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Regulation of circular dichroism behavior and construction of tunable solid-state circularly polarized luminescence based on BINOL derivatives[†]

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The development of chiral fluorescent materials has attracted great interest. [1,1'-binaphthalene]-2,2'-diol (BINOL), a privileged C_2 -symmetric molecular skeleton, is one of the most frequently used chiral optical backbones. However, a phenomenon of circular dichroism (CD) annihilation in the aggregated state was observed in BINOL based molecules, which limits the application of CD in the condensed state. In this work, by inserting various bridged alkyl chains into the hydroxyl groups of 3,3'-dicyanomethylene functionalized (*R*)-BINOL, a series of chiral luminogens (**BINB-*n***, *n* = 1 to 8) was obtained. All **BINB-*n*** luminogens exhibited aggregation-induced emission (AIE) characteristics and their molecular conformation was significantly dependent on the length of the alkyl chain, which further regulated their CD behavior from annihilation to preservation in the aggregated state. Moreover, in virtue of the AIE characteristic of **BINB-6**, judiciously introducing suitable electron donors successfully realized enhanced and tunable solid-state circularly polarized luminescence with the maximum g_{lum} value of 1×10^{-2} .

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Introduction

Chirality is a ubiquitous phenomenon in nature. Chiral molecules play crucial roles in most fundamental processes including the synthesis of deoxyribonucleic acid (DNA) or proteins, exploring new drug candidates and developing chiral functional materials.¹ Unlike the significant progress of chiral molecules made in biological science and the pharmaceutical industry, their applications in the field of material science, especially in the fabrication of chiral organic materials, are relatively less investigated. Indeed, owing to their distinct optical information and angular independence, chiral organic materials are of pivotal importance for opto-electronic applications and chiral

recognition processes.^{2–4} In order to obtain fine chiral information to clarify the working mechanism and further optimize the performance of chiral materials, various optical methods have been established. Among these methods, circular dichroism (CD) is without doubt the most commonly used technique.⁵ CD spectrometry, which originated from ground-state electronic transition of π -conjugated chromophores, is extremely sensitive and accurate towards the chirality variations. Benefited by CD spectroscopy, the chirality information of chiral materials in different molecular states can be readily obtained.

[1,1'-Binaphthalene]-2,2'-diol (BINOL), one of the most privileged C_2 -symmetric molecules, was employed as an ideal chiral source to fabricate chiral organic materials.⁶ In recent years, an abnormal effect termed aggregation-annihilated CD (AACD) was reported in BINOL based molecules. Further studies revealed that the variation of the torsion angle (θ) between two naphthalene rings after molecular aggregation is responsible for this AACD behavior.⁷ The AACD phenomenon obstructed the application of CD in the aggregated state. Some elegant strategies were reported recently to surpass the annihilation of CD in BINOL derived molecules.^{7a,8} Nevertheless, precisely regulating the CD response in the process of aggregation through rational molecular design and synthesis is still a formidable challenge.

In addition, circularly polarized luminescence (CPL) is another key parameter of chiral materials which provides the excited-state chiral information. The CPL active materials, especially solid-state

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CPL materials have potential applications in the fields of 3D organic light-emitting diodes and optical data recording devices.^{9–14} Recently, a concept of aggregation-induced emission (AIE) has opened up great opportunities to develop solid-state CPL materials.¹⁵ For instance, naturally chiral auxiliaries such as amino acids, sugars, and lipids were decorated into achiral AIE luminogens (AIEgens) to obtain an enhanced CPL response in the condensed state.¹⁶ Meanwhile, axial BINOL was used as a chiral source to construct solid-state CPL materials.¹⁷ Beside superior chiral characteristics, BINOL also possess excellent luminescence properties due to its favorable π -conjugated structure and most of the reported studies focused on its CPL properties in the solution state.¹⁸ In contrast, development of enhanced and tunable solid-state CPL materials using BINOL as a chiral fluorescent skeleton is still rare.

