



Alkyl length dependent reversible mechanofluorochromism of phenothiazine derivatives functionalized with formyl group



Junhui Jia^{*}, Yuying Wu

Key Laboratory of Magnetic Molecules and Magnetic Information Material, Ministry of Education, The School of Chemical and Material Science, Shanxi Normal University, Linfen, 041004, PR China

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ABSTRACT

A series of D-A typed phenothiazine derivatives functionalized by formyl group (PCAn, $n = 1, 2, 4$ and 6) with different lengths of *N*-alkyl chains have been designed and synthesized to systematically investigate the effect of chain length on their solid-state fluorescence properties. The results showed that these compounds emitted strong fluorescence in solutions and solid states with 52%, 42%, 49% and 45% solid-state absolute fluorescence quantum yield (Φ_F), respectively. Their emission wavelengths were strongly affected by solvent polarity, indicating intramolecular charge transfer (ICT) transitions. Interestingly, PCAn solids exhibit not only naked-eye visible and reversible mechanochromic behavior, but chain length-dependent emission properties. **PCA1** shows smaller fluorescence spectrum shifts (22 nm) under mechanical force stimuli. Homologs with longer alkyl chains exhibit similar mechanochromic behaviors but larger fluorescence contrasts after grinding except for **PCA6**. Moreover, the fluorescence emission of ground solid **PCA1** and **PCA4** can recover at room temperature, **PCA2** need high temperatures for fluorescence to be restored, and XRD and DSC revealed that the transformation between crystalline and amorphous states upon various external stimuli was responsible for the MFC behavior. This work demonstrates the feasibility of tuning the solid-state optical properties of fluorescent organic compounds by combining the simple alteration of chemical structure and the physical change of aggregate morphology under external stimuli.

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1. Introduction

Smart conjugated luminescent materials have attracted a great deal of attention due to their multi-stimuli responsive emission characteristics and broad applications in the fields of molecular probes, organic light-emitting devices (OLED), optical data recording and data security protection. Particularly, dynamic altering and switching of solid-state luminescence of organic materials upon light, heat, pressure or other external factors, is attracting a lot of interest. Especially, some fluorescent organic molecules can alter their luminescent properties in response to external mechanical stimuli such as shearing, grinding, or pressing, which is known as mechanofluorochromism (MFC) [1–4]. As a kind of “smart material,” MFC compounds have attracted significant attention because of their promising applications in pressure sensors, optical storage, rewritable media, and security ink [5–8].

These fluorescent organic molecules can give changes in the color of their fluorescence under mechanical stress and be restored to their original state by annealing or fuming with solvent vapor instead of the chemical alteration of molecular structures [9–14]. However, MFC materials have started to draw increasing research attention only within the past few years and the types of MFC materials and in-depth understanding of MFC phenomena are limited. To date, many kinds of organic molecules have been exploited to show MFC properties [15–19]. Especially, some nonplanar π -conjugated fluorescent molecules, such as tetraphenylethene (TPE), 9,10-divinylanthracene, triphenylamine (TPA) derivatives and organoboron compounds, were preferentially considered to act as MFC materials, and interestingly, some D- π -A emissive molecules always contribute to the realization of fluorescence change under mechanical stimuli [20–31]. It is worth mentioning that phenothiazine was usually introduced to construct organic luminescent materials as an excellent functional blocks [32,33]. It has a nonplanar, bowl-shaped configuration, and recently some studies have found that it can be introduced into molecular structures to obtain MFC-active fluorescent molecules [34,35].

^{*} Corresponding author.

E-mail address: jjajunhui@sxnu.edu.cn (J. Jia).

As is well known the alkyl length can influence molecular conformations, and change intermolecular interactions and even packing mode in solid states, which result in different MFC properties. However, the studies on the effects of alkyl length on MFC materials are limited owing to the scarcity of MFC materials and the mechanism is still unclear [36,37]. Therefore, there is still a great challenge for designing and synthesizing new MFC materials, as well as the accumulation of knowledge of the relationships between molecular structures and properties. In this context, much more systematic molecular design and structure-property investigation on MFC materials are becoming very necessary. To further understand the effect of alkyl chains on the solid-state fluorescence and mechanochromic luminescence, in the current work, we have prepared a series of phenothiazine derivatives functionalized with benzoyl group (PCAn, $n = 1, 2, 4$ and 6) with different lengths of N -alkyl chains (Scheme 1), and their photophysical properties and MFC behaviors were investigated in detail. The results showed that these molecules exhibited different MFC activities and their fluorescence emission and MFC behaviors are alkyl length-dependent.

2. Experimental section

2.1. General information

All the raw materials were used without further purification. All the analytical pure solvents were purchased from Beijing Chemical Works (Beijing, China). ^1H NMR and ^{13}C NMR spectra were recorded with a Mercury Plus instrument at 600 MHz and 151 MHz by using CDCl_3 as the solvent in all cases. High resolution mass spectra were performed on AB SCIEX Triple TOF™ 5600+ LC-MS/MS series. FT-IR spectra were recorded with a Varian 660-IR FT-IR spectrometer by incorporation of samples into KBr disks. The UV–vis absorption spectra were obtained using a VARIAN Cary 5000 spectrophotometer. Photoluminescence measurements were obtained on a Cary Eclipse fluorescence spectrophotometer. The fluorescence quantum yields of PCAn ($n = 1, 2, 4$, and 6) in various solvents were measured by comparing with a standard (quinine in $0.1\text{ N H}_2\text{SO}_4$, $\Phi_{\text{F}} = 0.546$) and the excitation wavelength was 365 nm. The solid fluorescence quantum yields were measured using an Edinburgh Instrument FLS920 with integrating cavity scanning (ICS) method. Cyclic voltammogram was performed using CHI 604B electrochemical workstation and measurement was carried out in dry CH_2Cl_2 with a scan rate at 100 mV/s. Three electrode configurations were used for the measurement: a platinum button was used as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The solution of Bu_4NBF_4 in DCM (0.1 M) was used as the supporting electrolyte. C, H, and N elemental analyses were performed with a vario MACRO cube elemental analyzer. The XRD patterns were obtained on an Empyrean X-ray diffraction instrument equipped with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$) by employing a scanning rate of $0.026^\circ\text{ s}^{-1}$ in the 2θ range from 5 to 50. Differential scanning

