

Stereoselective synthesis of folded luminogens with arene–arene stacking interactions and aggregation-enhanced emission†

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Tetraphenylethene derivatives with a folded Z-conformation and aggregation-enhanced emission characteristics are synthesized from 2-arylbzophenones. The intramolecular rotation of the folded luminogens is partially suppressed, resulting in improved emission efficiencies in solutions.

Since the discovery of aggregation-induced emission (AIE) by Tang *et al.* in 2001,¹ the design and synthesis of new AIE luminogens and exploration of their potential applications have attracted rapidly increasing interest. The novel AIE phenomenon is the direct opposite of aggregation-caused quenching (ACQ), which is well-known and widely observed from conventional chromophores. Delineating the mechanism of the AIE phenomenon is essential not only for fundamental understanding, but also, for advancing various new AIE systems. For propeller-like luminogens, *e.g.*, tetraphenylethene (TPE), the restriction of intramolecular rotation (RIR) is hypothesized to be the main reason underlying their AIE effects.^{2,3} While many indirect experimental and computational results support the RIR hypothesis, direct evidence from intramolecular control of the rotations is limited. Most subtle structural alterations to achieve RIR involve chemical bonding between aromatic rotors, which may alter the chemical nature, and thus the optical properties of the luminogens to a certain extent.⁴

McMurry coupling is an effective method of building C=C double bonds from ketones or aldehydes.⁵ It has been widely applied to the preparation of TPE and its derivatives.^{3,6} The reaction proceeds efficiently and affords stereo-uniform products by adopting symmetrically modified benzophenones as substrates. The products, however, are stereo-random, with nearly equal amounts of *Z/E*-isomers, when unsymmetrical benzophenone derivatives are treated under the same conditions, owing to the non-stereoselectivity of the reaction. Recently, we found that McMurry coupling could undergo divergent reaction pathways and furnish diverse products, which were greatly dependent on the nature of the substituents and their positions on benzophenones.⁷ The aromatic group at the 2-position of benzophenone influences the stereoselectivity of the reaction, leading to stereoregular TPE derivatives, which are rarely reported by other groups.⁸ In this work, we wish to focus on the synthesis of folded TPE derivatives and elucidate a mechanism for AIE.

The synthesis of an archetypal folded luminogen ((*Z*)-*o*-BPTPE) from 2-phenylbenzophenone (**1**) is shown in Scheme 1. Three kinds of phenyl rings in (*Z*)-*o*-BPTPE are labelled ϕ_1 , ϕ_2 and ϕ_3 for convenient description. The same labelling applies to other folded luminogens as discussed below. The treatment of **1** with TiCl₄ and zinc dust generates (*Z*)-*o*-BPTPE in a moderate yield of 50%. The reaction yields no other TPE derivative apart from (*Z*)-*o*-BPTPE. The product is isolated and easily purified by column chromatography. Single crystals of (*Z*)-*o*-BPTPE are grown from a THF–ethanol mixture and analyzed by X-ray diffraction crystallography. The crystal structure of (*Z*)-*o*-BPTPE illustrated in Fig. 1 confirms that (*Z*)-*o*-BPTPE is a *Z*-isomer. It has a folded conformation, in which ϕ_1 and ϕ_2 are located in a nearly parallel manner with the shortest distances of 3.264 Å and 3.274 Å being shorter than the typical distance for π – π stacking interactions (3.5 Å). The ϕ_1 and ϕ_2 surfaces have an overlap of approximately 50%. This type of parallel, stacked and offset geometry is favorable to the formation of π – π stacking interactions between ϕ_1 and ϕ_2 .^{9,10} The ¹H NMR spectrum of (*Z*)-*o*-BPTPE shows distinctive peaks at ~5.7 ppm (Fig. S1, ESI†), which are assigned to the H_a protons. The H_a in ϕ_2 overlies ϕ_1 with a distance of 3.141 Å, or 3.187 Å from H_a to the center of ϕ_1 , indicating that H_a is located within the

