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# Diversified AIE and mechanochromic luminescence based on carbazole derivatives decorated dicyanovinyl groups: Effects of Substitution Site and Molecular Packing

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Aggregation-induced emission (AIE) properties have been widely investigated not only because they thoroughly circumvent the notorious aggregation-caused quenching effect confronted in conventional fluorophores but also their promising applications in organic light-emitting diodes, fluorescent sensors and bioimaging. In this work, we reported a study of the molecular packing and luminescence properties of AIE active positional isomers (m-BPCDM and p-BPCDM) with carbazole and dicyanovinyl groups. The compound of m-BPCDM based on the meta-substitution showed more evident AIE processes than the compound of p-BPCDM based on the para-substitution, which can be attributed to the strong  $\pi$ - $\pi$  stacking effect brought by the plane spatial structure of p-BPCDM. Moreover, the two positional isomers also exhibited distinct mechanochromic luminescence properties.

### Introduction

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Organic luminescent materials, because of their intense and tunable emission intensity, have attracted tremendous attention and been widely used in fields such as organic lightemitting diodes,<sup>[1,2]</sup> biological imaging,<sup>[3-5]</sup> and fluorescent sensors.<sup>[6-8]</sup> However, the common investigation of luminescence processes is often carried out in dilute solution, and when extended to the concentrated solution, the luminescent behaviors of those molecules changed adversely.<sup>[9]</sup> In the aggregation state, if the luminophores adopt a planar conformation, which often consists of aromatic rings, those molecules may experience strong  $\pi$ - $\pi$  stacking interaction, and prone to form some detrimental species such as excimers and H-aggregation,<sup>[10,11]</sup> thus leading to the well-known notorious effect: aggregation-caused quenching (ACQ) effect.<sup>[12-14]</sup> Due to the ACQ effect, conventional methods of enhancing fluorescence quantum efficiency by increasing the number of conjugated unit in its molecular structure cannot be effectively implemented. Therefore, it can seriously hinder the performance of traditional fluorophores in the lighting and display industries. For instance, most luminescent materials are inapplicable in working condition due to its weak emission intensity when utilized in aqueous environment. [15,16]

In 2001, Tang<sup>[17]</sup> et al. carried out a momentous and valuable discovery, termed "aggregation-induced emission (AIE)" in a series of propeller-like luminogens. They are weakly or nonluminescent in dilute solution, but the emission intensity and fluorescence quantum efficiency are greatly increased in the aggregated state. In a dilute solution, when the AIE luminogens absorb energy and get excited, the peripheral rotors, such as phenyl rings, rotate against the central stator and consume its energy, which is called non-radiative transition, thereby annihilates its excited state and attenuates its luminescence.<sup>[18]</sup> In contrast, in the aggregate state, the steric hindrance produced by the distorted molecular configuration cripples its intermolecular  $\pi$ - $\pi$  interaction and limits its intramolecular rotation, as a result, enhances its luminescence intensity.<sup>[3,19-21]</sup> This restriction of intramolecular rotation (RIR) is considered as the main cause for the AIE effect. Generally, introducing different kinds of rotatable units into its molecular structure can be an efficient way to obtain materials with AIE effect.

Among many AIE luminogens, molecules with D- $\pi$ -A structure shows advanced photoluminescence properties.<sup>[22]</sup> The interaction of electron donor and electron acceptor on both sides of the benzene ring can cause intramolecular charge transfer (ICT), which considerably alter photophysical behaviors of the luminogens, especially emission color tunability.<sup>[23,24]</sup> Therefore, assembling with different types of electron donor and electron acceptor can effectively change the luminescence process of organic luminescent materials.<sup>[25-28]</sup> Cyano group is an ideal functional unit for the design of advanced optical materials due to its strong electron-withdrawing ability and structural simplicity.<sup>[29]</sup> More remarkably, the steric effect of the cyano group can distort the conformation of the luminogen, making the molecule immune to the ACQ effect.<sup>[30,31]</sup> Carbazole, an essential nitrogen-containing aromatic heterocyclic ring with a special rigid fused ring, and its derivatives, exhibit many

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unique photoelectric properties and bioactivities.<sup>[32]</sup> Owing to its electron-donating ability, high thermal stability and photochemical stability, carbazole groups have been widely exploited in the design of AIEgens.<sup>[33]</sup> Herein, we synthesized two new D-π-A types of AlEgens based on electron acceptor of cyano groups, and electron donor of carbazole groups. These two novel molecules exhibit similar spatial structures, except for the meta- substitution site of m-BPCDM and parasubstitution site of p-BPCDM on central benzene which causes different degrees of distortion of their spatial conformation, and therefore dramatically alters their AIE properties. More interesting, we further ascribe the significantly different AIE and mechanochromic luminescence performance of these  $D-\pi$ -A compounds to their different intermolecular packing in the crystalline phase. Meanwhile, preliminary DFT studies confirmed the above proposed mechanism.

