDBC in THF solution treated with HCl and NaOH solutions repeatedly. (C) Plots of the changes in peak intensity and wavelength in three acid–base treating cycles. Concentrations of HCl and NaOH: 1.0 M in H_2O; concentrations of TPE–DBA and TPE–DDBC: 5×10^{-4} M in THF; λ_{ex}: 360 nm. Letters A, B and N stand for acid and base treatments and neutral THF solution. 1, 2 and 3 stand for the number of acid–base cycles.

of an AIE molecule are also dynamic processes, the correlation between a supramolecular system and AIE will be of significant importance.[5] Herein, we report our concept-proof work by using TPE as the AIE-gen and the host–guest interaction between dibenzo[24]crown-8 and benzylamino moieties as the driving force to construct a self-assembling induced emission system.

Based on the above-mentioned idea, we designed and synthesized two TPE-derivatives, *i.e.* TPE–DDBC and TPE–DBA (Scheme 1 and the inset of Fig. 1), which perform as the host and guest molecules due to their dibenzo[24]crown-8 moieties and benzylamino groups, respectively. The details of syntheses can be found in the ESI.† The target compound TPE–DBA including both of the *E-/Z*-isomers was prepared from dialdehyde-functionalized TPE utilising a Schiff base reaction followed by a reduction of imine groups in one pot in a yield of 68%. Dibenzo[24]-crown-8 was brominized by ceric ammonium nitrate with sodium bromide, and product 2-bromo-dibenzo[24]crown-8 underwent a Suzuki coupling reaction to get attached onto TPE. Characterizations of the two target compounds are described in the ESI† (Fig. S1–S9, Schemes S1 and S2).

The AIE activity of the building blocks of TPE–DBA and TPE–DDBC was examined and the results are shown in Fig. 1. TPE–DBA shows no emission in dilute tetrahydrofuran (THF) solution when excited at a wavelength of 360 nm (λ_{ex}), which is close to the maximum of the UV-vis absorption spectrum of TPE–DBA (Fig. S10, ESI†). It remains non-emissive in the THF–water mixture solvent with the water fraction (f_W, by volume) being up to 80%. When the f_W reaches 90%, the system becomes highly emissive and the emission peak (λ_{em}) appears at around 485 nm. This λ_{em} is nearly identical to that of TPE itself,[7] because the conjugation of TPE–DBA is no larger than that of TPE, thanks to the blocking role of the methylene group between TPE and the benzylamino group. In addition, the water fraction required to
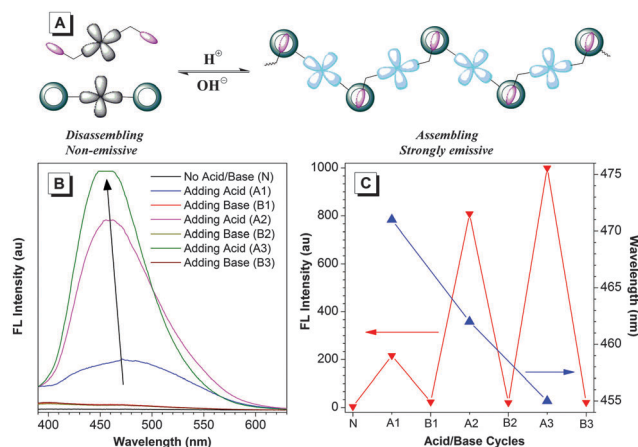
induce the aggregation in TPE–DBA is higher than that required for most AIE molecules,[2,5,6] due to the enhancement of the hydrophilicity contributed from the secondary amino groups.

Since both of the building blocks possess AIE characteristics, we expect that the AIE trait will be inherited by the supramolecular system. The working scheme is illustrated in Fig. 2A. The secondary amines in TPE–DBA are protonated by adding acid into the solution (Scheme S3, ESI†), and the protonated amines are capable of recognizing the crown ethers, and thereby the interaction of the ionic TPE–DBA and TPE–DDBC molecules. The non-covalent inter-action of the host will lock on the rotations of benzylamino groups, which involve the phenyl rotations of TPE units. According to the RIR mechanism, the FL from TPE–DBA will be turned on, as observed for boronic acid modified TPEs and β-cyclodextrin and TPE-containing metal organic frameworks.[7] Meanwhile, the emis-sion from the TPE moiety in TPE–DDBC can also be partially initiated, due to the damped intramolecular phenyl rotations caused by the formation of the supramolecular macro-molecules. The acidification induced assemblies will disassemble when treated with base, because deionized amines cannot be hosted by crown ethers and the restriction effect disappears accordingly.

