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A-π-D-π-A carbzazole derivatives with remarkable solvatochromism and mechanoreponsive luminescence turn-on

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Two A- π -D- π -A molecules with carbazole donor and dicyanovinyl acceptor but differing in the N-hexyl **(***h***-CPDM)** and Nisooctyl substitute (*i*-CPDM) were synthesized, and both of them presented remarkable dual properties of solvatochromism and mechanoreponsive luminescence (MRL) turn-on. The intrinsic intramolecular charge transfer (ICT) characteristic endowed both luminophors with prominent solvatochromic effect, with emission color tuning from blue to orange-red by changing the solvent from nonpolar hexane to polar dimethyl sulfoxide. Meanwhile, the none/weakly emissive original powders of *h*-CPDM and *i*-CPDM gave bright orange (610 nm) and yellow (596 nm) emission with photoluminescence quantum yields increasing as high as 85-fold after being ground. Investigations revealed this mechanoreponsive luminescence turn-on could be ascribed to the disturbance of the π - π stacking interactions in the non/weakly emissive *J*-aggregates by the mechanical force. This work offers carbazole derivatives with applications as sensitive fluorescent indicators for organic solvents and mechanical sensors.

Introduction

Organic compounds with molecules built up from alternating electron-donating (D) and electron-accepting (A) segments have attracted considerable attention by virtue of their wide applications in the fields of fluorescence sensors,¹ pH indicators,² viscosity probes,³ and mechanochromic materials.⁴ Among them, the A- π -D- π -A molecules are of particular interest due to their symmetrical structure and balanced dipole moment, which often exhibit intense fluorescence resulting from the reduced dipole-dipole interactions.⁵ Owing to their intrinsic intramolecular charge transfer (ICT) character, these molecules are promising candidates for solvent polarity detection because of the solvatochromic luminescence effect.^b However, highly sensitive detector molecules whose emitting colors can be tuned in a wide range of wavelength with intense luminescence distinguished by naked eyes are still rare.7

Similar to their applications as polarity sensor in solvents, ICT molecules that exhibit mechanoreponsive luminescence (MRL) characteristics in the solid state have drawn great attention due to their potential applications in mechano-sensors, and deformation detectors.⁸ To date, MRL materials displaying luminescence dichromic behavior have been reported and



In this work, two A- π -D- π -A carbazole derivatives using dicyanovinyl groups as the electron-accepting moieties, but

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Scheme 1 Molecular structures of *h*-CPDM and *i*-CPDM.

differing in the N-hexyl (h-CPDM) and N-isooctyl substitute (i-CPDM) were designed and synthesized to address the problems identified above (Scheme 1). Due to their strong ICT characteristics, these two compounds exhibited remarkable solvatochromic effects, suggesting their applications in solvents polarity detection. Moreover, their luminescence properties in the solid state were highly dependent on the molecular structure as well as the stability of the crystalline phases in response to external force stimuli. For example, upon grinding, the almost non-emissive solids demonstrated stimuli-responsive fluorescence not only changing in colors from red to orange (h-CPDM) and red to yellow (i-CPDM), but also with absolute photoluminescence quantum yields ($\Phi_{\rm F}$ s) raised as much as 85-fold. Based on these results, the relationship between the molecular structure and the diversity of luminescence behaviour, and the mechanism of MRL turnon in the solid state were investigated.

Experimental

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Materials and characterization

