PAPER

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Highly efficient FRET from aggregation-induced emission to BODIPY emission based on host–guest interaction for mimicking the light-harvesting system†

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A novel fluorescence resonance energy transfer (FRET) system based on the interaction of an AIE luminogen (tetraphenylethene, TPE) and BODIPY derivative as the host and guest, respectively, was disclosed. This FRET system worked well for mimicking a light harvesting system with highly energy transfer efficiency up to 93% from aggregation-induced emission to BODIPY emission and shows excellent tolerance to acidic and basic environments.

Fluorescence resonance energy transfer (FRET) is a photophysical process through which an electronically excited fluorescent "donor" molecule transfers its excitation energy to an "acceptor" molecule nonradiatively through a long-range dipole–dipole interaction.[1,2] FRET is widely studied and proved to be a powerful spectroscopic technique to accurately measure the distance between two fluorescent sources at the nanometer scale,[3,4] enabling the study of molecular conformations[5] and interaction dynamics.[6] Moreover, FRET is a core phenomenon in photosynthesis,[7,8] organic photovoltaics,[9] lighting sources,[10,11] biosensing,[12–14] or drug delivery tracing.[15] Furthermore, for practical applications, two requirements are necessary for the FRET process to occur: (1) a substantial overlap of the donor emission spectrum with the acceptor absorption; (2) an appropriate linker and distance between the donor and the acceptor.[16]

The light-harvesting system, which collects sunlight efficiently and funnels the excitation energy to the reaction center, which converting solar to chemical energy, plays a very important role in natural photosynthesis.[17] Many artificial light-harvesting molecules are synthesized in succession.[18] An ideal light-harvesting system absorbs light efficiently in a relatively broad region covering most of the sunlight spectrum and carries the energy smoothly to the reaction center. In order to achieve this for mimicking the light-harvesting system, the integration of multiple excellent chromophores or fluorophores is necessary based on FRET process. With the broad field of FRET applications at hand, the impressive progress of mimicking the photosynthetic light-harvesting system with synthetic models, which is significantly meaningful not only for our understanding of the function and mechanism of photosynthesis but also in the development of potential applications in terms of organic light-emitting diodes (OLED),[19] dye-sensitized solar cells (DSSC),[19a,20] and other optoelectronic devices,[21] offers appealing opportunities to enhance FRET and extend its versatility and is currently attracting increasing interest from biologists and chemists.

So far, lots of covalent and non-covalent artificial light-harvesting systems based on FRET have been developed, most of which were constructed by fluorescent donor–acceptor models.[22] Recently, with the rapid development of supramolecular chemistry, more and more efforts were contributed towards developing the non-covalent artificial light-harvesting systems, and among them crown ethers,[23] cyclodextrins,[24] pillararenes,[25] and host–guest complexes containing multiple hydrogen bonds[23,26] were frequently employed as building scaffolds.

It was well-known that most conventional luminophores such as the fluorescent donor and acceptor in host–guest systems with strong luminescence in solution become weakly emissive or nonemissive in the aggregate or solid state due to the notorious aggregation-caused quenching (ACQ),[27] which has greatly limited the applications of luminescent materials. To overcome the drawback of ACQ, Tang et al. developed an effective methodology named aggregation-induced emission (AIE) which has drawn increasing research interest as the opposite of ACQ systems.[27a,28] Because of their exactly opposite luminescent behaviours, AIE and ACQ materials are not easily

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coupled to construct new efficient luminescent materials. Recently, some attempts to combine AIE and ACQ luminophores by covalent bonding were made,[29] but they failed in realising the advantages of combining both classes of dye. The development of a feasible approach for achieving the effective collaboration of AIE and ACQ luminophores and constructing highly efficient FRET-based light-harvesting materials for practical applications remains an important challenge.

Herein, we introduce an efficient strategy to achieve the coupling of AIE and ACQ chromophores *via* FRET for the construction of high-efficiency light-harvesting system. As a prototypical AIE luminogen (AIEgen), tetraphenylethene (TPE) was chosen to combine with crown ether moieties as a host and energy donor in FRET system. Meanwhile, due to their outstanding and desirable properties such as high absorption coefficients, sharp emissions, high fluorescence quantum yields, and excellent chemical and photostability, borondipyrromethene (BODIPY) dyes were chosen as the chromophores in light-harvesting systems.[25,30] We prepared a borondipyrromethene (BODIPY) derivative containing benzylamino group as the guest and energy acceptor (Scheme 1). The details of syntheses of the host and guest compounds can be found in the Fig. S1 and S2 (ESI†). The target host compound **M1** was prepared from dimethyl TPE and dibenzo[24]-crown-8 (DB24C8). The target guest compound **M2** was prepared from BODIPY derivative after several steps. The chemical structures of the target compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and MS (ESI†).

