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Axial chiral aggregation-induced emission luminogens with aggregation-annihilated circular dichroism effect†

Haoke Zhang,[a] Hongkun Li,[b] Jia Wang,[c] Jingzhi Sun,[a] Anjun Qin*[ac] and Ben Zhong Tang*[abc]

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Axial chiral aggregation-induced emission (AIE) luminogens of (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA were synthesized for the first time by covalently attaching the AIE-active tetraphenylethene (TPE) units to the axial chiral binaphthol (BINOL) moieties at their 3,3′- or 6,6′-positions. It was found that the circular dichroism (CD) value when TPE was attached to BINOL at its 3,3′-positions was much larger than that found after its attachment at 6,6′-positions. The resultant AIE-active luminogens (AIEgens) show high quantum yields (up to 42.4%) in their aggregated states. Interestingly, these AIEgens exhibit an abnormal aggregation-annihilation CD (AACD) phenomenon. The decrease in the twisted angle between the two naphthalene rings upon aggregation was rationalized as the cause of this unique effect.

Introduction

Aggregation-induced emission (AIE), first described by Tang *et al.* in 2001,[1] refers to a unique phenomenon displayed by some propeller-shaped emitters, such as 1,1-dimethyl-2,3,4,5-tetraphenylsilole and tetraphenylethene (TPE). They are weakly or non-emissive when dissolved as molecules, but induced to emit intensely by aggregate formation upon the addition of poor solvents.[2,3] The AIE effect is exactly opposite to the aggregation-caused quenching (ACQ) exhibited by most of the traditional luminophores and will make the emitters perform efficiently in aggregated or solid states. Attracted by this prospect, researchers worldwide are enthusiastically studying this emerging area and several kinds of AIE-active luminogens (AIEgens) have been generated and applied in high-tech fields, like high performance organic light-emitting diodes, highly efficient chemo- and bio-sensors, and highly resolved cell imaging, *etc.*[2–6]

However, chiral AIEgens, which will play indispensable roles and have huge development potentials in the areas of bio-sensing and highly sophisticated optical devices,[7] have rarely been reported.[8] In 2011, Zhang *et al.* observed a pair of enantiomeric circular dichroism (CD) signals in two different crystals of TPE.[9] However, under general circumstances, TPE performed like a raceme or mesomer. As a result, CD signals could not be detected in its solution or amorphous states. An alternative impressive way to generate chiral AIEgens is to introduce sugar or amino acid groups into AIE units like TPE and siloles.[8] In this way, self-assembly, enantioselective recognition, circularly polarized luminescence, aggregation-induced CD *etc.* were realized. Although these AIEgens were chiral, some shortcomings still existed, such as poor thermal stability and difficult wavelength tunability. Moreover, these AIEgens are not suitable for optical and electrical device fabrication due to the presence of sugar or amino acid groups. Thus, other types of chiral AIEgens are in high demand.[10]

Besides point chirality, there is axial, planar and inherent chirality.[11] Inspired by previous work, we conceived an idea that an appropriate welding of AIEgen units and axial chiral moieties might create new types of AIEgens. Among the reported axial chiral chromophores, binaphthol (BINOL) is the most investigated.[12] It has been widely applied in the areas of asymmetric catalysis,[13] bio-sensors,[14] chiral inducers[15] and optical devices.[16] However, BINOL suffers from the ACQ effect. It is emissive when molecularly dissolved but becomes nonluminescent upon addition of its poor solvent, water (Fig. S1, ESI†), making its application as a fluorescent material rare. Meanwhile, TPE is an outstanding

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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*
[b] *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. E-mail: tangbenz@ust.hk*
[c] *Guangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

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AIEgen but an achiral compound in most cases. It is worth noting that covalently bonding the TPE units to a traditional ACQ luminophore has readily generated a new AIEgen with integrated functions in our previous work.[17] Therefore, we employed this strategy and covalently bonded chiral BINOL and TPE together in the hope of generating new AIEgens with axial chirality.