#### Experimental

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#### **Materials and Instrumentation**

All reagents and solvents were used as received from commercial suppliers without further purification. The <sup>1</sup>H and <sup>13</sup>C NMR was recorded at 298 K using Bruker Advance III 500 MHz spectrometer. Fourier-transform infrared spectroscopy (FT-IR) was performed on a Nicolet 5700 spectrometer. Elemental analyses (C, H, N) were carried out on a Vario EL analyzer. Mass spectra were obtained on an Agilent 6520B spectrometer. The powder X-ray diffraction (PXRD) data were collected on a Miniflex 600 diffractometer at room temperature using Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm) with 15 mA, 40 kV, and a scan rate of 3° min<sup>-1</sup> (2 $\theta$ , 5°-40°). The UV absorption spectra were attained by PE LAMBDA365 at ambient temperature. The PL spectra, fluorescence lifetimes and PL quantum yields were conducted on an Edinburgh FLS1000 fluorescence spectrophotometer at room temperature. The slit widths of excitation and emission were set the same in AIE experiment, and before fluorescence measurement, the solution of both two compounds was evenly dissolved in corresponding solvents. Particle size distributions of both molecules in acetone/water mixture were conducted by Malvern Zetasizer Nano ZS for several times to attain average values.

#### Synthesis and Characterization

m-BPMCz and p-BPMCz were synthesized by classical Friedel-Crafts acylation reaction and purified for the next reaction. m-BPCDM (2,2'-(1,3-phenylenebis((4-(9H-carbazol-9yl)phenyl)methaneylylidene))dimalononitrile) and p-BPCDM (2,2'-(1,4-phenylenebis((4-(9H-carbazol-9-

yl)phenyl)methaneylylidene))dimalononitrile) were synthesized by the respective reactions of m-BPMCz and p-BPMCz with malononitrile in the presence of titanium tetrachloride and pyridine (Scheme 1), and comprehensively characterized by Fourier transform infrared (FT-IR) spectroscopy (Fig. S1), and <sup>1</sup>H NMR and <sup>13</sup>C NMR (Fig. S2-S9).

Synthesis of 1,3-phenylenebis((4-(9H-carbazol-9yl)phenyl)methanone) (m-BPMCz) and 1,4-phenylenebis((4-



(9H-carbazol-9-yl)phenyl)methanone) (p-BPMCz). Compounds 1 and 2 were synthesized by classical Friedel-Crafts acylation reaction.<sup>[34]</sup> Isophthaloyl dichloride (2.52 g, 13 mmol) was dissolved in fluorobenzene (15 mL) under nitrogen atmosphere, and anhydrous aluminium chloride (3.50 g, 52 mmol) was added after mixing uniformly. After 8 h, the mixture was poured into crushed ice and filtered to obtain a white precipitate. The precipitate was then washed with a 10% NaOH solution for several times to obtain a fluffy white powder (3.24 g) (1). Compound 1 (0.65 g, 2 mmol) was mixed with carbazole (0.73 g, 4.4 mmol) in anhydrous N, N'-dimethylformamide (DMF) (25 ml) under nitrogen atmosphere, and t-BuOK (0.52 g, 4.6 mmol) was added in room temperature. The reaction system was then heated to 120 °C for 24 h. The mixture was poured into crushed ice to obtain a yellow precipitate, and then the precipitate was dissolved in dichloromethane and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the residue was purified by silica gel chromatography eluting with 50% petroleum ether in dichloromethane. The product (m-BPMCz, 0.92 g) was dried to afford the pure yellow solid product. The synthetic procedure of p-BPMCz is like m-BPMCz. m-BPMCz: Yield 12%. Light yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.42 (t, J = 1.7 Hz, 1H), 8.18-8.12 (m, 10H), 7.81-7.77 (m, 4H), 7.75 (d, J = 7.6 Hz, 1H), 7.54 (dd, J = 8.2, 0.9 Hz, 4H), 7.42 (ddd, J = 8.2, 7.1, 1.2 Hz, 4H), 7.32 (td, J = 7.5, 1.0 Hz, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 194.79, 142.30, 140.72, 140.20, 135.24, 132.00, 129.86, 126.45, 126.28, 123.95, 120.76, 120.54, 109.78. FTIR (KBr, cm<sup>-1</sup>): 1662 (C=O), 1598, 1511, 1450, 740. Anal. calcd for C44H28N2O2: C, 85.69; H, 4.58; N, 4.54. Found: C, 85.61; H, 4.60; N, 4.52. p-BPMCz: Yield 15%. Yellow solid. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.22-8.13 (m, 8H), 8.08 (s, 4H), 7.82 (d, J = 8.5 Hz, 4H), 7.57 (dd, J = 8.3, 0.9 Hz, 4H), 7.48 (ddd, J = 8.3, 7.1, 1.2 Hz, 4H), 7.36 (td, J = 7.5, 1.0 Hz, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 194.64, 142.26, 140.20, 137.93, 135.29, 133.62, 131.98, 131.04, 128.80, 126.46, 126.29, 123.93, 109.79. FTIR (KBr, cm<sup>-1</sup>): 1660 (C=O), 1598, 1510, 1450, 921, 750. Anal. calcd. for C<sub>44</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 85.69; H, 4.58; N, 4.54. Found: C, 85.63; H, 4.60; N, 4.51.