All reagents and solvents were purchased from J&K Chemical and used without purification. NMR spectra measurements were carried out at a Bruker NMR 600 spectrometer. MALDI-TOF mass spectrometric measurements were performed on a Waters MALDI Micro MX mass spectrometer, with 2,5dihydroxy benzoic acid (DHB) as the matrix. Elemental analysis was run on a Vario EL III Elemental Analyzer. UV-Vis spectra were recorded on a HTIACH U-3900 Spectrometer. Photoluminescent (PL) spectra were recorded on a HORIBA FluoroMax-4 spectrometer. The fluorescence quantum yields of the compounds in solutions were measured by comparing a standard (quinine sulfate in 1 N H₂SO₄ aqueous solution, Φ_F = 0.56). The absolute fluorescence quantum yields of the solids were measured on a HORIBA FluoroMax-4 spectrometer using an integrating sphere. The transient photoluminescence decay profiles of the solids were recorded using an Edinburgh Instrument FLS980 spectrometer equipped with an EPL-375 picosecond pulsed diode laser. Differential scanning calorimetry (DSC) experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of 5 K min⁻¹. Powder Xray diffraction measurements were performed on a Bruker Xray diffractometer.

Synthesis

bromohexane (5.94 g, 36 mmol) was dissolved in toluene (50 mL). The solution of KOH (4.5 g, 80 mmol) and tetrabutyl ammonium bromide (**TBAB**) (976 mg, 3 mmol) in H₂O (15 mL) was added. Then the reaction mixture was stirred at 110 °C for 4 h. After cooling, the mixture was poured into H₂O and extracted with chloroform. The combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. **1h** was recrystallized from ethyl ether to produce white crystals in an 89% yield. ¹H NMR (600 MHz, CDCl₃) δ = 8.13 (d, *J* = 2.4 Hz, 2H), 7.54 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 4.23 (t, *J* = 7.2 Hz, 2H), 1.85 - 1.76 (m, 2H), 1.36 - 1.19 (m, 6H), 0.85 (t, *J* = 7.2 Hz, 3H).

Synthesis of 1h. 3, 6-Dibromo-carbazole (9.75 g, 30 mmol) and

Synthesis of 1i. The procedure is similar to the synthesis of **1h** but using bromo-iso-octane instead of bromohexane. Compound **1i** was obtained as pale yellow oil by silica gel column chromatography (petroleum ether) in an 80% yield. ¹H NMR (600 MHz, $CDCl_3$) $\delta = 8.13$ (d, J = 1.8 Hz, 2H), 7.54 (dd, J = 8.7, 1.9 Hz, 2H), 7.22 (t, J = 5.8 Hz, 2H), 4.09 - 4.02 (m, 2H), 1.37 -1.15 (m, 9H), 0.86 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H).

Synthesis of 2h. Under a nitrogen atmosphere, 1h (4.12 g, 10 mmol), tetrakis(triphenylphosphine)palladium(0) $(Pd(PPh_3)_4)$ (576 mg, 0.5 mmol), K₂CO₃ (6.9 g, 50 mmol), 4-(dihydroxyboryl)benzaldehyde (3.3 g, 22 mmol) and 1,2-glycol dimethyl ether (200 mL) were added into a 500 mL threenecked flask. The mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the mixture was poured into H₂O, extracted with chloroform and dried over anhydrous MgSO₄. After filtration and concentration under reduced pressure, product 2h was obtained as yellow solid by silica gel column chromatography (ethyl acetate: ethyl acetate= 1: 12 by volume) in a 21% yield. ¹H NMR (600 MHz, CDCl₃) δ = 10.08 (s, 2H), 8.45 (d, J = 1.2 Hz, 2H), 8.01 (dt, J = 8.4, 1.8 Hz, 4H), 7.92 (dt, J = 8.4, 1.8 Hz, 4H), 7.81 (dd, J = 8.4, 1.8 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 4.38 (t, J = 7.2 Hz, 2H), 1.94 (m, 2H), 1.45 - 1.29 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H).

Synthesis of 2i. The procedure is similar to the synthesis of **2h** but using **1i** instead of **1h**. Compound **2i** as yellow solid was obtained by silica gel column chromatography (ethyl acetate: ethyl acetate= 1: 12 by volume) in a 41% yield. ¹H NMR (600 MHz, CDCl₃) δ = 10.08 (s, 2H), 8.447 (d, *J* = 1.8 Hz, 2H), 7.93 (dt, *J* = 7.8, 1.2 Hz, 4H), 7.971 (dt, *J* = 7.8, 1.2 Hz, 4H), 7.803 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.517 (d, *J* = 4.2 Hz, 2H), 4.250 (t, *J* = 7.2 Hz, 2H), 1.436 - 1.254 (m, 9H), 0.958 (t, *J* = 7.2 Hz, 3H), 0.884 (t, *J* = 7.2 Hz, 3H).

