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Influence of the 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 is unambiguously revealed.

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

Since AIE luminogens (AIEgens) exhibit remarkable advantages over typical ACQ molecules, especially in their aggregate and solid states, investigations into new AIEgens is of great importance. One direct and effective strategy is to decorate an AIEgen onto an ACQ fluorophore, converting the whole into a new AIEgen.[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 investigated whether the simple addition of rotatable phenyl rings onto an ACQ fluorophore would cause it to behave similarly.

In the field of organic conjugated emitters, polyphenyl is one of the most popularly used species due to the phenyl group being an elementary unit that can effectively extend conjugation.[7] Nevertheless, the ACQ effect in such systems has hampered its further application.[8] However, few efforts have been made to analyse and understand the photo-physical properties of polyphenyls and the effect of varying the number and position of substituted phenyl rings on the benzene cores.

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

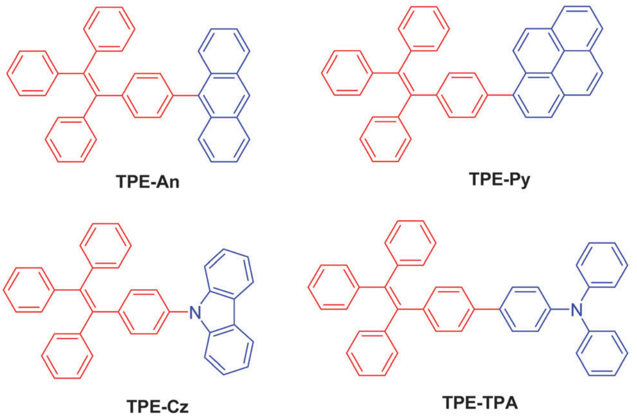

Chart 1 Molecular structures of AIEgens with TPE as rotors (red) and ACQ moieties (blue) as stators.

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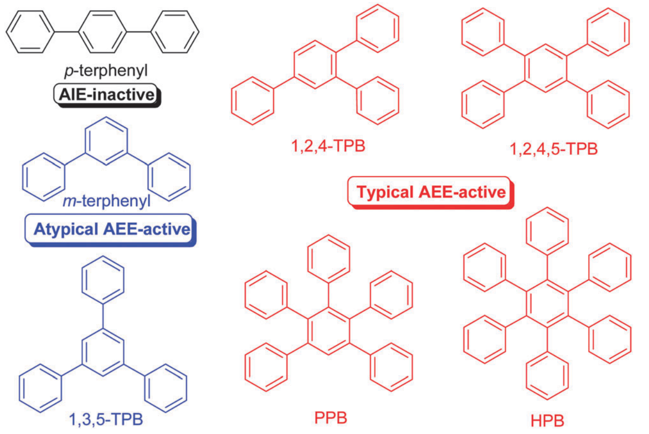

Chart 2 Molecular structures of the polyphenyls studied in this work.

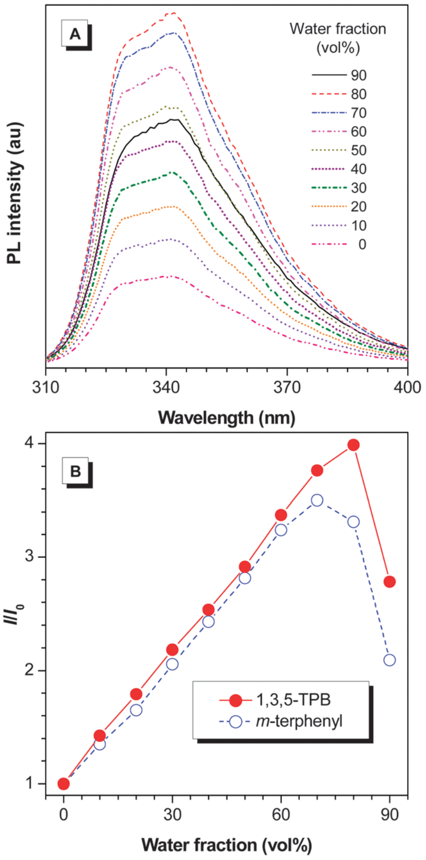

Fig. 1 (A) PL spectra of *m*-terphenyl in THF–water mixtures with different water fractions; λ_{ex}: 248 nm, concentration: 10 μM. (B) Changes in the PL intensity of *m*-terphenyl and 1,3,5-TPB in THF–water mixtures with different water fractions.

The molecular structures of the polyphenyls studied in this work are shown in Chart 2. From these, 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 previously reported methods.[9] Their structures were fully characterized by spectroscopic methods and satisfactory analysis data were obtained (Fig. S1–S8, ESI†). The structure–photo-physical property relationships of these polyphenyl substituted benzenes were studied using fluorescence spectroscopy and X-ray diffraction.

