Mechanofluorochromic properties of aggregation-induced emission-active tetraphenylethene-containing cruciform luminophores

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ABSTRACT

Two twisted donor–acceptor cruciform luminophores (DHCS-TPE and DMCS-TPE) that were composed of two π-conjugated segments connected via a central benzene core have been prepared. Such cruciforms showed unique intramolecular charge transfer (ICT) emission, obvious aggregation-induced emission (AIE) properties (ΦAIE = 19 and 20, respectively) and high solid state efficiency (0.913 and 0.424, respectively). Especially, the two compounds exhibited substituent-dependent mechanofluorochromic (MFC) behavior. The as-prepared powders of the more twisted DMCS-TPE could emit strong blue-green light centered at 474 nm, and the fluorescence color changed into yellowish green (531 nm) after grinding, a red shift of 57 nm was observed. Such mechanochromism was reversible upon the treatment of grinding and fuming with DCM. The high contrast MFC behavior of DMCS-TPE originated from the planarization of the molecular conformation and subsequent planar intramolecular charge transfer (PICT) under external force. By sharp contrast, the less twisted DHCS-TPE exhibited no MFC behavior. The reason is that the less twisted molecular conformation of DHCS-TPE generates strong intermolecular forces and close packing. Thus compared to DMCS-TPE, the crystalline solid powders of DHCS-TPE possess higher lattice energy and better structural stability. The grinding of the crystalline solid powders of DHCS-TPE cannot lead to amorphization and mechanofluorochromic luminescence.

1. Introduction

The development of mechanofluorochromic (MFC) materials [1] that change their solid-state emission color in response to external force stimuli (such as grinding, pressing, shearing, deformation, etc.) remains an interesting but challenging subject because such materials not only possess significance in fundamental research but also have potential applications in memory devices [2], sensors [3], security inks [4] and optoelectronic devices [5]. Up to now, there has been an increasing interest in the design and characterization of MFC materials including tetraphenylenethene [6], 9,10-divinylanthracene [7], triphenylacrylonitrile [5c,8] and organoboron complexes [9,10]. Nevertheless, MFC materialspossessing high solid-state luminescence efficiency and an obvious color contrast are still rare. The main reason is that many organic luminescent dyes usually exhibit strong fluorescence in dilute solution, and most of their emissions become weak or thoroughly quenched in solid or aggregation states due to the ACQ effect [11]. To overcome this problem, developing aggregation-induced emission (AIE) luminophore, which was first discovered by Tang and co-workers in 2001 [12], is a rational and promising choice. Generally, AIE molecules possess the strongly twisted conjugated backbones, which can hinder intermolecular close stacking and intense π–π interaction to probably endow such materials with strong solid emission and MFC behavior. And a number of AIE fluorophores have been found to be promising MFC materials [6,7a-c,10,13]. However, creating such organic AIE MFC materials, which combine high contrast mechanofluorochromism, excellent reversibility, and high solid-state fluorescence efficiency, is still strikingly desirable. Thus, great attention should be paid to the design and synthesis of new AIE MFC luminophores, in particular, based on novel frameworks, with high emission in the solid states.

Cruciform fluorophores, which are donor- and/or acceptor-functionalized cross-shaped chromophores with an aromatic ring as the common π-center, have gained an increasing interest owing to their potential applications in chemosensors [14], organic light-emitting
2.1.3. 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.

2.1.4. Materials

THF was distilled from sodium and benzophenone under nitrogen immediately prior to use. Ethanol was distilled under normal pressure over sodium under nitrogen before use. The other chemicals were used as received without further purification. Compound 2 was synthesized according to the literature [18].