Synthesis of *h***-CPDM. 2h** (459 mg, 1 mmol) was dissolved in absolute ethyl alcohol (25 mL) and tetrahydrofuran (15 mL) and stirred for 30 min at 75 °C. Then malononitrile (145 mg, 2.2 mmol) was added into the solution. After stirred for additional 8 h, the precipitate was filtered and dried. The crude product was recrystallized from ethyl ether to afford *h*-CPDM as orange-red solid in a 64% yield. ¹H NMR (600 MHz, CDCl₃) δ = 8.45 (d, *J* = 1.2 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 4H, 7.91 (d, *J* = 8.4, 4H), 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.79 (s, 2H), 7.55 (d, *J* = 9.0 Hz, 2H), 4.38 (t, *J* = 7.2 Hz, 2H), 1.27-1.46 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ = 159.17,



148.08, 141.45, 131.60, 130.32, 129.11, 127.79, 125.66, 123.61, 119.41, 114.13, 113.05, 109.86, 81.09, 77.28, 77.03, 76.77, 43.56, 31.54, 29.02, 26.96, 22.54, 14.01. MS (MALDI-TOF, m/z): 710.4 [M + matrix]⁺, 558.4 [M]⁺. Anal. Calcd for $C_{38}H_{29}N_5$: C, 82.14; H, 5.26; N, 12.6. Found: C, 82.02; H, 5.16; N, 12.53.

Synthesis of *i***-CPDM.** The procedure is similar to the synthesis of *h*-CPDM but using **2i** instead of **2h**. Compound *i*-CPDM was afforded as red solid by recrystallization in a 34% yield. ¹H NMR (600 MHz, CDCl₃) δ = 8.45 (d, *J* = 7.8 Hz, 2H), 8.03 (dt, *J* = 8.4, 2.4 Hz, 4H), 7.91 (dt, *J* = 9.0, 1.8 Hz, 4H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.79 (s, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 1.46 - 1.27 (m, 9H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ = 159.19, 148.07, 141.91, 131.61, 130.29, 129.13, 127.79, 125.63, 123.57, 119.36, 114.14, 113.05, 110.14, 81.11, 76.89, 76.77, 47.83, 39.53, 31.02, 28.81, 25.62, 24.42, 23.04, 14.04, 10.92. MS (MALDI-TOF, m/z): 738.4 [M + matrix]⁺, 586.4 [M]⁺. Anal. Calcd for C₄₀H₃₃N₅: C, 82.3; H, 5.7; N, 12.00. Found: C, 82.15; H, 5.62; N, 12.23

Result and discussion

Synthesis

The target **CPDM** homologues were synthesized according to literatures by a three-step procedure as depicted in Scheme 2.¹⁴ Compounds **1h** and **1i** were synthesized by the alkylation reaction of 3,6-dibromo-carbazole with bromohexane and bromo-iso-octane, respectively. **2h** and **2i** were obtained by Suzuki reaction of 4-formylphenylboronic acid with **1h** and **1i**, respectively. Finally, *h*-CPDM and *i*-CPDM were synthesized by Knoevenagel condensation reaction of malononitrile with **2h** and **2i**, respectively. The chemical structures of *h*-CPDM and *i*-CPDM were fully characterized by ¹H NMR, ¹³C NMR, mass spectrometry and elemental analysis. Both *h*-CPDM and *i*-CPDM are soluble in common organic solvents such as CHCl₃, CH₂Cl₂ and THF, but insoluble in methanol and water.

