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Remarkable substitution influence on the mechanochromism of cyanostilbene derivatives†

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Five twisted donor- π -acceptor cyanostilbene derivatives containing carbazole have been designed and synthesized with high yields. Their emission could be tuned from blue to orange by simply altering electron acceptors (donors). It was found that larger molecular dipole and the Stokes shifts of the donor- π -acceptor dyes could result in bathochromic shifts of absorption and emission. The density functional theory calculations further demonstrated that with the increase of the electron-donating or accepting abilities of the substituents, the energy gaps of the fluorophores gradually decreased, which elucidated the substituent effect of the organic fluorophores on their photophysical properties. Moreover, they exhibit typical intramolecular charge transfer (ICT), aggregation-induced emission (AIE), and crystallization-induced emission enhancement (CIEE) characteristics. Furthermore, the hydrogen- (2a), methyl- (2d) and chlorine-substituted (2e) derivatives exhibit remarkable reversible mechanochromic features (with emission wavelength changes up to 119 nm), while the methoxyl- (2b) and nityl- substituted (2c) derivatives have no mechanochromic characteristics owing to the fact that they have strong crystallizability. The analysis of the X-ray crystal structure proved that the AIE-, CIEE-active and mechanochromic behavior was associated with the stator-rotor structures, twisted conformations and crystal packing modes. More importantly, the substitution effect of cyanostilbene derivatives would provide an effective way to obtain full-color optoelectronic materials with AIE and mechanochromic properties.

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Introduction

Stimuli-responsive emission switching, such as mechano-, thermo- and vapochromism, was considered to be of the utmost importance for developing sensors, camouflage and rewritable optical media in recent years.¹⁻³ Mechanochromic fluorescent (MCF) materials play an especially important role in practical applications.⁴⁻⁸ The luminescent colors of MCF materials can be reversibly switched *via* some external stimuli such as heating, organic vapour, acids and bases.⁹⁻¹³ This reversible

mechanochromic behavior is an integral feature which allows the reuse of the material. The resulting high contrast in luminescent intensity or color is beneficial to naked-eye detection in practical applications. Up to now, a number of compounds based on liquid crystals, organic molecules, organometallic complexes, polymers and dye-doped polymers have shown MCF properties.¹⁴⁻¹⁶ Mechanochromic behavior typically displays some relation with the variation of molecular spacing, molecular packing modes and/or molecular conformations. A simple structure, short synthetic route and high yield are preferred. However, a clear design strategy for molecule construction which achieves the required large photoluminescence wavelength shift is still lacking.

Nevertheless, some aggregation-induced emission (AIE) active materials have already been reported to exhibit emission color switching because of their unique properties, and these materials demonstrate promise for use in practical applications.¹⁷⁻¹⁹ Generally, AIE active molecules possess propeller-like twisted conformation that necessitates loose molecular packing.^{18,20} Under external mechanical stimuli, this loose molecular packing is easily destroyed, resulting in a more planar molecule conformation and redder fluorescence-emission.²¹ In particular, electron donor- π -bridge-electron acceptor (D- π -A) structured luminogens often show solvatochromic effects due to intramolecular charge transfer (ICT), taking advantage of the transformation from local excited (LE) state to charge-transfer

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(CT) excited state.^{9,22–25} In addition, some compounds emit more efficiently in the crystalline state than in their solution or amorphous phases. This novel phenomenon is referred to as crystallization-induced emission enhancement (CIEE).^{26,27} The CIEE effect can easily switch the fluorescence of luminogens between amorphous and crystalline states through reversibly tuning the molecular packing patterns, which facilitates the transformation of luminogens aggregates between various states through thermal, vapor and mechanical stimuli. Thus, ICT dyes with AIE or CIEE-active materials are expected to become a foundation for high contrast mechanochromic materials.