Results and discussion

Three compounds, named (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA, were designed and synthesized in satisfactory yields by the typical Suzuki coupling of dibromo-substituted BINOL derivatives and borate-substituted TPE (Chart 1; the synthetic details are provided in ESI†). In these molecules, hexyl groups were used to decorate the hydroxyl groups at the 2,2′-positions of BINOL to improve its solubility and stability.

Indeed, these molecules are soluble in commonly used organic solvents such as tetrahydrofuran (THF) and chloroform, but are insoluble in water. These molecules were carefully purified and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and high resolution mass spectroscopy (Fig. S2–S13, ESI†), and satisfactory analysis data corresponding to their expected structures were obtained (see ESI† for details). The thermal stabilities of these molecules were evaluated by thermogravimetric analysis (TGA). The results showed that (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA possess the 5%-weight loss (T_d) temperatures of 392, 420 and 425 °C, respectively (Fig. S14, ESI†), suggesting that they have great resistibility to heat and that the substitution positions also affect their thermal stability. More importantly, their T_d values are 78 °C higher than that of the point chiral silole derivative,[8a] further confirming the validity of our design strategy.

After confirming their structures, we investigated the photophysical properties of the BTPE-BINA derivatives. TPE is a typical AIEgen, so we tested whether this property could be transferred to the (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA. We measured their photoluminescence (PL) spectra in THF–water mixtures with different water fractions (f_w). As shown in Fig. 1 and Fig. S15 and S16 (ESI†) and Table 1, they are all weakly emissive with negligible quantum yields (Φ_F < 0.5%) in THF–water mixtures with f_w lower than 50%. Afterwards, the emission intensities increase swiftly with the addition of water. The highest intensities and Φ_F values were recorded in THF–water mixtures with an f_w of 90%, with intensities more than 700 times and Φ_F values 88 times larger than those in THF solution, indicating that these molecules are all AIE-active. Interestingly, the Φ_F values of (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA are larger and their maximum absorption and emissive wavelengths are longer than those of (*R*)-3,3′-BTPE-BINA (Table 1 and Fig. S15–S17, ESI†), suggesting that the conjugation is better at the 6,6′ positions of BINOL than at the 3,3′ positions.

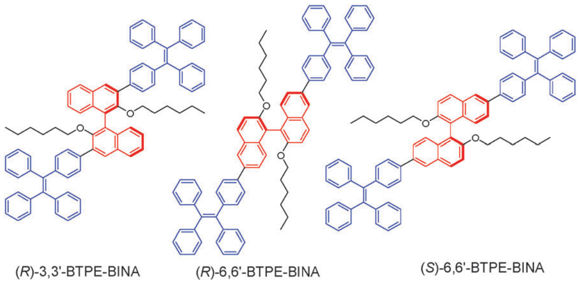

Chart 1 Chemical structures of BTPE-BINA derivatives.

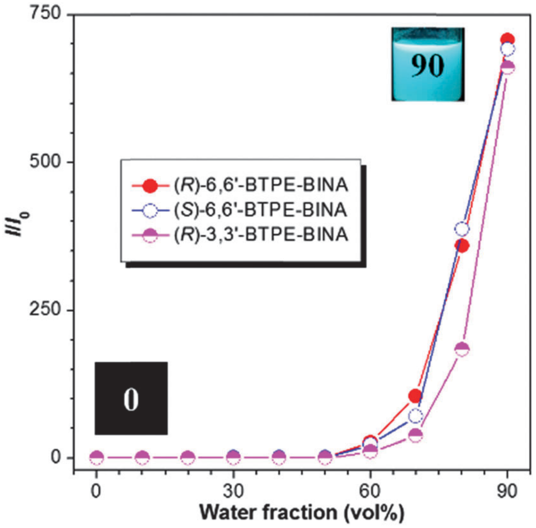

Fig. 1 Plots of relative PL intensity of (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA *versus* the water fraction (f_w) in THF–water mixtures. Concentration = 10^{-5} M; *I* = PL intensity, I_0 = PL intensity at f_w = 0%. Inset: photographs of THF–water mixtures of (*R*)-3,3′-BTPE-BINA with f_w = 0 and 90%, irradiated with a 365 nm hand-held UV lamp.

