Fine-tuning the mechanofluorochromic properties of benzothiadiazole-cored cyano-substituted diphenylethene derivatives through D–A effect

Xiqi Zhang,*a Zhiyong Ma,b Yang Yang,a Xiaoyong Zhang,ac Xinru Jia b and Yen Wei*a

We synthesized three new benzothiadiazole-cored cyano-substituted diphenylethene derivatives (PT-OMe, PT-H, and PT-CF3) with different methoxy, hydrogen, and trifluoromethyl end groups, and the synthesis confirmed by standard spectroscopic methods. These end groups endowed them with different donor–acceptor (D–A) effects, and they provide them with a peculiar and completely opposite mechanofluorochromic property. Red-shifted mechanofluorochromic features were found in the PT-OMe and PT-H compounds, while on the contrary, PT-CF3 showed blue-shifted mechanofluorochromic behavior. The mechanofluorochromic mechanism was explored and attributed to the metastable state of the ground compounds and the crystalline-amorphous phase transformation between the original and ground states. Moreover, these derivatives showed reversible significant mechanofluorochromic properties and reproducibility between ground and annealed states, making them promising stimuli-responsive and smart luminescent materials for mechanoensors, fluorescence switches and light-emitting device applications. The introduction of the D–A effect strategy demonstrated in this work would provide a new path to fine tune the optical features of mechanofluorochromic materials with unique and diverse fluorescent properties.

1. Introduction

Mechanofluorochromic materials are a class of smart materials that change their fluorescent behaviors in response to external force stimuli with superior efficiency and reproducibility, and have aroused great interest because of their mechanosensors, fluorescence switches, security papers, and data storage applications.1–3 Mechanofluorochromic behavior can be achieved by either chemical structural changes in the materials or by transformations of the molecular arrangement and packing mode.1 The number of successful examples reported for mechanofluorochromic materials is still limited because of the insufficient conversion and irreversible reactions involved in the solid-state reactions.4,5 By contrast, the transformation of molecular arrangements to achieve a mechanofluorochromic behavior is more attractive because of the good reversibility and the low demand for these materials.5–9 However, mechanofluorochromic materials that are dependent on changes in the molecular arrangement and packing are still rare, which may be due to two reasons.1 The first one is the lack of guidelines on the structure–property relationships of mechanofluorochromic materials. Another one is the aggregation-caused quenching (ACQ), an effect that exists in most of planar organic compounds at solid state, which constitutes a notorious problem and makes the mechanofluorochromic phenomenon difficult to observe.10–12 In this regard, aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) materials with anti-ACQ features have been developed with various architectures and utilized for chemosensor and bioimaging applications.13–16 These unique anti-fluorescence quenching materials have opened up a new path for the development of new mechanofluorochromic materials.1 Since 2010, a number of new mechanofluorochromic materials based on AIE (or AIEE) materials have been reported with various fluorogens, including tetraphenylethene,17–21 diarylvinylnanthracene,22–24 cyano-substituted diarylethene,25–28 and triphenylethene derivatives.29–31

Fully understanding the structure–property relationship is very important to investigate the mechanofluorochromic mechanism and to further broaden the field of mechanofluorochromic materials. Some recent design strategies have demonstrated the importance of the crystallinity,32–34 the alky (alkoxy) length,35–37 the excimers,38 and the interactions with D–A molecules,39–41 factors that could directly affect the performance of mechanofluorochromic materials. These studies
provided some clues to better understand the structure–property relationship in these materials. Most recently, the Shiki Yagai group reported a strategy for mechanofluorochromic materials by imparting amphiphilic and dipolar characteristics to a luminescent π-conjugated system, and studied the effect of amphiphilic and polar groups. However, systematic investigation of the D–A effect to mechanofluorochromic materials is still pending. Therefore, fine-tuning the mechanofluorochromic properties of these smart materials through the D–A effect is of great scientific interest and highly demanded. In this contribution, we have designed and easily synthesized three novel benzothiadiazole-cored cyano-substituted diphenylethene derivatives with different methoxy, hydrogen, and trifluoromethyl end groups [PT-OMe, PT-H, and PT-CF3, see Scheme 1], which endowed them with different D–A effects. Quantum mechanical computations were conducted to reveal the electronic effect and the twisted conformation of these compounds. Then, solid fluorescence spectra were studied to explore their interesting and unique mechanofluorochromic properties. Afterwards, the mechanofluorochromism was investigated by small and wide-angle X-ray scattering (SWAXS), differential scanning calorimetry (DSC), and time-resolved emission-decay behaviors. The results demonstrated that the introduction of the D–A effect could fine tune the optical properties of the as-prepared compounds with peculiar and completely opposite mechanofluorochromic properties.