2.2. Synthesis

2.2.1. 4,4′-bis(1,2,2-triphenylvinyl)-[1,1′,4′,1″-terphenyl]-2,5″-dicarbaldyde (3)

Compound 1 (4.00 g, 13.70 mmol), 2 (15.47 g, 41.11 mmol), Pd (PPh3)4 (200 mg, 0.173 mmol), Na2CO3 (8.00 g, 75.48 mmol) were added into toluene/H2O (400 mL, v/v = 3/2). The mixture was heated to reflux under nitrogen atmosphere for 48 h. 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, CH2Cl2) affording a light yellow solid (10.13 g), yield 93%. 1H NMR (400 MHz, CDCl3) δ 8.00 (s, 2H), 7.81–7.09 (m, 38H), 6.98 (d, J = 10.8 Hz, 4H), 6.72 (s, 4H), 6.54 (s, 2H), 3.86 (s, 12H) (Fig. S17); 13C NMR (100 MHz, CDCl3) δ 191.87, 144.47, 144.24, 143.42, 143.37, 143.26, 142.06, 139.97, 137.87, 136.38, 134.24, 131.66, 131.34, 131.29, 129.97, 129.42, 129.04, 128.23, 127.85, 127.82, 127.72, 126.87, 126.71, 126.67, 125.31 (Fig. S18); HRMS (MALDI-TOF) m/z: [M]+ Calcd for C60H42O2 794.3185; Found 794.3192 (Fig. S19). Anal. Calcd (%) for C60H42O2: C 90.65, H 6.33; Found: C 90.58, H 5.41.

2.2.2. (2Z,2′Z)-3,3″-(4,4′-bis(1,2,2-triphenylvinyl)-[1,1′,4′,1″-terphenyl]-2,5″-dylv)bis(2-(4-hexyloxy)phenylacylonitrile) (DHCS-TPE)

Compound 3 (1.50 g, 1.89 mmol) and 4 (1.23 g, 5.66 mmol) were added into dry ethanol (150 mL) and dry THF (15 mL), and then CH3ONa (0.31 g, 5.74 mmol) was added quickly. The mixture was refluxed with stirring for 24 h under an atmosphere of nitrogen. 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, CH2Cl2/petroleum ether, v/v = 2/1), affording a bright yellowish-green solid (1.62 g). Yield 72%. 1H NMR (400 MHz, CDCl3) δ 8.16 (s, 2H), 7.47 (d, J = 8.8 Hz, 4H), 7.35 (s, 2H), 7.26 (d, J = 10.8 Hz, 6H), 7.16–7.06 (m, 32H), 6.98 (d, J = 8.8 Hz, 4H), 4.05 (t, J = 6.4 Hz, J = 6.8 Hz, 4H), 1.88–1.81 (m, 4H), 1.54–1.48 (m, 4H), 1.41–1.37 (m, 8H), 0.94 (t, J = 6.8 Hz, J = 7.2 Hz, 6H) (Figs. S20 and S21); 13C NMR (100 MHz, CDCl3) δ 160.17, 143.66, 143.61, 143.54, 143.40, 141.57, 140.91, 140.41, 139.11, 139.16, 139.40, 134.50, 134.41, 130.91, 130.90, 130.32, 129.41, 127.77, 127.68, 127.35, 126.60, 126.57, 126.38, 118.13, 115.03, 113.21, 68.29, 31.58, 29.16, 25.72, 22.62, 14.05 (Fig. S22); HRMS (MALDI-TOF) m/z: [M]+ Calcd for C88H76N2O2 1192.5918; Found 1192.5918 (Fig. S23). Anal. Calcd (%) for C88H76N2O2: C 88.55, H 6.42, N 5.41; Found: C 88.55, H 6.42, N 5.39.

2.2.3. (2Z,2′Z)-3,3″-(4,4′-bis(1,2,2-triphenylvinyl)-[1,1′,4′,1″-terphenyl]-2,5″-dylv)bis(2-(3,5-dimethoxyphenyl)acylonitrile) (DMCS-TPE)

By following the synthetic procedure for DHCS-TPE, DMCS-TPE was synthesized by using 3 (1.60 g, 2.01 mmol), 5 (1.07 g, 6.03 mmol) and CH3ONa (0.33 g, 6.11 mmol) as the reagents. The crude product was purified by column chromatography (silica gel, CH2Cl2/petroleum ether, v/v = 2/1), affording a light yellow solid (1.68 g). Yield 75%. 1H NMR (400 MHz, CDCl3) δ 7.47 (s, 2H), 7.35 (d, J = 8 Hz, 4H), 7.14–6.99 (m, 34H), 6.72 (s, 4H), 6.54 (s, 2H), 3.86 (s, 12H) (Fig. S24); 13C NMR (100 MHz, CDCl3) δ 161.24, 143.81, 143.49, 143.45.
3. Result and discussion