AIEgen TPE derivatives such as **M1** becomes highly emissive in the aggregate state with the gradual increasing of the fraction of the poor solvent (Fig. S3, ESI†). But usually the traditional ACQ luminophores turn to be none or weakly fluorescence emissive under this condition. Numerous endeavors can be made to prevent or alleviate the ACQ problem, including the introduction of bulky substituents,[31] enhanced intramolecular charge transfer (ICT) transition,[32] cross-dipole packing,[33] and Jaggregated formation.[34] With the molecular structure of guest **M2** in hand, we try to obtain the fluorescence behaviour of **M2**

in pure organic solvent (THF) and the solution with the increasing addition of the poor solvent. As expected, no remarkable emission intensity of **M2** at 510 nm was observed upon the addition of water, even up to 90% fraction of water (Fig. S4(d), ESI†).

As shown in Fig. S4(e) (ESI†), the recording of the absorption and AIE emission spectra for guest **M2** and host **M1** verified them as the appreciable combinatorial duo to establish the FRET system, where the emission range of donor TPE (400–570 nm) almost coincided with the absorption range of acceptor BODIPY (430–530 nm). Furthermore, the maximum excitation wavelength of **M2** was determined as 475 nm, which is consistent with AIE emission wavelength of **M1**, suggesting the occurrence of FRET.

In order to investigate the complexation of host with guest in solution, the fluorescence titration experiments were first performed to monitor the AIE emission at 465 nm corresponding to **M1** and emission at 515 nm for **M2** by adding increasing amount of guest **M2** into the solution (THF : H$_2$O, 2 : 8, v/v) of host **M1**. As shown as in Fig. 1 and S6 (ESI†), with gradual addition of **M2**, the AIE emission peak of **M1** at 465 nm decreased gradually, while the emission peak of **M2** at 510 nm appeared and then increased remarkably, indicating the formation of a new complex between **M1** and **M2**. When more than 0.30 equiv. of **M2** was added to the **M1** solution, the fluorescence intensities at both 480 nm and 510 nm showed almost no change. Moreover, the change in fluorescence emission colour before and after the addition of the guest could be easily distinguished by the naked eye (Fig. S7, ESI†). The above results clearly demonstrated that an efficient FRET effect from donor **M1** to acceptor **M2** existed in the host–guest complex. From the fluorescence titration result, the FRET efficiency was further calculated to be 93% for the host–guest system. In order to get more evidence for interaction of host and guest, the TEM images were performed. As shown in Fig. 2, the nanoparticle of spherical morphology of host **M1** in aggregation state turn to prismatic crystal after the addition of guest **M2**, which directly representing the host–guest recognition occurred and resulted in the formation of complex system to generate FRET.
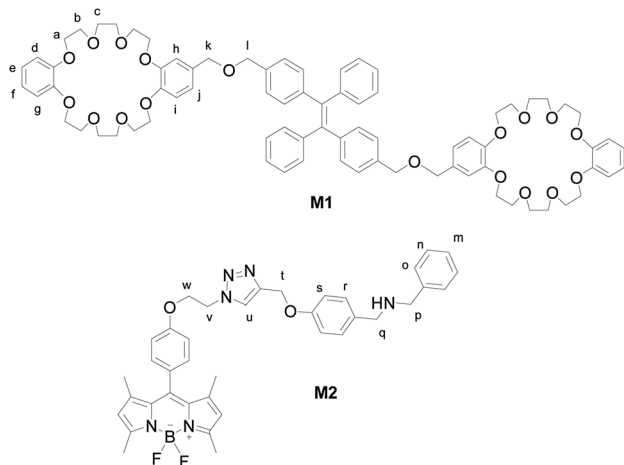
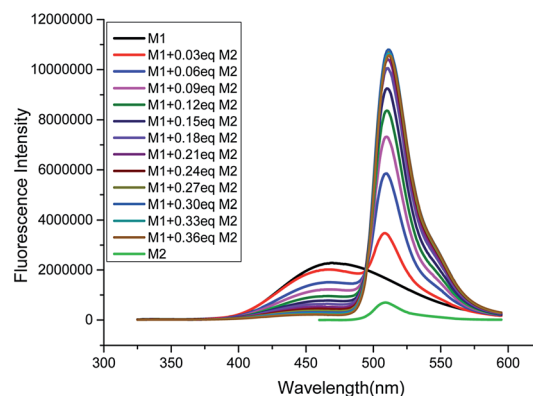**Scheme 1** FRET donor (host) **M1** and acceptor (guest) **M2**.