Herein, by inserting various bridged alkyl chains into the hydroxyl groups of 3,3'-dicyanomethylene functionalized (*R*)-BINOL, a series of chiral luminogens (**BINB-*n***, *n* = 1 to 8) was obtained (Fig. 1). All **BINB-*n*** exhibited typical AIE features. Meanwhile, the molecular conformation of **BINB-*n*** was successfully controlled by the length of the alkyl chain, which resulted in the CD behavior converted from annihilation to preservation. Combining the experimental result with molecular dynamic simulation, the molecular conformation of **BINB-*n*** significantly influenced the change of θ during the aggregation process, and further affected their CD behaviors. Moreover, thanks to the AIE characteristic, introducing various electron donors into **BINB-6** successfully yielded enhanced and tunable solid-state CPL.

Results and discussion

Following the molecular design concept, we began our investigation by introducing bridged alkyl chains with different lengths into the hydroxyl groups of 3,3'-dicyanomethylene functionalized (*R*)-BINOL to form a series of bridged structures termed as **BINB-*n*** (*n* = 1 to 8). All luminogens displayed a higher absorption peak at approximately 280 nm in acetonitrile solution, which can be attributed to the $\pi-\pi^*$ transition. The longest absorption band at around 340 nm was observed, which can be ascribed to intramolecular charge transfer

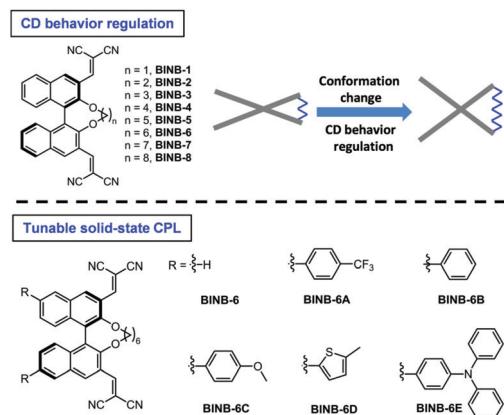


Fig. 1 Chemical structures of the (top) **BINB-*n*** and (bottom) **BINB-6** derivatives.

(ICT) transition (Fig. S1A, ESI[†]). Meanwhile, a remarkable solvent effect was observed for **BINB-6** as an example, which further confirmed their ICT characteristics (Fig. S1D, ESI[†]).¹⁹ After adding water into the acetonitrile solution, the emission intensity of all luminogens initially decreased owing to the intensive ICT process, but later increased and reached a maximum when the water fraction (f_w) was up to 99%, demonstrating their typical AIE feature (Fig. 2A, B and Fig. S5, ESI[†]). The AIE effect was mainly attributed to the restriction of the free motion of dicyanomethylene groups.^{7b} It is noteworthy that the emission in the aggregated state exhibited a blue shift compared to that in the solution state, which could be caused by the reduction of polarity inside the aggregates. Molecular aggregation was further confirmed by dynamic light scattering measurement (Fig. S8, ESI[†]).

Because of the identical absolute configuration of BINOL, similar Cotton effects were observed for **BINB-1** to **BINB-8** at 230, 270, 320 and 350 nm in their solution state (Fig. 2C and Fig. S11, ESI[†]). The strong Cotton effects in the wavelength range from 230 to 320 nm can be attributed to the characteristic absorption of chiral binaphthyl moieties, while the CD peak at 350 nm originated from the whole molecular chirality.²⁰ By increasing f_w , the bridged chiral AIEgens presented distinct changes in CD response. Taking **BINB-2** and **BINB-6** as examples (Fig. 2C–E), almost no significant change in the CD spectra was detected when f_w was less than 60%. However, with continuously increasing f_w , the change of CD response exhibited a different tendency. For **BINB-2**, the CD signal dramatically decreased and approximately 25% intensity remained at 230 nm with the f_w up to 99%. The decrease in CD response became weaker for **BINB-6** while the CD intensity maintained more than 75% even at f_w of 99%. Other **BINB** derivatives also displayed significantly alkyl

