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Reversible solid-state mechanochromic luminescence originated from aggregation-induced enhanced emission-active Donor–Acceptor cruciform luminophores containing triphenylamine

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Abstract

Two D-A type cruciform luminophores **FB-CTPAEB** and **DFB-CTPAEB** were designed and prepared. The two compounds exhibited unique intramolecular charge-transfer (ICT) and solid-state fluorescence behavior. The results show that both compounds exhibit AIEE behavior and high solid-state luminescence efficiency (up to 0.693 and 0.442, respectively). Moreover, **FB-CTPAEB** and **DFB-CTPAEB** show remarkable mechanofluorochromic (MFC) properties. Once the as-prepared samples were subjected to grinding, the emission of the two cruciform luminophores was red shifted by 52 nm and 46 nm, correspondingly, their fluorescence colors changed from yellow and reddish orange to red, respectively. The fluorescence emission changes induced by grinding can be restored by solvent-fuming and regenerated by grinding. PXRD analysis revealed that the MFC behavior of **FB-CTPAEB** and **DFB-CTPAEB** came from the transformation between crystalline and amorphous states upon external stimuli. Meanwhile, the

extension in molecular conjugation caused by planarization of molecular conformation and subsequent planar intramolecular charge transfer (PICT) process were responsible for the red-shifts in the PL spectra.

Keywords: cruciform; triphenylamine; intramolecular charge-transfer; aggregation-induced enhanced emission; mechanofluorochromism

1. Introduction

Mechanofluorochromic (MFC) materials are a class of "smart" materials that change their solid-state emission color in response to external force stimuli (such as grinding, pressing, shearing, deformation, etc.) [1]. As the switchable emissions could be easily obtained by destroying their relative loose structure arrangement under the external stimulus instead of altering the chemical structures, these materials have attracted wide attention due to their potential applications in optical data storage devices [2], mechano-sensors [3], security inks [4], optoelectronic devices [5] and other fields. To date, many MFC materials, such as 3,6-bis(aryl)-1,4-diketo-pyrrolo[3,4-c]pyrroles (DPPs) [6], tetraphenylethene [1f,7], oligo(p-phenylene vinylene) [8], 9,10-divinylanthracene [9], triphenylacrylonitrile [5c,7e,10] and organoboron complexes [11,12], have been developed. However, MFC materials that exhibit high solid-state luminescence efficiency and an obvious color contrast are still rare, partly because many organic luminescent dyes usually suffer from aggregation caused quenching (ACQ) [13], which leads to poor solid state emission, and then it is disadvantageous to the observation of MFC phenomenon. In 2001, Tang et al. reported on an important class of landmark

materials with anti-ACQ effects, namely aggregation-induced emission (AIE) materials [14], which are nonluminescent in the dilute solutions, but become highly emissive in the aggregate states. In the next year, Park's group reported on aggregation-induced enhanced emission (AIEE) materials [15], and then in 2010, this group published the cyano-distyrylbenzene derivative that exhibited both AIE activity and MFC behavior [16], which made people realize that there was a certain relationship between AIE and MFC properties of the luminophore. Thus, great attention has been paid to the design and synthesis of new AIE- or AIEE-MFC luminophores, and a number of AIE or AIEE fluorophores with MFC behavior have been reported in Chi's laboratory and by other groups [7,17]. However, the development of organic AIE- or AIEE-MFC materials that possess high contrast mechanofluorochromism, excellent reversibility, and high solid-state fluorescence efficiency is still strikingly desirable. In addition, MFC phenomena and mechanisms are still debated, and there is still no clear general design strategy to design AIE- or AIEE-MFC materials at present. It is difficult to predict in advance whether a new AIE fluorescent chromophore has MFC performance. Therefore, it is important to develop new MFC dyes for an in-depth understanding of the underlying mechanism of AIE- or AIEE-MFC behavior at the molecular level and establish the structure-property relationships of these compounds.