Synthesis of 2,2'-(1,3-phenylenebis((4-(9H-carbazol-9yl)phenyl)methaneylylidene))dimalononitrile (m-BPCDM) and 2,2'-(1,4-phenylenebis((4-(9H-carbazol-9-

yl)phenyl)methaneylylidene))dimalononitrile (p-BPCDM). m-

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BPMCz (0.25 g, 0.41 mmol) and malononitrile (0.26 g, 4 mmol) were dissolved in anhydrous dichloromethane (20 ml). After mixing uniformly, the mixture was cooled to 0 °C under nitrogen atmosphere. Anhydrous titanium tetrachloride (0.52 ml, 4.8 mmol) was then slowly added to the solution via a syringe. The mixture was stirred at 0 °C for 2 h before pyridine (1.04 ml, 13 mmol) was added dropwise to the solution. The reaction mixture was then warmed to room temperature and then heated to reflux for 24 h. The reaction mixture was poured into dichloromethane and subsequently collected the filtrate. The filtrate was extracted with 10% HCl aqueous solution (200 ml) and 10% NaHCO<sub>3</sub> aqueous solution (200 ml), respectively. Then the filtrate was collected and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the residue was purified via silica gel chromatography with dichloromethane/petroleum ether (2:1 v/v) as eluent. The product was then dried to afford the pure orangish solid product (0.20 g, 0.28 mmol). p-BPCDM was also prepared by the above method. m-BPCDM: Yield 68%. Orange solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.15 (d, J = 7.8 Hz, 4H), 7.85-7.74 (m, 12H), 7.57 (d, J = 8.2 Hz, 4H), 7.46 (t, J = 7.7 Hz, 4H), 7.35 (t, J = 7.4 Hz, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 171.56, 142.88, 139.80, 137.13, 133.75, 132.62, 132.51, 131.68, 130.11, 126.66, 126.45, 124.20, 121.18, 120.57, 113.54, 113.50, 109.90, 82.91. FTIR (KBr, cm<sup>-1</sup>): 2223 (CN), 1598, 1512, 1450, 752. Anal. calcd. for C<sub>50</sub>H<sub>28</sub>N<sub>6</sub>: C, 84.25; H, 3.96; N, 11.79. Found: C, 84.21; H, 3.98; N, 11.76. ESI-MS: calcd. for C<sub>50</sub>H<sub>28</sub>N<sub>6</sub>, [M+Cl]: 747.2064. Found: 747.2069. p-BPCDM: Yield 71%. Orange solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.22-8.06 (m, 8H), 7.76 (ddd, J = 15.7, 12.3, 7.7 Hz, 8H), 7.55 (d, J = 8.1 Hz, 4H), 7.48-7.37 (m, 4H), 7.33 (dt, J = 7.5, 4.0 Hz, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ (ppm) 171.43, 142.76, 139.82, 132.89, 132.28, 130.92, 126.67, 126.45, 124.18, 121.19, 120.62, 113.47, 113.39, 109.81, 83.25. FTIR (KBr, cm<sup>-1</sup>): 2223 (CN), 1598, 1510, 1450, 750. Anal. calcd. for C<sub>50</sub>H<sub>28</sub>N<sub>6</sub>: C, 84.25; H, 3.96; N, 11.79. Found: C, 84.22; H, 3.98; N, 11.77. ESI-MS: calcd. for C<sub>50</sub>H<sub>28</sub>N<sub>6</sub>, [M+CI]<sup>-</sup>: 747.2064. Found: 747.2069.