Photophysical properties

UV-Vis absorption and photoluminescence properties of *h*-**CPDM** and *i***-CPDM** were studied in solvents with different polarities as shown in Fig. 1 and Fig. 2, and the corresponding data were illustrated in Table 1. The absorption spectra of the

two compounds in various solvents exhibited one characteristic absorption band in the range of 414-431 nm (Fig. 1). Meanwhile, both of the two compounds showed similar absorption maxima and profiles in solutions, indicating a small change of dipole moment at the ground state in different solvents.¹⁵ On the contrary, the emission spectra of *h*-CPDM and *i*-CPDM showed strong solvent polarity dependence (Fig. 2a and 2b). As illustrated in Table 1, the emission bands were bathochromic shifted from 457 nm to 606 nm and from 451nm to 619 nm as increasing the solvent polarity from nonpolar hexane to polar DMSO, respectively, which was typical ICT effect. It was noted that such large solvatochromic shifts of 49 nm (h-CPDM) and 68 nm (i-CPDM) led to distinct fluorescence colors covering from blue to orange-red, which could be clearly distinguished by naked eyes under a 365 UV lamp (Fig. 2c and2d). The $\Phi_{\rm F}$ s of the compounds increased with solvent



Fig. 1 UV-vis absorption spectra of (a) $\pmb{h}\text{-CPDM}$ and (b) $\pmb{i}\text{-CPDM}$ in various solvents (10 5 M).



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polarity just in the primary region, and decreased in the very strong polar solvents, producing a distinct maximum. This updown phenomenon has been observed in some compounds with ICT characteristics.¹⁶ From hexane to THF, the increased $\mathcal{D}_{\rm F}$ of "negative solvation effect" can be ascribed to the reduction of "the proximity effect" of π - π * and n- π * transition and the "conformation change" of the molecule with the increased solvent polarity.¹⁶ With a further increase of the solvent polarity from THF to DMSO, the decreased $\mathcal{D}_{\rm F}$ of "positive solvation effect" is attributed to the domination of the ICT process. The two competing mechanisms resulted in the observed maximum fluorescence quantum yields of 29.0% and 33.6% for *h*-CPDM and *i*-CPDM in THF, respectively.

To better evaluate the effects of solvents on the emission features, the relationship between the solvent polarity parameter and the Stokes shift according to the Lippert–Mataga equation was investigated. 17

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$
 (eq. 1)

$$\Delta v = v_a - v_e = \frac{2(\mu_e - \mu_g)^2}{4\pi\varepsilon_e hca^3} \Delta f + consistant$$
 (eq. 2)

In which Δv stands for the Stokes shift, v_a and v_e represent the maximum absorption and emission wavenumbers (cm⁻¹), respectively. The letter *h* is Planck's constant, *c* is the speed of light in vacuum, *a* is the Onsager radius. μ_e and μ_g are the

Table 1 Photophysical properties of the compounds in various solvents

	,					
Compound	Solvent	Δf	λ _{Abs} (nm)	λ _{PL} (nm)	Stokes shift (cm ⁻¹)	Ф _F (%)
h-CPDM	Hexane	0	415	457	2215	10.9
	Toluene	0.012	427	504	3578	12.7
	THF	0.21	423	550	5459	29.0
	Acetone	0.28	420	598	7087	1.3
	Acetonitrile	0.29	418	602	7312	0.34
	DMSO	0.26	430	606	6754	0.32
<i>i</i> -CPDM	Hexane	0	423	451	1468	15.0
	Toluene	0.012	428	493	3080	20.9
	THF	0.21	422	556	5711	33.6
	Acetone	0.28	416	599	7344	4.3
	Acetonitrile	0.29	417	617	7773	0.67
	DMSO	0.26	427	619	7264	0.55



