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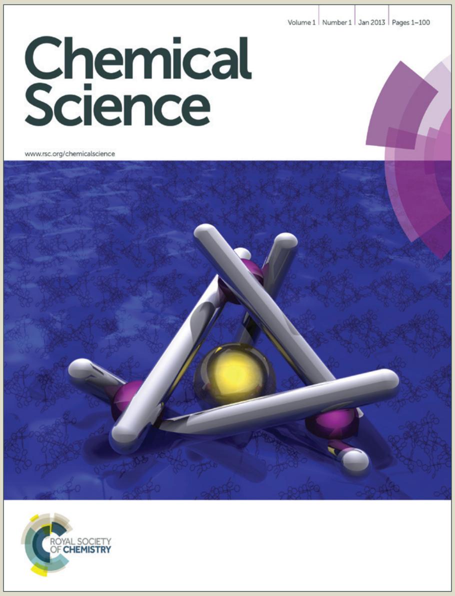

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EDGE ARTICLE

Tetraphenylpyrazine-Based AIEgens: Facile Preparation and Tunable Light Emission

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Ming Chen,[a] Lingzhi Li,[a] Han Nie,[b] Jiaqi Tong,[a] Lulin Yan,[d] Bin Xu,[d] Jing Zhi Sun,[a] Wenjing Tian,[d] Zujin Zhao,[b] Anjun Qin,*[ab] and Ben Zhong Tang*[abc]

The research on aggregation-induced emission (AIE) has been a hot topic. With enthusiastic efforts paid by the researchers, hundreds of AIE luminogens (AIEgens) have been generated but mainly based on archetypal silole, tetraphenylethene, distyrylanthracene, triphenylethene, and tetraphenyl-1,4-butadiene etc. To enlarge the family of AIEgen and to enrich their functions, new AIEgens are highly demanded. In this work, we report a new kind of AIEgen based on tetraphenylpyrazine (TPP), which could be facilely prepared under mild reaction conditions. Furthermore, TPP derivatives possess good thermal stability and their emission could be fine-tuned by varying the substituents on their phenyl rings. It is anticipated that TPP derivatives could be another widely investigated AIEgens in combining their facile preparation, good thermo-, photo- and chemo-stability, and efficient emission.

Introduction

The organic light-emitting materials are one of the key issues during development of efficient organic light-emitting diodes, organic lasers, and fluorescent sensors etc. However, the thorny problem encountered for the traditional organic light-emitting molecules is the well-known concentration/aggregation-caused quenching, which has greatly limited the enhancement of device performance. One of the methods to surmount this difficulty is to enable the aggregation to play positive instead of negative roles in enhancing the efficiency of molecule emission in the condensed phases. Indeed, such strategy has been successfully developed, that is, aggregation-induced emission (AIE).[1]

Compared with traditional organic emitters, AIE luminogens (AIEgens) are a class of burgeoning conjugated molecules with propeller-shaped structures. They are weakly or non-luminescent in their dilute solutions, but emit efficiently when aggregated or fabricated into solid films.[2] Due to their twisted conformations, the peripheral rotors like phenyl rings of AIEgens rotate against the central stator like (hetero) aromatic rings or vinyl groups to annihilate the excitons in a non-radiative fashion in solution, while in the aggregate state this rotation is greatly restricted, which in turn opens up the radiative channel and makes the molecule emissive.[3] This intriguing property endows AIEgens with potential applications in highly efficient optoelectronic devices, fluorescent sensors, cell imaging, and so on.