It has been reported that electron-accepting 2,3,3-triphenylacrylonitrile (TPAN) is a prototypical CIEE molecule because of its facile synthesis and superb CIEE effect.²⁸ If a reasonable electron-donor can be chosen to modify the periphery of TPAN, it will assuredly be advantageous for the creation of ICT materials that are AIE and CIEE-active with high contrast. Carbazole derivatives became first candidates due to their strong donor power.^{29–31} According to these inspirations, a combination of TPAN and carbazole may be advantageous for construct a high contrast mechanochromic materials. Moreover, adjusting the mechanochromic property of these smart materials through simply altering electron acceptors (donors) is of great scientific interest and highly demanded. Thus, five D- π -A structured luminogens of cyanostilbene derivatives containing carbazole were designed and synthesized, in which a benzene ring portion of TPAN with various electron acceptors (donors) (Chart 1). These luminogens exhibit typical AIE-, CIEE-active and ICT characteristics. It is noteworthy that the emission color of the carbazole-based AIE luminogens varies from blue to orange by simply altering electron acceptors (donors). Additionally, three of these luminogens show remarkable mechanochromism, with changes in emission wavelengths up to 119 nm. To the extent of our knowledge, such high contrast for solid emitters under mild conditions has rarely been reported.^{32–35} Therefore, these results will provide an effective way to obtain full-color

AIE and mechanochromic optoelectronic materials with high contrast.

Results and discussion

Synthesis

The target compounds (2a–2e) were prepared according to the synthetic routes shown in Scheme S1 (ESI[†]). Briefly, 9-phenyl-9H-carbazole-3-carbaldehyde³⁶ (1) was prepared in 80% yields through the classical Vilsmeier–Haack reaction. Compound 2a–2e^{10,37} was prepared from the Knoevenagel condensation reaction of compound 1 with benzylcyanide derivative in anhydrous ethanol in the presence of sodium hydroxide (40%). The resulting luminogens were produced with high yields (90–98%). Crystals of 2a–2e suitable for X-ray diffraction were obtained from mixture of *n*-hexane/tetrahydrofuran and toluene/dichloromethane (2e) at room temperature, respectively. The X-ray structures of compound 2a–2e confirms their configuration (Fig. 6). The final products were characterized by ¹H NMR, ¹³C NMR, LRMS and HRMS spectral (Fig. S1–S17, ESI[†]).

Photophysical properties

The photophysical characterizations in solution are highly dependent on the solvent polarity for the D- π -A conjugated molecules.³⁸ Therefore, the absorption and emission properties of target compounds in varying solvents were tested. Luminogens exhibited two characteristic absorption bands in varying solvents, which are attributable to the π - π^* and ICT transitions, respectively (Fig. 1A and S18–S21, ESI[†]). The absorption profiles of 2a–2e show altered little in varying solvents, evidencing a rather small dipole change in the ground state.⁹

Moreover, the absorption spectra of the five molecules possessed maximum absorption peaks at 372, 375, 413, 375 and 380 nm in DCM, respectively. The obvious bathochromic shift of 2c should be ascribed to the increasing electron affinity, which strengthens D-A effect and thereby reduces the energy gaps between the excited and ground states.³⁹ However, their emission spectra exhibited a typical bathochromic shift with increasing solvent polarity (Fig. 1B and S18–S21, ESI[†]). And the solution emission color ranging from blue to orange almost covered the whole visible region. The maximum emission of 2b (444 nm) with -OCH₃ groups exhibited 5 nm and 3 nm

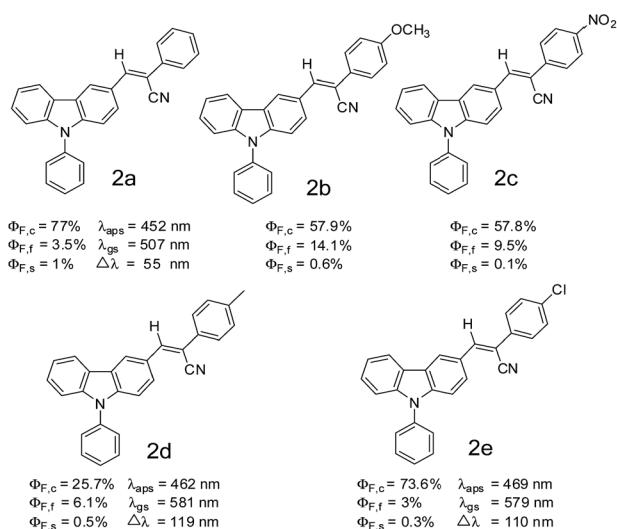


Chart 1 Chemical structures and photophysical properties of 2a–2e.