2. Experimental details

2.1 Materials and characterization

Tetrakis(triphenylphosphine)palladium(0), 4,7-dibromo-2,1,3-benzothiadiazole, 4-formylphenylboronic acid, tetrabutylammonium hydroxide solution (0.8 M, 5 drops) was added and the mixture was heated to reflux for 2 h with a precipitated yellow solid. The reaction mixture was cooled to room temperature and filtered and washed with ethanol for three times to afford PT-OMe (0.28 g, yield 73%).1H NMR (400 MHz, CDCl3) δ: 3.86 (s, 6H), 6.94–7.04 (m, 4H), 7.45–7.54 (m, 2H), 7.61–7.70 (m, 4H), 7.71–7.80 (m, 2H), 7.89 (s, 1H), 7.97 (d, 1H, J = 8.4 Hz), 8.02–8.17 (m, 6H). 13C NMR (100 MHz, CDCl3) δ (ppm): 160.65, 139.39, 138.92, 134.09, 128.43, 127.58, 127.16, 121.82, 118.14, 112.10, 100.00. MS (FAB) calcd for C38H20F6N4S: C 67.25, H 2.97, N 8.26, S 4.72%; found: C 67.25, H 2.97, N 8.26, S 4.72%.

Fluorescence spectra and life time were measured on FLS 920 lifetime and steady state spectrometer. Differential scanning calorimetry (DSC) curves were performed on TA Instruments DSC Q2000 at a heating rate of 10 °C min⁻¹ under a N2 atmosphere. 1D small and wide angle X-ray scattering (SWAXS) experiments were carried out with a SAXS instrument (SAXSess, Anton Paar) containing Kratky block-collimation system. An image plate was used to record the scattering patterns form from 0.06 to 29 nm⁻¹.

2.2 Synthesis of PT-OMe, PT-H, and PT-CF3

Synthetic routes of the compounds PT-OMe, PT-H, and PT-CF3 are shown in Scheme 1. The intermediate of PTA2 was synthesized according to previous literature. For the synthesis of PT-OMe, a solution of PTA2 (0.22 g, 0.64 mmol) and 4-methoxyphenylacetonitrile (0.28 g, 1.92 mmol) in ethanol (20 mL) was stirred at room temperature. Then tetrabutylammonium hydroxide solution (0.8 M, 5 drops) was added and the mixture was heated to reflux for 2 h with a precipitated yellow solid. The reaction mixture was cooled to room temperature and filtered and washed with ethanol for three times to afford PT-OMe (0.28 g, yield 73%). 1H NMR (400 MHz, CDCl3) δ: 3.86 (s, 6H), 6.94–7.04 (m, 4H), 7.45–7.54 (m, 2H), 7.61–7.70 (m, 4H), 7.71–7.80 (m, 2H), 7.89 (s, 1H), 7.97 (d, 1H, J = 8.4 Hz), 8.02–8.17 (m, 6H). 13C NMR (100 MHz, CDCl3) δ (ppm): 160.65, 139.39, 138.92, 134.09, 128.43, 127.58, 127.16, 121.82, 118.14, 112.10, 100.00. MS (FAB) calcd for C38H20F6N4S: C 67.25, H 2.97, N 8.26, S 4.72%; found: C 67.25, H 2.97, N 8.26, S 4.72%.

The synthetic routes of PT-H and PT-CF3 were similar to that of PT-OMe.

PT-H (72% yield). 1H NMR (400 MHz, CDCl3) δ: 7.39–7.51 (m, 6H), 7.62 (s, 2H), 7.68–7.78 (m, 5H), 7.90 (s, 2H), 8.06–8.19 (m, 7H). 13C NMR (100 MHz, CDCl3) δ (ppm): 154.00, 141.53, 139.30, 134.52, 133.83, 132.84, 129.79, 129.84, 129.22, 128.43, 127.58, 126.16, 121.14, 112.10, 100.00. MS (FAB) calcd for C38H20F6N4S: C 67.25, H 4.31, N 9.35, S 5.37%.

PT-CF3 (70% yield). 1H NMR (400 MHz, CDCl3) δ: 7.61–7.77 (m, 5H), 7.78–7.87 (m, 4H), 7.90 (s, 2H), 8.00–8.09 (m, 3H), 8.10–8.23 (m, 6H). MS (FAB) calcd for C38H20F6N4S: C 79.68, H 4.09, N 10.32, S 5.91%; found: C 79.75, H 4.04, N 10.27, S 5.92%.