As an important kind of fluorescent chromophores, cruciform fluorophores have gained an increasing interest because of their unique molecular structures and fascinating optical properties [18]. Recently, some cruciform fluorophores exhibiting both obvious AIE character and high contrast MFC properties have been reported by our group [19]. In the current work, we have designed and synthesized another structural type of cruciform molecules FB-CTPAEB and DFB-CTPAEB (Scheme 1). In these two molecules, two different arms with different functions intersected at a central benzene core: in the middle of one arm is electron-withdrawing dicyanovinylbenzene segment, and at both ends of this arm is electron-donating triphenylamine unit. Thus, the spatially separated frontier molecular orbitals (FMOs) in species could be realized. Meanwhile, in the other arm there are two benzene rings, on which the substituents can effectively regulate the electronic structure of the whole molecule. On the other hand, the space congestion caused by four large substituents on the central benzene ring forces them distort from the ring plane, which would depress the molecular close π - π packing and enhance solid luminescence efficiency. As expected, FB-CTPAEB and DFB-CTPAEB possess significant AIEE characteristics with high solid state efficiency of 0.693 and 0.442, respectively. The crystalline to amorphous phase transition of the two luminophores by grinding resulted in excellent MFC performance and well distinguishable color contrast with emission peak shifts of 52 nm and 46 nm was obtained, respectively.



Scheme 1 The molecular structures of FB-CTPAEB and DFB-CTPAEB.

2. Experimental section

2.1. Materials and Measurements

General. The ¹H (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained with a Bruker-Avance III spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. The high-resolution mass spectrometry (HRMS) was carried out with a MALDI-TOF MS Performance instrument (Shimadzu, Japan). C, H, and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. The UV-vis absorption spectrum was recorded on a Shimadzu UV-2550 spectrophotometer. Fluorescent measurements were obtained on a Cary Eclipse Fluorescence Spectrophotometer. The absolute fluorescence quantum yields for the as-prepared solids were measured on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. Powder X-ray diffraction (XRD) was performed on a Bruker D8 Focus Powder X-ray diffraction instrument. Dynamic light scattering (DLS) measurements were performed on the BI-200SM Laser Light Scattering System (Brookhaven). Density functional theory (DFT) calculations were performed on FB-CTPAEB and **DFB-CTPAEB** at the B3LYP/6-31G(d) level using the Gaussian 09W program package.

Preparation of the samples for AIEE study. A stock solution of luminogen in THF with a concentration of 1.0×10^{-3} M was prepared. An aliquot (0.1 mL) of the stock solution was transferred to a 10 mL volumetric flask. After the appropriate amount of THF was added, distilled water was added slowly under sonication to

give 1.0×10^{-5} M solution with different fractions of water. The PL measurement of the resultant solutions was performed immediately.

Preparation of the samples for mechanofluorochromism study. The ground powders were prepared by grinding the initial powders with a pestle and mortar. The fumed samples were obtained by fuming the ground powders with DCM for 2 min.

Materials. Ethanol was distilled under normal pressure over sodium under nitrogen before use. The other chemicals were used as received without further purification.

2.2. Synthesis

4,4''-bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (3a)

2,5-Dibromoterephthalaldehyde **1** (4.00 g, 13.70 mmol), **2a** (7.30 g, 38.44 mmol), Na₂CO₃ (8.00 g, 75.48 mmol) and Pd(PPh₃)₄ (150 mg, 0.130 mmol) were added into toluene/H₂O (300 mL, v/v = 3/2). Then the mixture was heated to reflux and stirred for 48 h under a nitrogen atmosphere. After cooling to room temperature, the organic layer was separated, the aqueous layer extracted with DCM, the combined organic layer dried over anhydrous Na₂SO₄. Upon evaporating off the solvent, the crude product was subjected to purification by column chromatography (silica gel; petroleum ether/DCM, v/v = 2/1), affording a light yellow solid (5.15 g). Yield 89%. ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 2H), 8.14 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.60 (d, *J* = 7.6 Hz, 4H) (Fig. S5); ¹³C NMR (100 MHz, CDCl₃) δ 190.49, 143.57, 139.91, 136.57, 130.64, 130.58, 130.30, 125.84, 125.81 (Fig. S6);

HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₂₂H₁₂F₆O₂ 422.0741; Found 422.3416 (Fig. S7). Anal. Calcd (%) for C₂₂H₁₂F₆O₂: C 62.57, H 2.86; Found: C 62.63, H 2.78.