#### **DFT calculations**

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The ground-state geometries were optimized at the level of B3LYP/6-31G(d), spatial distributions of the HOMOs and LUMOs of the compounds were obtained from the optimized ground state structures. Based on the optimized configuration of the ground state (S<sub>0</sub>), the high excitation energy levels of singlet and triplet states were evaluated using B3LYP/6-31G(d).





## **Results and discussion**

#### Solvatochromism

The existence of electron-withdrawing dicyanovinyl groups and electron-donating carbazole groups implies that m-BPCDM and p-BPCDM both are typical D-π-A structure, except for a difference in their spatial construction. Based on the dependence of the photophysics of the D- $\pi$ -A conjugates on the polarity of the solution, the UV absorption spectra of these two compounds in different solvents were investigated (Fig. S10). The characteristic absorption peaks of m-BPCDM and p-BPCDM underwent an obvious blue shift from 435 nm to 403 nm and 439 nm to 407 nm following with the polarity of the solvents, respectively. By further investigation, the emission spectra data of m-BPCDM and p-BPCDM were performed in Fig. 1 and Table S1. Clearly, with the change of the polarity of different solutions from low polar toluene to highly polar acetone, the emission of m-BPCDM and p-BPCDM are gradually red-shifted from 555 nm to 608 nm and 477 nm to 603 nm respectively, exhibiting an evident bathochromic effect. These results indicate that the fluorescence behaviours of m-BPCDM and p-BPCDM are highly dependent on the solvent polarity, which can be ascribed to the fact that the combination of the electron-donating carbazole groups and the electron-accepting dicyanovinyl group enables ICT processes in the molecule. Optical and electronic properties of m-BPCDM and p-BPCDM and their precursors were summed in Table 1.

#### **Aggregation-Induced Emission**

By further inspecting the structures of these two molecules, the single bond connecting the carbazole group and the adjacent benzene ring entered our sight. It is well known that molecules

#### Table 1 Optical and electronic properties of m-BPCDM and p-BPCDM.

compound	solnª				crystal			Еномо (eV)	Eumo (eV)	Еномо <sup>е</sup> (eV)	<i>Е</i> шмо <sup>е</sup> (eV)
	λ <sub>abs</sub> (nm)	$\lambda_{\text{em}}$ (nm)	Φ <sub>F</sub> <sup>b</sup> (%)	τ <sup>c</sup> (ns)	λ <sub>em</sub> (nm)	Φ <sub>F</sub> <sup>b</sup> (%)	τ <sup>c</sup> (ns)				
m-BPCDM	412	596	0.30	4.51	565	69.74	7.89	-5.04 <sup>d</sup>	-2.43	-5.40	-3.06
p-BPCDM	420	592	0.20	3.97	609	17.39	4.43	-5.46	-3.35 <sup>d</sup>	-5.67	-3.16
m-BPMCz	339	498	0.50	2.81	521	23.45	2.50	-5.36 <sup>d</sup>	-2.14	-5.39	-1.99
p-BPMCz	336	550	0.20	4.22	565	3.72	2.04	-5.53 <sup>d</sup>	-2.37	-5.51	-2.34

<sup>a</sup> Tested in a THF solution (10<sup>-5</sup> M). <sup>b</sup> Fluorescence quantum yield determined by a calibrated integrating sphere in THF. <sup>c</sup> Lifetime of the prompt component in transient PL. <sup>d</sup> Calculated from cyclic voltammetry experiments calibrated by Fc/Fc<sup>+</sup> and UV absorption spectra. <sup>e</sup> Calculated from the B3LYP/6-31G(d) basis set.

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Fig. 2 (a) PL spectra of m-BPCDM and p-BPCDM in acetone/water mixtures with different water fractions ( $f_w$ ). (b) PL spectra of p-BPCDM in acetone/water mixtures with different water fractions ( $f_w$ ). (c) Plots of the PL peak intensity of m-BPCDM vs the water fraction  $(f_w)$ . (d) Plots of the PL peak intensity of p-BPCDM vs the water fraction  $(f_w)$ . (e) Particle size distribution of m-BPCDM in an acetone/water mixture with a  $f_w$  value of 70%. (f) Particle size distribution of p-BPCDM in an acetone/water mixture with a  $f_w$  value of 70%. Concentration:  $10^{-5}$  M ( $f_w$ = 0%); excitation wavelength: 377 nm.

with rotors, here are carbazole groups, in the non-aggregated state, are easy to consume energy through the rotation of the rotors and diminish the emission subsequently. According to the RIR mechanism of AIE, m-BPCDM and p-BPCDM could also feature the AIE effect.