3. Results and discussion

The fluorogens PT-OMe, PT-H, and PT-CF3 were prepared following the synthetic routes shown in Scheme 1 and produced yields of 70–73%. Their structures were characterized and confirmed by standard spectroscopic methods. To obtain the lowest energy spatial conformations of the compounds, we conducted quantum mechanical computations via Gaussian 03 software. The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOS) of these...
compounds were obtained (Fig. 1) according to the density functional method at the B3LYP/6-31 G level after the structural optimization.43

The HOMOs of these compounds exhibited dispersed electron cloud distributions located at the conjugated benzothiadiazole-cored cyano-substituted diphenylethene system of the molecules, whereas the electron clouds of the LUMOs showed migration from both sides of the molecules to the benzothiadiazole core. The migration trend of the electron clouds from HOMO to LUMO is in this order: PT-OMe > PT-H > PT-CF3. Moreover, all the as-prepared compounds adopted twisted spatial conformations according to the optimized structures. The dihedral angles of the benzothiadiazole group and the adjacent phenyl group (Plans A and B) were calculated to be 36° for the three compounds, however, the dihedral angle of the two phenyl groups (Plans B and C) in the cyano-substituted diphenylethene conjugated system were found to be markedly different and determined as follows: 26° for PT-OMe, 32° for PT-H and 36° for PT-CF3.

The twisted conformations of the molecules may generate mechanochromic properties for them.17 Therefore, we scratched the compounds with a metal spatula directly, while they were cast on filter paper directly. The fluorescent color of PT-OMe immediately changed from yellow to orange (Fig. 2, left), revealing a conspicuous red-shifted mechnanofluorochromatic feature. The as-prepared PT-H also showed red-shifted mechanofluorochromatic property. However, the PT-CF3 compound exhibited a peculiar and completely opposite blue-shifted mechanofluorochromatic performance, as the original orange fluorescence changed to yellow light after scratching. This interesting, unique and diverse mechanofluorochromatic property based on benzothiadiazole-cored cyano-substituted diphenylethene derivative has not been reported in the literature to this day. Therefore, a series of characterization methods including solid fluorescence spectra, SWAXS, DSC, and time-resolved emission-decay behaviors have been used to reveal the mechanofluorochromism.

To quantitatively measure the fluorescent wavelength changes of the synthesized compounds among the different states, solid-state fluorescent spectra were carried out. As shown in Fig. 3A, the maximum fluorescent emission wavelength of the original PT-OMe sample was located at 556 nm. When it was ground, the emission wavelength was red-shifted to 578 nm, gaining a 22 nm red-shift of wavelength. The as-prepared ground sample could easily recover to the original fluorescence by annealing on a hot plate at 100 °C for 5 min (Fig. 3A), demonstrating the excellent reversibility of the obtained mechanofluorochromatic material. The maximum fluorescent emission wavelength of the original PT-H sample was 544 nm (Fig. 3B), while its ground state showed a red-shift of 12 nm to 556 nm. Furthermore, the excellent reversibility between the ground state and annealed state was also demonstrated. Compared with the PT-OMe and PT-H compounds, the as-prepared PT-CF3 with trifluoromethyl electron-withdrawing end...
groups was endowed with unique and completely opposite blue-shifted mechanofluorochromic performance. When the original PT-CF₃ was ground in a mortar, the maximum fluorescent emission wavelength was changed from the original 566 nm to 551 nm, indicating a blue-shifted wavelength of 15 nm. Moreover, its original state with longer emission wavelength could be easily recovered through an annealing process. The above result proved that the mechanofluorochromic properties of benzo-thiadiazole-cored cyano-substituted diphenylethene derivatives could be fine tuned from red-shift to blue-shift by altering their electron-donating end groups to electron-withdrawing end groups.

It has been proposed that the mechanofluorochromic phenomenon usually occurs along with the destruction of an ordered structure by external mechanical forces. Thus, SWAXS measurements were conducted to determine the aggregation state changes of these mechanofluorochromic compounds (Fig. 4), and they were employed to elucidate the micro-structures of the compounds in the original, ground, and annealed states. The sharp scattering peaks were observed for the original samples, indicating ordered crystalline structures. After the as-prepared samples were grounded by external mechanical forces, a trend from crystalline structure to amorphous state occurred along with the original sharp peaks attenuating or even disappearing. Interestingly, when the as-prepared ground samples were annealed, the annealed samples led to the recovery of the crystalline structure, accompanied with the appearance of sharp peaks that coincided with the original samples. The above SWAXS results indicate that the reversible transition between the ordered and disordered molecular aggregations is crucial for the mechanofluorochromic behaviors.