3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':4',1''-terphenyl]-2',5'-dicarbaldehyde (3b)

By following the synthetic procedure for **3a**, **3b** was synthesized by using 2,5-Dibromoterephthalaldehyde **1** (4.00 g, 13.70 mmol), **2b** (9.91 g, 38.44 mmol), Na₂CO₃ (8.00 g, 75.48 mmol) and Pd(PPh₃)₄ (150 mg, 0.130 mmol) as the reagents. The crude product was purified by column chromatography (silica gel, DCM/petroleum ether, v/v = 1/1), affording a yellow solid (6.36 g). Yield 83%. ¹H NMR (400 MHz, CDCl₃) δ 10.08 (s, 2H), 8.16 (s, 2H), 8.08 (s, 2H), 7.92 (s, 4H) (Fig. S8); ¹³C NMR (100 MHz, CDCl₃) δ 189.27, 142.30, 138.35, 136.58, 132.74, 132.41, 131.73, 129.73, 129.70, 124.23, 122.98, 121.50 (Fig. S9); HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₂₄H₁₀F₁₂O₂ 558.3158; Found 558.3179 (Fig. S10). Anal. Calcd (%) for C₂₄H₁₀F₁₂O₂: C 51.63, H 1.81; Found: C 51.70, H 1.89. (**2Z,2'Z)-3,3'-(4,4''-bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-2',5'-diyl)bis(2-(4 -(diphenylamino)phenyl)acrylonitrile) (FB-CTPAEB)**

Compound **3a** (0.74 g, 1.75 mmol) and 2-(4-(diphenylamino)phenyl)acetonitrile (1.25 g, 4.40 mmol) were added into dry ethanol (50 mL), and then CH₃ONa (0.25 g, 4.63 mmol) was added quickly. The mixture was refluxed with stirring for 6 h under a nitrogen atmosphere. After cooling to room temperature, the resulting precipitate was collected by filtration, and dried under vacuum. The crude product was purified

by column chromatography (silica gel, DCM/petroleum ether, v/v = 1/1), affording a bright orange red solid (1.46 g). Yield 87%. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 8 Hz, 4H), 7.42 (d, *J* = 8.8 Hz, 4H), 7.36-7.30 (m, 10H), 7.15-7.10 (m, 12H), 7.06 (d, *J* = 8.8 Hz, 4H) (Fig. S11); ¹³C NMR (100 MHz, CDCl₃) δ 149.42, 146.80, 142.52, 140.38, 136.85, 133.67, 130.74, 130.57, 130.35, 130.24, 129.55, 126.98, 126.18, 125.69, 125.65, 125.40, 124.16, 122.70, 121.83, 117.92, 114.67 (Fig. S12); HRMS (MALDI-TOF) m/z: [M+H]⁺ Calcd for C₆₂H₄₁F₆N₄ 955.3235; Found 955.1653 (Fig. S13 and S14). Anal. Calcd (%) for C₆₂H₄₀F₆N₄: C 77.98, H 4.22, N 5.87; Found: C 77.91, H 4.18, N 5.94.

(2Z,2'Z)-3,3'-(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':4',1''-terphenyl]-2',5'-di yl)bis(2-(4-(diphenylamino)phenyl)acrylonitrile) (DFB-CTPAEB)

By following the synthetic procedure for FB-CTPAEB, DFB-CTPAEB was 3b (1.00)synthesized by using 1.79 mmol), g, 2-(4-(diphenylamino)phenyl)acetonitrile (1.27 g, 4.48 mmol) and CH₃ONa (0.26 g, 4.81 mmol) as the reagents. The crude product was purified by column chromatography (silica gel, DCM/petroleum ether, v/v = 3/2), affording a bright orange red solid (1.68 g). Yield 86%. ¹H NMR (400 MHz, CDCl₃) δ 8.29 (s, 2H), 8.02 (s, 6H), 7.41 (d, J = 8.8Hz, 4H), 7.34-7.28 (m, 10H), 7.16-7.11 (m, 12H), 7.05 (d, J = 8.4Hz, 4H) (Fig. S15); ¹³C NMR (100 MHz, CDCl₃) δ 149.70, 146.75, 140.79, 139.15, 135.14, 133.94, 132.77, 132.44, 132.10, 131.77, 130.75, 130.04, 129.54, 126.99, 125.79, 125.42, 124.42, 124.21, 122.21, 122.17, 122.14, 121.78, 121.71, 118.99, 117.60, 116.27 (Fig. S16); HRMS (MALDI-TOF) m/z: [M]⁺ Calcd for C₆₄H₃₈F₁₂N₄ 1090.2905; Found 1090.5599 (Fig. S17 and S18). Anal. Calcd. (%) for C₆₄H₃₈F₁₂N₄: C 70.46, H 3.51, N 5.14; Found: C 70.51, H 3.44, N 5.21.