Thanks to enthusiastic efforts scientists paid, lots of AIEgens, with versatile functionalities and diverse applications have been developed (Chart 1).[4,5] Currently, most of the AIEgens are the derivatives of silole,[6] tetraphenylethene (TPE),[7] distyrylanthracene (DSA),[8] triphenylethene,[9] and tetraphenyl-1,4-butadiene (TPBD).[10] Although these molecules could be regarded as the archetypal AIEgens, their intrinsic disadvantages should not be ignored. For example, silole and its derivatives are troublesome in preparation especially in purification and unstable under basic condition;[10a] TPE and DSA, triphenylethene, TPBD and their derivatives contain double bonds, which may lead to potential photoxidation and photobleaching. The involved E/Z isomerizations of their containing double bonds also complicated the mechanism understanding though we and others have theoretically and experimentally proved that restriction of intramolecular rotation (RIR) is the cause for the AIE effect.[3] Thus, new AIE cores, which are easy to be synthesized and functionalized under mild reaction conditions, stable upon exposure to light and heat, and survived in acidic and basic conditions, are highly desirable.[11]

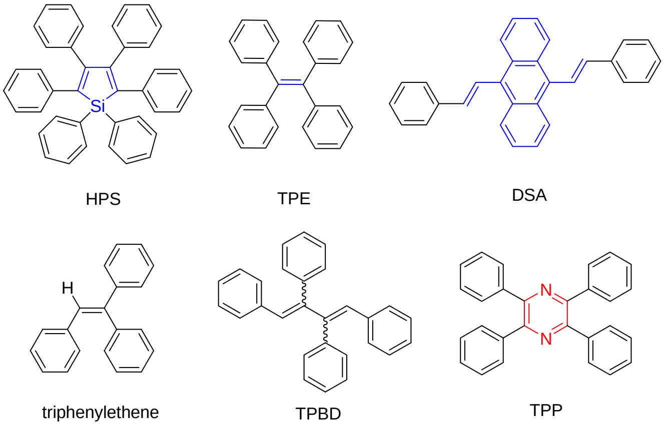


Chart 1 Molecular structures of AIEgens of hexaphenylsilole (HPS), tetraphenylethene (TPE), distyrylanthracene (DSA), triphenylethene, tetraphenyl-1,4-butadiene (TPBD) and tetraphenylpyrazine (TPP).

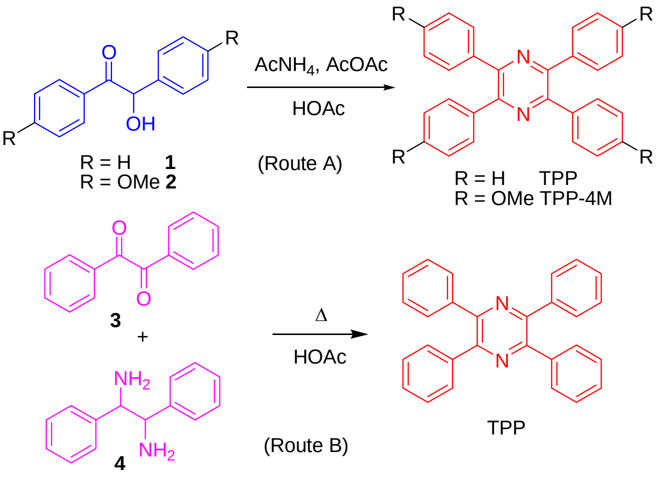
In 2009, we developed a new AIEgen of 2,3-dicyano-5,6-diphenylpyrazine (DCDPP), which was synthesized under very mild reaction conditions in high yield by simple heating the mixtures of dione and diamine in acetic acid.[12] It is worth noting that there is no vinyl group contained in DCDPP, which makes it more stable and greatly simplify the mechanism elucidation. Furthermore, the pyrazine ring is an electron deficient group and could enrich the properties of resultant AIEgens.[13]

Inspired by the facile preparation and encouraged by AIE property of DCDPP, in this work, we report a new type of AIEgen of tetraphenylpyrazine (TPP), which could be synthesized via one-pot procedure under mild reaction conditions (its structure is shown in Chart 1). It is worth noting that the TPP core is ready to be functionalized by varying the structures of starting molecules or post-reactions of the bromo-substituted TPP with aromatic boronic acid via Suzuki coupling, which provides an ideal platform to fine-tune the light emission of resultant molecules from deep-blue to pure blue.