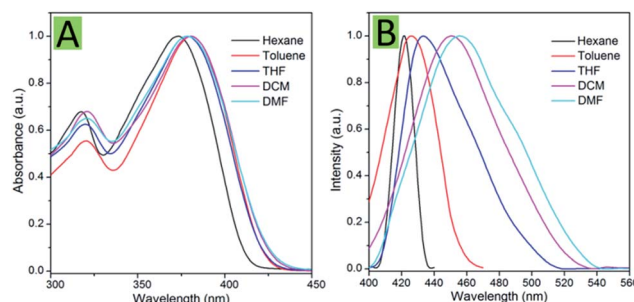


Fig. 1 Normalised (A) absorption and (B) emission spectra of 2e in various organic solvents.

bathochromic shifts compared with 2a (439 nm) and 2d (441 nm), respectively. When the stronger electron-accepting ability groups $-\text{NO}_2$ were introduced, fluorophores 2c (562 nm) exhibited more dramatically bathochromic shifts. It is very interesting that fluorophores 2c exhibited large Stokes shifts (149 nm), which will be vital to their real world applications.^{40,41} Hence, the enhancement of the molecular dipole of the D- π -A fluorophores resulted in the bathochromic shift of the UV-vis absorption and the fluorescent emission, so do the Stokes shifts.⁴² As shown in Fig. S22 (ESI[†]), the emission spectra of the powders of 2a (H), 2b (OCH_3), 2c (NO_2), 2d (CH_3) and 2e (Cl) clearly exhibited tunable emission colors from blue to orange, which agreed with their corresponding emission maxima at 452, 515, 575, 462 and 469 nm. The solid emissions of fluorophores 2a–2e nearly covered the whole visible region and had further bathochromic shifts compared with those in solution. This result showed that emission could be tuned from blue to orange (even red) by simply altering electron acceptors (donors) (Table S1, ESI[†]).

Density functional theory calculations were performed using the B3LYP/6-31G(d,p) basis set to better understand the optical characteristics of the luminogens. As shown in Fig. 2 and S23 (ESI[†]), while the electron clouds in HOMO levels are predominantly placed on the electron-donating carbazole and bridged π units, those of LUMO levels are mainly located on the 2-phenylacrylonitrile moiety and electron-withdrawing groups, indicative of ICT characteristic in the molecules in accordance with spectroscopic results. Compared with compound 2a, the HOMOs of compounds 2b and 2d with the strong electron-donating $-\text{OCH}_3$ and $-\text{CH}_3$ group showed upshift more seriously than their LUMOs, respectively. Thus, the energy gaps of compounds 2b (2.22 eV) and 2d (2.31 eV) were smaller than that of compound 2a (2.32 eV), which well explained that the absorption and emission bands of compounds 2b and 2d were longer than those of compound 2a. But the HOMO of compound 2c with the strong electron-accepting $-\text{NO}_2$ group moved to downshift, while the LUMO showed downshift more badly. Therefore, the energy gaps of compound 2c (1.84 eV) was smallest that of all compounds, which well explained that the absorption and emission bands of compound 2c was longer than those of other compounds. Hence, the panchromatic emissive properties of the fluorophores could be theoretically explained. On the other hand, the optical band gaps estimated from the onset wavelength of the absorption spectra showed a dramatically decrease of 2.76 eV for 2c (Table S1, ESI[†]). All these data agreed fairly well with the theory calculations.

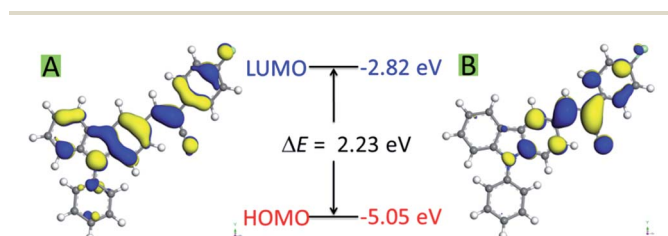


Fig. 2 B3LYP/6-31G(d,p) calculated molecular orbital amplitude plots of (A) HOMO and (B) LUMO levels for 2e.

