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ARTICLE

Axial Chiral Aggregation-Induced Emission Luminogens with Aggregation-Annihilated Circular Dichroism Effect

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

Introduction

Aggregation-induced emission (AIE), first termed by Tang et al. in 2001,¹ refers to a unique phenomenon that some propeller-shaped emitters, such as 1,1-dimethyl-2,3,4,5-tetraphenylsilole and tetraphenylethene (TPE), are weakly or non-emissive when molecularly dissolved but induced to emit intensely by aggregate formation upon addition of poor solvents.^{2,3} The AIE effect is exactly opposite to the aggregation-caused quenching (ACQ) existed in most of traditional luminophores and will make the emitters perform efficiently in the aggregate or solid states. Attracted by this prospect, researchers worldwide are enthusiastically involving in this emerging area and several kinds of AIE-active luminogens (AIEgens) have been generated and applied in high-tech fields, like high performed 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 has 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 But under general circumstance, 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 in generating chiral AIEgens is to introduce sugar or amino acid groups into AIE units like TPE and siloles.⁸ The 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 type of chiral AIEgens are in highly demanded.¹⁰

Besides the point chirality, there are axial, planar and inherent chirality.¹¹ Inspired by previous work, we conceive an idea that an appropriate welding of AIEgen units and axial chiral moieties may create new type of AIEgens. Among the reported axial chiral chromophores, binaphthol (BINOL) is the most investigated one.¹² It has been widely applied in the areas of asymmetric catalysis,¹³ bio-sensor,¹⁴ chiral inducer¹⁵ and optical devices.¹⁶ However, BINOL suffers from the ACQ effect. It is emissive when molecularly dissolved but becomes nonluminescent upon adding its poor-solvent of water (Figure S1, ESI[†]), making its applications as fluorescent materials rare. Meanwhile, TPE is an outstanding AIEgen but achiral compound in most cases. It is worth noting that when covalently bonding the TPE units to a traditional ACQ luminophore has readily generated new AIEgen with integrated functions in our previous work.¹⁷ So, we employed this strategy and combined chiral BINOL and TPE together by covalent bonds in the hope to generate 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 by the typical Suzuki coupling of dibromo-substituted BINOL derivatives and borate-substituted TPE in satisfactory yields (Chart 1, the synthetic details are provided in ESI[†]). In these molecules, hexyl groups were used to decorate the hydroxyl groups at 2,2'-positions of BINOL to improve its solubility and stability.

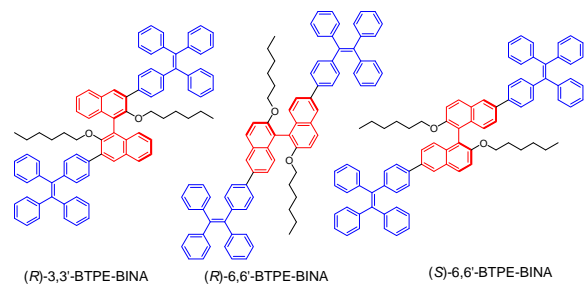


Chart 1. Chemical structures of BTPE-BINA derivatives.

Indeed, these molecules are soluble in commonly used organic solvents such as tetrahydrofuran (THF) and chloroform, but insoluble in water. These molecules were carefully purified and fully characterized by ^1H and ^{13}C NMR, and high resolution mass spectroscopies (Figures 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 $^\circ\text{C}$, respectively (Figure S14, ESI †), suggesting that they have great resistibility to heat and the substitution positions also affect their thermal stability. More importantly, their T_d values are 78 $^\circ\text{C}$ higher than the point chiral silole derivative,^{8a} further confirming the validity of our design strategy.