Results and discussion

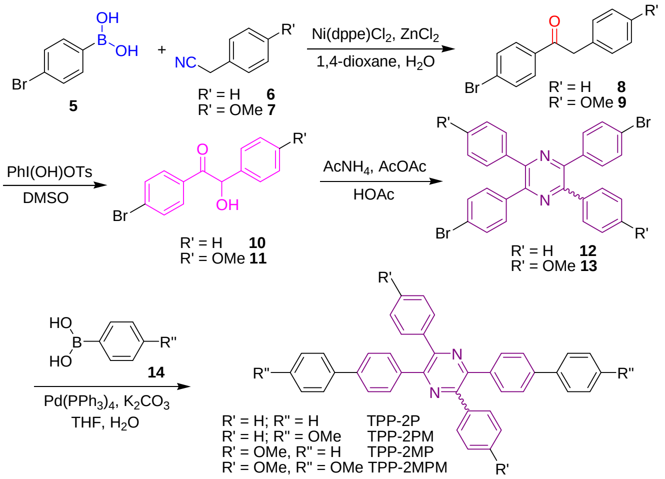
Synthesis of TPP and its derivatives

In general, there are two routes to prepare TPP and its derivatives (Scheme 1). In route A, the commercially available starting compounds of benzoin (**1**) or anisoin (**2**) could be readily converted to TPP or its methoxyl substituted molecule of TPP-4M in the presence of acetic anhydride, ammonium acetate in refluxed acetic acid after only 3.5 h.[14] Whereas, the route B is similar to our previous report.[12,15] Mixing benzyl and 1,2-diphenylethane 1,2-diamine in acetic acid and refluxing for 4 h produced TPP in moderate yield. More importantly, the produced TPP and its derivatives from both routes could be purified by recrystallization and no tedious column chromatography is needed, making these routes the simplest ones in preparation of AIEgens.



Scheme 1. Synthetic routes to tetraphenylpyrazine (TPP) and its derivative.

To verify the universality of these routes, we applied them to synthesize TPP derivatives. In this paper, we will focus on route A and demonstrate its advantages (Scheme 2). The route B will be used in another work. The bromo-substituted intermediates **12** and **13** shown in Scheme 2 could be facilely prepared via three-steps from commercially available bromo-substituted aromatic boronic acid and phenylacetonitrile in the presence of catalytic systems of Ni/Zn, PhI(OH)OTs, and AcNH4/AcOAc, respectively. Afterwards, the Suzuki coupling reaction between the resultant intermediates and aromatic boronic acid **14** readily furnished TPP derivatives with donor-π-acceptor structures in satisfactory yields. The detailed synthetic procedures are provided in Electronic Supplementary Information (ESI†).



Scheme 2. Synthetic routes to TPP-based AIEgens.

All the TPP derivatives were characterized by ^{1}H and ^{13}C NMR spectra (Figures S1-S24, ESI†) and high resolution Mass spectra (Figures S25-S30, ESI†). Satisfactory data corresponding to their structures were obtained. These TPP derivatives structurally exclude the unstable vinyl groups and are thermally stable. Taking the TPP as an example, the temperature of 5% loss of its weight (T_d) is 275 °C, which is quite similar to that of HPS and DSA, but is 62 °C higher than that of TPE (Figure S31, ESI†). Interestingly, functionalization of the TPP could further enhance the T_d of the resultant products to 60 °C higher (Figure S32, ESI†), which will increase the device stability if they are applied in this field. It is worth noting that unlike the HPS, TPP remains intact under both of the acidic and basic conditions as suggested by their remaining PL intensities in the aggregate states (Figure S33, ESI†). Moreover, unlike the photo-oxidable DSA (Figure S34, ESI†), no any new peak could be found in the ^{1}H NMR spectrum of TPP after it was irradiated by a UV lamp of 365 nm with a power of 1.10 mW/cm^2 (Figure S35, ESI†) for 2 h, demonstrating it possesses good photo-stability.