AIE properties

When illuminated under a UV light, the dilute THF solutions of the luminogens exhibited almost no visible light, whereas their powdered forms emitted strong blue, yellow, or orange lights indicating their AIE characteristics. Further measurement of the emission spectra of 2a–2e in THF and THF/water aqueous mixtures were conducted to discern the presence or absence of AIE-active attributes. As depicted in Fig. 3, compound 2e exhibited extremely weak emission signal in pure THF. However, with increasing water fraction (f_w), the fluorescence intensity initially decreased, as the addition of water into THF increased the solvent polarity.^{28,43} Moreover, when f_w was $\leq 70\%$, only weak signals were observed, which was ascribed to the solvating powers of the mixtures still genuinely dissolve the luminogenic molecules. With a f_w of 85%, the luminogen molecules began to aggregate and the fluorescence intensity started to increase. At a high f_w of 90%, 2e had a strong emission at 490 nm with an intensity ~ 5 -fold higher than that in THF, thus solidifying the AIE nature of 2e. Owing to the increasing polarity of the solvent mixtures, the emission showed a clear redshifted. Similar AIE behaviors were also found in 2a–2d with an emission enhancement (I_{90}/I_0) of ~ 5 -, 6-, 8- and 4-fold, respectively (Fig. S24–S27, ESI[†]).

CIEE properties

Interestingly, when the test solutions of the compound 2a–2e were prepared in THF and THF/water mixtures with varying water fractions and kept at room temperature above 2 h, the test results are entirely different. As shown in Fig. 4, the fluorescence intensity of 2e remained almost constant in the $\text{H}_2\text{O}/\text{THF}$ mixtures with up to 60% (f_w). However, there was a sharp increase when the water content reached 70%. The fluorescence intensity of 2e in the 70% (f_w) $\text{H}_2\text{O}/\text{THF}$ mixture was about 24 times higher than that in pure THF solution. Contrary to predictions, the fluorescent intensity decreased as a further increase of the f_w . One possible explanation could be that the luminophores had a morphological change in the aqueous medium. In mixtures with a lower f_w , the molecules of luminophores might aggregate slowly, which could form ordered crystalline particles by steady aggregation. In mixtures with

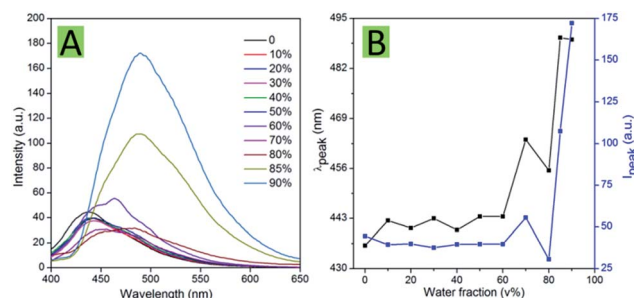


Fig. 3 (A) Emission spectra of 2e in THF and THF/water mixtures with varying water fractions (f_w). (B) Plots of fluorescence peak location and intensity vs. f_w for 2e. Concentration = 20 μM ; excitation wavelength = 360 nm.

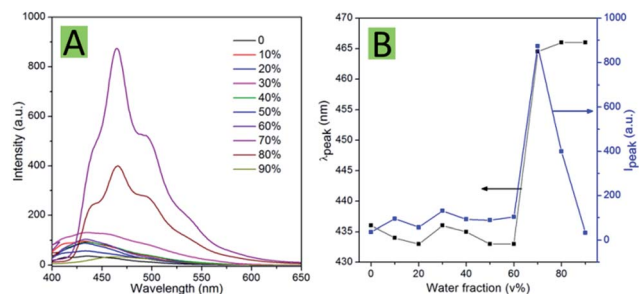


Fig. 4 (A) Emission spectra of 2e in THF and THF/water mixtures with varying water fractions (f_w) and kept at room temperature above 2 h. (B) Plots of fluorescence peak location and intensity vs. f_w for 2e. Concentration = 20 μ M; excitation wavelength = 360 nm.

a high f_w , however, the dye molecules may aggregate quickly and in a random, less emissive manner which leads to a low ratio of crystalline particles and redder amorphous particles.^{26,44–46} Therefore, compound 2e exhibited CIEE properties. Similar CIEE behavior was also found in 2a, 2b and 2d, giving an emission enhancement of >305-, 14- and 22-fold in 30/70 THF–water compared to those in THF (Fig. S28, S29 and S31, ESI[†]). However, 2c showed discrepant CIEE behavior to that of 2e in that it displayed strong emission at a high f_w of 90%, with an intensity \sim 10-fold higher than that in THF (Fig. S30, ESI[†]). However, we found that the quantum yields of 2c in the solution state, the amorphous state and the crystalline states were 0.1%, 9.5% and 57.8%, respectively, evidently suggesting that 2c is indeed CIEE-active.³⁹