3.1. Synthesis of DHCS-TPE and DMCS-TPE

The synthetic routes for cruciform luminophores DHCS-TPE and DMCS-TPE are shown in Scheme 2. The key intermediate was prepared by Suzuki-Miyaura coupling reaction between 1 and boronic acid 2 catalyzed by Pd(PPh₃)₄ in toluene-H₂O in a high yield of 93%. The target molecules DHCS-TPE and DMCS-TPE were synthesized between 3 and substituted phenylacetonitriles 4 and 5 via standard Knoevenagel condensation in the presence of sodium methoxide, respectively, to give good yields of 72% and 75%. DHCS-TPE and DMCS-TPE are soluble in common organic solvents, such as CHCl₃, CH₂Cl₂, THF, benzene and toluene, but show poor solubility in alcohols and aliphatic hydrocarbon solvents, such as cyclohexane, hexane, methanol and ethanol. It is worth mentioning that we have tried to allow the condensation reaction between 3 and 2-(4-methoxyphenyl)acetonitrile, unfortunately, the product obtained had so poor solubility that it was not soluble in common organic solvents. Therefore, 2-(4-hexyloxyphenyl)acetonitrile was selected to react with 3, which enabled the product DHCS-TPE to possess moderate solubility. All the intermediates and target molecules were characterized by ¹H and ¹³C NMR, MALDI-TOF mass spectrometry, and C, H, N elemental analyses.

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

To investigate the solvent effect on the photophysical properties, the absorption and emission spectra of DHCS-TPE and DMCS-TPE were measured in various solvents, and the corresponding photophysical data were collected in Tables S1 and S2. As shown in Fig. 1a, for compound DHCS-TPE, in different solvents, it exhibited a strong absorption peak at ca. 340 nm originating from π–π* transition and weak bands at the longer wavelength ca. 400 nm attributed to the CT transition between electron donor (tetrphenylethene unit) and electron acceptor (dicyanodistyrylbenzene axis) [19], which could be confirmed by the solvent-dependent emission spectra. Fig. 1c showed the solvent-dependent photoluminescence (PL) spectra of DHCS-TPE. It was found that the maximum emission bands of DHCS-TPE became broad and red-shifted significantly with increasing polarity of the solvent. For example, in cyclohexane, DHCS-TPE gave a strong emission band at 464 nm, but with the increasing solvent polarity, its emission band was red-shifted to 509 nm in DCM accompanied by emission bands broaden. Combined with the large Stokes shifts, the broadening and red-shift of the emission bands, we suggested that intramolecular charge-transfer (ICT) transitions of DHCS-TPE took place in more polar solvents [20]. And the longer wavelength emissions can be assigned to ICT emissions. Similarly, DMCS-TPE displayed the π–π* transition bands at ca. 330 nm and CT transition bands ca. 400 nm (Fig. 1b), and its emission spectra also showed the broadening and red-shift of the emission bands from cyclohexane to DCM (Fig. 1d), indicating an ICT character for the excited state. The effects of solvents on the emission features can be further evaluated by the relationship between the solvent polarity parameter (Δf) and Stokes shift (Δυ) and emission maxima (Lippert–Mataga equation) [21,22]. Δf and Δυ of the two compounds in different solvents are listed in Tables S1 and S2. It was clear that both DHCS-TPE and DMCS-TPE showed positive solvatochromism. Their emission peaks red-shifted and quantum yields decreased gradually with the increasing of Δf. From the plots of Δυ – Δf (Fig. S1), we could find that the slopes of the fitting line for DHCS-TPE and DMCS-TPE were as high as 7448 and 14657, exhibiting significant solvatochromism effect. In addition, in the same solvent, the maximum ICT emission wavelength of DHCS-TPE was smaller than that of DMCS-TPE, indicating the ICT degrees of the two compounds in the excited state increased in a sequence of DHCS-TPE < DMCS-TPE [18,23], which were same as the order of the onset wavelength in absorption (Figs. S2–S7).