Fig. 3 Fluorescence Stokes shifts as a function of orientational polarizability Δf in various solvents

permanent dipole moments of the excited state and the ground state, respectively. The letter ε_0 is the permittivity of the vacuum, ε is the static dielectric constant of the solvent, nis the refractive index, and Δf is the orientation polarizability. Fig. 3 showed the plots of the Stokes shifts (Δv) versus orientational polarizability (Δf). According to the Lippert-Mataga equation, the slope of the best-fit line was related to the dipole moment change between the ground state and the excited state (μ_e - μ_g). The values were calculated to be 15224 and 17100 for *h*-CPDM and *i*-CPDM, respectively. Comparing to some typical molecules that show ICT fluorescence, these results indicate a large dipole moment change between the excited state and the ground state.¹⁸ In other words, when the charges transfer from the electron-donating carbazole unit to the electron-withdrawing dicyanovinyl units in a more polar solvent, the dipole moment is increased in the excited state. As a result, the polarized excited state is stabilized to adapt to the enhanced dipole moment through the relocation of the polar solvent molecules, resulting in lowered energy and the red-shifted PL maximum.¹¹ Thus, *h*- CPDM and *i*-CPDM whose ICT states are highly sensitive to the solvent polarity may be applied to the development of efficient chemical sensors for the detection of volatile organic compounds.

Theoretical calculation

The ICT characteristics of the compounds are further supported by the density functional theory (DFT) calculation results. As can be seen in Fig. 4a, for both of the molecules, the highest occupied molecular orbitals (HOMOs) are mainly localized on the central carbazole core with sizeable distribution on the two phenyl rings, whereas the lowest unoccupied molecular orbitals (LUMOs) are mostly distributed on the dicyanovinyl units as well as the phenyl rings. Thus, the spatial separation between the HOMO and LUMO indicated a typical ICT effect between the electron-donating moiety and the electron-withdrawing moieties.¹⁹

Additionally, it was found that both *h*-CPDM and *i*-CPDM molecules adopted moderately twisted conformations, but they were different in the symmetry of the skeletons. Molecule *h*-CPDM possessed almost symmetrical structure with the dihedral angles between the substituted phenyl ring and the central carbazole unit 34.4°/34.5°, while *i*-CPDM was less symmetrical, and the corresponding dihedral angles were34.2°/34.9° (Fig 4b). The geometry parameters of the

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Fig. 4 (a) HOMO and LUMO spatial distributions and (b) geometrically optimized 3D molecular models in the ground/excited state from the side view of *h*-CPDM and *i*-CPDM by TD-DFT B3LYP/6-31G(d) calculation.

excited states were calculated by means of the timedependent density functional theory (TD-DFT). Upon excitation, the corresponding dihedral angles were decreased to $27.5^{\circ}/29.0^{\circ}$ and $28.0^{\circ}/29.1^{\circ}$ for *h*-CPDM and *i*-CPDM respectively. Furthermore, the C-C distance between the phenyl ring and the central carbazole unit was declined by 0.01 Å going from the optimized ground state to the excited state for both of the molecules. These changes of molecular geometry in the excited state led to large Stokes shift,²⁰ as verified by the experimental results.

On the other hand, comparing with the organic fluorophores with planar or rigid twisted conformation,²¹ this moderately twisted skeleton may exhibit fantastic luminescent behaviors, for example, mechanoresponsive properties in the solid state.²² Moreover, the linear and branched N-alkyl substituents afforded different steric hindrance, which would be expected to play an important role in tuning the intermolecular interactions or the stability of the crystalline phases in their aggregated state, and as a result influenced the corresponding luminescence.

Aggregation-caused emission quenching

To investigate the fluorescence behaviors of *h*-CPDM and *i*-CPDM in aggregated states, the UV-vis absorption and PL spectra in THF/water mixtures with different fraction of water (f_w) were studied (Fig. 5). When the f_w was up to 80 and 90%, the absorption spectra exhibited significant changes and leveled-off tails clearly appeared in long-wavelength region (Fig 5a and 5b). This can be ascribed to the well-known Mie scattering caused by nanosized particles, which indicates that *h*-CPDM and *i*-CPDM molecules aggregate in high water fractions.^{8a,23} The red-shifts of λ_{Abs} to 438 nm and 430 nm for *h*-CPDM and *i*-CPDM when f_w reaches 90% indicate that *J*-aggregations may occur.^{13,24}