Guided by this assumption, we monitored the FL changes upon repeatedly adding acid and base into the THF solution containing TPE–DBA and TPE–DDBC in a 1 : 1 mole ratio. The experimental data collected in a typical run are presented in Fig. 2B and C. In neutral THF solution, the two compounds were unable to aggregate, so that no FL could be detected. When 10 μL of HCl aqueous solution was added into 5 mL of THF solution, a white precipitate appeared after sonication for 10 min and the system emitted bright blue FL under 365 nm UV-light illumination (Fig. 3). Afterwards, the mixture was treated with 10 and 20 μL of NaOH solution to neutralize HCl turning the solution basic, the FL disappeared with the disappearance of the precipitate. The FL "turn-on/turn-off" behaviours are reversible and can be repeated, as demonstrated in Fig. 2B.
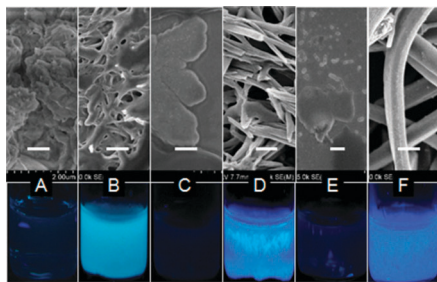
Fig. 3 SEM images of the morphologies (scale bar: 500 nm) for the microstructures formed in the mixture of TPE–DBA and TPE–DDBC (1:1, mole ratio, in THF) treated with HCl–NaOH solutions. Shown in the bottom row are the corresponding FL images. (A): neutral THF solution; (B), (D) and (F): treated with 1.0 M HCl; (C) and (E): treated with 1.0 M NaOH following steps (B) and (D), respectively.

The origin of the FL is ascribed to the formation of the insoluble assembly, which is induced by the host–guest interaction, and not to the insolubility of TPE–DBA and TPE–DDBC induced by water addition. In fact, f_W in the mixture is very small. Specifically, the volume of THF solution used in the experiment was 5 mL, while the volume of HCl solution or NaOH solution was only 10–20 μL each time. As a result, after 3 cycles of treatments, the volume of water should be 100–110 μL. Compared with the volume of THF, the water fraction is as low as 2% eventually. As indicated by the results shown in Fig. 1, such low water fraction cannot lead to the aggregation of TPE–DBA and TPE–DDBC. From Fig. 2B it can be noted that the emission became stronger and the emission peak blue-shifted after every cycle. This "stepwise" FL amplification can be associated with the stepwise addition of water in the mixture, which leads the hydrophobic TPE moieties to tighter packing thus inducing stronger emission, according to the RIR mechanism. The blue-shift may be associated with the formation of a higher ordered microstructure in the fluorescent precipitate. It has been proved that in crystals or in highly ordered structures, the TPE moiety takes a more twisted conformation.[5,6]

To gain further understanding of the observed phenomenon, the microstructures formed in the supramolecular systems were checked by scanning electron microscopy (SEM). Fig. 3 exhibits the SEM images of samples taken from the TPE–DBA/TPE–DDBC mixtures treated with acid and base for the first three cycles. Without the protonation of the secondary amine groups, the self-assembly could not occur, and the precipitate obtained by solvent evaporation showed an irregularly shaped morphology (Fig. 3A). Upon acidification, the host–guest recognition occurred and resulted in the formation of supramolecular polymers, which precipitated in the solution due to the rigid and hydrophobic TPE units and the increased molecular weight. The morphology is characterized by microscopic wires with diameters of about 100 nm (Fig. 3B). Several wires twisted together to make a bunch. Such string-like networks were often observed in the supramolecular organogels.[8] Strong FL was emitted from the organized microstructures presented here. When the precipitate was treated with base, the micro-networks collapsed and a featureless morphology was observed again by SEM (Fig. 3C). Similar morphological changes took place in each acid–base treatment cycle (Fig. 3A–F and Fig. S12–S17, ESI†). A distinction

is that the width of the microwires became larger (from ∼100 nm to over 500 nm) as the treatment cycle increased. The microscopic morphology changes are responsible for the FL enhancement and the blue-shift.

In summary, we have demonstrated a novel self-assembly induced emission (SAIE) system. The host–guest interaction initiates the "polymerization" of the TPE-containing building blocks and the RIR process, and turns on the emission of the AIE-gen. The breaking of the non-covalent bonds eliminates the restriction and turns the emission off. The assembling–disassembling processes accompanied by FL turn-on/off are dynamic, reversible and tuneable by treating the system with acid–base. Yet, Cl^- can form a strongly-bonded counter-ion pair with a protonated secondary amine and PF_6^- or BF_4^- may be a better candidate for anion to manifest better host–guest interaction. As a concept-proof work, the existing results have offered sufficient evidence to support the SAIE idea. Host–guest interaction is only one of the various supramolecular interactions and AIE-gens can be chemically modified to accommodate different situations, thus the present concept is helpful and useful to construct more supramolecular AIE systems and to fabricate novel chemo-/biosensors and stimuli-responsive materials with FL emission properties.

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