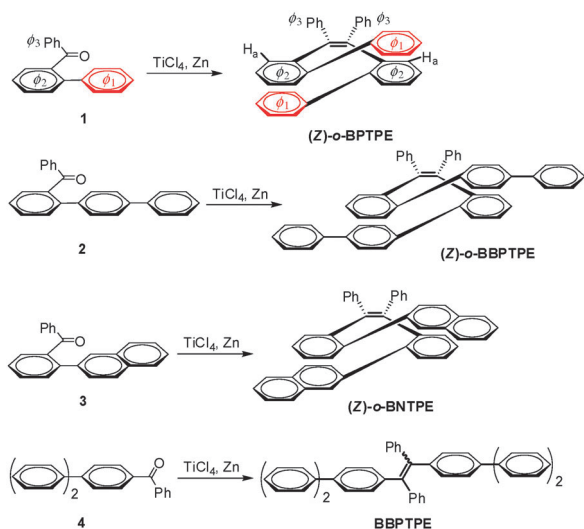
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† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallography, ¹H NMR spectra, proposed mechanism of the reaction, crystal structure of compound **10**, and Table S1. CCDC 955718–955721. For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/c3cc47696k



Scheme 1 Syntheses of folded and linear TPE derivatives. The H_a protons in (Z)-o-BPTPE are indicated as an example.

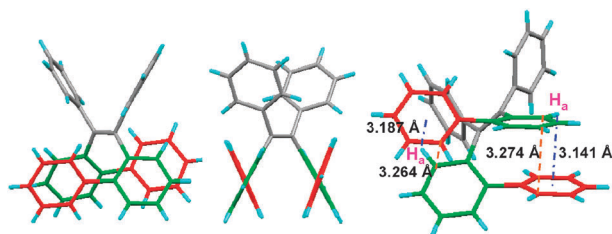
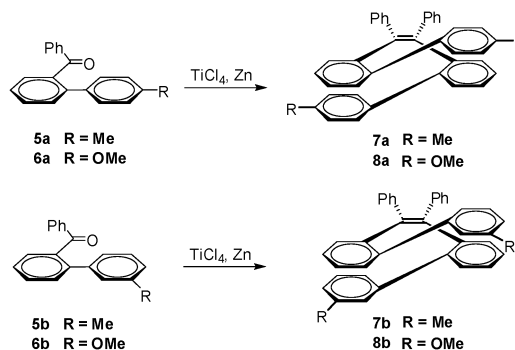


Fig. 1 The X-ray crystallography-determined molecular structure of (Z)-o-BPTPE (CCDC 955718). The shortest distances between ϕ_1 and ϕ_2 and distances from the H_a s to the center of ϕ_1 s are indicated.

shielding cone of ϕ_1 . Thereby, the resonance associated with H_a moves upfield due to the shielding effect of ϕ_1 .¹¹

With the successful synthesis of the model molecule (Z)-o-BPTPE, we wondered whether such folded luminogens could be prepared if ϕ_1 s were replaced with bulky groups, e.g., biphenyl and naphthalenyl. To our delight, the folded luminogens (Z)-o-BBPTPE and (Z)-o-BNTPE are obtained from 2-biphenyl-4-ylbenzophenone (2) and 2-(naphthalen-2-yl)benzophenone (3) in yields of 56 and 46%, respectively. The distinctive signals from the H_a s are recorded at ~ 5.8 ppm in the ^1H NMR spectrum of (Z)-o-BBPTPE (Fig. S2, ESI[†]), which are similar to those of (Z)-o-BPTPE. Those of (Z)-o-BNTPE are shifted to a higher field of ~ 5.3 ppm (Fig. S3, ESI[†]), presumably due to the fact that naphthalenyl is richer in π -electrons and thus, has a stronger shielding effect. However, the reaction of 4-biphenyl-4-ylbenzophenone (4), performed under the same conditions as the control, gives a mixture of Z/E-isomers (BBPTPE). The upfield proton resonance signals are absent from the ^1H NMR spectrum of BBPTPE (Fig. S8, ESI[†]), indicating it has a straight conformation rather than a folded one.

