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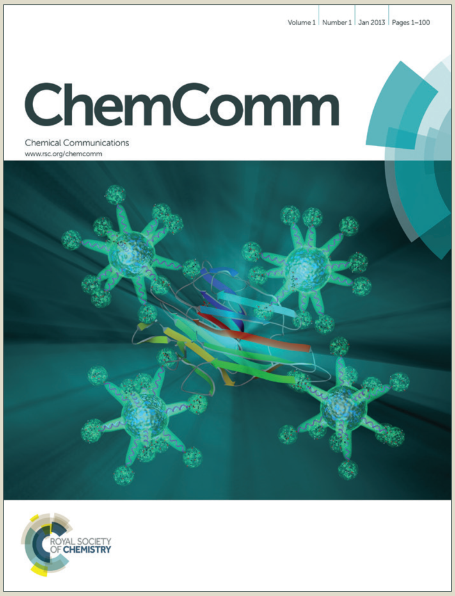

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Influence of number and substitution position of phenyl groups on the aggregation-enhanced emission of benzene-cored luminogens

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The influence of the number and substitution position of phenyl groups on the aggregation-enhanced emission of benzene-cored luminogens was unambiguous unveiled.

Aggregation induced emission (AIE) conceptually developed in 2001 is drawing increasing attention for it could solve the notorious aggregation-caused quenching (ACQ) problem encountered in most traditional fluorephores.[1] Objectively, AIE is both of great academic and practical implies. It can help to enrich the basic photo-physical knowledge by rationalizing the working mechanism of restriction of intramolecular rotation (RIR).[2] Furthermore, it satisfies the application requirements of luminogens that are always used in their aggregate or solid states, such as solid films in organic light emitting diode (OLED) and nanoparticles with high contrast and photo-bleaching stability in chemo- and biosensor.[3,4]

Since AIE luminogens (AIEgens) exhibit remarkable advantages over typical ACQ molecules, especially in their aggregate and solid states, the exploration of new AIEgens is of great importance. One direct and effective strategy is to convert an ACQ fluorophore to an AIE one by decorating an AIEgen on it.[5] For example, anthracene (An), pyrene (Py), carbazole (Cz) and triphenylamine (TPA) show typical ACQ effects due to their inevitable π-π stacking in the aggregate states. The attachment of the AIE-active tetraphenylethene (TPE) readily generates new AIEgens of TPE-An, TPE-Py, TPE-Cz and TPE-TPA, respectively (Chart 1).[6] Inspired by such a powerful strategy, we thus made our efforts on investigating whether simply adding rotatable phenyl rings to an ACQ fluorophore behaves similarly.

In the family of organic conjugated emitters, polyphenyl is one of the most popularly used species, because phenyl group is an elementary unit that can extend conjugation effectively.[7] Nevertheless, the ACQ effect in such system has hampered its further application.[8] While, rare efforts have been paid on analysing and understanding the photo-physical properties of polyphenyls via varying the number and position of substituted phenyl rings on the benzene cores.

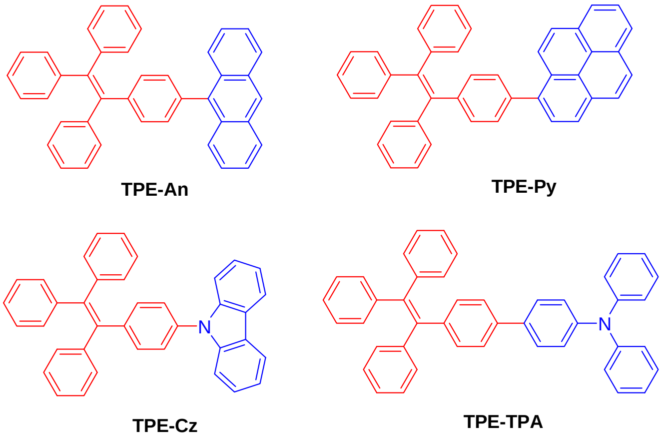
TPE-An TPE-Py
TPE-Cz TPE-TPA

Chart 1. Molecular structures of AIEgens with TPE as rotors (red) and ACQ moieties (blue) as stators.