For better insight into the influence of the geometric and electronic structures of DHCS-TPE and DMCS-TPE on their photophysical properties, density functional theory (DFT) calculations were performed on the two compounds with the Gaussian 09W package. The geometrical structures are optimized at the B3LYP/6-31G(d) level. Fig. 2 shows the optimized molecular configuration and the electron distribution of the HOMOs and LUMOs for DHCS-TPE and DMCS-TPE. It is found that the LUMO densities for DHCS-TPE and DMCS-TPE are mainly distributed along the acceptor dicyanodistrylbenzene axis. The HOMO densities for DHCS-TPE are located in the whole molecule, and in the case of DMCS-TPE, the HOMO densities were distributed in over the donor tetraphenylethene unit. The reason for the difference in the distribution of the HOMO densities for two molecules is below: the electron-donating ability of the alkoxy can weaken the electron-withdrawing ability of the acceptor dicyanodistrylbenzene axis. And thus the electron-withdrawing ability of the acceptor dicyanodistrylbenzene axis in DHCS-TPE is weaker than that of DMCS-TPE because the electron-donating ability of para-hexyloxy in DHCS-TPE is stronger than that of meta-methoxyl in DMCS-TPE. As a result, the ICT would occur from the donor (tetrphenylethene) to the acceptor (dicyanodistrylbenzene axis) for the excited state. Moreover, DMCS-TPE possesses larger CT degree in the excited state than that of DHCS-TPE. The above inference is consistent with the observed optical property. In addition, for DHCS-TPE, the dihedral angles between two vinyl planes and the central benzene are 28.1° and 32.6°, respectively. And dihedral
angles between two side benzene rings and the central core are 46.6° and 60.3°, respectively. And for DMCS-TPE, the corresponding dihedral angles are 32.5°, 35.5°, 48.4° and 64.5°, which are larger than that of DHCS-TPE. Such high torsional angles should be ascribed to the steric hindrance between tetraphenylethene and substituted cyanostyryl groups. As a result, DHCS-TPE and DMCS-TPE show specially twisted conformation, which disfavors close molecular packing and π–π interactions in the solid state and this may endow them, especially DMCS-TPE, with solid state emission, AIE characteristics and MFC behavior.

3.3. Aggregation induced emission (AIE)

Tetraphenylethene (TPE) is a well-known AIE luminogen. So far, a large number of the molecules containing TPE unit have been developed for their simple synthetic routes and notable AIE performance [6]. When excited with 365 nm UV light, the as-prepared powders of DHCS-TPE and DMCS-TPE could emit strong green and blue-green light, respectively. However, relatively weak blue and yellow light was observed from their dilute THF solutions, revealing their AIE feature. To confirm the AIE nature of DHCS-TPE and DMCS-TPE, we measured their PL spectra in dilute mixtures of water–THF with different water fractions (fw, the volume percentage of water in THF/water mixtures). Because the two compounds are insoluble in water and soluble in THF, increasing the water fraction in the mixed solvent could thus change their existing forms from a solution state in the pure THF to the aggregated particles in the mixtures with high water contents, thereby changing their PL spectra. As shown in Fig. 3, in pure THF, DHCS-TPE and DMCS-TPE could emit blue and yellow fluorescence with maxima at 493 and 561 nm, respectively, but the intensity was weak and Φf is only 0.049 and 0.021. When the proper amount of water is added into THF solution, the PL intensities initially decreased and the emission peaks show red shifts due to the increased solvent polarity. The fluorescence quenching is attributed to the ICT effect in polar solvent for DHCS-TPE and DMCS-TPE with D-A structures. As fw is above 40% and 50%, the emission peaks were recovered and the PL intensities started to increase rapidly for the two luminogens, respectively, at which solvating powers of the mixtures are so worse 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. At a high fw of 90%, the bright blue and yellow-green light emitting of DHCS-TPE and DMCS-TPE is observed for the aggregates, which is about 3 and 2 times higher than that in the pure THF, respectively. At the same time, the emission peaks of the two luminogens blue-shift from 515 (fw = 40% for DHCS-TPE) and 583 nm (fw = 50% for DMCS-TPE) to 484 and 520 nm, respectively. Thus, the increase in PL intensity could be attributed to the AIE effect derived from the formation of molecular aggregates when
adding water to the solution. The aggregated particles obtained are characterized using dynamic light scattering (DLS) and shows the existence of nano-aggregates as their main constituent in the solvent mixtures with high water contents (Figs. S8 and S9). The AIE nature of DHCS-TPE and DMCS-TPE can also be further confirmed by the vivid contrast fluorescent images of the solvent mixtures from 0% to 90% (Fig. 3c and f).

