Supramolecular assembly-induced yellow emission of 9,10-distyrylanthracene bridged bis(pillar[5]arene)s†

Nan Song, Dai-Xiong Chen, Meng-Chan Xia, Xi-Long Qiu, Ke Ma, Bin Xu, Wenjing Tian and Ying-Wei Yang*

9,10-Distyrylanthracene has been introduced to bridge two pillararenes to form a dimeric host, which can assemble into a linear supramolecular polymer upon cooperatively binding to a neutral guest linker, exhibiting yellow fluorescence emission in solution and solid states.

During the past fifteen years, the concept of aggregation-induced emission (AIE) and aggregation-induced enhanced emission (AIEE), in addition to the mechanism of analyte-modulated conventional photophysical processes such as photo-induced electron transfer (PET), photo-induced charge transfer (PCT), and fluorescence resonance energy transfer (FRET), has appeared to be a powerful and versatile approach for the fabrication of novel types of fluorescent probes and chemical sensors. Representative compounds with AIE properties, such as tetraphenylethene (TPE) and 9,10-distyrylanthracene (DSA), are non-emissive in the molecularly dissolved solution states, whereas enhanced fluorescence emission can be achieved in their aggregated states. Tang et al. have ascribed the AIE phenomenon to the restriction of intramolecular rotation (RIR) of fluorogenic molecules within aggregates, which effectively blocks the non-radiative energy dissipation pathways and favors the radiative decay of excitons. In recent years, various AIE-based chemosensors and biosensors for analytes ranging from heavy-metal ions, explosives, carbohydrates, melamine, and DNA to proteins and enzymes have been successfully developed.

Pillarenes, representing a new class of synthetic supramolecular macrocycles, have advanced dramatically and have been employed widely in supramolecular chemistry and materials science due to their superior structures, facile functionalization and typical host–guest properties. A variety of functionalized pillararenes have been synthesized for the fabrication of supramolecular polymers and hybrid materials. Taking advantage of the mechanism of AIE, we reported the construction of stimuli-responsive supramolecular gels with strong blue fluorescence by the self-assembly of the first TPE-bridged pillar[5]arene (P5) tetramer and a triazole-based neutral guest linker.

Compared with TPE, DSA is a typical yellow emission compound with AIE/AIEE properties. Yellow fluorescence emission shares many advantages, e.g., (a) yellow emission is the most sensitive light visually, since the sensitivity of the eye to yellow light of 570 nm is 20 times higher than red or blue light under the same light intensity; (b) the yellow light is softer and will not produce visual fatigue. This warm color light is superior for fetal psychological development, giving a sense of pleasure; (c) yellow light-emitting diodes are still in high demand in the market of emitting devices. Thus, the design and construction of switchable yellow fluorescent supramolecular materials are in urgent need.

Herein, we first introduced DSA as a bridge to link two pillararene hosts to obtain DSA-bridged bis[pillar[5]arene]s, i.e., DSA-(P5)2, which can further serve as a new building block to self-assemble with a triazole-based neutral linker (NG2) for the fabrication of fluorescent supramolecular materials (Scheme 1).
The on–off switchable fluorescence properties of NG2⊂DSA-(P5)₂ based on supramolecular assembly–disassembly via an AIE mechanism may facilitate the evolution of a novel fluorescent probe technology for labeling and tracking cells, proteins and nucleic acids.

9,10-Bis(4-hydroxystyryl)anthracene was synthesized according to our previous report. DSA-(P5)₂ and DSA-(monomer)₂ were synthesized by introducing a bromobutyl mono-substituted P5 moiety or its monomer 1-(4-bromobutoxy)-4-methoxybenzene to react with the two hydroxyl groups of 9,10-bis(4-hydroxystyryl)-anthracene, catalyzed by K₂CO₃ and KI in MeCN. The resulting compounds were fully characterized by ¹H NMR, ¹³C NMR and MALDI-TOF MS spectroscopy (Fig. S1–S7, ESI†).

We envision that DSA-(P5)₂ and DSA-(monomer)₂ will be endowed with AIE characteristics benefiting from the DSA cores. Different amounts of water, a poor solvent for DSA-(P5)₂, have been added to the THF solution of DSA-(P5)₂. DSA-(P5)₂ exhibits no fluorescence when completely dissolved in pure THF. However, the fluorescence intensity of DSA-(P5)₂ increased dramatically upon increasing the water fraction and reached the highest level when the volume of water was 90% (Fig. S8 and S9, ESI†). Meanwhile, another mixed solvent, i.e., chloroform–hexane, has also been used to confirm the AIE properties of DSA-(P5)₂. Chloroform is a favourable solvent for the compound while hexane is an unfavourable solvent. DSA-(P5)₂ shows weak fluorescence when dissolved in pure chloroform. Upon addition of hexane, the fluorescence intensity gradually increased and reached the maximum when the volume fraction of hexane was 99% and DSA-(P5)₂ emits strong yellow light with the PL emission peak centered at 543 nm (Fig. 1a and b). All the experimental results indicated that DSA-(P5)₂ possesses obvious AIE properties in the mixed solvent of H₂O–THF and AIE characteristics in the mixed solvent of hexane–chloroform. On the other hand, non-fluorescent DSA-(monomer)₂ in pure THF also exhibited AIE properties via the addition of water into its THF solution (Fig. S10 and S11, ESI†) and AIEE properties in the mixed solvent of hexane–chloroform (Fig. 1c and d). As mentioned above, the results suggested that covalent grafting of synthetic macrocyclic host compounds to DSA bridges maintained appreciable AIE/AIEE properties of DSA cores, providing a new macrocyclic building block with exceptional fluorescence behaviour.