To confirm this speculation, the PL spectra of m-BPCDM and p-BPCDM in the solid state and in acetone solution were recorded under UV light (Fig. S13). Both m-BPCDM and p-BPCDM are highly emissive in the solid and aggregated state with fluorescence quantum yield of m-BPCDM and p-BPCDM is 69.74% and 17.39% respectively. However, both are rather weakly emissive in liquid medium.

The above tests showed BPCDM isomers with excellent fluorescence quantum efficiency in the solid state which indicates the existence of the AIE effect. Hence, their AIE properties were tested delicately in a solution of acetone and water which served as a good and poor solvent, respectively. For both compounds, they showed a weak emission in acetone, and with the increase of the water infraction  $(f_w)$ , the emission intensity boosted a lot from 30% for m-BPCDM (for p-BPCDM, from 40%), and yielded approximately a 240-fold (30-fold for p-BPCDM) of luminescence intensity enhancement when the  $f_w$ was increased up to 70% (Fig. 2c and d). The slight increase of the  $f_w$  resulted in an augment of the polarity of the solvent, followed by the abatement of the PL intensity. Besides, the

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fluorescent emission exhibited a certain red-shift as a result of intramolecular charge transfer, whicP이:iも0.1839級에도여20% photophysical phenomenon that common exists in the D-π-A conjugated organic dyes.<sup>[35,36]</sup> As the  $f_w$  continued to increase, most of the molecules began to aggregate, which encumbered the rotation of the carbazole units and reduced the nonradiative transition, ultimately enhanced the PL intensity.<sup>[37]</sup> After the aggregation process finished, the suspension solution was diluted as  $f_w$  increased from 70% to 90% and thus the PL intensity decreased. The particle sizes of m-BPCDM and p-BPCDM in the mixture with a  $f_w$  of 70% were determined to be 166 nm and 157 nm respectively, using dynamic light scattering (DLS), confirming the formation of nanoaggregates (Fig. 2e and f).

#### **Crystal Structure**

To further explore the underlying reasons for this significant substitution site dependent emission behavior, an inspection of their single crystal structures was performed (Fig. 3 and Fig. S17). Fig. 3 presents the single x-ray crystal structures of m-BPCDM and p-BPCDM. Crystal p-BPCDM adopted a near-planar conformation and the torsion angles of the carbazole group relative to the attached benzene ring, the attached benzene ring relative to the dicyanovinyl group, the central benzene ring towards the dicyanovinyl group were 48.13°, 36.61° and 46.49°, respectively (Fig. 3b). In comparison, the crystal of its positional isomer m-BPCDM showed an obvious twisted conformation in its crystal structure. The torsion angle between the carbazole group and the attached benzene ring nearly 33.22°, while the torsion angles of the attached benzene ring towards the dicyanovinyl, the central benzene ring towards the dicyanovinyl group go contrary, which were 36.27° and 46.72° respectively. Besides, the distances between two neighboring carbazole units in m-BPCDM and p-BPCDM are 4.759 Å and 5.381 Å (Fig. 3). On the other hand, the vertical distances between two neighboring



Fig. 3 Single crystal structures and molecular packing patterns of m-BPCDM (a) and p-BPCDM (b), and the molecular packing viewed from the bottom and side of adjacent molecules

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Fig. 4 Optimized molecular structures and molecular amplitude plots of HOMO and LUMO energy levels of m-BPCDM and p-BPCDM.

molecules were calculated to be 4.309 Å and 4.886 Å (Fig. S17), respectively. The above results suggest that p-BPCDM encounter stronger intermolecular  $\pi$ - $\pi$  stacking interactions and thus resulting in weaker fluorescence in its solid state. Adversely, m-BPCDM experiences comparative weaker intermolecular  $\pi$ - $\pi$  stacking interactions and therefore exhibits higher PL intensity in the solid state (Fig. S14). The fluorescence quantum yields of m-BPCDM and p-BPCDM were measured to be 69.74% and 17.39%, respectively. The above results further indicate that the quenching effect is relevant with crystal packing style. As we assumed, the distortion of the molecular skeleton in these D- $\pi$ -A type positional isomers can induce AIE effect reasonably.<sup>[38,39]</sup> Besides, a moderately twisted configuration within the molecular framework may bring about some specific luminescent behaviors, such as mechanically responsive luminescence.