Table 1 Optical properties of (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA[a]

Compound	λ_{ab}/nm	λ_{em}/nm	$\Phi_{F,sol}$/%	$\Phi_{F,agg}$/%
(*R*)-3,3′-BTPE-BINA	323	476	0.2	27.8
(*R*)-6,6′-BTPE-BINA	337	488	0.5	42.4
(*S*)-6,6′-BTPE-BINA	337	488	0.4	41.9

[a] λ_{ab}: maximum absorption wavelength; λ_{em}: maximum emissive wavelength; $\Phi_{F,sol}$: quantum yield in THF; $\Phi_{F,agg}$: quantum yield in THF–water mixtures with f_w = 90%. The Φ_F were estimated using quinine sulfate in 0.1 N sulfuric acid (Φ_F = 54.6%) as standard.

To better understand this observation, we performed theoretical calculations (Table 2 and Fig. S18, ESI†). The twisted angles (*a*)

Table 2 Optimized molecular configurations for (*R*)-6,6′-BTPE-BINA, (*S*)-6,6′-BTPE-BINA and (*R*)-3,3′-BTPE-BINA

Twist angle	(*R*)-6,6′-BTPE-BINA	(*S*)-6,6′-BTPE-BINA	(*R*)-3,3′-BTPE-BINA
a[a] (°)	96.7	96.7	112.7
β[b] (°)	35.9	35.6	46.5

[a] Twisted angle between two naphthalene rings. [b] Twisted angle between naphthalene–benzene (in TPE) rings.

between the two naphthalene rings of 3,3′-BTPE-BINA and 6,6′-BTPE-BINA are 112.7 and 96.7° respectively, which make the electron communication inactive.[18] Thus, the dominant conjugation occurred between the naphthalene–benzene rings of TPE. The twisted angle (β) between naphthalene and benzene (in TPE) rings in 3,3′-BTPE-BINA is 46.5° due to the structural congestion, whereas that in 6,6′-BTPE-BINA is less than 36°. The relatively smaller twisted angles mean better conjugation, which readily leads to longer absorption and emission wavelengths.

Next, we investigated whether the embedded BINOL could endow these AIEgens with chirality. We measured their CD spectra; CD is an accurate and reliable technique to confirm an enantiomer's absolute configuration.[19] CD spectra of (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA in THF verified that they are a pair of enantiomers, suggesting that the Suzuki coupling has not changed the chirality of BINOL (Fig. S19, ESI†). The maximum CD wavelengths (λ_{CD}) of (*R*)-3,3′-BTPE-BINA and (*R*)-6,6′-BTPE-BINA appeared at 341 and 367 nm, respectively, which are much longer than that of BINOL (*ca.* 320 nm),[20] indicating that the whole molecules instead of only the BINOL moieties become chiral (Fig. 2). Moreover, the molar ellipticity ([Θ]) value of (*R*)-3,3′-BTPE-BINA at 341 nm is deduced to be 60 000 mdeg mL mmol^{-1} mm^{-1}, whereas that of (*R*)-6,6′-BTPE-BINA at 367 nm is only 8000 mdeg mL mmol^{-1} mm^{-1}. These results suggest that the effect on the chirality of substitution by TPE at the 3,3′-positions of the BINOL moiety is larger than that at its 6,6′-positions.

For the reported AIEgens with point chirality, the unique phenomenon of aggeregation-induced CD was observed.[8a–d] To check whether our AIEgens possess the same feature, we measured their CD spectra in THF–water mixtures with different f_{w}. Surprisingly, these AIEgens display an abnormal aggregation-annihilation CD (AACD) phenomenon (Fig. 3). The CD signals of the AIEgens remain unchanged or slightly increase in the THF–water mixtures with f_{w} lower than 40% but sharply collapse at 40 or 50% until f_{w} increases to 60%. Afterwards, the CD signals remain constant at very low values but with a red-shift of their λ_{CD} (Fig. 3 and Fig. S20, ESI†).