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

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

Interestingly, one of the isomers of *p*-terphenyl, *m*-terphenyl, in which the central benzene is substituted by two phenyl rings in the *meta*-positions, behaves differently. Its solution with THF is weakly emissive at 341 nm. Since the absolute Φ_F could not be measured due to the test limit of the equipment, we used the PL intensity to characterize the photo-physical properties. The PL intensity linearly increased with the addition of non-solvent water into the THF solution, exhibiting atypical aggregation-enhanced emission (AEE) characteristics (Fig. 1A). The slight drop of PL intensity in the THF–water mixture with a 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 causes the two substituted phenyl rings to twist out of the central plane of the benzene core, prohibiting the π–π stacking interaction between molecules in the aggregate state. Meanwhile, the RIR enables this AIEgen to emit intensely in its aggregate state.

The addition of another phenyl ring onto the *meta* position of *m*-terphenyl will generate another AIEgen, 1,3,5-TPB. The photo-physical properties of this molecule are similar to that of *m*-terphenyl. It also displays the atypical AEE effect but emits at the longer wavelength of 354 nm due to the lengthening of the conjugation (Fig. 1B and Fig. S10, ESI†). It is worth noting that the maximum emission peaks remain almost unchanged, suggesting that no strong π–π interactions exist due to the non-planar structure conformation. Fortunately, a 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 in the emission intensity upon the addition of water is probably due to the poor solubility of 1,3,5-TPB in THF.

Surprisingly, slightly changing the structure of 1,3,5-TPB to its isomer 1,2,4-TPB, in which only one substitution position by a phenyl group is different, causes remarkable differences in their photo-physical properties. As aforementioned, 1,3,5-TPB is atypically AEE-active, whereas, 1,2,4-TPB is a typical AEE-active molecule.

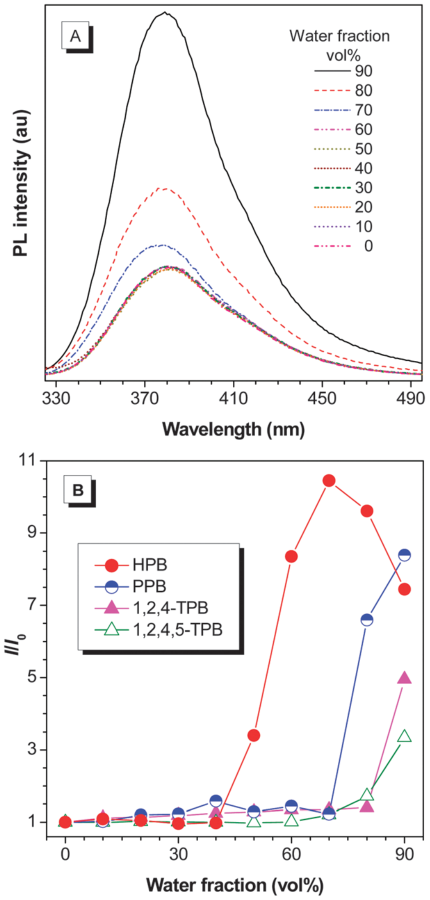

Fig. 2 (A) PL spectra of 1,2,4,5-TPB in THF–water mixtures with different water fractions; λ_{ex}: 275 nm, concentration: 10 μM. (B) Changes in the fluorescence intensity of 1,2,4-TPB, 1,2,4,5-TPB, PPB and HPB in THF–water mixtures with different water fractions.

This AIEgen emits weakly with a maximum peak at *ca.* 375 nm in THF and THF–water mixtures with f_w less than 80% but efficiently in THF–water mixtures with f_w of 90% due to the RIR (Fig. 2 and Fig. S12A, ESI†). In addition, the absolute Φ_F measurements show a similar behaviour (Fig. S12B, ESI†). In comparison with its congener of 1,3,5-TPB, the strong steric hindrance in 1,2,4–TPB 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° (Fig. S13, ESI†),[12] which are much larger than those of 1,3,5-TPB. This structural conformation enables 1,2,4-TPB to dissolve in THF well and emit weakly in THF–water mixtures with f_w less than 80%.