#### **Theoretical Calculation and Analysis**

Given the introduction of electron-withdrawing dicyanovinyl groups and electron-donating carbazole groups, and the positional isomers m-BPCDM and p-BPCDM, some evident distinctions can be observed in their molecular structure and their packing mode in crystal. In view of this, the molecular orbital amplitude plots of the positional isomers (m-BPCDM and p-BPCDM) are theoretically calculated by density functional theory (DFT) at the level of B3LYP/6-31G(d) (Fig. 4).

The highest occupied molecular orbitals (HOMOs) of both two compounds are mainly concentrated on the electron-rich carbazole groups, scarcely distributed on the benzene rings. The lowest unoccupied molecular orbitals (LUMOs) of m-BPCDM and p-BPCDM are chiefly concentrated on the electrondeficient dicyanovinyl groups and the benzene rings. Compared



Fig. 5 (a) PL spectra of m-BPCDM and its precursor. (b) PL spectra of p-BPCDM and its precursor.

to their precursors m-BPMCz and p-BPMCz (Table S3), the OTHE A type structure in positional isomers m-BPCDMPANG P-BPCDM makes the ICT effect more apparent,<sup>[40]</sup> the polarization degree more significant, accordingly resulting in an obvious red shift of their PL spectra (Fig. 5).

Intriguingly, the maximum emission peak of p-BPCDM towards its precursor p-BPMCz, red-shifted from 504 nm to 606 nm, while for its positional isomer m-BPCDM, red-shifted from 500 nm to 568 nm. Thus, altering the substitution pattern of the molecules can tune the distribution of HOMOs and LUMOs, leading into the changes of ICT effect, and eventually, partially changing the PL properties of the molecules.

#### Mechanochromic Luminescence Property

Because of the distortion of relevant molecular structures, under external force, the arrangement or accumulation mode of the molecules may change and therefore alter the luminescence properties of these compounds.<sup>[41]</sup> Accordingly, the luminescence behaviors and structure changes by grinding the three compounds under external force were investigated.

As shown in Fig. 6a and c, the pristine crystals of m-BPCDM and p-BPCDM emitted at 565 nm and 609 nm, respectively. After grinding, the spectra of these compounds were red-shifted to 590 nm and 617 nm. During the grinding process, the crystal lattice collapses, and the molecules adopted a more planar conformation that altered the luminescence behaviors. Intriguingly, as compared to p-BPCDM, m-BPCDM with more distort structure displayed more obvious red-shift in its fluorescence spectra. From a crystallographic point of view, there is less free space in p-BPCDM, so its PL spectra almost keep the same before and after grinding. As shown in Fig. 6b and d, both p-BPCDM and m-BPCDM in their pristine form displayed sharp and intense diffraction peaks that can be attributed to crystalline structures. The sharp diffraction peaks disappeared after grinding, yielding a broad band indicating that its morphology became amorphous. After recrystallization under dichloromethane vapor for 6 h, the crystallinity and fluorescence of the two compounds was



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resumed after fuming, indicating the reversible mechanochromic luminescence properties of m-BPCDM and p-BPCDM in response to external stimuli.

## Conclusions

In summary, two carbazole derived fluorescent molecules functionalized by strong electron withdrawing dicyanovinyl groups were designed and synthesized. The effects of positional isomers on AIE and mechanochromic luminescence properties were systematically investigated. The results showed that the space steric of bulky aromatic groups and dicyanovinyl groups enabled the two isomers to crystallize with a twisted molecular conformation, which subsequently endowed them with AIE features by emitting a strong fluorescence in the aggregated state. The single crystal X-ray analysis further confirmed that the  $\pi$ - $\pi$  stacking interaction in p-BPCDM is stronger than that of m-BPCDM, therefore it exhibited much weaker emission intensity in the solid state of p-BPCDM. Moreover, m-BPCDM presented reversible mechanochromic luminescence properties due to its non-face by face packing configuration. It is anticipated that such positional isomer strategy can be extended to other molecular systems allowing many new types of stimuli-responsive luminescent and AIE effective materials to be fabricated.

# **Conflicts of interest**

There are no conflicts to declare.

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# Notes and references

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