Fig. 1 Fluorescence titration spectra of compound **M1** (10 μM) towards **M2** (0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27, 0.30, 0.33, 0.36 equiv.) in THF/H$_2$O (1 : 9, v/v) medium (λ_{ex}: 305 nm).
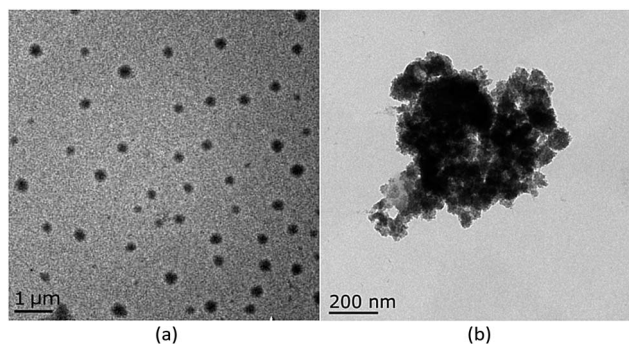
Fig. 2 (a) Imagine of **M1** (10 μM) in TEM at 1000 nm, (b) imagine of **M1** (10 μM) upon addition of **M2** (0.3 equiv.) in TEM at 200 nm.

To gain further understanding the pH-responsibility of the observed FRET phenomenon, we monitored the fluorescence changes upon adding acid and base into the THF/water solution containing **M1** and **M2** in a 1 : 1 mole ratio. The pH-responsive titration was performed by the addition of CF_3COOH and DBU to the host/guest complex solution gradually to adjust the pH value of the solution. To our surprise, no obvious changes of the fluorescence emission intensities of the FRET system under acid and base condition were observed. Moreover, the fluorescence emission intensity of the FRET upon the K^+ addition also did not change remarkably. Furthermore, the absorbance of **M1** and **M2** in aggregation state was obtained (Fig. S4(b), ESI†). This FRET system absorbs light efficiently in broad region covering most of the sunlight spectrum (200–550 nm). The above results indicated that this complex of **M1** and **M2** was a highly efficient and pH stable FRET system for mimicking very stable light-harvesting system. Under acidic condition, the interaction of crown ether in host with dibenzylammonium salt in guest occurred. After the addition of base, the interaction of host and guest was changed to the interaction of crown ether with trizole unit and the distances between donor and acceptor chromophores or fluorophores changed slightly, so this complex of **M1** and **M2** shows pH stable FRET property.

The host–guest interaction between donor and acceptor was investigated by ^1H NMR to obtain important insights into the complexation behavior of **M1** with **M2** in aggregation state (Fig. 3). After the addition of acceptor **M2** to donor **M1**, the slight changes in the chemical shifts of the protons H_a (from 4.190 to 4.192 ppm), H_b (from 3.941 to 3.945 ppm), and H_c (from 3.842 to 3.860 ppm), and the benzyl protons H_k and H_l (from 4.452 to 4.453 ppm) in the crown ether units were observed by comparison of the ^1H NMR spectra of **M1** and the mixture. The multiplet and doublet peaks at 6.877–6.929 ppm corresponds to the aromatic protons H_d–H_j of crown ether units turn into sharp peaks. This result indicated the occurrence of host–guest interactions between donor **M1** and acceptor **M2**, which agreed with the FRET behaviour of host–guest system. Furthermore, the ^1H NMR titration under acid and base conditions was also carried out. Upon the addition of two equivalent of CF_3COOH to the solution of **M1** and **M2**, obvious changes in the chemical shift were observed. Upfield shifts were observed for cyclohexylmethylene protons H_b (from 3.945 to 3.873 ppm), and H_c