3. Result and discussion

3.1. Synthesis of FB-CTPAEB and DFB-CTPAEB

The preparations of the cruciform luminophores FB-CTPAEB and DFB-CTPAEB are summarized in Scheme 1. Suzuki-Miyaura coupling of 2,5-dibromoterephthalaldehyde 1 with the aromatic boric acid 2a or 2b was carried out in the mixed solvent of toluene and H₂O by using Pd(PPh₃)₄ as a catalyst in high yields of 89% and 83%, respectively. Then a subsequent standard Knoevenagel condensation catalyzed by sodium methoxide produced the target compounds **FB-CTPAEB** and **DFB-CTPAEB** with good yields of 87% and 86%, by treating the intermediate compounds 3a or 3b with 2-(4-(diphenylamino)phenyl)acetonitrile, respectively. Both FB-CTPAEB and DFB-CTPAEB have good solubility in organic solvents such as chloroform, DCM, THF, benzene and toluene, but show poor solubility in alcohols and aliphatic hydrocarbon solvents, such as cyclohexane, *n*-hexane, methanol and ethanol. The structures of all the intermediates and target molecules were fully characterized by different spectroscopic methods, including ¹H and ¹³C NMR spectroscopy and MALDI-TOF high resolution mass spectrometry, as well as C, H, N elemental analysis.



Scheme 2 Synthetic routes of FB-CTPAEB and DFB-CTPAEB.

3.2. UV-vis absorption and fluorescent emission spectra in solutions

Due to the existence of typical electron-donating triphenylamine and electron-accepting cyano groups, FB-CTPAEB and DFB-CTPAEB become typical D-A molecules, and it offers ready ICT process in these two molecules [18d,19a]. Since photophysical properties of the D–A conjugates in solutions are strongly dependent on the solvent polarity, we thus examined the absorption and emission properties of both compounds in varying solvents, and the corresponding photophysical data were collected in Table S1 and S2. As shown in Fig. 1a, each compounds displayed two intense absorption bands, the one that located at approximately $\lambda < 360$ nm was attributed to the $\pi - \pi^*$ transition delocalized along the π -electronic system, while the other absorption band ranging from 380 nm to 550 nm with a high molar extinction coefficient $(10^4 \text{ M}^{-1} \text{ cm}^{-1})$ was assigned to the intramolecular charge transfer (ICT) transition from electron rich triphenylamine units to the dicyanovinylbenzene segments, it can be confirmed by the solvent-dependent absorption spectra, which blue-shifted slightly with increasing solvent polarity. For example, the ICT bands of FB-CTPAEB and DFB-CTPAEB

emerged at 450 nm and 461 nm in cyclohexane, and blue-shifted to 435 nm and 436 nm in DMF, respectively (Table S1 and S2). The above phenomenon might be due to the less conjugation degree of the compounds resulted from a larger dihedral angle in more polar solvents [11d, 20].

The emission spectra of FB-CTPAEB and DFB-CTPAEB in different solvents showed obvious positive solvatochromicity properties (Fig. 1c and d, Table S1 and S2). In nonpolar cyclohexane, the two compounds could emit green and yellow lights located at 540 nm and 556 nm, respectively, and the emission bands gave the vibrational structures, which is the LE (locally excited) ones [21]. With the of FB-CTPAEB increasing solvent polarity, the emission bands and **DFB-CTPAEB** red-shifted significantly. For example, they emitted both red lights centered at 624 nm and 642 nm in the moderately polar THF, respectively, and in highly polar DMF, the lights that the two compounds emitted were extremely weak with the emission wavelengths of 658 nm and 667 nm. The above results are consistent with the strong ICT character of the solvent relaxed emissive state. The solvatochromic behaviors of FB-CTPAEB and DFB-CTPAEB can be further quantitatively described by the Lippert–Mataga equation [22]. The Stokes shifts (Δv) of the two compounds in varying solvents were calculated and listed in Table S1 and S2. From the plots of $\Delta v - \Delta f$ (Fig. S1), we could find that the slopes of the fitting line for FB-CTPAEB and DFB-CTPAEB were as high as 12546 and 14772, exhibiting significant solvatochromism effect. In addition, in the same solvent, the maximum ICT absorption and emission wavelengths of FB-CTPAEB is smaller