calorimetry (DSC) curves were obtained on a DSC 200 F3 at a heating rate of $10^\circ\text{C min}^{-1}$, and the data of all samples (pristine and ground) were collected when they were heated for the first time. Pressing experiment: A quantity of PCAn and KBr powder was simply mixed in a mortar and then pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. Annealing experiment: The pressed sample was put into an oven whose temperature was 30°C over Tc (cold-crystallization temperature of each compound) for 3 min. Solvent-fuming experiment: The ground sample was placed above the dichloromethane level and was exposed to the vapor for 1 min at room temperature. The molecular configuration was used to obtain the frontier orbitals of PCAn by density functional theory (DFT) calculations at the B3LYP/6-31G (d, p) level with the Gaussian 09W program package.

2.2. Synthesis, procedures, and characterization

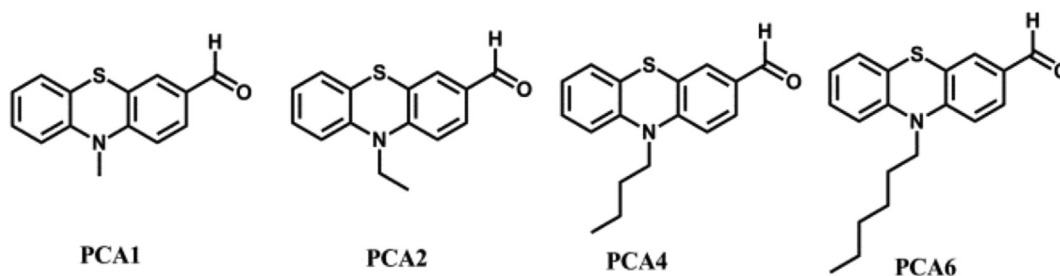
Compounds **1** and target compounds PCAn were synthesized by the reported methods [32,33], and the synthetic routes were shown in Scheme 2.

2.2.1. 10-Methyl-10H-phenothiazine-3-carbaldehyde (PCA1)

1.3 mL POCl_3 (16 mmol) was added into 2 mL DMF in 25 mL flask under ice-water bath, after being stirred for 10 min at room temperature, 10-methyl-10H-phenothiazine (1.7 g, 8 mmol) dissolved in 1, 2-dichloroethane (10 mL) was added into the above mixture drop-wise under ice-water bath, and then the resulting mixture was heated to reflux for 12 h. The reaction mixture was cooled to room temperature and poured into ice-water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using petroleum ether/dichloromethane ($v:v = 1:1$) as eluent, yellow-green solid was obtained after recrystallization from dichloromethane and diethyl ether. Yield: 0.96 g, 50%. mp: $88\text{--}90^\circ\text{C}$. IR (KBr, cm^{-1}): 1676, 1600, 1568, 1464, 1396, 1380, 1328, 1256, 1204, 752. ^1H NMR (600 MHz, CDCl_3) δ 9.81 (1 H, s), 7.66 (1 H, dd, $J_1 = 1.8\text{ Hz}$, $J_2 = 1.8\text{ Hz}$), 7.60 (1 H, d, $J = 1.8\text{ Hz}$), 7.21–7.18 (1 H, m), 7.14–7.12 (1 H, m), 7.00–6.98 (1 H, m), 6.85 (2 H, t, $J = 8.2\text{ Hz}$), 3.43 (3 H, s) (Fig. S1). ^{13}C NMR (151 MHz, CDCl_3) δ 190.09, 151.11, 144.13, 131.22, 130.46, 127.99, 127.78, 127.42, 127.32, 127.15, 124.03, 123.65, 122.59, 122.44, 114.78, 114.06, 113.72, 77.23, 77.02, 76.80, 35.84. (Fig. S2); MS (HR-MS): m/z 242.0537 [$\text{M}+\text{H}$] $^+$ (Fig. S3, Calcd for $\text{C}_{14}\text{H}_{11}\text{NOS}$: 241.0561); Anal. Calcd. (%) for $\text{C}_{14}\text{H}_{11}\text{NOS}$: C, 69.68; H, 4.59; N, 5.80. Found (%): C, 69.72; H, 4.61; N, 5.77.

2.2.2. 10-Ethyl-10H-phenothiazine-3-carbaldehyde (PCA2)

The synthetic method for compound PCA2 was similar to that of compound PCA1. It was purified by column chromatography (silica gel, petroleum ether/ $\text{CH}_2\text{Cl}_2 = 1/1$) to give yellow solid (49% in yield). mp: $100\text{--}101^\circ\text{C}$. IR (KBr, cm^{-1}): 1672, 1600, 1576, 1468, 1398,



Scheme 1. The structures of PCA1, PCA2, PCA4 and PCA6.

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