Absorption of TPP-based AIEgens

After confirming the structures of TPP and its derivatives, we investigated their photo-physical properties. It is well-known that pyrazine is an electron withdrawing group, thus, substitution of the phenyl rings of TPP with additional phenyl rings or electron-donating methoxyl groups will extend the conjugation and facilitate the charge transfer from phenyl or methoxyl groups to the central pyrazine rings, and in turn red-shift the maximum absorption (λ_{ab}) (Figure 1 and Table S1, ESI†). Indeed, from TPP, TPP-2P and TPP-2PM to TPP-2MPM, enlarging the conjugation and introducing the D-A structures by incorporating phenyl and methoxyl groups have red-shifted their λ_{ab} gradually from 338 to 362 nm. Meanwhile, when the methoxylphenyl groups were directly attached to the pyrazine rings (TPP-4M, TPP-2MP, and TPP-2MPM), longer

λ_{ab} with very small difference (2-3 nm) was observed, suggesting that the charge-transfer plays a crucial role in deciding their absorption.

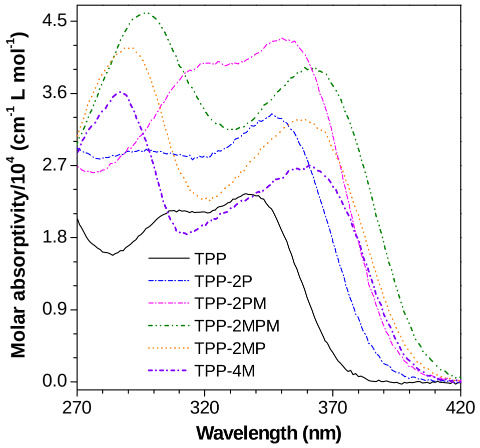


Figure 1. UV-vis absorption of TPP and its derivatives in THF.

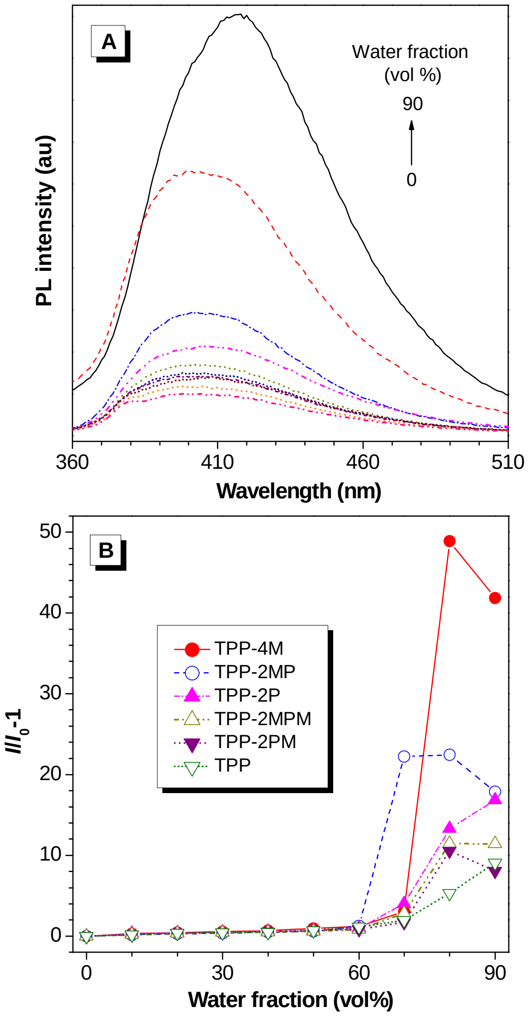


Figure 2. (A) PL spectra of TPP in THF/water mixtures with different water fraction; λ_{ex} = 338 nm (10 μM). (B) Variation in the PL intensity of TPP and TPP derivatives in THF/water mixtures with different water fraction.