We thus embarked a research on this aspect in order to develop new AIEgens and to further deciphering the AIE mechanism. Delightfully, an unambiguous structure-property relationship for such system was established. The AIE-inactive polyphenyls could be successfully converted to AIE-active ones by attached certain amount of phenyl rings on the benzene cores with subtle change of the substitution positions.

The molecular structures of polyphenyls studied in this work are shown in Chart 2. Among which, 1,3,5-triphenylbenzene (1,3,5-TPB), 1,2,4-triphenylbenzene (1,2,4-TPB), 1,2,4,5-tetraphenylbenzene (1,2,4,5-TPB) and pentaphenylbenzene (PPB) were synthesized according to the reported methods.[9] Their structures were fully characterized by spectroscopic methods and satisfactory analysis data were obtained (Fig. S1-S8, electronic supplementary information, ESI†). The relationship of the structure-photophysical property of these multiple phenyl

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substituted benzenes was studied using fluorescence spectroscopy technique and X-ray diffraction analysis.

We first investigated the emission behaviour of *p*-terphenyl, in which the central benzene was substituted by two phenyl rings on its *para*-positions (Chart 2). The photoluminescence (PL) measurements showed that its THF solution emits intensely at 350 nm with absolute quantum yield (Φ_F) of 64.5% and fine emission structure could be observed in its PL spectrum. However, upon addition of water, the non-solvent of it, into the THF solution, distinctly decrease of the absolute Φ_F was recorded (Fig. S9; ESI†), indicative of a typical ACQ effect.

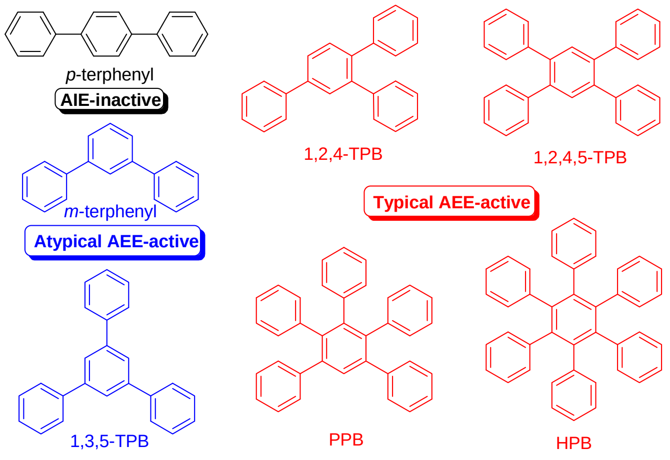

Chart 2. Molecular structures of polyphenyls.

The linear structure of *p*-terphenyl is apt to adopt a stable planar conformation to maintain the minimal potential energy for intramolecular rotation with a maximal electronic conjugation.[10] Such conformation of the molecule tends to form quenching species like excimers via π-π stacking interaction in the aggregate state, making *p*-terphenyl AIE-inactive.[3i]

Interestingly, one of the isomers of *p*-terphenyl, *i.e.* *m*-terphenyl, in which the central benzene was substituted by two phenyl rings on its *metal*-positions, behaves differently. Its THF solution is weakly emissive at 341 nm. Since the absolute Φ_F could not be measured due to the equipment test limit, we used the PL intensity to characterize the photo-physical property. The PL intensity linearly increased upon addition of non-solvent of water into its THF solution, exhibiting the atypical aggregation-enhanced emission (AEE) characteristics (Fig. 1A). The slight drop of PL intensity in the THF/water mixture with 90% water fraction (f_w) is probably due to the formation of less emissive amorphous nanoaggregates via random packing of the molecules.[11] The AEE feature of *m*-terphenyl could be ascribed to its V-shaped structure, which makes two substituted phenyl rings twisted out the central plane of benzene core and prohibits the π-π stacking interaction between molecules in the aggregate state. Meanwhile, the RIR enables this AIEgen to emit intensely in its aggregate state.

