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Aggregation-induced emission enhancement of polycyclic aromatic alkaloid derivatives and the crucial role of excited-state proton-transfer[†]

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Aggregation-induced emission enhancement (AIEE) phenomenon is observed in the polycyclic aromatic alkaloid derivatives due to the configuration changes in the excited state, which is attributed to intramolecular proton-transfer and the formation of a new structure of enol form.

Most organic chromophores are highly emissive in solution but weakly luminescent in the solid state due to the aggregation-caused quenching (ACQ) effect. Since the first aggregation-induced emission (AIE) active material, 1-methyl-1,2,3,4,5-pentaphenylsilole, was reported by Tang's group,¹ materials with AIE or AIEE properties have attracted much attention due to their potential applications in many fields.² In the past few years, more and more compounds with AIE or AIEE properties have been developed, such as siloles,³ 1-cyano-trans-1,2-bis-(4'-methylbiphenyl)ethylene (CN-MBE),⁴ 2,5-diphenyl-1,4-distyrylbenzene (DPDSB) derivatives,⁵ diphenyldibenzofulvene (DPDBF) derivatives,⁶ conjugated polymers,⁷ and others.⁸ The previous works have been focused on the exploration of the mechanism of those AIE- or AIEE-active molecules. It is concluded that the AIE or AIEE resulted from the inhibition of the nonradiative channel, that is, the vibrational/torsional energy relaxation process is blocked by the stacking of the intermolecular interaction in the aggregate state. Hence, the AIE or AIEE effect of the molecules has been found to be usually associated with aromatic groups by rotatable C-C, C-N or N-N single bonds.³⁻⁸ In addition, they are usually explained on the basis of the theory of restriction of intermolecular rotation (RIR), intramolecular charge-transfer (ICT), excimer formation, and excited-state proton-transfer (ESPT).³⁻⁹ The theory of RIR and ICT in explaining the AIEE phenomenon

has already been rationalized by molecular interactions and packing. However, the AIEE effect is rarely discussed in the light of ESPT theory,¹⁰ especially from intramolecular interactions. Although a few articles refer to ESPT theory, the spectrum of the transition state has not been investigated in depth and crystal structures are not reported.

In the processes of exploring how the ESPT is impacted on AIEE, two new alkaloid derivatives 4-(2-(3-trifluoroacetylamino)propionylphenylamino)-9-(2-trifluoroacetylamino)ethylacridine-1,2-dione (TBBF) and 4-(2-acetylphenylamino)-9methylacridine-1,2-dione (TBBH) were synthesized (Scheme 1).¹¹ They show differences from the general AIEE phenomenon. because configuration changes have taken place by protontransfer when they are excited. In this paper, the optical properties, crystal structure, pH effect, dynamic conversion of nanoparticles, NMR and IR spectra were investigated. It is concluded that TBBF and TBBH are normally more stable as keto forms in the ground state, whereas, in the excited state, enol forms are more stable owing to the formation of a new structure with a conjugated heptacyclic ring. In combination with the theory of the transition state (Keto-Keto*-Enol*-Enol), the configuration changes in photoexcitation and an abnormally large Stokes shift of photoluminescence (PL) spectrum from 470 to 585 nm upon addition of water have been well explained.9,10 Our results will not only enlarge the family of the specific AIEE-active compounds from polycyclic aromatic alkaloid derivatives, but also enrich the AIEE mechanism of ESPT theory.

The solutions (such as CH₂Cl₂, CHCl₃, ethanol and DMF) of **TBBH** and **TBBF** were somewhat luminescent, while both



Scheme 1 Synthesis and molecular structure of TBBH and TBBF.

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[†] Electronic supplementary information (ESI) available: Synthetic procedures; fluorescence images of solution, aggregates and solid; time-resolved fluorescence spectra; SEM images; nano-particle size; HOMO-LUMO energy orbitals; PL spectra in solvents with different polarity and pH; NMR spectra at various concentrations and IR spectra; crystallographic data. CCDC 799380. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c0cc04827e



Fig. 1 Absorption and PL spectra of TBBF in ethanol-water mixtures with different fractions of water; $c = 5 \,\mu$ M.

of the solids exhibit strong orange fluorescence under UV-lamp illumination (365 nm) (Fig. S1, ESI†). The AIEE feature is also quantitatively characterized by the measurement of their PL spectra and UV-visible absorption spectra in ethanol and in water–ethanol mixtures (concentration kept at 5 μ M) (Fig. 1 and S2, ESI†). The main absorption band peaks are located at around 295 and 460 nm, respectively.

For TBBF, the emissions from pure ethanol solution is weak and the fluorescence quantum yield ($\Phi_{\rm F}$) value is small (6.5%) (Fig. 1 and Table S1, ESI[†]). With increasing the fraction of water, the PL of TBBF is switched on and red-shifted from 469 to 481 nm, accompanied by a gradual increase in the emission intensity which reaches a maximum for 70% water-ethanol solutions. Then the fluorescence at 481 nm decreases gradually, and a new peak at 570 nm develops and becomes stronger with further increasing the water fraction. When the water fraction is increased to 90%, the $\Phi_{\rm F}$ value rises to 71.9% with a much longer lifetime (3.795 ns) shown, which is about 50-fold higher than that of (0.072 ns) in pure ethanol (Table S1, ESI⁺). The PL of TBBF in the film state is red-shifted to 585 nm. The Stokes shift for TBBF is 116 nm in the film compared with that of in the pure ethanol solution, indicating that there is a large configurational conversion from the twisted ground state to a more planar excited state (Fig. 2). For the sake of better understanding the role of ESPT, we only consider the singlemolecular rotation group. In dilute ethanol solution without water added, molecules have two points that can twist without any restriction imposed on the intramolecular torsional motions. This is regarded as the hypothetical "free" state and TBBF should have no emission. However, in the actual excited state, intramolecular proton transfer occurs via N-H and O-H bonds, which hinders molecular rotation. In this "half free" state, due to restriction of intramolecular rotation,



Fig. 2 Configuration changes from keto to enol forms are influenced by proton-transfer in the excited-state.