To study the impact of substituent positions on the formation of folded luminogens, 2-phenylbenzophenone derivatives carrying methyl or methoxyl groups at different positions of ϕ_1 are prepared and tested. The reactions of substrates 5a and 5b, and 6a and 6b, which possessed methyl or methoxyl groups at the meta- or para-positions of ϕ_1 , were carried out successfully to yield single folded



Scheme 2 Syntheses of folded TPE derivatives with methyl or methoxyl substituents at different positions.

TPE derivatives in moderate yields of 40–55% (Scheme 2). However, the reactions of 2-phenylbenzophenone derivatives with substituents at the ortho-position became complicated and target products were barely isolated. This can be ascribed to the severe steric hindrance of the products. These results reveal that the location of substituents on 2-phenylbenzophenone has a significant impact on the formation of folded luminogens. X-ray diffraction analysis of single crystals of 7a and 8a, grown from THF–ethanol, confirms that both luminogens are Z-isomers with a folded conformation (Fig. 2). ϕ_1 and ϕ_2 adopt a cofacial, slightly tilted arrangement with their centers offset, and the shortest distances between them are 3.260–3.339 Å, demonstrating intramolecular π - π stacking interactions. The H_a s in 7a and 8a are located in a similar position within the crystals as those in (Z)-o-BPTPE. The characteristic chemical shifts of the H_a s of 7a and 7b, and 8a and 8b, are also recorded upfield at ~ 5.8 ppm (Fig. S4–S7, ESI[†]).

The mechanism behind the formation of the folded Z-products was also investigated. Intramolecular π - π stacking interactions are evidently helpful in stabilizing the intermediate complex of titanium species, the subsequent deoxygenation of which furnishes the folded Z-isomers. The coupling of 1-(biphenyl-2-yl)ethanone, an analogue of 2-phenylbenzophenone with a methyl group rather than ϕ_3 , only yields an unfolded E-product (10, Scheme S1, Fig. S9 and S10, ESI[†]) and no folded products. When a methyl group takes the place of ϕ_3 ,

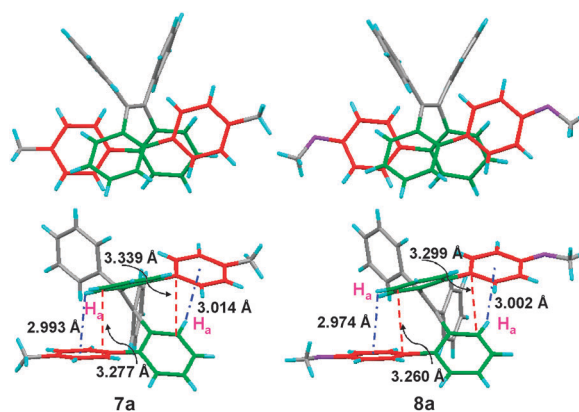


Fig. 2 Crystal structures of 7a (CCDC 955719) and 8a (CCDC 955720). The shortest distances between ϕ_1 and ϕ_2 and distances from the H_a s to the center of the ϕ_1 s are indicated.

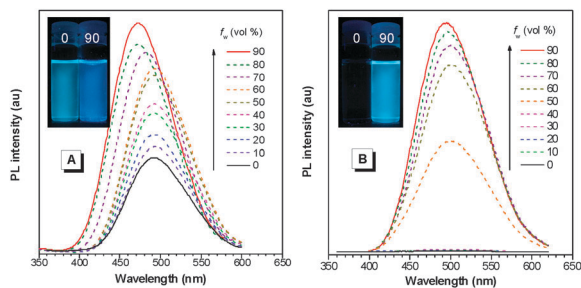


Fig. 3 PL spectra of (A) (*Z*)-*o*-BBPTPE and (B) BBPTPE in THF–water mixtures with different water fractions (f_w). Inset: Photo of (A) (*Z*)-*o*-BBPTPE and (B) BBPTPE in THF–water mixtures ($f_w = 0$ and 90%), taken under the illumination of a UV lamp.