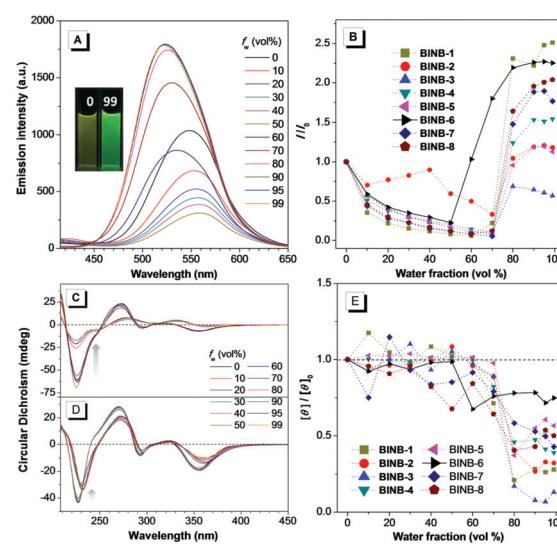


Fig. 2 (A) Emission spectra of **BINB-6** in acetonitrile/water mixtures with different f_w . (B) Plot of emission intensity versus the composition of f_w for **BINB-1** to **BINB-8**. CD spectra of (C) **BINB-2** and (D) **BINB-6** in acetonitrile/water mixtures with different f_w . (E) Plot of CD signal intensity versus the composition of f_w for **BINB-1** to **BINB-8**. Inset in (A): Photograph of **BINB-6** in acetonitrile/water mixtures with 0 and 99% f_w under 365 nm UV irradiation.

chain dependent CD behavior with either preservation or annihilation. As described in Fig. 2E, **BINB-6** displayed the utmost capability to preserve the CD intensity in the aggregated state. This remarkable conversion of CD behavior proved that the alkyl chain length can serve as an efficient way to modulate the CD property of chiral AIEgens in the process of molecular aggregation.

On the other hand, unbridged substituents with different steric hindrance, including methyl, tertbutyldimethylsilyl and tertbutyldiphenylsilyl groups, were introduced to generate **BINUB-1** to **BINUB-3** in order to investigate the influence of steric hindrance on the CD behavior (Scheme S3, ESI[†]). A similar AIE phenomenon was observed for the three unbridged luminogens (Fig. S2A, B, S6 and S9, ESI[†]). However, the CD signal gradually decreased with increasing f_w , while the intensity at 230 nm dropped more than 55% at f_w of 99% (Fig. S2C, D and S12, ESI[†]). This result suggested that, due to the flexible nature of the unbridged BINOL backbone, varying the degree of steric hinderance of the unbridged groups cannot effectively restrain the CD annihilation effect.

To determine the underlying reasons for the special optical behavior of these bridged chiral AIEgens, single crystals of the corresponding AIEgens were grown by slow evaporation from a suitable mixture of solvents. All single crystals of **BINB-n** were successfully obtained except **BINB-3** and **BINB-6** owing to their poor crystallization ability. Fortunately, a single crystal of the **BINB-6** derivative that bears a trifluoromethylphenyl group at the 6,6'-position (**BINB-6A**), was obtained.²¹ The single crystal data are summarized in Tables S6 and S7 (ESI[†]). As shown in Fig. 3 and Fig. S14–S20 (ESI[†]), all corresponding molecules adopted highly nonplanar configurations inherited from BINOL while multiple intermolecular C–H · · · N interactions (2.472–2.645 Å) were found throughout most of the crystal lattice. The twisted structure combined with weak intermolecular interactions helped to rigidify the molecular conformation, prevented the molecules from forming π – π or dipole–dipole interactions, and endowed **BINB-n** with high solid-state emission efficiency.

Further analysis of the molecular conformation revealed that the different lengths of alkyl chain at the 2,2'-position of **BINB-n** generated various θ values in the crystal. From **BINB-1** to **BINB-4**, the θ value increased from 52.27 to 106.81°. By extending the alkyl chain from *n*-pentyl to *n*-heptyl (**BINB-5** to **BINB-7**), the θ value showed little difference which was more than 111° (111.52 to 113.52°). However, continuously prolonging the length of the alkyl chain (**BINB-8**), the θ value decreased to 89.83°. To understand the origin of alkyl chain-dependent CD behavior, molecular dynamics (MD) simulation of chiral AIEgens in a molecularly dissolved state was carried out by using **BINB-2** and **BINB-6A** as representative examples (Fig. S21, ESI[†]). The simulation results indicated that the θ value was 71.00° and 111.00° for **BINB-2** and **BINB-6A** in their dissolved state. The change of θ value between the dissolved and crystal state was 9.68° and 0.52° for **BINB-2** and **BINB-6A**, respectively. Clearly, the variation of the θ value for **BINB-6A** is smaller than that of **BINB-2**, which resulted in the preservation of the CD response of **BINB-6A** rather than **BINB-2** in their aggregated state.^{8,22}