than that of **DFB-CTPAEB**, indicating the ICT degrees of the two compounds in the excited state increased in a sequence of **FB-CTPAEB** < **DFB-CTPAEB** [19,23]. The fluorescence quantum yields (Φ_f) of **FB-CTPAEB** and **DFB-CTPAEB** in different solvents are also determined by using quinine sulfate ($\Phi_f = 0.546, 0.5 \text{ mol}$ L^{-1} H₂SO₄) as the standard (Table S1 and S2). The Φ_f of the two compounds in solution decreases from 0.328 and 0.270 (cyclohexane) to 0.131 and 0.104 (chloroform) and less than 0.001 (DMF), respectively, which is consistent with a positive solvatokinetic effect [11d]. **FB-CTPAEB** and **DFB-CTPAEB** show weak fluorescence in highly polar solvents due to the fast interconversion from the emissive LE state to the low emissive ICT state; however, they exhibit much stronger emission in nonpolar solvents due to restricted ICT transitions.



Fig. 1 Normalized UV-vis absorption spectra of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b), and normalized PL spectra of **FB-CTPAEB** (c, $\lambda_{ex} = 450$ nm) and **DFB-CTPAEB** (d, $\lambda_{ex} = 465$ nm) in different solvents (1.0×10^{-5} mol L⁻¹).

To reveal the influence of the geometric and electronic structures of FB-CTPAEB and DFB-CTPAEB on their photophysical properties, we performed density functional theory (DFT) calculations on the two cruciforms with the Gaussian 09W program using the DFT/B3LYP/6-31G(d,p) method. Fig. 2 shows the optimized molecular configuration and the electron distribution of the HOMOs and LUMOs for FB-CTPAEB and DFB-CTPAEB. Obviously, the overall electron density of the HOMOs of FB-CTPAEB and DFB-CTPAEB is mainly localized on the electron-donating triphenylamine frameworks, whereas the overall electron density of LOMOs of the two compounds is distributed on the electron-accepting dicyanovinylbenzene fragments. Generally, such electron distribution imparts the dye molecules with an intrinsic ICT property, which is consistent with the measured photophysical data. Furthermore, the above theoretical calculation results illustrate that FB-CTPAEB and DFB-CTPAEB adopt a twisted spatial conformation at their optimized lowest energy states. For FB-CTPAEB, both the dihedral angles between two vinyl planes and the central benzene are 30.2°. And both dihedral angles between two side benzene rings and the central core are 45.3°. In the case of **DFB-CTPAEB**, the corresponding dihedral angles are 30.8° and 46.7°, respectively. The reason for such large twist angles is that the crowding in the central benzene ring forces the surrounding substituents to distort from the ring plane. The specially twisted conformation of the two cruciforms would lead to effective depression of molecular close π - π packing and enhancement of emission quantum yields in the solid state, which may endow the two compounds with AIE characteristics and

MFC behavior.



Fig. 2 The calculated HOMO and LUMO density maps and optimized molecular geometry of **FB-CTPAEB** and **DFB-CTPAEB** at the B3LYP/6-31G(d) level.

3.3. Aggregation-induced enhanced emission (AIEE)

Keeping in mind the reports and our design strategy that constructing molecular framework with large twisted conformation may contribute to interesting AIEE behavior, we explored the AIEE properties of **FB-CTPAEB** and **DFB-CTPAEB** by measuring their absorption and PL spectra in dilute mixtures of water–THF with different water fractions (f_w , the volume percentage of water in THF–water mixtures). The absorption spectra of **FB-CTPAEB** and **DFB-CTPAEB** in the THF/water mixtures are depicted in Fig. 3, which shows that the spectral profiles of the two compounds are significantly changed when f_w was above 50%, the whole