These results indicate that the more twisted the structural conformation and the more phenyl rings attached to the central benzene, will allow for more pronounced AEE features to be achieved. However, is this law applicable for more complex systems of polyphenyls? To answer this question, we investigated the molecular structures and photo-physical properties of 1,2,4,5-TPB, PPB and HPB. As seen from their single crystal structures (CCDC 703163), 1,2,4,5-TPB possesses moderate dihedral angles of 40.50–65.98° (Fig. S14, ESI†), which are larger than those of 1,2,4-TPB. It is worthy to note that 1,2,4,5-TPB also features AEE characteristics (Fig. 2 and Fig. S15, ESI†). It remains weakly emissive with an absolute Φ_F (1.5%) in THF and THF–water mixtures with f_w of lower than 60%. Beyond 60% the emission intensity increases gradually but without shifting the 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 the THF–water mixture with f_w of 90%. This is probably due to a tighter molecular packing, which further restricts the intramolecular rotations.

Similarly, thanks to the intramolecular rotation in other numbers of phenyl rings substituted on the benzene cores, PPB and HPB are also AEE-active (Fig. 2B and Fig. S16 and S17, ESI†). Furthermore, the more crowded substituted phenyl rings on the benzene cores of PPB (CCDC 769270)[13] and HPB (CCDC 609800),[14] as indicated by their single crystals, enable them to possess dihedral angles of 56.09–72.921° and 65.14–88.591°, respectively (Fig. S18 and S19, ESI†), which are more twisted than those of 1,2,4,5-TPB. Such large dihedral angles between substituted phenyl rings and the central benzene core inevitably shortens the effective conjugation length and blue-shifts their emission to 30 nm shorter than that of 1,2,4,5-TPB (Fig. S16 and S17, ESI†).

Interestingly, a 37 nm red-shift for *p*-terphenyl was observed moving from its solution to film state, further suggesting that π–π stacking interactions occur in this molecule (Fig. S20 and Table S2, ESI†). The AEE-active luminogens, however, show no red-shift or blue-shift of their maximum emission going from their solution to film states, which are typical photo-physical properties for AIEgens.[3h]

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

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Notes and references

1 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740.

2 (*a*) C. Q. Zhang, S. B. Jin, K. N. Yang, X. D. Xue, Z. P. Li, Y. G. Jiang, W. Q. Chen, L. R. Dai, G. Z. Zou and X. J. Liang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 8971; (*b*) G. F. Zhang, Z. Q. Chen,

M. P. Aldred, Z. Hu, T. Chen, Z. L. Huang, X. G. Meng and M. Q. Zhu, *Chem. Commun.*, 2014, **50**, 12058; (*c*) G. D. Liang, J. W. Y. Lam, W. Qin, J. Li, N. Xie and B. Z. Tang, *Chem. Commun.*, 2014, **50**, 1725; (*d*) S. L. Deng, T. L. Chen, W. L. Chien and J. L. Hong, *J. Mater. Chem. C*, 2014, **2**, 651; (*e*) D. D. Chen, X. Feng, S. Z. Gu, B. Tong, J. B. Shi, J. G. Zhi and Y. P. Dong, *Chin. Sci. Bull.*, 2013, **58**, 2728; (*f*) H. Yao and K. Ashiba, *RSC Adv.*, 2011, **1**, 834; (*g*) Q. Y. Wu, Q. Peng, Y. L. Niu, X. Gao and Z. G. Shuai, *J. Phys. Chem. A*, 2012, **116**, 3881; (*h*) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. B. Zhu and B. Z. Tang, *Chem. Mater.*, 2003, **15**, 1535; (*i*) Z. Li, Y. Dong, B. Mi, Y. Tang, M. Häussler, H. Tong, Y. Dong, J. W. Y. Lam, Y. Ren, H. H. Y. Sung, K. S. Wong, P. Gao, I. D. Williams, H. S. Kwok and B. Z. Tang, *J. Phys. Chem. B*, 2005, **109**, 10061; (*j*) S. Dong, Z. Li and J. Qin, *J. Phys. Chem. B*, 2009, **113**, 434.

3 For reviews, see: (*a*) R. R. Hu, N. L. Leung and B. Z. Tang, *Chem. Soc. Rev.*, 2014, **43**, 4494; (*b*) D. Ding, K. Li, B. Liu and B. Z. Tang, *Acc. Chem. Res.*, 2013, **46**, 2441; (*c*) Y. Z. Zhao, M. M. Cai, Y. Qian, L. H. Xie and W. Huang, *Prog. Chem.*, 2013, **25**, 296; (*d*) J. J. Zhang, Q. Zou and H. Tian, *Adv. Mater.*, 2013, **25**, 378; (*e*) A. J. Qin, J. W. Y. Lam and B. Z. Tang, *Prog. Polym. Sci.*, 2012, **37**, 182; (*f*) Z. G. Chi, X. Q. Zhang, B. J. Xu, X. Zhou, C. P. Ma, Y. Zhang, S. W. Liu and J. R. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878; (*g*) M. Wang, G. Zhang, D. Zhang, D. Zhu and B. Z. Tang, *J. Mater. Chem.*, 2010, **20**, 1858; (*h*) J. Mei, Y. N. Hong, J. W. Y. Lam, A. J. Qin, Y. H. Tang and B. Z. Tang, *Adv. Mater.*, 2014, **26**, 5429; (*i*) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361; (*j*) Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun.*, 2009, 4332.