Since **BINB-6** exhibited a relatively notable AIE effect, we expected to construct chiral AIEgens with tunable emission by introducing different donors into **BINB-6** as suitable donor–acceptor systems can sufficiently control the separation of the highest occupied molecular orbital and lowest unoccupied molecular orbital.^{19,23} The electron-donating potential increased in the following order: 4-(trifluoromethyl)phenyl, phenyl, 4-methoxyphenyl, 5-methylthiophenyl, and 4-(diphenylamino)phenyl, which formed a series of chiral AIEgens (**BINB-6A** to **BINB-6E**). The ICT absorption bands exhibited typical bathochromic-shift from 340 to 350 nm, which is in line with the electron donating ability. Meanwhile, the longest CD response also shifted from 340 to 375 nm in the order from **BINB-6** to **BINB-6E**. Importantly, the installed different electron donor has negligible influence on CD behavior since the CD intensity of **BINB-6** derivatives is preserved in the process of aggregation. As shown in Fig. 4D and Fig. S13 (ESI[†]), the CD signals at around 260 nm for **BINB-6** derivatives maintained

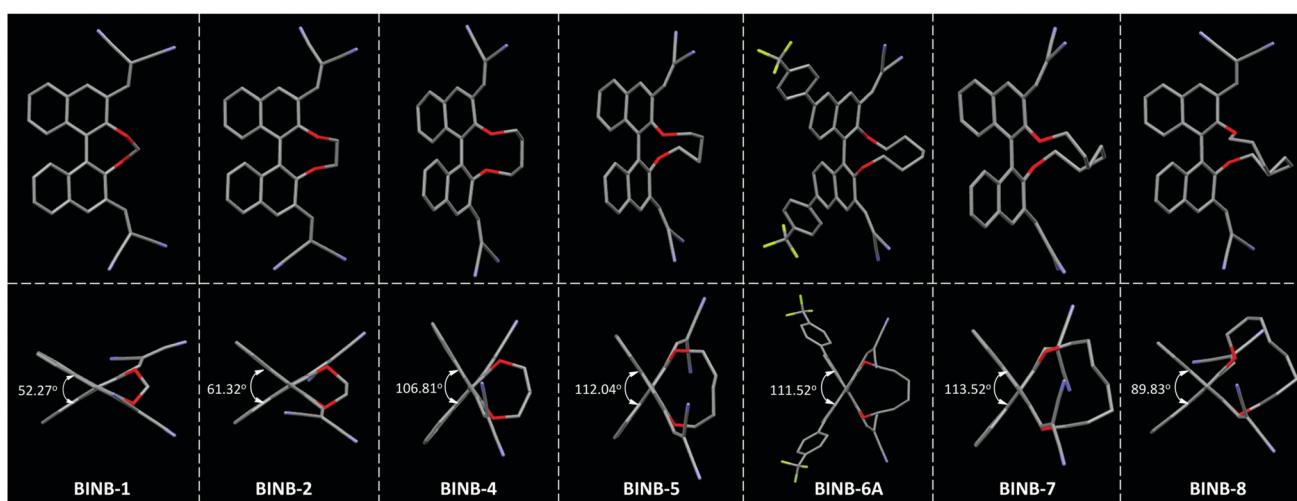


Fig. 3 The view of (top) molecular conformation and (bottom) θ value for the corresponding **BINB** derivatives. Hydrogen atoms are omitted for clarity.