Reproducible heating DSC results showed that the ground state of PT-OMe had an endothermic peak, which represented a reproducible cold-crystallization transition, located at 67.5 °C before the melting point with an enthalpy value of 2.9 kJ mol⁻¹, however, no endothermic peak appeared near this temperature point for the original and annealed states (Fig. 5). This result indicates that the aggregation structure in the ground sample is a metastable state, which could transform into a more stable packing structure through an annealing procedure. The endothermic peaks of the as-prepared ground samples of PT-H and PT-CF₃ were also observed and located at 70.9 °C and 69.8 °C, with enthalpy values of 1.9 kJ mol⁻¹ and 2.4 kJ mol⁻¹, respectively. Similarly, the original and annealed samples of PT-H and PT-CF₃ had no endothermic peak near the corresponding state.
temperature point. The DSC results indicated that the cold-crystallization transition of the ground sample was attributed to the obvious morphological change of the compound induced by grinding, and the metastable state was responsible to the mechano-fluorochromic behaviors. Moreover, it also revealed that the morphological change of the compound induced by grinding and annealing was reversible.

The time-resolved emission-decay behaviors of PT-OMe, PT-H, and PT-CF₃ in original, ground, and annealed states were investigated to obtain further information of the mechano-fluorochromic materials. The time-resolved fluorescence curves and the lifetime data were illustrated in Fig. 6 and Table 1, respectively. Two relaxation pathways were found for the fluorescence decays, indicating that the time-resolved FL spectra of the compound included independent emissions from the segments with different π-conjugation extent, according to the two detected lifetimes. The weighted mean lifetimes (τ) of the original, ground, and annealed states of three samples were determined. The original and annealed states of the sample did not exhibit significant differences, which was consistent with their maximum fluorescent emission wavelength. However, the ground states of these samples showed the smallest (τ) as compared to the original and annealed states, which could be easily observed in Fig. 6. These results indicated that the mechano-fluorochromic behavior of the compounds happened along with the decrease of the weighted mean lifetimes.

As reported by Wang et al.⁴¹ this type of molecule is likely packed in a J-packing fashion in the aggregation state by an intermolecular π–π interaction. Previous works have demonstrated that different aggregation types of aromatic π systems might result in different changes of the emission bands in the aggregated states, and strong intermolecular π–π interactions commonly induce obvious red-shift absorption and fluorescence because of exciton delocalization.⁴² More red-shift fluorescence of the original or annealed sample was induced by much stronger π–π interactions and closer intermolecular packing in the case of PT-CF₃. When the electron-withdrawing group of −CF₃ was substituting an electron-donating group like −H or −OMe, the mechano-fluorochromic behavior was completely reversed. As the benzothiadiazole core is a strong electron-withdrawing group, PT-CF₃ is considered as an A–A–A type compound, while PT-H and PT-OMe are considered as D–A–D types. A proposed explanation for the red-shift mechano-fluorochromic properties of PT-H and PT-OMe is that the distorted conformation, especially the D–A system,⁴⁰ are subject to conformational changes and rotate to a more planar conformation under external pressure, leading to extended conjugation and the subsequent red-shift.

4. Conclusions

In summary, we have reported three new benzothiadiazole-cored cyan-substituted diphenylethene derivatives (PT-OMe, PT-H, and PT-CF₃) with different methoxy, hydrogen, and trifluoromethyl end groups. The designed end groups endowed them with different D–A effects, and gave birth to unique and diverse mechano-fluorochromic properties. After grinding the original compounds, PT-OMe and PT-H showed a red-shift of maximum fluorescent emission wavelength of 22 nm and 12 nm, respectively, while on the contrary, PT-CF₃ exhibited a mechano-fluorochromic blue-shift of 15 nm. The original states of these compounds could be easily recovered from the ground states through an annealing process. The SWAXS, DSC, and time-resolved emission-decay behaviors studies revealed that

![Fig. 6](image-url) Time-resolved emission decay curves of (A) PT-OMe, (B) PT-H, and (C) PT-CF₃ in original, ground, and annealed states.
the mechanofluorochrome mechanism was ascribed to the metastable state of the ground compounds and the crystalline-amorphous phase transformation between the original and ground state. This D–A effect strategy was demonstrated as an effective way to fine tune the fluorescent behavior of the mechanofluorochrome materials.

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References