4 (*a*) J. Huang, N. Sun, Y. Dong, R. L. Tang, P. Lu, P. Cai, Q. Q. Li, D. G. Ma, J. H. Qin and Z. Li, *Adv. Funct. Mater.*, 2013, **23**, 2329–2337; (*b*) Z. Zhao, C. M. Deng, S. M. Chen, J. W. Y. Lam, Q. Wei, P. Lu, Z. Wang, H. S. Kwok, Y. G. Ma, H. Y. Qiu and B. Z. Tang, *Chem. Commun.*, 2011, **47**, 8847; (*c*) X. Zhang, X. Zhang, L. Tao, Z. Chi, J. Xu and Y. Wei, *J. Mater. Chem. B*, 2014, **2**, 4398; (*d*) Z. Xie, B. Yang, W. Xie, L. Liu, F. Shen, H. Wang, X. Yang, Z. Wang, Y. Li, M. Hanif, G. Yang, L. Ye and Y. Ma, *J. Phys. Chem. B*, 2006, **110**, 20993; (*e*) C. T. Lai and J. L. Hong, *J. Phys. Chem. B*, 2010, **114**, 10302; (*f*) C. J. Bhongale, C. W. Chang, C. S. Lee, E. W. G. Diau and C. S. Hsu, *J. Phys. Chem. B*, 2005, **109**, 13472; (*g*) M. Shimizu, K. Mochida and T. Hiyama, *Angew. Chem., Int. Ed.*, 2008, **47**, 9760; (*h*) H. Li, Z. Chi, X. Zhang, B. Xu, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2011, **47**, 11273; (*i*) K. R. Ghosh, S. K. Saha and Z. Y. Wang, *Polym. Chem.*, 2014, **5**, 4048; (*j*) X. G. Gu, J. J. Yao, G. X. Zhang, C. Zhang, Y. L. Yan, Y. S. Zhao and D. Q. Zhang, *Chem. – Asian J.*, 2013, **8**, 2362.

5 (*a*) W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159; (*b*) Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 2221.

6 Z. Zhao, P. Lu, J. W. Y. Lam, Z. Wang, C. Y. K. Chen, H. H. Y. Sung, I. D. Williams, Y. Ma and B. Z. Tang, *Chem. Sci.*, 2011, **2**, 672.

7 (*a*) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897; (*b*) Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. A. Li, Y. Liu, J. Qin and B. Z. Tang, *Chem. Commun.*, 2007, 70.

8 (*a*) X. Yang, L. Liu, C. B. He, W. S. Chin, T. Lin, K. Y. Mya, J. Huang and X. Lu, *J. Mater. Chem.*, 2006, **16**, 829; (*b*) C. He, Y. Xiao, J. Huang, T. Lin, K. Y. Mya and X. Zhang, *J. Am. Chem. Soc.*, 2004, **126**, 792.

9 (*a*) X. Y. Shen, W. Z. Yuan, Y. Liu, Q. Zhao, P. Lu, Y. Ma, I. D. Williams, A. Qin, J. Z. Sun and B. Z. Tang, *J. Phys. Chem. C*, 2012, **116**, 10541; (*b*) K. E. Maly, E. Gagnon, T. Maris and J. D. Wuest, *J. Am. Chem. Soc.*, 2007, **129**, 4306.

10 (*a*) N. A. Murugan and S. Yashonath, *J. Phys. Chem. B*, 2005, **109**, 1433; (*b*) B. Schatschneider and E. L. Chronister, *J. Phys. Chem. B*, 2011, **115**, 407.

11 M. Chen, L. Li, H. Nie, J. Tong, L. Yan, B. Xu, J. Z. Sun, W. Tian, Z. Zhao, A. Qin and B. Z. Tang, *Chem. Sci.*, 2015, **6**, DOI: 10.1039/c4sc03365e.

12 C. F. R. A. C. Lima, M. A. A. Rocha, A. Melo, L. R. Gomes, J. N. Low and L. M. N. B. F. Santos, *J. Phys. Chem. A*, 2011, **115**, 11876.

13 E. Gagnon, T. Maris, P. M. Arseneault, K. E. Maly and J. D. Wuest, *Cryst. Growth Des.*, 2010, **10**, 648.

14 M. Lutz, A. L. Spek, S. Bonnet, R. J. M. K. Gebbink, G. Koten, private communication, 2006.