the molecules become less congested, which leads to the formation of an *E*-isomer as it has a lower total electronic energy than a *Z*-isomer, as revealed by theoretical calculations (Fig. S11, ESI[†]). However, in the case of (*Z*)-*o*-BPTPE, the *Z*-isomer is more stable than the *E*-isomer. Therefore, it is deduced that the spatial repulsion from ϕ_3 should have functioned as a crucial driving force to bring about the parallel location of ϕ_1 and ϕ_2 . Intramolecular π - π stacking interactions and spatial congestion work collectively, resulting in the stereoselectivity of the reactions and the folded conformation of the products (Scheme S2, ESI[†]).

Unlike most TPE derivatives that are almost non-fluorescent in a solution state, these folded TPE derivatives show good emissions in THF solutions. As an example, (*Z*)-*o*-BBPTPE shows an acceptable emission peak at 492 nm. The fluorescence quantum yield (Φ_F) is 45%, measured in dilute THF solution, which is much higher than that of BBPTPE (0.62%) (Table S1, ESI[†]). As revealed by the crystal structures of folded luminogens, the ϕ_2 s in the TPE unit are located close to and in an approximately parallel pattern with the ϕ_1 s. As the rotations of the ϕ_2 s are restricted greatly, the nonradiative decay of the excited state is thus reduced, leading to reasonably high emissions in solutions. These folded luminogens show better emissions in aggregates. Fig. 3A displays the photoluminescence (PL) spectra of (*Z*)-*o*-BBPTPE in THF–water mixtures as an example. It can be seen that the emission of (*Z*)-*o*-BBPTPE intensifies progressively without a significant change in the maximum absorption wavelength (Fig. S12, ESI[†]), with the addition of water. Since (*Z*)-*o*-BBPTPE is insoluble in water, its molecules should have aggregated in the aqueous medium, demonstrating that the enhanced emission is caused by the formation of aggregates. A slight hypsochromic shift is observed in high water fractions, which is attributed to the morphological change from amorphous to crystalline.⁸ The linear analogue BBPTPE, however, shows typical AIE characteristics (Fig. 3B). The film of (*Z*)-*o*-BBPTPE shows intense emission with a maximum at 472 nm. The absolute Φ_F of the film is 72%, which is much higher than that in solution. This is because the motions of rotatable phenyl rings (ϕ_3 s) are also suppressed by the spatial constraint in the aggregate state. The radiative relaxation of the excited state becomes dominant, affording improved emission efficiencies. Similar emission behaviors are also detected in other folded luminogens, revealing aggregation-enhanced emission (AEE) attributes.

The computational results from the analysis of (*Z*)-*o*-BPTPE verify that the phenyl rotors in the TPE unit are sensitive to

various rotation barriers because of the folded conformation (Fig. S13, ESI[†]). ϕ_2 experiences a much higher rotation barrier than ϕ_3 , indicating that the rotational motions of ϕ_2 are basically suppressed but ϕ_3 is rotatable with little constraint.¹² In other words, the intramolecular rotation of the TPE unit is restricted by $\sim 50\%$ in the isolated state. The intramolecular rotation of ϕ_3 can be further suppressed by spatial constraint in the condensed phase. These results strongly support that RIR is responsible for the AIE effect of most TPE derivatives.

In summary, a stereoselective synthesis of TPE derivatives with a folded *Z*-conformation is presented. The intramolecular π - π stacking interaction and spatial congestion are responsible for the stereoselectivity of the reaction and the formation of the folded structure. These folded TPE derivatives show good fluorescence with much higher emission efficiencies than the linear TPE derivatives, owing to the partial suppression of the intramolecular rotation of phenyl rotors in the TPE unit. They possess AEE attributes and become more emissive in the solid state. These results reveal that internal control of the intramolecular rotations endows the luminogens with improved emissions in solution, suggesting that RIR is responsible for the AIE phenomenon. Further exploration of this folded system is in progress.

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