The PL spectra of h-CPDM and i-CPDM in THF/water

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Fig. 5 UV-Vis absorption spectra of (a) *h*-CPDM and (b) *i*-CPDM, and fluorescence spectra of (c) *h*-CPDM and (d) *i*-CPDM (10⁻⁵ M) in THF/water mixtures with different water fractions. The effect of water fractions on the maximum emission intensity of (e) *h*-CPDM and (f) *i*-CPDM.

mixtures and the effect of f_w on the emission intensity were shown in Fig. 5c-5f. *h*-CPDM and *i*-CPDM exhibited strongest yellow fluorescence in pure THF peaking at 550 and 556 nm, respectively. When the water fraction was increased, the fluorescence maximums showed apparent redshift with a dramatic decrease in the intensity. This aggregation-caused emission quenching (ACQ) effect may be attributable to the the unfavorable π - π interactions between the molecules in the *J*-aggregates.¹³

Mechanoresponsive luminescence properties

To evaluate the possible MRL characteristics of *h*-CPDM and *i*-CPDM, their luminescence behaviors in the solid states were studied under mechanical stimuli. As shown in Fig. 6 and Table2, the original powders of *h*-CPDM and *i*-CPDM obtained from the evaporation of the CH₂Cl₂ solvent emitted very weak red and orange-red light at 678 nm (Φ_F = 0.9%) and 661 nm



Fig. 6 Fluorescence spectra of the original and the ground samples of (a) h-CPDM

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Fig. 7 Time-resolved fluorescence spectra of (a) h-CPDM and (b) i-CPDM in original and ground state. $\lambda_{\rm ex}$ = 375 nm

($\Phi_{\rm F}$ = 0.3%), respectively, which can be regarded as the fluorescent "off" states due to the formed *J*-aggregates.¹³ Upon grinding with a pestle, the ground samples showed luminescence not only in dramactially enhanced intensity, but also with obvious blue-shift. For *h*-CPDM, the blue-shift value was 68 nm, and the $\Phi_{\rm F}$ value was increased by 9.7-fold. In the case of *i*-CPDM, the fluorescent peak was blue-shifted for 65 nm, while the $\Phi_{\rm F}$ value was enlarged by as much as 85-fold respect to that of the original powders. Thus, both *h*-CPDM and *i*-CPDM exhibited remarkable MRL turn-on behaviors.

The time-resolved emission-decay behaviors of the samples in original and ground states were investigated to obtain further information of the MRL turn-on. The fluorescence lifetimes of *h*-CPDM and *i*-CPDM became longer after being ground (Fig. 7 and Table 2), indicating that phase transition might exist during the grinding treatment.²⁴ Moreover, the radiative rate constants (k_r s) of the ground samples were much larger than the original ones, which should be attributable to the activation of radiative pathways in the molecular arrangement of the ground states.

To determine the mechanism of the MRL turn-on, X-ray diffraction measurement was carried out for each sample (Fig. 8). For the original powders of *h*-CPDM, there were two sharp diffraction peaks in the small-angle region at 5.93° and 11.74° with the *d*-spacings of 14.83 Å and 7.53 Å, respectively. After being ground, these two peaks moved to 8.31° and 15.16°, resulting in decreased *d*-spacings of 10.63 Å and 5.84 Å, respectively. Meanwhile, two peaks in the wide-angle region were considerably weakened or diminished: the peaks at 21.85° and 25.67° with the *d*-spacings of 4.06 and 3.47 Å, which were probably caused by the ordered packing of the hexyl chains through the van der Waals interactions and the $\pi\text{-}\pi$ stacking of the aromatic rings, respectively.²⁵ This result indicated that the grinding treatment decreased the intermolecular distance, and impaired the ordered arrangement of the hexyl chains and the π - π stacking interactions in *J*-aggregates, which brought out the enhanced intensity as well as the blue-shift of the fluorescence. Similar to h-CPDM, the original powders of i-**CPDM** also exhibited a well-ordered microcrystalline structure. The peaks at 8.27° and 15.07° with the *d*-spacings of 10.68 Å and 5.87 Å could be indexed to the intermolecular distances. After being ground, these two diffraction peaks were disappeared, and the peak for π - π stacking (25.52°, 3.49 Å) was weakened obviously. The result suggested that most of the π - π stacking was disturbed to random molecular packing,