To understand this unusual AACD, we carried out several control experiments. Firstly, we investigated the effect of the aggregation behavior of (*R*)-**11** (Fig. 4A), which is the starting material for the synthesis of (*R*)-3,3′-BTPE-BINA (ESI†), on the CD changes under the same conditions. The results showed that the [Θ] still had a sharp annihilation at f_{w} = 60%, manifesting that the AACD originated from the binaphthalene moieties and has no relationship with the TPE units. Furthermore, it is reported that the a value has an entirely quantitative relationship with the CD signals, such as Davydov splitting width and molar ellipticity.[21] By combining the smaller a value (85.3°) of crystalline (*R*)-3,3′-BTPE-BINA (CCDC 1031983, Fig. S21, ESI†)

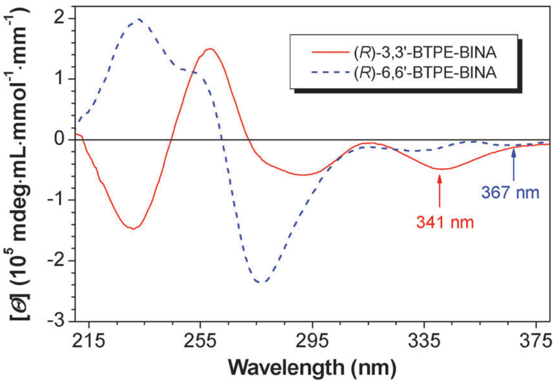

Fig. 2 CD spectra of (*R*)-3,3′-BTPE-BINA and (*R*)-6,6′-BTPE-BINA in THF. Concentration = 10^{-4} M.

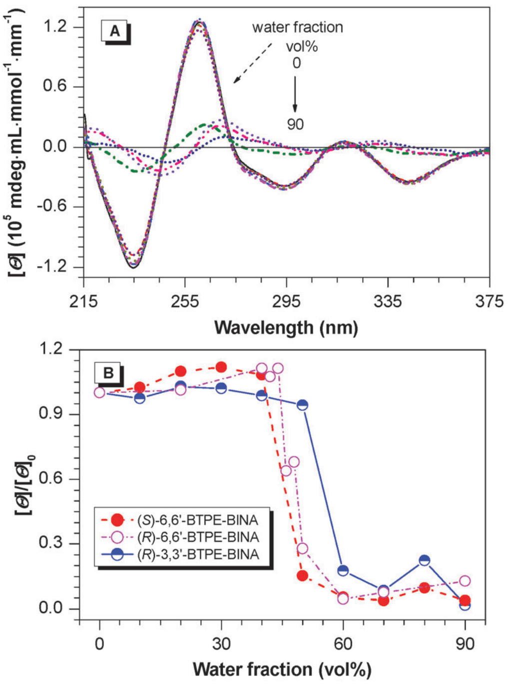

Fig. 3 (A) CD spectra of (*R*)-3,3′-BTPE-BINA in THF–water mixtures with different f_{w}. Concentration = 10^{-4} M. (B) Plots of relative molar ellipticity of (*S*)-6,6′-BTPE-BINA (@280 nm), (*R*)-6,6′-BTPE-BINA (@280 nm), and (*R*)-3,3′-BTPE-BINA (@ 260 nm) *versus* f_{w}. [Θ] = molar ellipticity, [Θ]$_0$ = molar ellipticity at f_{w} = 0%.