Fig. 3 SEM images of **TBBF** (volume percent of water: (a) 0, (b) 30, (c) 50, (d) 70, (e) 90, (f) 100%).

the enhancement of planarity and the increase of conjugation lead to weak and broad emission, and also promote the aggregation of nanoparticles to some extent owing to the increase of intermolecular interactions. Because water is a poor solvent of TBBF, some molecules begin to pack in the aggregate state upon addition of water. Therefore the restriction imposed on the intramolecular torsional motions is strengthened, which aids proton transfer by the formation of O-H and N-H hydrogen bonds. In 0-30% water-ethanol mixtures, one-dimensional nanowires were obtained after solvent evaporation (Fig. 3a and b), while when the water fraction is above $\sim 40\%$, a large number of nanoparticles are formed (Fig. 3c and d). Despite this, all the solutions prepared are homogeneous without visible deposits observed after mixing. The large portion of the TBBF molecules remaining in the solvent mixture gradually deposit in a way similar to recrystallization. So the rotation has been partially limited and fluorescence intensity is enhanced in the "half free" state. Upon using a higher fraction of water in the system, for example, up to 90%, the TBBF molecules quickly agglomerate to form reddish amorphous ramiform aggregates (Fig. 3e and f). The aggregate particles predominate in the mixture and their size is large enough to be easily observed. One can see that the diameter of particles is hundreds of nanometres (Fig. S4b, ESI⁺). With increasing water content molecules gradually change from the "half free" state to the "locked" state (Fig. 2). Thus the fluorescence intensity at 481 nm decreases and then disappears gradually while a peak of 570 nm becomes evident. Similar results are obtained to TBBH (Fig. S3 and S4a, ESI⁺), which exhibit weaker fluorescence in the aggregate state, owing to the shorter substituent group.

In order to verify whether proton-transfer exists and how it impacts on the excited state of TBBF and TBBH, we measured the PL spectra in solvents with different polarity and pH. At the same concentration, it is noticed that the emission peaks increase with the increase of the polarity of the solution (Fig. S5, ESI[†]). This indicates that a significant intramolecular electronic push-pull phenomenon exists in the bonds of N-H-O. Proton-transfer leads to occupied orbital energy transfer from the aniline group in the ground state to the whole molecule in the excited state (Fig. S6, ESI[†]). In addition, TBBF is weakly luminescent in acidic solution when the pH value is lower than 4.31. At a pH of 12.64, the PL intensity is 15-fold higher than that at pH of 3.09 (Fig. 4a). The peak intensity at 475 nm is decreased and then increased compared with the peak at 580 nm when the pH is reduced from 12.64 to 3.09 (Fig. 4b), which demonstrates that N-H-O bond is broken in strong acid or alkali solutions, though it is easier



Fig. 4 PL spectra of **TBBF** (20 μ M) at different pH values (left) and in normalized form (right) in ethanol–water mixture (1:9 v/v).

to form the enol molecular structure. At low pH, molecules in the "locked" state are destroyed and converted into an ammonium salt form, which dissolves in water, so the solution is weakly emissive; at high pH, the ammonium salt form of **TBBF** returns to its free amine form, which is insoluble and aggregates in water. Thus, the stronger fluorescence coming from the aggregate state is turned on. A similar phenomenon is observed for TBBH (Fig. S7, ESI⁺). In fact, the configuration changes caused by aggregation can be further confirmed by NMR and IR. The "half-free" state of the larger conjugated structure gives rise to an increase of the chemical shift upon increase in concentration (Fig. S8, ESI[†]). From the IR spectra, the rocking vibration peak of N–H (1661 cm^{-1}), the stretching vibration peak of C=O (1737 cm^{-1}) and the enhanced symmetric stretching vibration of H bonds in CH_3 (2852 cm⁻¹) are observed in solution (Fig. S9a, ESI⁺), however, they can not be seen in the solid state (Fig. S9b, ESI[†]). All of these results indicate the formation of new rings of the enol form due to the configuration changes.

The proposal that ESPT is operative is also supported by crystallography (Fig. 5). The torsional angle between the backbone and adjacent aniline group is 29.11° and rotational motions of the aniline group leads to weak fluorescence in ethanol solution. In the single molecule, there are strong intramolecular interactions, which make **TBBH** easily form a new structure containing a conjugated heptacyclic ring by O-H and N-H bonds (Fig. S10a, ESI[†]) and is the reason why **TBBH** has only one emission peak at 580 nm in the film state. Besides the intramolecular interactions, there are also strong intermolecular interactions (Table S2, ESI[†]). Each molecule is fixed with eight molecules up and down by $C-H-\pi$ interactions and H-O bonds (including one water molecule) (Fig. S10b and S10c, ESI[†]). These interactions lead to the large Stokes shift of the emission peak and a gradual increase in the emission intensity upon the addition of water.

In summary, in this work, we have successfully developed two novel alkaloid derivatives with an AIEE effect. We propose



Fig. 5 Molecular structure of **TBBH** (left) and packing arrangement of **TBBH** in a unit cell (right).

that the AIEE effect is attributed to ESPT, as established by observation of optical spectra, solution polarity effects, pH effect, NMR spectra, IR data and crystallography. ESPT plays a critical role not only on explaining the AIEE effect, but also on the synthesis of further AIEE-active compounds. In addition, we forecast that they could be used as metal ion probes by replacing the water molecules in the crystal structure.

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