



Halogen effect on mechanofluorochromic properties of alkyl phenothiazinyl phenylacrylonitrile derivatives



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ABSTRACT

Three novel alkyl phenothiazinyl phenylacrylonitrile derivatives (**C12F**, **C12Cl**, and **C12Br**) with different halogen end groups (fluorine, chlorine, and bromine) were synthesized with ultra-high yield (>90%) and successfully confirmed according to standard spectroscopic methods. All these compounds were demonstrated with apparent twisted intramolecular charge transfer (TICT) and aggregation-induced emission (AIE) features. The halogen effect rendered them different electronic donor-acceptor behaviours, and gave birth to peculiar different mechanofluorochromic properties. The fluorine-substituted compound (**C12F**) showed obvious red-shifted mechanofluorochromic feature, while almost no mechanofluorochromic characteristic existed in the chlorine- (**C12Cl**) and bromine-substituted (**C12Br**) compounds. The mechanofluorochromic mechanism of **C12F** was investigated and attributed to the phase transformation from crystalline to amorphous state between the original and ground samples, easy crystallinity of the compound, straight conformation of alkyl chain, higher energy gap, and significant decrease of weighted mean lifetime. Moreover, **C12F** showed reversible mechanofluorochromic behaviour and reproducibility by annealing the ground sample, making it promising dual responsive and smart fluorescent materials for fluorescence switches and mechanosensors. The discussion of halogen effect on mechanofluorochromic properties in this work would provide a new way to adjust the fluorescent feature of mechanofluorochromic materials.

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1. Introduction

Mechanofluorochromic materials have attracted great interest in mechanosensors, fluorescence switches, and data storage applications in the past decade due to superior high efficiency and reproducibility [1–3]. However, mechanofluorochromic materials dependent on changes in molecular arrangement and packing are still rare ascribed to the lack of clear structure-property

relationship of mechanofluorochromic materials [4–6]. Another problem that limit the development of these materials is the fluorescent quenching phenomenon in many planar conjugated molecules [7,8]. On the contrary, aggregation-induced emission (AIE) materials with anti-quenching feature have been developed with various architectures and utilized for chemosensor and bio-imaging applications [9–12]. More importantly, many AIE compounds have been demonstrated with mechanofluorochromic feature, which would open up a new path to fabricate more and more mechanofluorochromic compounds [13–18].

Based on the previous work, deeply understanding the structure-property relationship is of great importance to investigate the mechanofluorochromic mechanism, which will further broaden the area of mechanofluorochromic materials. Some recent design strategies have demonstrated the structure adjustment could directly affect the performance of mechanofluorochromic

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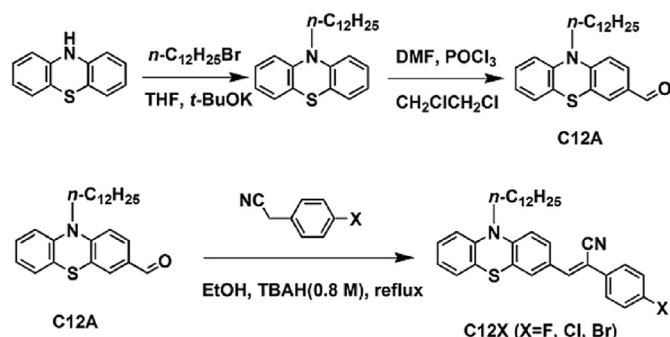
materials, and provided some aids to better understand their structure-property relationship [1]. In 2011, Harima et al. reported heteropolycyclic fluorescent dyes with donor–acceptor (D–A) π -conjugated structure showed mechanofluorochromism, and the degrees of mechanofluorochromism were dependent on the electron-accepting ability of acceptor, steric sizes of the substituents, and intermolecular π – π interaction [19]. Other D–A associated mechanofluorochromic systems have been studied by Yagai's group, Wei's group, and Wang's group [20–22]. Alkoxy (alkyl) length is another important structural factor affecting mechanofluorochromism, which has been studied by Xu and Chi's group, indicating the mechanofluorochromism of 9,10-distyrylanthracene derivatives was more obvious when the length of alkoxy group increased [23]. The Yang's group also reported alkyl length-dependent solid-state fluorescence properties of 9,10-bis[(N-alkylcarbazol-3-yl)vinyl]anthracenes under various external stimuli, demonstrating the opposite phenomenon that the shorter the N-alkyl chain, the more remarkable the mechanofluorochromic behaviour [24]. In 2012, Xu and Chi's group reported the influence of carbazolyl groups on mechanofluorochromic properties of the distyrylanthracene derivatives, proving more obvious mechanofluorochromism with the increase of carbazolyl groups [25]. Most recently, Fraser's group examined the effect of halide substituted group to the mechanochromic luminescence of difluoroboron β -diketonate compounds, suggesting no obvious different mechanofluorochromism among the fluorine, chlorine, and bromine substituted compounds [26]. However, systematic investigation of halogen effect to mechanofluorochromic materials is still highly rare. Therefore, adjusting the mechanofluorochromic property of these smart materials through halogen effect is of great scientific interest and highly demanded.