Addition of another phenyl ring on the *meta* position of *m*-terphenyl will generate another AIEgen of 1,3,5-TPB. The photo-physical property of this molecule is similar to that of *m*-terphenyl. It also displays the atypical AEE effect but emit at a longer wavelength of 354 nm due to the lengthening of the conjugation (Fig. 1B and S10, ESI†). It is worth noting that the maximum emission peaks remain almost unchanged, suggesting that no strong π-π interaction existed due to the non-planar structure conformation. Fortunately, single crystal of 1,3,5-TPB suitable for X-ray diffraction analysis was obtained (CCDC 1032746). The measurement showed that 1,3,5-TPB adopts a non-planar conformation with twisted angles in the range of 34.58-38.60° (Fig. S11, ESI†), further confirming its propeller-shaped conformation. The linear increase of the emission intensity upon addition of water is probably ascribed to the poor solubility of 1,3,5-TPB in THF.

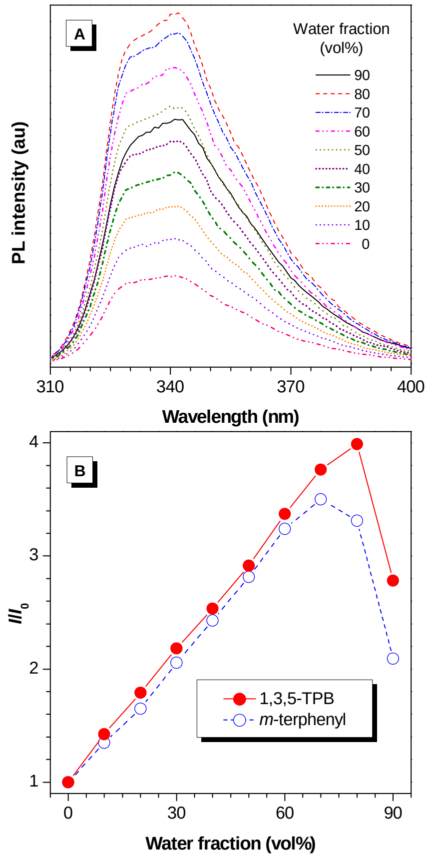

Figure 1. (A) PL spectra of *m*-terphenyl in THF/water mixtures with different water fractions; λ_{ex}: 248 nm, concentration: 10 µM. (B) Changes in the PL intensity of *m*-terphenyl and 1,3,5-TPB in THF/water mixtures with different water fractions.

Surprisingly, slight changing the structure of 1,3,5-TPB to its isomer of 1,2,4-TPB, in which only one substitution position of phenyl group was different, remarkably differentiates their photo-physical properties. As aforementioned, 1,3,5-TPB is atypically AEE-active, whereas, 1,2,4-TPB is an typical AEE-active molecule. This AIEgen emits weakly with maximum peak at *ca.* 375 nm in THF solution and THF/water mixtures with f_w lower than 80%, but efficiently in THF/water mixtures with f_w of 90% due to the RIR (Fig. 2A and Fig. S12A; ESI†). Moreover, the

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absolute Φ_F measurements show similar behaviours (Fig. S12B; ESI†). In comparison with its congener of 1,3,5-TPB, the strong steric hindrance leads to high twisting angles between the surrounding phenyl rings and the central benzene. As can be seen from the single crystal structure (CCDC 736467) of 1,2,4-TPB, the dihedral angles are in the range of 42.03-50.06^{o} (Fig. S13, ESI†),[12] which are much larger than that of 1,3,5-TPB. This structural conformation enables 1,2,4-TPB to dissolve in THF well and emit weakly in its THF solution/water mixtures with f_w less than 80%.