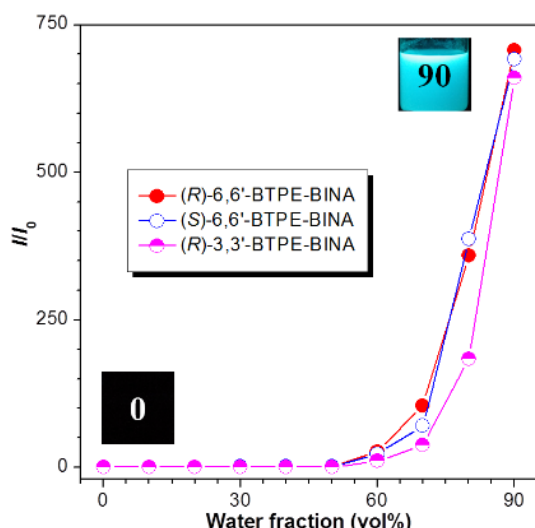


Figure 1. Plots of relative PL intensity (*R*)-3,3'-BTPE-BINA, (*R*)-6,6'-BTPE-BINA and (*S*)-6,6'-BTPE-BINA versus the water fraction (f_w) in THF/water mixtures. Concentration = 10^{-5} M; I = PL intensity, I_0 = PL intensity at $f_w = 0\%$. Inset: photographs of THF/water mixtures of (*R*)-3,3'-BTPE-BINA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

After confirming their structures, we investigated their photo-physical properties. TPE is a typical AIEgen, could this property be transferred to the (*R*)-3,3'-BTPE-BINA, (*R*)-6,6'-BTPE-BINA and (*S*)-6,6'-BTPE-BINA? To answer this question, we measured their photoluminescence (PL) spectra in THF/water mixtures with different water fractions (f_w). As shown in Figures 1, S15 and S16 (ESI †), and Table 1, they are weakly emissive with negligible quantum yields ($\Phi_F < 0.5\%$) in THF/water mixtures with f_w lower than 50%. Afterwards, the emission intensity increase swiftly with

the addition of water. The highest intensities and Φ_F values were recorded in THF/water mixtures with f_w of 90%, which are more than 700 and 88 times larger than those in their THF solution, respectively, 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, Figures S15-S17, ESI †), suggesting the conjugation is better at 6,6' positions of BINOL than its 3,3' positions.

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	$\Phi_{F,\text{sol}}/\%$	$\Phi_{F,\text{agg}}/\%$
(<i>R</i>)-3,3'-BTPE-BINA	323	476	0.2	27.8
(<i>R</i>)-6,6'-BTPE-BINA	337	488	0.5	42.4
(<i>S</i>)-6,6'-BTPE-BINA	337	488	0.4	41.9

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

To better understand this observation, we performed the theoretical calculation (Table 2, Figure S18, ESI †). The twisted angles (α) between two naphthalene rings of 3,3'-BTPE-BINA and 6,6'-BTPE-BINA are 112.7 and 96.7 $^\circ$ respectively, which make the electron communication inactive.¹⁸ Thus, the dominated conjugation occurred between naphthalene-benzene rings of TPE. The twisted angle (β) between naphthalene and benzene (in TPE) rings in 3,3'-BTPE-BINA is 46.5 $^\circ$ due to the structural congestion, whereas, that in 6,6'-BTPE-BINA is less than 36 $^\circ$. The relative smaller twisted angles mean better conjugation, which readily lead to longer absorption and emission wavelength.

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

Twist angle	(<i>R</i>)-6,6'-BTPE-BINA	(<i>S</i>)-6,6'-BTPE-BINA	(<i>R</i>)-3,3'-BTPE-BINA
α ($^\circ$) ^a	96.7	96.7	112.7
β ($^\circ$) ^b	35.9	35.6	46.5

^a Twisted angle between two naphthalene rings. ^b Twisted angle between naphthalene-benzene (in TPE) rings.

Next, we investigated whether the embedded BINOL could endow these AIEgens with chirality by measuring their CD spectra, which is an accurate and reliable technique to confirm 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 change the chirality of BINOL (Figure S19, ESI †). The maximum CD wavelengths (λ_{CD}) of (*R*)-3,3'-BTPE-BINA and (*R*)-6,6'-BTPE-BINA were 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 BINOL moieties become chiral (Figure 2). Moreover, the molar ellipticity ($[\theta]$) value of (*R*)-3,3'-BTPE-BINA at 341 nm is deduced to be 60000 mdeg $\cdot\text{mL}\cdot\text{mmol}^{-1}\cdot\text{mm}^{-1}$, 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 of substitution of TPE at 3,3'-positions of BINOL moiety on the chirality is larger than that at its 6,6'-positions.