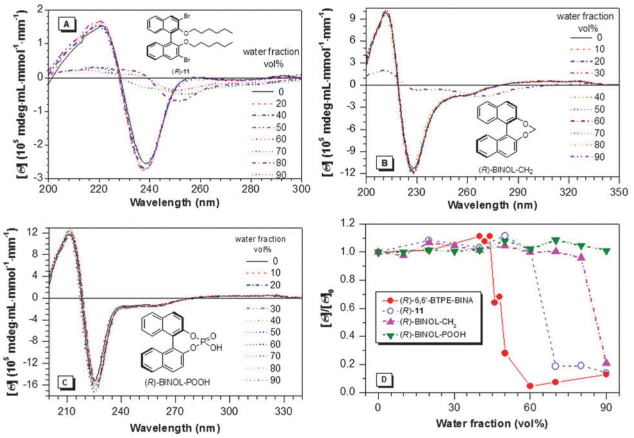

Fig. 4 CD spectra of (A) (*R*)-**11**, (B) (*R*)-BINOL-CH$_2$ and (C) (*R*)-BINOL-POOH in THF–water mixtures with different f_{w}. Concentration = 10^{-4} M. (D) Plots of relative molar ellipticity of (*R*)-**11** (@240 nm), (*R*)-BINOL-CH$_2$ (@230 nm) and (*R*)-BINOL-POOH (@230 nm) *versus* f_{w}.

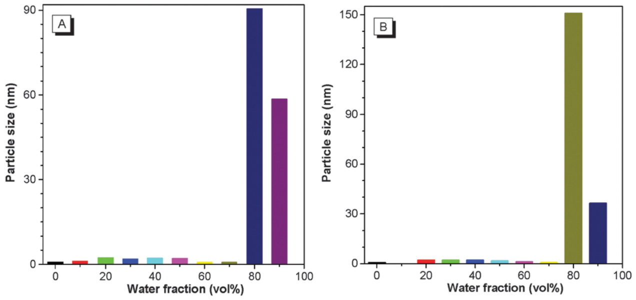

Fig. 5 Particle size of compounds (A) (*R*)-BINOL-CH_2 and (B) (*R*)-BINOL-POOH in THF–water mixtures with different f_w. Concentration = 10^{-4} M.

instead of that (112.7°) of its single molecule, we thus speculated that aggregation might induce a decrease of *a* and then lead to the annihilation of [Θ].

One of the methods used to study the effect of the *a* value on the CD changes is to "lock" it.[22] We first used methylene to lock two naphthalenes of BINOL. The aggregation experiments of the resultant (*R*)-BINOL-CH_2 showed that when the f_w was lower than 80%, the [Θ] remained almost the same. However, the annihilation still happened in the THF–water mixture with f_w larger than 80% (Fig. 4B), suggesting that the locking force is not strong enough to restrain the decrease of the *a* value. Therefore, we used a stronger locker based on the fact that the bond energy of P–O (597.2 kJ mol^{-1}) is much larger than that of C–O (255.2 kJ mol^{-1}).[23] As shown in Fig. 4C, the [Θ] of this molecule of (*R*)-BINOL-POOH remained almost unchanged during the whole process of aggregation. Fig. 5 further confirms that aggregates have been formed with f_w larger than 80%, both in compounds (*R*)-BINOL-CH_2 and (*R*)-BINOL-POOH. These results confirm that AACD is caused by the decrease in the *a* values in these AIEgens.

Conclusions

In conclusion, we created new kinds of axial chiral AIEgens, (*R*)-3,3′-BTPE-BINA, (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA, by attaching TPE to BINOL moieties for the first time. These molecules share the advantages of both TPE and BINOL: (i) they are AIE-active and possess high Φ_F in aggregated states; (ii) they exhibit axial chirality and the CD value of (*R*)-3,3′-BTPE-BINA is larger than those of (*R*)-6,6′-BTPE-BINA and (*S*)-6,6′-BTPE-BINA. Interestingly, these AIEgens show an abnormal AACD effect. The decrease of the twisted angle between the naphthalene rings in the BINOL unit upon aggregation was rationalized as the cause for this phenomenon. It is anticipated that this AACD could be potentially applied in chiral sensors. Moreover, according to the AACD mechanism, strong emission and CD intensities could be realized in this axial chiral system by covalently locking two naphthalene rings, which will be of benefit to the fabrication of high performance chiroptical devices.

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