To determine the reason for the AIE effect of DHCS-TPE and DMCS-TPE, the dependencies of the optical properties on solvent temperature were examined. With the decreasing of the system temperature, for the two compounds, their emission peaks red-shift and their fluorescence intensities increased in THF (Fig. S10). Because low-temperature environments can suppress molecular motions (such as torsion and vibration), which might be beneficial to extend the conjugate length of the molecules, and thus the red-shifts of the emission peaks and the enhancement of the PL intensities would occur. Therefore, the main reason for AIE of DHCS-TPE and DMCS-TPE could be attributed to be the restriction of intramolecular rotation (RIR) associated with the aromatic groups and decreased solvent polarity effect when molecules precipitate [10a,b]. To quantitatively evaluate the AIE effect of DHCS-

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**Fig. 3.** PL spectra of DHCS-TPE ((a), $\lambda_{\text{ex}} = 400$ nm) and DMCS-TPE ((d), $\lambda_{\text{ex}} = 370$ nm) in THF/water mixtures with different $f_w$. Normalized fluorescence emission intensities of DHCS-TPE (b) and DMCS-TPE (e) in THF/water mixtures with different $f_w$. The fluorescence images of DHCS-TPE (c) and DMCS-TPE (f) with various water fractions (from 0% to 90%) under UV light (365 nm).
3.4. Mechanofluorochromic (MFC) properties

As discussed above, the two luminogens DHCS-TPE and DMCS-TPE possessing the highly torsional molecular conformations, the AIE feature, ICT characteristics, and moreover high solid state efficiency, would be promising candidates as stimuli responsive smart materials [10]. To investigate whether the two luminogens DHCS-TPE and DMCS-TPE exhibit mechanochromic luminescence, their solid emission properties were studied. The fluorescence responses of DMCS-TPE toward grinding and fuming processes are illustrated in Fig. 4. Upon exciting with UV light, the as-prepared DMCS-TPE solid powders exhibit strong blue-green emission. After the grinding treatment using a pestle and a mortar, the emitting color of DMCS-TPE samples unexpectedly changes into yellowish green (Fig. 4b), indicating the obvious MFC feature. The mechanochromic effect of DMCS-TPE could be reverted to its original color by fuming with DCM vapor for 2 min. And when the fumed samples are re-ground, the fluorescence colors are again changed as the first grinding. The wavelength changes in solid-state emission could be repeated many times without fatigue, suggesting excellent reversibility in the switching processes (Fig. S11). PL spectra were used to monitor such naked-eye-visible fluorescence color changes under grinding and fuming stimuli. As depicted in Fig. 4a, the maximum emission wavelength of the as-prepared DMCS-TPE sample is 474 nm, and red-shifts to 531 nm in the ground powders, implying the PL spectrum of amorphous sample exhibits a significant 57 nm red-shift compared with the initial powders. Moreover, upon DCM fuming, its maximum emission wavelength can blue-shifted to the initial wavelength, which further suggests the reversibility of the mechanochromic fluorescence. Unexpectedly, the luminogen DHCS-TPE has no MFC properties. Grinding did not result in any change in the fluorescence color of DHCS-TPE, and the maximum emission wavelength remains almost unchanged and only the change of 1 nm is observed (Fig. S12).