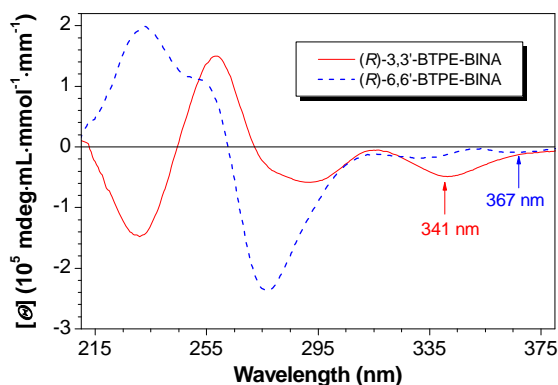


Figure 2. CD spectra of (R)-3,3'-BTPE-BINA and (R)-6,6'-BTPE-BINA in THF. Concentration: 10⁻⁴ M.

For the reported AIEgens with point chirality, the unique phenomenon of aggregation-induced CD was observed.^{8a-8d} 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 (Figure 3). The CD signals of the AIEgens remain unchanged or slightly increase in the THF/water mixtures with f_w lower than 40% but sharp collapsed at 40 or 50% until f_w increased to 60%. Afterward, the CD signals remain constant at very low values but with ref-shift of their λ_{CD} (Figures 3 and S20, ESI[†]).

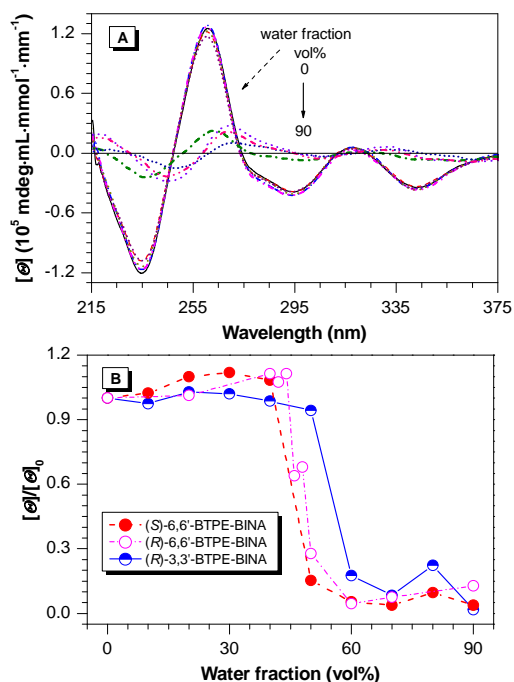


Figure 3. (A) CD spectra of (R)-3,3'-BTPE-BINA in THF/water mixtures with different f_w . Concentration = 10⁻⁴ M. (B) Plots of relative molar ellipticity of (S)-6,6'-BTPE-BINA (@280 nm), (R)-6,6'-BTPE-BINA (@280 nm), and (R)-3,3'-BTPE-BINA (@260 nm) versus f_w . $[\theta]$ = molar ellipticity, $[\theta]_0$ = molar ellipticity at $f_w = 0\%$.

To understand this unusual AACD, we carried out several control experiments. Firstly, we investigated the effect of the aggregation behavior of (R)-11 (Figure 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 $[\theta]$ still had a sharp annihilation at f_w of 60%, manifesting that the AACD originated from the binaphthalene moieties and has no relationship with TPE units. Furthermore, it is reported that the a value has an entirely quantitative relationship with 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, Figure S21, ESI[†]) than that (112.7°) of its single molecule, we thus speculated that aggregation may induce the decrease of a and then lead to the annihilation of $[\theta]$.