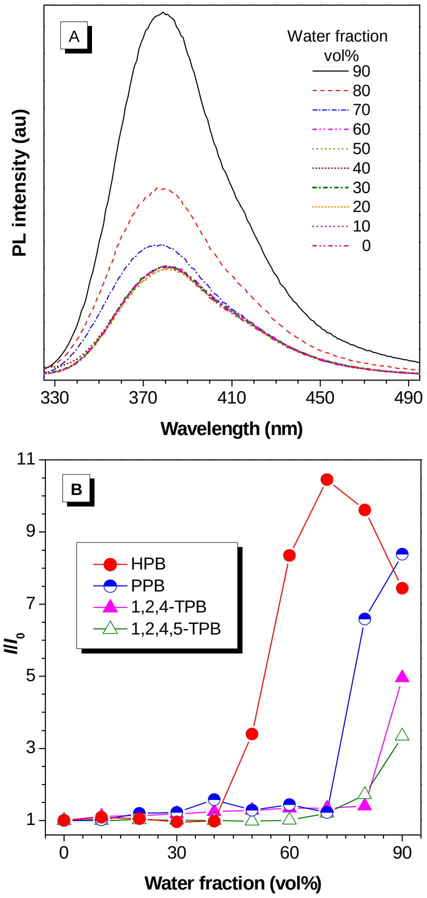

Figure 2. (A) PL spectra of 1,2,4,5-TPB in THF/water mixtures with different water fractions; λ_{ex}: 275 nm, concentration: 10 μM. (B) Changes in the fluorescence intensity of 1,2,4-TPB, 1,2,4,5-TPB, PPB and HPB in THF/water mixtures with different water fractions.

These results indicate that more twisted the structural conformation and more phenyl rings attached on the central benzene, more pronounced AEE features will be achieved. Is this law applicable for much more complex system of polyphenyls? To answer this question, we investigated the molecular structure and photo-physical property of 1,2,4,5-TPB, PPB and HPB. As could be found from their single crystal structures (CCDC 703163), the 1,2,4,5-TPB possesses the moderate dihedral angles of 40.50-65.98^{o} (Fig. S14, ESI†), which are larger than 1,2,4-TPB. It is worthy to note that 1,2,4,5-TPB also features the AEE characteristics (Fig. 2B and S15). It remains weak emissive with absolute Φ_F (1.5%) in THF and THF/water mixtures with f_w lower than 60%. Afterwards, the emission intensity increases gradually but without shifting its maximum emission peaks at 380 nm. The highest intensity and absolute Φ_F (6.4%) were recorded in THF/water mixtures with f_w of 90%. It is worth noting that the absolute Φ_F (20.9%, Table S1, ESI†) is much higher than the aggregates formed in THF/water mixture with f_w of 90% probably due to more tight molecular packing, which further restrict the intramolecular rotations.

Similarly, thanks to the intramolecular rotation in certain degree of substituted phenyl rings on the benzene cores, PPB and HPB are also AEE-active (Fig. 2B, S16 and S17, ESI†). Moreover, due to the more crowded substituted phenyl rings on the benzene cores as indicated by their single crystals, PPB (CCDC 769270)[13] and HPB (CCDC 609800)[14] possess the dihedral angles of 56.09-72.92^{o} and 65.14-88.59^{o}, respectively (Fig. S18 and S19, ESI†), which are more twisted than that of 1,2,4,5-TPB. Such large dihedral angles between substituted phenyl rings and central benzene cores inevitably shorten the effective conjugation length and blue-shifted their emission 30 nm shorter than that of 1,2,4,5-TPB (Fig. S16 and S17, ESI†).

Interestingly, 37 nm of red-shift of *p*-terphenyl was observed from its solution to film states, further suggesting the π-π stacking interaction occurred in this molecule (Fig. S20 and Table S2, ESI†). The AEE-active luminogens, however, show no shift or blue-shift of their maximum emission from their solution to film states, which are general photophysical properties for AIEgens.[3h]

In summary, we successfully establish an unambiguous structure-property relationship of polyphenyls via tuning the number and position of substituted phenyl rings on the benzene core. The general rule concluded from this study is that more phenyl rings attached on the central benzenes will induce a pronounced AEE effect due to its much more twisted conformation influenced by steric effect. Unlike TPE, the polyphenyls contain no double-bonds, which exclude the *E-Z* isomerization, simplifies the mechanism understanding for the AIE/AEE phenomenon, and enhance their thermal stabilities (Fig. S21, ESI†), making them a new kind of AIEgens.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis and characterization, PL spectra, and single crystal structures of polyphenyls. See DOI: 10.1039/c000000x/

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