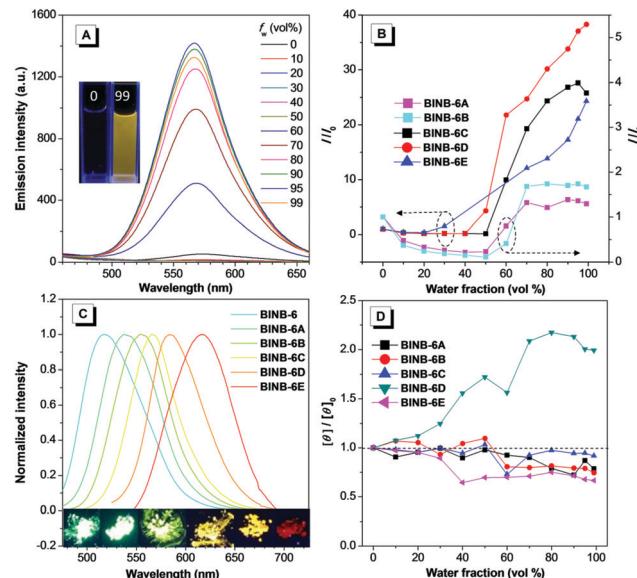


Fig. 4 (A) Emission spectra of **BINB-6C** in acetonitrile/water mixtures with different f_w . (C) Emission spectra of **BINB-6** to **BINB-6E** in their solid state. (B) Plot of emission intensity at specific wavelengths and (D) CD intensity at specific wavelengths versus the composition of f_w for **BINB-6A** to **BINB-6E**. Inset in (A): Photograph of **BINB-6C** in acetonitrile/water mixtures with 0 and 99% f_w under 365 nm UV irradiation. Inset in (C): Photograph of **BINB-6** to **BINB-6E** in solid state under 365 nm UV irradiation.

more than 75% at f_w of 99%. It is interesting that 2-fold enhancement of the CD intensity was observed for **BINB-6D**, which could be associated with its well-ordered aggregates.²⁴

All **BINB-6** derivatives exhibited enhanced emission in their aggregated state (Fig. 4A, B and Fig. S6, S9, ESI[†]). Meanwhile, their solid-state quantum yields were higher than that in solution, which is consistent with their AIE feature (Table 1). Owing to the gradual strengthening of the electron-donating ability, the significant red-shift in solid-state emission ranging from 522 to 623 nm was observed (Fig. 4C). The CIE chromaticity diagrams (Fig. S3 and Table S1, ESI[†]) demonstrated the same tunable emission color from green CIE (0.2634, 0.6195) to red CIE (0.646, 0.3536).

We further investigated the solid-state CPL properties of **BINB-6** derivatives due to their AIE characteristics. Self-assembly of chiral organic molecules was reported to efficiently amplify the CPL signal

Table 1 Optical properties of **BINB-6** derivatives

Compd.	Solution state ^a			Solid state					
	λ_{abs} [nm]	λ_{em} [nm]	Φ_{F}^b [%]	τ_{avg}^c [ns]	λ_{em} [nm]	Φ_{F}^b [%]	τ_{avg}^c [ns]	λ_{CPL}^d [nm]	
BINB-6	338	547	8.6	4.98	518	11.2	5.38	547	0.6
BINB-6A	338	555	9.2	5.03	538	9.5	4.85	536	-5.0
BINB-6B	342	562	6.6	4.35	555	7.9	6.34	557	4.0
BINB-6C	345	575	0.5	0.99	566	6.8	7.54	580	1.0
BINB-6D	338	577	0.7	3.59	584	4.0	6.15	597	-10.0
BINB-6E	350	623	0.3	4.35	617	0.7	9.06	— ^e	— ^e

^a Acetonitrile solution (10 μM). ^b Absolute fluorescence quantum yield measured using the calibrated integrating sphere system. ^c Mean fluorescence lifetime (τ_{avg}) calculated using the equation $\tau_{\text{avg}} = A_1\tau_1 + A_2\tau_2$. ^d Self-assembled microstructure. ^e No CPL was detected due to its microparticle form.

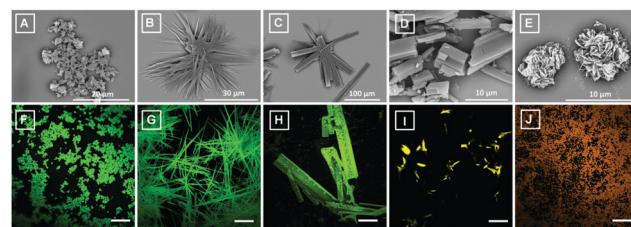


Fig. 5 The SEM images (A–E) and confocal fluorescent images (F–J) of self-assembled **BINB-6** to **BINB-6D**. Scale bar for F–J: 20 μm .