To further understand the MFC behavior of DHCS-TPE and DMCS-TPE, the X-ray diffraction (XRD) measurements were carried out on their solid-state samples. As shown in Fig. 5, the XRD diffraction curves of the as-prepared DMCS-TPE solid powders display many sharp and intense reflections that are indicative of their regular crystalline nature. By sharp contrast, the ground solids show rather weak, broad, and diffused peaks, indicating disordered molecular packing or amorphous states. However, when fumed with DCM vapor, sharp diffractions, similar to those of the as-prepared solids, emerge again. These results show that after grinding, most of the ordered structures are disrupted. The grinding treatment can convert the crystalline phase to the amorphous state, and the fuming treatments can convert the amorphous phase to the crystalline state through molecular repacking, which realizes the reversible inter-conversion of mechanochromism. Therefore, the mechanochromism of DMCS-TPE is attributed to the transformations between the ordered crystalline and amorphous states. This is a general mechanism for many other mechanochromic compounds. In addition, the different MFC properties of the two compounds may be due to the electronic and steric effects of the peripheral substituents on the acceptor dicyanodimethoxybenzene axis with two para-hexyloxy and four meta-methoxy linkages. The large red-shifts of DMCS-TPE after grinding might be original from the conformational change and rotate to a position more parallel to the coplanar under external force, leading to extended conjugation and subsequent planar intramolecular charge transfer (PICT). This proposal could be evidenced by the UV-vis absorption spectra of as-prepared and ground samples (Fig. S13). It is obvious that the ground DMCS-TPE samples show a clear red-shift relative to that of as-prepared ones, indicating the extension of \( \pi \)-conjugation after grinding. Therefore, the planarization of the molecular conformation and subsequent PICT accounts for the MFC behavior of DMCS-TPE. However, for DHCS-TPE, the diffraction peaks in XRD pattern are coincident with those of the as-prepared powders (Fig. S14), confirming the fact that the green emission samples before and after grinding belong to the same crystalline morphology (Fig. S15). Moreover, the UV-vis absorption and PL spectra of its ground samples are almost the same as those of as-prepared ones, respectively (Figs. S12 and S16). Consequently, the color of the as-prepared and ground DHCS-TPE samples shows no changes. The no MFC behavior of DHCS-TPE might be due to its less twisted molecular conformation, which generates strong intermolecular forces and close packing. Therefore, the crystalline solid powders of DHCS-TPE possess higher lattice energy.
and better structural stability than those of DMCS-TPE. The force of mechanical grinding cannot destroy the unit cell structure of DHCS-TPE crystals.

4. Conclusion

Two twisted donor-acceptor cruciform luminophores DHCS-TPE and DMCS-TPE, which were constructed by two π-conjugated electron-rich tetraphenylenes and electron-poor cyanostyril intersecting at a central benzene core, have been designed and successfully prepared. The impact of molecular structure on photophysical properties was studied from the perspective of electronic and steric effects. It was found that the two cruciforms exhibited unique ICT emission, obvious AIE properties, and strong solid-state fluorescence. The solid fluorescence quantum yield of DHCS-TPE and DMCS-TPE reach 0.913 and 0.424, respectively. More interestingly, the two compounds possess substituent-dependent MFC behavior. Owing to a more twisted molecular conformation, DMCS-TPE with four meta-methoxys on the acceptor dicyanodistyrilbenzene axis shows reversible high contrast MFC nature with large spectral shift of up to 57 nm, while the less twisted DHCS-TPE with two para-hexyloxys on the acceptor dicyanodistyrylbenzene axis has no MFC behavior. Due to the stronger intermolecular force and closer packing of DHCS-TPE, grinding of the crystalline solid powders doesn’t affect their crystalline lattice, and thus grinding of DHCS-TPE crystals cannot lead to amorphization and mechanochemical luminescence. This study not only discloses a particular structure-property relationship between the luminescent polymorphs of organic luminophores, but also provides a perspective of the potential applications of these luminescence-switching polymorphs in the fields of optical displays and visual sensors for multiple external stimuli.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2018.04.021.

References