Fluorescence quantum efficiency

To evaluate the emissions quantitatively, an amorphous thin film of 2a–2e was prepared and the quantum efficiencies of the dye molecules in dilute solution ($\Phi_{F,s}$), in amorphous thin film ($\Phi_{F,f}$) and in crystalline solid ($\Phi_{F,c}$) states were further studied. The $\Phi_{F,s}$ values of 2a–2e were as low as 1%, 0.6%, 0.1%, 0.5% and 0.3% (Chart 1), respectively, which were estimated in THF using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as standard.²⁸ The $\Phi_{F,f}$ and $\Phi_{F,c}$ of 2a–2e were measured using a calibrated integrating sphere. The $\Phi_{F,s}$, $\Phi_{F,f}$ and $\Phi_{F,c}$ values of 2a–2e are listed in Chart 1, and these results further validate their AIE and CIEE activity. It is irrevocably clear that the quantum yield of the crystalline particles was much higher than that of the amorphous particles. Therefore, emission intensity of luminophores decreased with a higher fraction of water. Moreover, it is obvious that, with an additional methyl group, 2d shows a much lower efficiency of 25.7% compared to that of the other compound. This may be attributed to the rotation and vibration of the methyl group, which induced exciton energy consumption even in the crystalline state.⁹

Mechanochromic

In comparison to the photophysical properties of the CIEE active luminogens, the morphology dependent emission and multiple colored emissions switching in the solid state were more dramatic. Hence, their solid emission properties were examined by grinding

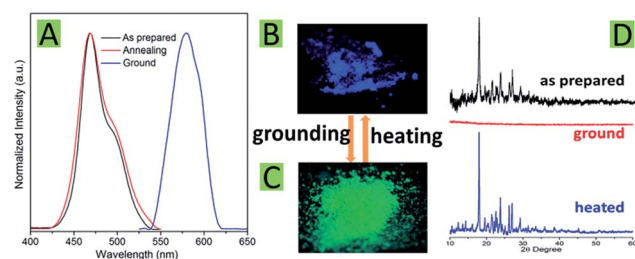


Fig. 5 (A) Emission spectra of the as prepared, ground and annealing 2e solids, (D) their XRD patterns and (B and C) their photographs taken under UV illumination.

the as prepared solids of luminogens. As shown in Fig. 5, while the as prepared solid powders of 2e revealed strong blue emission at 469 nm, they emitted yellow lights with a maximum at 579 nm upon gently grinding with a pestle. Meanwhile, as visualized by the naked eye, the emission of as prepared solid powders of 2e was much stronger than the ground ones. Upon further annealing at 60 °C for 10 min or fuming with solvent for 3 min, the emission color and intensity of ground samples was fully recovered, suggesting the reversibility of the mechanochromic fluorescence process. The invertibility of mechanochromic switching was examined by the grinding–annealing exposure processes. As depicted in Fig. S32 (ESI[†]), switching between blue and yellow emission colours can be repeated with many cycles without fatigue because of the non-destructive nature of the mechanical stimuli. These surveys further demonstrate the mechanochromic fluorescent behaviour of luminogens normally transforms from crystals to amorphous solids.

To obtain information on the mechanism, powder XRD analysis was conducted. The as prepared powder exhibited quite intense and sharp diffraction peak in Fig. 5D, which was indicative of their regular crystalline structure. No diffraction peak was observed with mechanical grinding, which reflected a disordered molecular packing. When annealed or fumed with solvent, sharp diffractions emerged again. This indicated the restoration of an ordered crystalline lattice. The results further prove that mechanochromic characteristic are distinctly associated with the arrangement of molecules, which highly influences their photophysical properties.⁴⁷ Similar phenomena were also observed for 2a and 2d, whose as prepared/ground solid emission maxima are 452/507 and 462/581 nm, respectively. 2d displayed markedly excellent mechanochromic behavior with high contrast of up to 119 nm, which is rarely found in ICT dyes upon a simple ground (Fig. S33–S36, ESI[†]). However, 2b and 2c had no such property because they had excellent crystallization capability. To test that hypothesis, the XRD analysis of 2b and 2c was conducted in as prepared and ground powder (Fig. S37, ESI[†]). Before and after grinding, 2b and 2c were always formed in the crystalline but not in the amorphous state. In other words, if an AIE compound was provided with strong crystallizability to form stable crystals such that the change from the crystalline to the amorphous phase could not be realized, the compound would not be mechanochromic.⁴⁸