absorption spectra start to increase, indicating the formation of nano-aggregates. The aggregated particles obtained are characterized by dynamic light scattering (DLS) and shows the existence of nano-aggregates as their main constituent in the solvent mixtures with high water contents (Fig. S2 and S3). The emergence of the increase in absorbance and levelling-off tail in the visible region of the absorption spectra originates from the light scattering, or Mie effect, of the nanoaggregate suspensions in the solvent mixtures, which effectively decreased the light transmission in the mixture [19a]. As shown in Fig. 4, FB-CTPAEB and **DFB-CTPAEB** show switched emission in THF-water mixture solutions with f_w , which directly elucidates the AIEE process. In pure THF, the weak reddish orange and red emission for the two compounds with λ_{max} at 625 nm and 643 nm, respectively, was observed. However, their $\Phi_{\rm f}$ is only 0.062 and 0.027. When the proper amount of water is added into THF solution, the PL intensities are gradually quenched and the emission peaks show red-shifts. This is because the addition of water significantly increases the polarity of the mixed solvent, which induces the quenching of fluorescence and the red-shifts of the emission band of the two D-A type compounds. Meanwhile, when f_w is over 50%, the emission peaks of the two luminogens are recovered and the PL intensities start to increase rapidly, respectively, at which solvating powers of the mixtures are so poor that the luminogen molecules tend to aggregate, inside which the encapsulated the two luminogen molecules locate in a nonpolar environment and the ICT process is limited, thus the fluorescence is recovered. When f_w is increased to 95%, the emission of solutions further blue-shifts to 603 nm and 618 nm, whose intensities increase by ca. 3.5-fold and 5.5-fold relative to those of in pure THF solutions, respectively, the bright orange and reddish orange light emitting for FB-CTPAEB and **DFB-CTPAEB** is observed for the aggregates. The changes in the above fluorescence spectra could be attributed to the AIEE effect derived from the formation of molecular aggregates when adding water to the solution. The AIEE nature of FB-CTPAEB and DFB-CTPAEB can also be further confirmed by the vivid contrast fluorescent images of the solvent mixtures from 0% to 95% (insets of Fig. 4b and d). To quantitatively evaluate the AIEE effect of FB-CTPAEB and **DFB-CTPAEB**, the fluorescence quantum yields of the luminogens in solution ($\Phi_{f,s}$) and as prepared solid ($\Phi_{f,aps}$) states are determined. The $\Phi_{f,aps}$ values for **FB-CTPAEB** and **DFB-CTPAEB** (0.693 and 0.442) were much higher than $\Phi_{f,s}$ (0.062 and 0.027), further suggesting the AIEE behavior of the two compounds. Thus, we could get the AIEE factors ($\alpha_{AIEE} = \Phi_{f,aps}/\Phi_{f,s}$) of **FB-CTPAEB** and DFB-CTPAEB as 11.3 and 16.4, respectively.



Fig. 3 UV-vis absorption spectra of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b) in THF/water mixtures with different f_w .



Fig. 4 PL spectra of **FB-CTPAEB** ((a), $\lambda_{ex} = 450$ nm) and **DFB-CTPAEB** ((c), $\lambda_{ex} = 470$ nm) in THF/water mixtures with different f_w . Plot of I/I₀ versus water fraction of **FB-CTPAEB** (b) and **DFB-CTPAEB** (d), where I and I₀ represent the PL intensities in a THF/water mixture with a specific f_w and in pure THF, respectively. The insets of b and d depict the fluorescence images of **FB-CTPAEB** and **DFB-CTPAEB** with various water fractions (from 0% to 90%, excitation wavelength: 365 nm), respectively.

3.5. Mechanofluorochromic (MFC) properties

Generally, the fluorophores that possess the AIE feature, ICT characteristics, and twisted spatial conformation may show mechanochromic luminescence [12,19]. Herein, **FB-CTPAEB** and **DFB-CTPAEB** are greatly anticipated to be mechanochromic active. Thus, the mechanochromic properties of the two compounds are studied. As shown in Fig. 5c and d, the as-prepared samples of **FB-CTPAEB** and **DFB-CTPAEB** could emit intense yellow and reddish orange light under UV irradiation, and both their emitting colors changed into red when