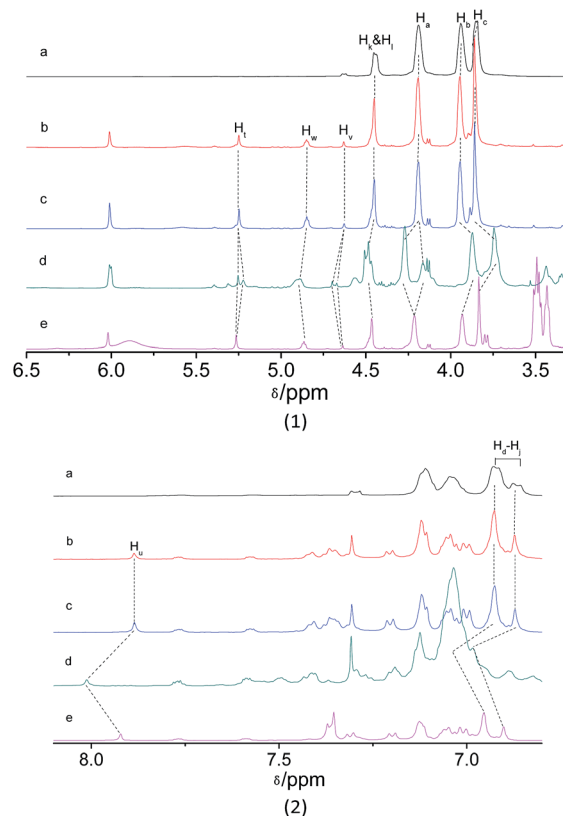**Fig. 3** Partial ^1H NMR spectra (500 MHz, CDCl$_3$): (a) ^1H NMR spectrum of host **M1** (1.0 mM), (b) ^1H NMR spectrum of host **M1** (1.0 mM) upon addition of 0.5 equiv. of guest **M2**, (c) ^1H NMR spectrum of host **M1** (1.0 mM) upon addition of 1.0 equiv. of guest **M2** in CDCl$_3$, (d) ^1H NMR spectrum of host–guest system in (b) upon addition of 2.0 equiv. of CF$_3$COOH, (e) ^1H NMR spectrum of host–guest system in (c) upon addition of 4.0 equiv. of DBU.

(from 3.860 to 3.745 ppm), but the signal peak corresponding to proton H_a splits into two sets of signals, one upshift from 4.192 to 4.165 ppm while another downshift from 4.192 to 4.271. Downfield shifts were also observed for the benzyl protons H_k and H_l (from 4.453 to 4.485 ppm) in host **M1**. Moreover, downfield shifts was observed for the protons H_v (from 4.626 to 4.686 ppm) and H_w (from 4.848 to 4.893 ppm) in CH$_2$CH$_2$ unit of guest **M2**. Most important, the remarkable downfield shift was observed for the vinyl proton H_u (from 7.885 to 8.012 ppm) in trizole unit of guest **M2**. Subsequently, upon the addition of four equivalent of base DBU to the previous solution of **M1** and **M2**, downfield shifts were observed for the protons H_b, H_c and H_t, meanwhile, upshifts were observed for the protons H_b, H_c, H_k, H_l, H_v, H_w, and H_u *etc.* (Fig. S14, ESI†). Based on the combination of the results of FRET titration and ^1H NMR titration, the plausible interaction mechanism of the host and guest was proposed as in Scheme 2. Under the acid condition, the recognition of crown ether to occurred. After the enough base addition, the crown ether switch from dibenzylammonium salt to chain unit near BODIPY core.

In conclusion, a new AIE fluorescence donor constructed by TPE with DB24C8 and a new fluorescence acceptor constructed by BODIPY with dibenzylamine linked with trizole were
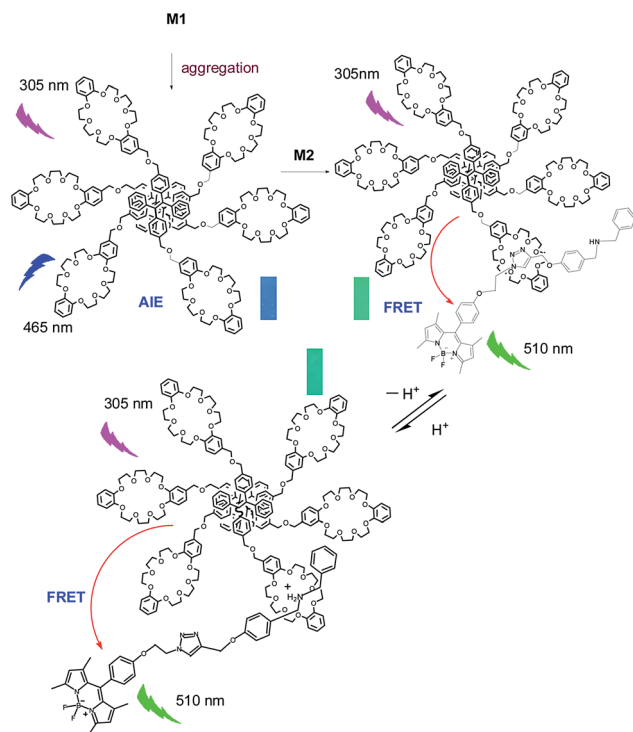
Scheme 2 Proposed interaction mechanism of the host–guest system.

synthesized. The interaction between the donor and acceptor, which act as host and guest respectively, occurred in the poor solution (THF/H_2O, 1 : 9, v/v) to generated highly efficient FRET from AIE emission to green emission of BODIPY. The fluorescence titration result shows that this novel FRET system is a pH-stable under acid and base conditions which will undoubtedly shed light on the practical application of FRET system based on host–guest interaction for mimicking the light harvesting system.

Acknowledgements

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