resulting in MRL luminescence turn-on. Comparing with the liner N-hexyl group of *h*-CPDM,





the branched N-isooctyl substituent of *i*-CPDM induced larger steric hindrance, which lowered the phase stability of the original powders and suppressed the adverse intermolecular interactions more effectively. So, we suppose that a more random molecular packing were responsible for the more significant enhancement of $\mathcal{D}_{\rm F}$ value for *i*-CPDM after being ground.

The phase changes in the aggregated states of *h*-CPDM and *i*-CPDM were further confirmed by the DSC analysis (Fig. 9). There was an endothermic peak at 220 °C (ΔH 49.9 J/g) for *h*-CPDM and 222 °C (ΔH 44.3 J/g) for *i*-CPDM corresponding to the melting point, respectively. After being ground, exothermic peaks were appeared at 145 °C (ΔH 36.8 J/g) for *h*-CPDM and 123 °C (ΔH 32.2 J/g) for *i*-CPDM, respectively, indicating that the ground samples were in a metastable state. Thus, the DFT calculation, combined with the XRD patterns and the DSC results well demonstrated that the MRL turn-on was derived from disturbing the molecular packing in the non/weakly emissive *J*-aggregates of the moderately twisted molecules in the π - π stacking directions.

Conclusions

In summary, two novel A- π -D- π -A molecules with carbazole donor and dicyanovinyl acceptor but differing in N-hexyl substitute (*h*-CPDM) and N-isooctyl substitute (*i*-CPDM) were designed and synthesized. Both luminophors showed remarkable solvatochromic effects: the emission color tuned in a wide wavelength region from blue to orange-red with the increase of the solvent polarity. Interestingly, the original powders of *h*-CPDM and *i*-CPDM based on ACQ effect exhibited MRL turn-on characteristics. XRD and DSC characterizations revealed that the MRL turn-on mechanism was ascribed to the disturbance of the π - π interactions in *J*aggregates of the moderately twisted molecules. The ground

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Table 2. Photophysical properties of the solids in original and ground state

Compound	Original sample				Ground sample					
	λ_{PL} (nm)	$arPhi_{ extsf{F}}$ (%)	τ (ns)	<i>k</i> _r (ns ⁻¹)	<i>k</i> _{nr} (ns⁻¹)	$\lambda_{\scriptscriptstyle PL}$ (nm)	Φ _F (%)	τ (ns)	<i>k</i> _r (ns⁻¹)	<i>k</i> _{nr} (ns⁻¹)
h-CPDM	678	0.9	6.37	0.0014	0.156	610	8.7	6.83	0.012	0.134
i-CPDM	661	0.3	1.37	0.0022	0.728	596	25.6	1.45	0.177	0.513

*i***-CPDM** samples displayed more remarkable $\Phi_{\rm F}$ value increase, which could be attributed a more random packing of the molecules caused by the larger steric hindrance of the N-isooctyl chain. This work would provide a new strategy for developing dual functional luminophors with solvatochromism and mechanical-induced emission turn-on behaviors.

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A-π-D-π-A carbzazole derivatives with remarkable solvatochromism

and mechanoreponsive luminescence turn-on

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Two A- π -D- π -A carbzazole derivatives differing in the N-hexyl and N-isooctyl substitute were developed. They exhibited prominent solvatochromic effect and luminescence turn-on characteristics upon mechanical force stimuli.