In this work, we have designed and facilely synthesized three new alkyl phenothiazinyl phenylacrylonitrile derivatives with different halogen end groups (**C12F**, **C12Cl**, and **C12Br**, see Scheme 1), which endowed them with different electronic donor–acceptor effects. The AIE features were firstly demonstrated in THF/water mixed solvents. Then, solid photoluminescence (PL) spectra were studied to explore their unique and interesting mechanofluorochromic properties. Finally, small and wide-angle X-ray scattering (SWAXS), quantum mechanical computations, and time-resolved emission-decay behaviours were conducted to understand their mechanofluorochromic features. The results demonstrated that introduction of halogen effect could endow the as-prepared compounds with peculiar and different mechanofluorochromic properties.

2. Experimental procedure

2.1. Materials and characterization

Phenothiazine, 1-bromododecane, potassium tert-butoxide, 4-



Scheme 1. Synthetic routes of **C12F**, **C12Cl**, and **C12Br**.

fluorophenyl acetonitrile, 4-chlorophenyl acetonitrile, 4-bromophenyl acetonitrile, tetrabutylammonium hydroxide (0.8 M in methanol) were purchased from Alfa Aesar and used as received. All other agents and solvents were purchased from commercial sources and used directly without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ultra-pure water was used in the experiments. The THF/water mixed solvents with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. The ground samples were obtained by grinding the original samples using a mortar and pestle. The annealing experiments were done on a hot-stage with an automatic temperature control system for 5 min with the annealing temperatures of 70 °C, 60 °C and 50 °C for **C12F**, **C12Cl**, and **C12Br**, respectively.

¹H NMR and ¹³C NMR spectra were measured on a JEOL 400 MHz spectrometer [CDCl₃ as solvent and tetramethylsilane (TMS) as the internal standard]. Standard FAB-MS was obtained on ZAB-HS mass spectrometry. 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 from 5 to 35 nm⁻¹. Fluorescence spectra and life time were measured on FLS 920 lifetime and steady state spectrometer. The fluorescence quantum yield values (Φ_F) of the compounds in solution were estimated using quinine sulfate in 0.1 N H₂SO₄ ($\Phi_F = 54.6\%$) as standard. The fluorescent quantum yield for the solid samples were measured on a MK-301 EL/PL Measurement Program (Bunkoukeiki Co., Ltd, Japan) equipped with an integrating sphere and a CCD spectrometer (Andor Tech, CCD-6685). Differential scanning calorimetry (DSC) curves were performed on TA Instruments DSC Q2000 at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

2.2. Syntheses of **C12F**, **C12Cl**, and **C12Br**

Synthetic routes of the compounds **C12F**, **C12Cl**, and **C12Br** were showed in Scheme 1. The intermediate of **C12A** was synthesized according to the previous literature [27–29].

Synthesis of **C12F**. A solution of **C12A** (0.395 g, 1.00 mmol) and 4-fluorophenyl acetonitrile (0.405 g, 3.00 mmol) in ethanol (20.0 mL) was stirred at room temperature. Then tetrabutylammonium hydroxide solution (TBAH, 0.8 M, 5 drops) was added and the mixture was heated to reflux for 2 h. The reaction mixture was cooled to room temperature and filtered, washed with ethanol for three times to afford **C12F** (0.490 g, yield 95.7%). ¹H NMR (400 MHz, CDCl₃) δ : 0.86 (t, 3 H, J = 6.8 Hz), 1.13–1.36 (m, 16 H), 1.36–1.48 (m, 2 H), 1.73–1.86 (m, 2 H), 3.85 (t, 2 H, J = 6.8 Hz), 6.75–6.89 (m, 2 H), 6.93 (t, 1 H, J = 7.2 Hz), 7.01–7.19 (m, 4 H), 7.26 (s, 1 H), 7.53 (s, 1 H), 7.54–7.64 (m, 2 H), 7.79 (d, 1 H, J = 8.8 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 164.26, 161.78, 147.31, 144.00, 140.84, 131.07, 131.04, 128.58, 128.51, 127.81, 127.71, 127.62, 127.60, 127.55, 124.89, 123.77, 123.18, 118.44, 116.26, 116.04, 115.67, 115.19, 107.51, 47.84, 31.94, 30.02, 29.87, 29.73, 29.65, 29.63, 29.32, 26.84, 22.80, 14.24. MS (FAB) calcd. for C₃₃H₃₇FN₂S, 512, found 512.

The synthetic routes of **C12Cl** and **C12Br** were similar to that of **C12F**.

C12Cl (93.2% yield). ¹H NMR (400 MHz, CDCl₃) δ : 0.86 (t, 3 H, J = 6.8 Hz), 1.14–1.36 (m, 16 H), 1.36–1.48 (m, 2 H), 1.73–1.87 (m, 2 H), 3.85 (t, 2 H, J = 7.2 Hz), 6.80–6.89 (m, 2 H), 6.93 (t, 1 H, J = 7.2 Hz), 7.04–7.19 (m, 2 H), 7.31 (s, 1 H), 7.38 (d, 2 H, J = 8.4 Hz), 7.47–7.61 (m, 3 H), 7.79 (d, 1 H, J = 8.4 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 147.46, 144.10, 141.19, 134.77, 133.39, 129.28, 128.75, 128.61, 127.69, 127.60, 127.57, 127.05, 125.78, 124.88, 123.72, 123.22, 118.26, 115.68, 115.18, 107.31, 47.68, 32.02, 29.73, 29.65, 29.63, 29.46,

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