Depending on the typical fluorescence characteristics and the inherent cavities of pillaranes, DSA-(P5)₂ can be used to fabricate efficient luminescent supramolecular polymers with unique optical and sensing properties. A neutral guest with two triazole-cyano units, i.e., NG₂, has been introduced for supramolecular assembly with DSA-(P5)₂ as a linker. Chloroform was chosen as a solvent medium for the assembly of NG₂⊂DSA-(P5)₂ considering its good solubility for all compounds and the highly efficient affinity between P5 and NG₂ in chloroform. DSA-(P5)₂ exhibits a relatively weak fluorescence when it was molecularly dissolved in chloroform. However, the continuous fluorescence intensity enhancement has been detected along with the gradual addition of NG₂, which can be ascribed to the restriction of intermolecular rotation induced by supramolecular assembly (Fig. 2b and e). The efficient host–guest binding affinity of DSA-(P5)₂ and NG₂ leads to a maximally diminished distance of DSA-(P5)₂ molecules and brings DSA cores much closer to each other, thus the rotations of the internal conjugated system have been largely restricted, resulting in the favourable radioactive relaxation accompanied by the emission of the supramolecular assembly.

Control experiments were performed to further prove the supramolecular assembly-induced fluorescence enhancement. First of all, DSA-(monomer)₂ without P5 host cavities was synthesized by linking the monomer with DSA. As expected (Fig. 2c and f), upon addition of NG₂, there is no obvious fluorescence enhancement compared with individual DSA-(monomer)₂ in chloroform, indicating that supramolecular assembly did not occur between DSA-(monomer)₂ and NG₂ due to the lack of host cavities and DSA-(monomer)₂ molecules were in their molecular dispersion states in chloroform. Meanwhile, no fluorescence intensity change was observed when NG₁ (Fig. 2a and d), an asymmetric neutral guest with only one triazole binding site for pillaranes, was gradually added into the chloroform solution of DSA-(P5)₂. DSA-(P5)₂ and NG₁ can only form a 1:2 inclusion complex instead of a supramolecular polymer, thus NG₁⊂DSA-(P5)₂ is molecularly dissolved in chloroform, accompanied by active nonradiative decay and no fluorescence emission.

The fluorescence lifetimes of all luminescent compounds have also been recorded by time-resolved fluorescence measurements. The emission of DSA-(P5)₂, NG₂⊂DSA-(P5)₂, and DSA-(monomer)₂, exhibited double-exponential decay with an average lifetime (τ) of 0.373 ns, 0.446 ns (Fig. 3) and 0.321 ns (Fig. S13, ESI†), respectively, without obvious distinction due to the same bearing chromophore, i.e., the DSA core. Furthermore, the fluorescence emission enhancement induced by supramolecular assembly.
assembly has also been verified by fluorescence quantum yields of their chloroform solutions, which were measured using an integrating sphere (Table 1). It can be determined that DSA-(P5)$_2$, after assembling into a linear polymer via the neutral guest linker, shows a relatively high quantum yield (QY) of 4.41% as compared with individual DSA-(P5)$_2$ (QY: $\phi = 3.52\%$) when dissolved in chloroform, corresponding to supramolecular assembly-induced fluorescence emission enhancement. However, compared with DSA-(P5)$_2$, DSA-(monomer)$_2$ exhibits a lower quantum yield of 2.56%, ascribed to the steric hindrance of the large P5 moieties of DSA-(P5)$_2$ that has limited the rotation within the molecule in favor of the radiative decay. The rate constant for radiative deactivation, i.e. $k_r$, or the rate constant for non-radiative deactivation, i.e. $k_{nr}$, can be easily calculated by the ratio of $\phi$ to $\tau$ or the ratio of $(1 - \phi)$ to $\tau$. NG2 $\subset$ DSA-(P5)$_2$ shows a relatively high radiative rate and low non-radiative rate compared with individual DSA-(P5)$_2$. Furthermore, more efficient fluorescence emission of DSA-(P5)$_2$ can be observed in accordance with its relatively high radiative decay rate (Table 1).

The supramolecular assembled structure and morphology of NG2 $\subset$ DSA-(P5)$_2$ have been further demonstrated by scanning electron microscopy, showing linear structures (Fig. S14, ESI†). Moreover, yellow fluorescence could also be observed from fluorescence microscopy images (Fig. S15, ESI†). Compared with the irregular large areas with yellow fluorescence from individual DSA-(P5)$_2$ and NG1 $\subset$ DSA-(P5)$_2$ dispersed as dimers, NG2 $\subset$ DSA-(P5)$_2$ shows the structure of a complex network due to the supramolecular interactions between the molecules.

In conclusion, we have successfully prepared new DSA-bridged bis(pillarene)s with typical aggregated enhanced fluorescence properties, which were constructed into supramolecular linear polymers mediated by a neutral guest possessing two triazole binding sites for pillarene cavities. DSA-(P5)$_2$ and DSA-(monomer)$_2$ exhibited typical AIE properties in the mixed solvents of THF–H$_2$O and chloroform–hexane, respectively. Significantly, compared with traditional AIE properties by the addition of unfavorable solvents, the strong yellow fluorescence of DSA-(P5)$_2$ was induced by supramolecular assembly via host–guest inclusion complexation. This result has been confirmed by the control experiments,
This research is supported by the National Natural Science Foundation of China (21272093 and 51473061).