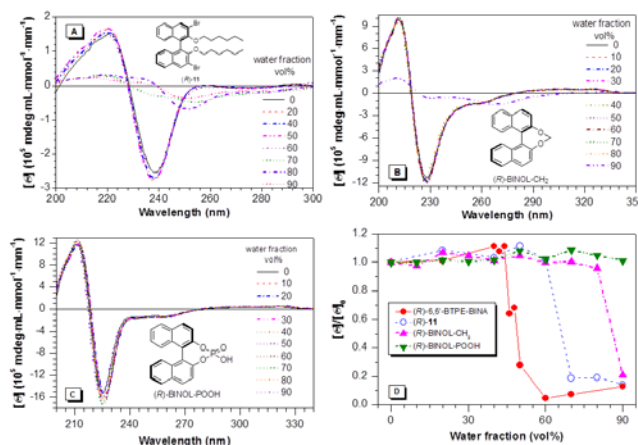


Figure 4. CD spectra of (A) (R)-11, (B) (R)-BINOL-CH₂ and (C) (R)-BINOL-POOH in THF/water mixtures with different f_w . Concentration = 10⁻⁴ M. (D) Plots of relative molar ellipticity of (R)-11 (@240 nm), (R)-BINOL-CH₂ (@230 nm) and (R)-BINOL-POOH (@230 nm) versus f_w .

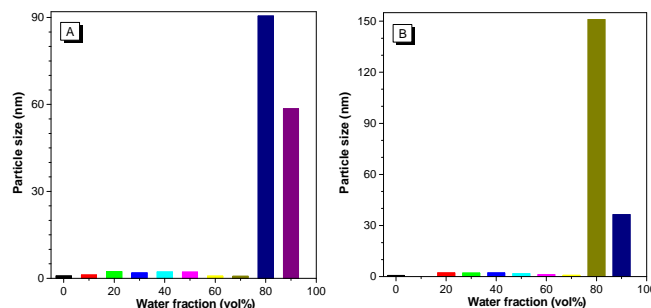


Figure 5. Particle size of compounds (A) (R)-BINOL-CH₂ and (B) (R)-BINOL-POOH in THF/water mixtures with different f_w . Concentration: 10⁻⁴ M.

One of the methods to study the effect of the a on the CD changes is to “lock” it.²² We first use methylene to lock two naphthalenes of BINOL. The aggregation experiments of the resultant (R)-BINOL-CH₂ showed that when the f_w was lower than 80%, the $[\theta]$ remained almost the same. However, the annihilation still happened in the THF/water mixture with f_w larger than 80% (Figure 4B), suggesting that locking force is still 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) is much larger than that of C-O (255.2 kJ/mol).²³ As shown in Figure 4C, the $[\theta]$ of this molecule of (R)-BINOL-POOH kept almost unchanged during the whole process of aggregation. Figure 5 further confirm that

aggregates have been formed with the f_w larger than 80%, both in compounds (*R*)-BINOL-CH₂ and (*R*)-BINOL-POOH. These results confirm that AACD is caused by the decrease of the a values in these AIEgens.

Conclusions

In conclusion, we created a new kind of axial chiral AIEgens of (*R*)-3,3'-BTPE-BINA, (*R*)-6,6'-BTPE-BINA and (*S*)-6,6'-BTPE-BINA by attaching the TPE to BINOL moieties for the first time. These molecules share the advantages of both of TPE and BINOL: (i) they are AIE-active and possess high Φ_F in the aggregate states; (ii) they also 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 showed the abnormal AACD effect. The decrease of the twisted angle between the naphthalene rings in 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 benefit to the fabrication of high performance chiroptical devices.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data and the relevant results. See DOI: 10.1039/b000000x/

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Table of Contents use only

Axial chiral luminogens with aggregation-induced emission (AIE) characteristics are designed and synthesized by covalently attached the AIE-active tetraphenylethene to the axial chiral binaphthol moieties. The resultant molecules exhibit unique aggregation-annihilated circular dichroism phenomenon and the decrease of the twist angles of two naphthalene rings in the aggregate state was rationalized as the cause for this unique effect.

AIE + Axial chirality = AIE axial chirality