Aggregation-enhanced emission

Structural inspection of the resultant molecules, we can find that the phenyl rings connected to the pyrazine cores via single bonds. According to the RIR mechanism of AIE, these TPP derivatives could also feature the AIE effect. To confirm this, we studied their photoluminescence (PL) behaviours (Figures 2 and S36-S40, ESI†). Figure 2A shows the PL spectra of TPP in THF/water mixtures with different water fractions (f_w) as an example. The emission of TPP is weak in THF solution and increases slowly until the f_w up to 60%. Afterwards, the emission intensified swiftly. Other TPP derivatives behave similarly: they are weakly emissive in THF solution and in THF/water mixtures with f_w less than 60%. When f_w was beyond 60%, their emission enhanced remarkably. Since water is a poor solvent for TPP and its derivatives, addition of water will induced them to form nanoaggregates with size in the range of 31 to 287 nm (Table S2). Thus, TPP and its derivatives feature the unique aggregation-enhanced emission (AEE) characteristics.

Moreover, when carefully inspected Figure 2B, we could find only the PL intensities of TPP and TPP-2P continue to increase in the THF/water mixtures with f_w of 90%. The decease of the PL intensities of other TPP-based AIEgens is related to their containing methoxyl groups, which probably lead to form less emissive amorphous nanoaggregates by the random packing of the molecules in THF/water mixtures with 90% water fraction.[16]

It is worth noting that the emission enhancement of TPP-2P, TPP-2PM, TPP-2MPM and TPP-2MP is much higher than that of TPP (Figure 2B) due to their contained additional phenyl rings, which will reinforce the RIR. The absolute quantum yield (Φ_F) measurements showed that these AIEgens possess high Φ_F in the range of 8.3-30.7% and most of them are above 15% (Table S1, ESI†).

Interestingly, the highest emission enhancement was recorded with TPP-4M in THF/water mixture with f_w of 80%, which is 49-fold higher than that in THF solution. Accordingly, the highest absolute Φ_F (30.7%) was also recorded with TPP-4M. The reason could be related to the molecular packing as discussed below.

Single crystal packing

To understand the emission behaviours of these AIEgens, we tried to grow their single crystals. Delightfully, the single crystals of TPP (CCDC 1031716), TPP-2P (CCDC 1031717), TPP-2PM (CCDC 1031718), and TPP-4M (CCDC 1031719) suitable for X-ray diffraction analyses were obtained. The analysis showed that all these TPP-based AIEgens adopt non-planar conformations with twisted angles between the phenyl rotors and pyrazine stators in the range of 33 to 66° (Figures S41-S44, ESI†).

Detailed survey of the molecular packing in the single crystals, we could find that multiple intermolecular C-H···π interactions with distance in the range of 2.82-3.18 Å (Figure 3) existed. Such interactions could assist in locking the molecular motion in the crystal lattice and reducing the non-radiative deactivation of excitons.[12] Moreover, the multiple C-H···π interactions in TPP-4M are much stronger than that in TPP because the interaction distance is much shorter in the former, which has helped to enhance the molecular rigidity, limit the conformational freedom much more effectively and turn on its emission in a greater magnitude.

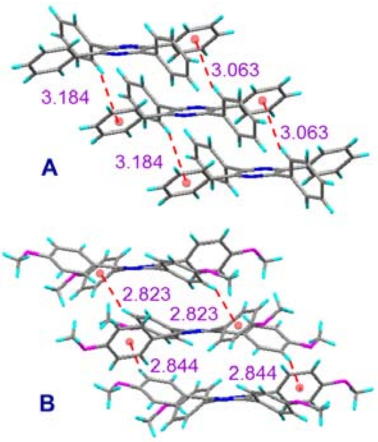


Figure 3. Single crystal packing diagrams and intermolecular C-H…π interactions of (A) TPP and (B) TPP-4M.