X-ray crystal structure

To further understand their AIE-, CIEE-active and mechanochromic behaviors, we have obtained the single crystal structures to disclose their molecular conformation and packing modes. The single crystal structures and molecular packing plots of 2a–2e are shown in Fig. 6, and crystal data of 2a–2e are listed Tables S2–S6 (ESI†). As the picture suggests, all compounds adopted highly twisted conformations and the twisted angles between the phenyl rings at 9-position of carbazole and carbazole varied from 47.39° to 119.89°, which resulted in intramolecular rotations in solutions, effectively consuming exciton energies and leading to poor fluorescence. However, when aggregated as nanosuspensions or solid powders, such rotations were restricted, thereby yielding enhanced emissions. We further investigated the twisted angles between the carbazole and the vinyl groups. It was found that the angles decreased from 12.00° to 2.10° with the redshifted emission. The smaller twisted angles demonstrated more planar conformation of vinylcarbazole moiety and better conjugation of the whole molecule, which was almost consistent with their emission maxima.

The origin of the luminescence switching can also be attributed to the extremely twisted conformations, which can be planarized through mild mechanical stimuli and restored upon thermal annealing or solvent fuming. In the crystalline state, the luminogens may assume a more twisted conformation so as to fit into the crystalline lattice. This twisted stacking architecture shortens their effective conjugation lengths, thereby making their emission wavelength blue shift. While the crystalline lattice collapses by external stimuli, the

dye molecules may change into a more planar conformation, thus producing much redder emissions. Besides van de Waals forces, compound 2a–2e showed weak intermolecular hydrogen bonding interactions such as C–H⋯C, C–H⋯N, C–H⋯O and C–H⋯Cl (Fig. 6). The molecular conformation have been locked and rigidified by these multiple interactions, which greatly decreasing the energy loss through non-radiative relaxation channels. Upon amorphization by mechanical force, some of these interactions are lost. That explains why the crystals show stronger emission than amorphous phase.⁴³ As for dye 2b, however, there was an offset face-to-face π – π packing modes and the molecule was packed very tight which enhanced the molecular rigidity and stability of the crystal lattice. While compound 2c with the smallest twisted angles adopted an almost planar conformation. Thus, 2b and 2c cannot change molecular conformation upon external stimulation. In addition, compound 2d and 2e exhibited looser molecular packing modes compared to 2a, resulting in the formation of some cavities, as shown in Fig. 6. The presence of large amounts of cavities in the crystals makes the molecules highly slideable and compressible. Therefore, the luminogens more easily lead to the planarization of molecular conformation upon facile mechanical stimuli.^{43,49} This may be the main reason that 2d and 2e have a bathochromic shift of the emission wavelength (nearly 120 nm) after grinding. All these data, including stator–rotor structures, twisted conformations and crystal packing modes, should be responsible for the AIE, CIEE and mechanochromic feature of the five compounds.

Thermal properties

Thermal properties of the luminogens were also evaluated. Thermal gravimetric analysis (TGA) (Fig. 7A and S38–S40, ESI†) results indicated that all luminogens are thermally stable, with T_d (defined as the temperature at which a sample loses its 5% weight) from 362 °C to 408 °C. The curves obtained by differential scanning calorimetry (DSC), which was used to study the behaviour of as prepared 2e (Fig. 7B) under heating, showed two marked exothermic transition peaks in DSC curves. One peak at the lower temperature was attributed to the phase transition from solid crystalline to liquid crystal ($T_{S-LC} = 81.4$ °C), and the other peak at the higher temperature was ascribed to the phase