because of the chirality transfer from small molecules to the self-assembled network.^{15d,16c,25} Therefore, we prepared self-assembled samples of **BINB-6** derivatives on a glass substrate by slowly evaporating the solvent (acetonitrile or dichloromethane). As shown in Fig. 5, the scanning electron microscope (SEM) images revealed that all **BINB-6** derivatives successfully self-organized into microstructures with different shapes except for **BINB-6E** which formed microparticles. Detailed morphological analysis indicated that irregular tiny microslices and microneedles were formed for **BINB-6** and **BINB-6A**, while **BINB-6B** and **BINB-6C** assembled into micro rods. The microflowers constituted by secondary microplates were observed for **BINB-6D**. Under the confocal fluorescence microscope, all self-assembled microstructures displayed intense emission. At the same time, the emission color ranged from green to orange (520 to 580 nm) following the order from self-assembled **BINB-6** to **BINB-6D** (Fig. S4, ESI[†]).

As expected, all self-assembled chiral AIEgens emitted CPL upon photoexcitation. As shown in Fig. 6A, the CPL peaks varied from 520 to 610 nm following the order from **BINB-6** to **BINB-6D**, which cover the region from green to red. The magnitude of CPL was evaluated by the luminescence dissymmetry factor (g_{lum}), which is defined as $g_{\text{lum}} = 2 \times (I_L - I_R)/(I_L + I_R)$, where I_L and I_R

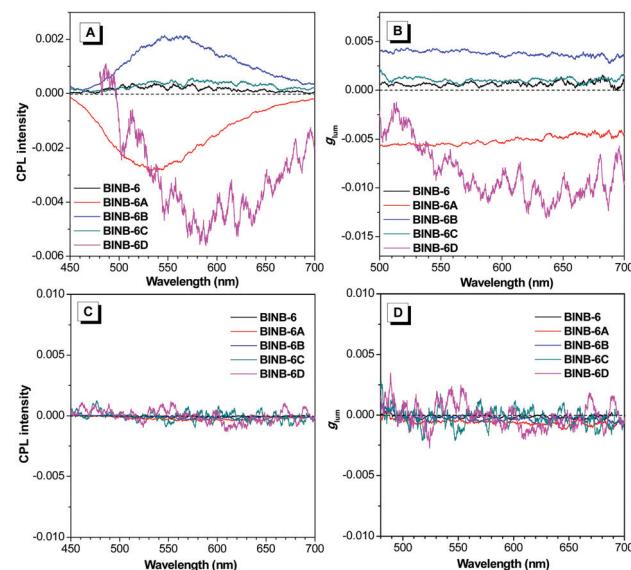


Fig. 6 The CPL spectra of (A) self-assembled microstructures and (C) the solution state of **BINB-6** to **BINB-6D**. The corresponding g_{lum} value of (B) self-assembled microstructures and (D) the solution state of **BINB-6** to **BINB-6D**.

refer to the intensity of left- and right-handed CPL, respectively. It is noted that the g_{lum} factor of all self-assembled AIEgens was greater than 10^{-4} , and the maximum g_{lum} factor can reach up to 1×10^{-2} for **BINB-6D** (Fig. 6B). In sharp contrast, almost no CPL response was detected in their dissolved state while nearly zero g_{lum} was obtained (Fig. 6C and D). Intriguingly, **BINB-6A** and **BINB-6D** gave opposite CPL signals compared with those of **BINB-6**, **BINB-6B** and **BINB-6C**, which could be attributed to their different macroscopic chirality when they underwent a self-assembly process.

Conclusions

In conclusion, we developed a strategy to regulate CD behavior in the process of molecular aggregation through controlling the molecular conformation. By inserting different alkyl chains into the hydroxyl groups of BINOL derivatives, a series of chiral AIEgens (**BINB-n**) with different conformations was obtained. The conversion of the CD response from annihilation to preservation for BINOL derivatives was observed. Combining single crystal analysis and theoretical simulation, the different CD behavior was associated with their varied molecular conformation, which further influences the variation of θ value in the process of molecular aggregation. In addition, introducing diverse electron donors into the molecular backbone of **BINB-6** yielded a series of chiral AIEgens with tunable emission. Moreover, these chiral AIEgens exhibited enhanced and tunable CPL after self-assembly. The maximum g_{lum} value reached up to 1×10^{-2} . This work provides a general method to regulate the CD behavior for chiral luminogens as well as a facile approach to construct tunable solid-state CPL materials.

Conflicts of interest

There are no conflicts to declare.

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