Tunable blue emission

Thanks to its facile functionalization, TPP-based AIEgens could emit light from deep blue to pure blue. As shown in Figures 4 and S45 as well as Table S1 (ESI†), the TPP in THF emits with maximum peak at *ca*. 390 nm and TPP-2MPM at *ca*. 460 nm, whereas, in the thin-solid film, the emission peaks of these AIEgens remain almost unchanged due to the propeller-shaped molecular structures. Interestingly, from solution to film, the maximum emission peaks of TPP-2P and TPP-2PM red-shifted from 423 and 438 nm to 442 and 453 nm, whereas, TPP-2MP and TPP-4M blue-shifted from 455 and 433 nm to 440 and 428 nm, respectively. The red-shift of emission peaks of TPP-2P and TPP-2PM implies that additional phenyl rings connected to the TPP cores play crucial roles, which will probably cause the intermolecular interactions from solution to film. The blue-shift of the emission of TPP-2MP and TPP-4M indicates that the charge-transfer from methoxyl groups to pyrazine rings was alleviated. Thus, these results suggest that the emission of TPP-based AIEgens could be fine-tuned by varying the substituted groups of TPP.

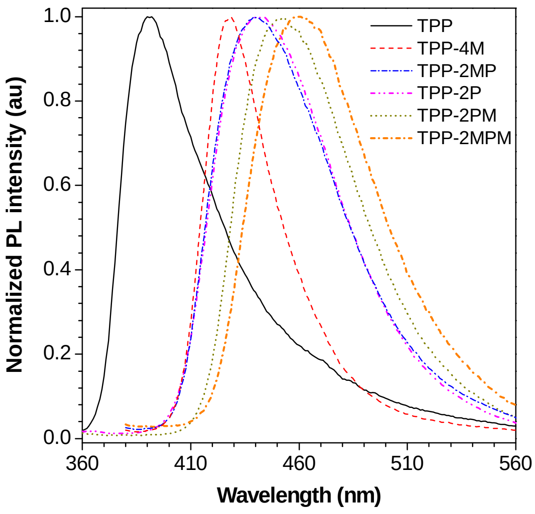


Figure 4. PL spectra of the thin films of TPP and its derivatives. The excitation wavelengths were selected as the maximum absorption in THF as shown in Table S1.

Conclusions

In conclusion, a new type of AIEgen of TPP and its derivatives were rationally designed according to the mechanism of RIR and facilely synthesized under mild reaction conditions. The TPP-based AIEgens simplify the mechanism understanding because they all contain no controversial vinyl groups. Furthermore, these AIEgens possess high thermo-, photo- and chemo-stabilities because they contain no the active double bonds, like in TPE and DSA, and instable Si-C bonds like in HPS under basic conditions. The emission of these AIEgens could be fine-tuned from deep-blue to pure blue by varying the substituted groups on the pyrazine rings. It is worthy to point that the AEE-active TPP-based derivative with electron-accepting substituent, such as cyano-group could also be facilely prepared in high yield via method A (Schemes S1, Figures S46 and S47), further manifesting the universality of this synthetic method. Moreover, thanks to the electron-withdrawing ability of pyrazine moieties, green or red emission is anticipated to be realized by attaching stronger electron-donating groups on the periphery of TPP. Thus, we believe that these TPP-based AIEgens will not only enrich the family of AIEgens and find wide application in light-emitting diodes, chemosensors and bioprobes etc., but also attract considerable interests of scientists in the areas of fundamental photophysical research and material sciences.

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[a] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: qinaj@zju.edu.cn (A.J.Q.).

[b] Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China.

[c] Department of Chemistry, Institute for Advanced Study, Institute of Molecular Functional Materials, and State Key Laboratory of Molecular Neuroscience, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong China. tangbenz@ust.hk (B.Z.T.).

[d] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China.

† Electronic Supplementary Information (ESI) available: Synthesis, characterization, TGA curves, PL spectra, crystal structures of TPP and its derivatives. See DOI: 10.1039/b000000x/

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Table of Content use only

New structural AIEgens with tunable emission based on tetraphenylpyrazine were rationally designed and facilely prepared.