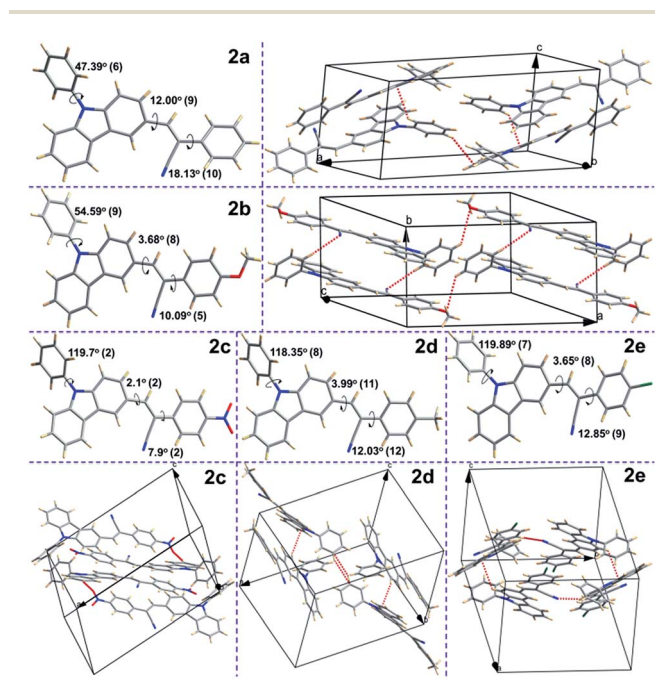


Fig. 6 Single-crystal structures and molecular packing plots of 2a–2e. Carbon, hydrogen, oxygen, nitrogen and chlorine atoms are shown in gray, yellow, red, blue and green, respectively.

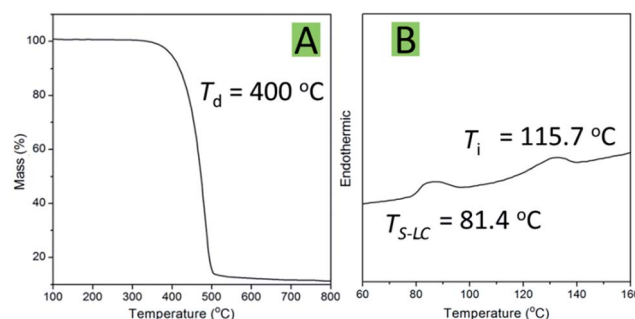


Fig. 7 (A) TGA thermograms of 2e recorded under nitrogen atmosphere at 10 °C min⁻¹ scan rates. (B) DSC curve of the as-prepared 2e.

transition from liquid crystal to isotropic melt ($T_i = 115.7\text{ }^\circ\text{C}$), reflecting that two phases were present before isotropic melting.⁵⁰ The T_g value of 2a–2d are were as high as 40.5, 40.2, 72.3 and 43.5 $^\circ\text{C}$, respectively.

Conclusions

In summary, multifunctional D- π -A luminogens based on carbazole and TPAN were designed and synthesized with high yields. These compounds showed typical ICT, AIE and CIEE characteristics, excellent thermal stability (T_d up to 408 $^\circ\text{C}$) and high crystalline states efficiency (up to 77%). What is more, their emission could be tuned from blue to orange by simply altering electron acceptors (donors). Additionally, the luminescent efficiency and the color of the compounds 2a, 2d and 2e can be reversibly converted by a simple grinding-vapour or a pure thermal treatment. Particularly, 2d exhibited remarkable mechanochromic properties with a contrast up to 119 nm, something rarely found in similar ICT luminogens. According to the analysis of the X-ray crystal structure, the destruction of the crystalline structure leads to the planarization of molecular conformation and the increase of the conjugation degree, which is considered as a possible reason for the redshift of fluorescence emission. However, 2b and 2c have no mechanochromic characteristics due to their excellent crystallization capability, which indicates that AIE compound with strong crystallizability cannot easily realize mechanochromic behavior. The analysis of X-ray crystal structure further proved that the mechanochromic property associated with the molecular packing modes and twisted conformations. Such attractive properties render these luminogens promising candidates for versatile potential applications in volatile organic compounds and stress sensors, two-photon absorption devices, OLEDs, optical data storage and bioimaging in the future. More importantly, the remarkable effect of substituent groups on the mechanochromism of cyanostilbene derivatives will provide an effective way to obtain full-color mechanochromic optoelectronic materials with high contrast.

Acknowledgements

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