they are ground in a mortar or on a quartz substrate by using a pestle, indicating obvious mechanochromic behavior of the two fluorophores. PL spectra are used to monitor such a color transformation under grinding stimuli. As dispicted in Fig. 5a and b, the emission of the as-prepared FB-CTPAEB and DFB-CTPAEB samples was located at 574 nm and 593 nm, and red-shifted to 626 nm and 639 nm in the ground powders, respectively. It means that the grinding treatment induces spectral red-shifts of 52 nm and 46 nm for the two compounds. An excellent mechanochromic material usually exhibits good reversible changes in color and emission. To check the reversibility of the mechanochromic phenomenon observed for the powders of FB-CTPAEB and DFB-CTPAEB, we treat their ground samples by fuming with DCM vapor. The red emitting ground powders of the two fluorophores could be transferred into yellow and reddish orange emitting solids, respectively, similar to the as-prepared solids, after fuming with DCM for 2 min. Meanwhile, their corresponding maximum emission wavelengths return to 578 nm and 598 nm, respectively. The obtained results indicate the good reversibility of the mechanochromic fluorescence for FB-CTPAEB and DFB-CTPAEB. Moreover, the grinding-fuming fluorochromic process could be repeated many times without any fatigue, suggesting the excellent reversibility in the switching processes (Fig. S4).



Fig. 5 (a) Normalized fluorescent spectra of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b) in different solid-states: as-prepared, grinding and fuming ($\lambda_{ex} = 390$ nm). Photographs of **FB-CTPAEB** (c) and **DFB-CTPAEB** (d) in different solid states under UV light (365 nm).

Generally, the emission behavior of solid emitters depended on the molecular packings. Thus, to gain further insight into the MFC phenomenon, the powder X-ray diffraction (PXRD) patterns for **FB-CTPAEB** and **DFB-CTPAEB** in different solid states are measured. As shown in Fig. 6, it is clear that the as-prepared solids of **FB-CTPAEB** and **DFB-CTPAEB** exhibit many sharp and intense diffraction peaks, indicative of the crystalline forms. By sharp contrast, the corresponding ground powders show very weak, broad, diffused or no diffraction peaks, indicating most of the ordered structures are disrupted, and the disordered molecular packing or amorphous samples are obtained. Moreover, when fumed with DCM vapor, sharp diffractions, similar to those of the as-prepared solids, emerge again, because of the transformation from an amorphous state back to a crystalline state. Therefore, the mechanochromism of **FB-CTPAEB** and **DFB-CTPAEB** originates from the transformations between the ordered crystalline and amorphous states. It is a general

mechanism for many other mechanochromic compounds. Moreover, we believe that the large red-shifts of **FB-CTPAEB** and **DFB-CTPAEB** after the external force applied to the as-prepared samples might come from the conformational change and rotate to a position more parallel to the coplanar under external pressure, leading to extended conjugation and subsequent planar intramolecular charge transfer (PICT) [18d], which can be confirmed by the UV-vis absorption spectra of as-prepared and ground samples (Fig. 7). The as-prepared samples of **FB-CTPAEB** and **DFB-CTPAEB** exhibit strong absorption peaks at 444 nm and 455 nm, after grinding, they red-shift to 449 nm and 450 nm, indicating the extension of π -conjugation after grinding [5c].



Fig. 6 PXRD patterns of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b) in different solid-states: as-prepared, grinding and fuming.



Fig. 7 Normalized UV-vis absorption spectra of as-prepared and ground samples of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b), respectively.

4. Conclusion

In summary, we have demonstrated the molecular design, synthesis, and properties of two twisted donor-acceptor cruciform luminophores FB-CTPAEB and **DFB-CTPAEB**, and studied the impact of molecular structure on photophysical properties from the perspective of electronic and steric effects. FB-CTPAEB and **DFB-CTPAEB** possess highly distorted spatial conformation and significant ICT triphenylamine process from electron-rich unit to electron-poor dicyanovinylbenzene fragment. The two cruciform luminophores show typical AIEE behavior with high solid state efficiency of 0.693 and 0.442, respectively. Moreover, FB-CTPAEB and DFB-CTPAEB exhibit high contrast MFC properties with good reversibility. Under external force stimuli, both yellow and reddish orange emitting as-prepared powders of the two fluorophores could be transferred into red emitting solids. The increase in molecular conjugation caused by planarization of molecular conformation and subsequent PICT process lead to the red-shifts in the PL spectra from 574 nm and 593 nm to 626 nm and 639 nm, respectively. All these excellent properties make the compounds promising stimuli-responsive, smart, luminescent materials for mechanical sensors, rewritable record media, security protection and light-emitting device applications.

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Supporting Information for

Reversible solid-state mechanochromic luminescence originated from aggregation-induced enhanced emission-active Donor–Acceptor cruciform luminophores containing triphenylamine

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solvent	Δf	$\lambda_{abs}/nm \ (\epsilon/M^{-1} \ cm^{-1})$	λ_{em}/nm	$\Delta v_{\rm st}^{\ a}/{\rm cm}^{-1}$	$\Phi_{ m f}^{\ b}$
cyclohexane	~0	307 (54300), 450 (53600)	540	3704	0.257
toluene	0.014	302 (50400), 452 (49800)	571	4611	0.162
chloroform	0.149	303 (53600), 450 (48600)	602	5611	0.131
ethyl acetate	0.201	300 (51800), 436 (45300)	618	6755	0.070
THF	0.210	301 (52100), 441 (45900)	624	6650	0.062
DCM	0.218	300 (53100), 442 (47300)	628	6701	0.082
DMF	0.275	300 (50000), 435 (40900)	658	7791	0.002

Table S1	. Photophy	ysical data	of FB-C	TPAEB	in diff	erent solvents.
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 ${}^{a}\Delta v_{st} = v_{abs}$ - v_{em} . ^bThe fluorescence quantum yield (Φ_{f}) was measured using quinine sulfate as a standard (Φ_{f} =0.546 in 0.5 mol L⁻¹ H₂SO₄).

 Table S2. Photophysical data of DFB-CTPAEB in different solvents.

solvent	Δf	$\lambda_{abs}/nm ~(\epsilon/M^{-1} ~cm^{-1})$	λ_{em}/nm	$\Delta v_{\rm st}^{\ a}/{\rm cm}^{-1}$	${\Phi_{\mathrm{f}}}^b$
cyclohexane	~0	304 (46100), 461 (48800)	556	3706	0.219
toluene	0.014	298 (45600), 460 (44500)	591	4819	0.128
chloroform	0.149	301 (48000), 458 (42500)	616	5600	0.104
ethyl acetate	0.201	302 (51600), 443 (45200)	636	6850	0.031
THF	0.210	301 (49000), 444 (42600)	642	6946	0.027
DCM	0.218	297 (58200), 447 (50300)	642	6795	0.035
DMF	0.275	300 (50200), 436 (41900)	667	7943	0.001

 ${}^{a}\Delta v_{st} = v_{abs}-v_{em}$, ^bThe fluorescence quantum yield (Φ_{f}) was measured using quinine sulfate as a standard ($\Phi_{f} = 0.546$ in 0.5 mol L⁻¹ H₂SO₄).

Fig. S1 Plot of Stokes shift (Δv) of **FB-CTPAEB** and **DFB-CTPAEB** versus Δf of their solutions ($1.0 \times 10^{-5} \text{ mol L}^{-1}$).

Fig. S2 DLS data of **FB-CTPAEB** ($1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$) in THF/water ($f_w = 95\%$).

Fig. S3 DLS data of **DFB-CTPAEB** (1.0×10^{-5} mol L⁻¹) in THF/water ($f_w = 95\%$).

Fig. S4 Maximum fluorescent emission of **FB-CTPAEB** (a) and **DFB-CTPAEB** (b) upon repeating treated by grinding and fuming with DCM.

Fig. S9 13 C NMR (100 MHz) spectrum of 3b.

Fig. S14 MALDI/TOF MS spectrum of FB-CTPAEB.

Fig. S17 MALDI/TOF MS spectrum of DFB-CTPAEB.

Fig. S18 MALDI/TOF MS spectrum of DFB-CTPAEB.

CHR ANA

Highlights for

Reversible solid-state mechanochromic luminescence originated from aggregation-induced enhanced emission-active Donor–Acceptor cruciform luminophores containing triphenylamine

Ying Wang, Dandan Cheng, Hongke Zhou, Xingliang Liu,* Yonghui Wang, Aixia Han, Chao Zhang

1. Two twisted donor–acceptor π -conjugated cruciform luminophores showing unique ICT properties were prepared.

2. The two cruciform luminophores displayed aggregation-induced emission characteristics and high solid state efficiency.

3. They possessed high contrast mechanofluorochromic behavior with good reversibility.