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Phenothiazine substituted phenanthroimidazole derivatives: Synthesis, photophysical properties and efficient piezochromic luminescence

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ABSTRACT

Two phenanthroimidazoles with phenothiazine substituents were synthesized. It was found that these novel molecules showed intense fluorescence in both solution and the solid state. Additionally, these phenanthroimidazoles displayed reversible piezofluorochromism. For example, a crystal of the monophenothiazinyl analogue gave an intense sky blue emission which changed to a green emission after grinding, the fluorescence emission could be recovered when the ground powders were fumed with organic vapors or heated. XRD patterns suggested that the reversible piezofluorochromism resulted from the transformation between crystalline and amorphous states. The single crystal X-ray structure of the monophenothiazinyl analogue revealed the twisted conformation and existence of weak C-H $\cdots$ π interactions, resulting loose packing in the crystal state, which was favorable for the piezofluorochromism. These results obtained will be of great help in designing new piezofluorochromic molecules, which might have potential applications in mechanical sensors and security printing.

1. Introduction

Recently, the exploitation of efficient solid-state fluorescent materials has received increasing attention in organic light emitting diodes (OLEDs), optoelectronic devices, solid-state organic lasers, and fluorescent sensors [1]. In particular, piezofluorochromic (PFC) materials exhibiting switchable colours in response to external stress are attracting substantial attention due to their potential applications in mechano-sensors, optical recording, security papers, data storage, and optoelectronic devices [2]. These materials change their luminescence color under mechanical force and can be recovered to their original state by fuming with organic solvent vapor or annealing [3]. A fluorescence color change indicates a control of reversible transformation of molecular packing because solid-state photophysical properties are critically dependent upon molecular arrangement [4]. High solid-state emission and an obvious color contrast are very significant for the application of PFC materials [5]. However, most of the organic dyes generally show extremely weak emission in the solid state owing to concentration quenching. To overcome this problem, the aggregation-induced emission (AIE)-active molecules are firstly reported by Tang and co-workers [6]. The AIE-gens are highly luminescence in the solid state, but very weak fluorescence is observed in the solution state, which limited their wide range of applications. So, organic materials with strong fluorescence emission in both solution and the solid state should be developed [7].

The phenanthroimidazole moiety (PI) has a rather rigid planar structure and is a wide-bandgap fluorophore, which can contribute to the desired high-energy emission of the compounds. PI based molecular systems have been explored in optoelectronics and molecular biology [8]. In particular, PI derivatives usually gave high fluorescence quantum yields in solution and the solid state. For example, Wang et al. synthesized two diazacarbazole substituted PI derivatives and found that they exhibited deep-blue emission and were used to fabricate undoped fluorescent OLEDs [9]. Tong and coworkers reported that asymmetric PI substituted sulfone derivatives showed high fluorescence quantum yields in solution and the solid state, which was suitable for application in OLEDs [10]. Recently, our group has prepared phenanthroimidazole derivatives with strong emission which could sense vapors of volatile acids [11]. Currently, most reported PFC materials consist of nonplanar π-conjugated molecules, such as tetraphenylethene [12], triphenylethene [13], 9,10-bis(arylvinyl)anthracene [14] and boron complex

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[15]. However, few reports have focused on the PFC materials with PI groups [16]. Till now, the development of phenanthroimidazole-based piezofluorochromic dyes with high contrast remains an interesting problem. Meanwhile, phenothiazine is an excellent functional block for the construction of organic materials [17]. It has a nonplanar, bowl-shaped configuration, and recently it has been introduced into molecular structures to obtain PFC-active fluorescent molecules [18]. With these foregoing features in mind, herein, we designed and synthesized new phenothiazine substituted phenanthroimidazole derivatives **P1** and **P2** (Scheme 1), and their fluorescent properties and piezofluorochromic behavior was investigated. The two compounds have high fluorescence quantum yields in the solid state because of restricted π-π stacking, and show apparent PFC properties. For example, an emission changes from sky blue to green for **P1**, from green to yellowish green for **P2**, respectively, resulting from external pressure. The emissions display 33 nm and 14 nm red shifts after grinding. Powder X-ray diffraction analyses and differential scanning calorimetry confirm that the phase transition between the crystalline and amorphous states upon application of external pressure is responsible for the reversible color change. The reason for the phase transformation is ascribed to the twisted conformations of the molecules which lead to loose molecular packing, as confirmed by single crystal X-ray diffraction analysis.

2. Experimental section

2.1. Materials and measurements

^{1}H NMR spectra and ^{13}C NMR spectra were measured on a Bruker AMX-400 NMR spectrometer at 400 MHz and 100 MHz in $CDCl_3$ as the solvent at room temperature. FT-IR spectra were measured with a Nicolet-360 FTIR spectrophotometer by the incorporation of samples in KBr disks. Mass spectra were recorded on an Agilent 1100 MS series and AXIMA CFR MALDI/TOF (Compact) mass spectrometers. C, H and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. The UV–vis absorption spectra were determined on a Beijing purkinje TU-1810 Spectrophotometer. Fluorescence emission spectra were obtained on a Shimadzu RF-5301 PC fluorimeter. The fluorescence quantum yields in solvents were estimated by comparing to a standard (quinine sulfate in 0.1 M H_2SO_4, $\Phi_F = 0.546$). The absolute fluorescence quantum yields were estimated on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. Cyclic voltammogram was performed using CHI 830D electrochemical workstation and measurement was carried out in 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_4NPF_6 in DCM (0.1 M) was used as the supporting electrolyte. XRD patterns were obtained on an Empyrean X-ray diffraction instrument. DSC measurements were carried out using a Mettler Toledo 3 thermos system at a heating rate of 10 °C/min. The frontier orbital plots of the HOMO and LUMO of target compounds were obtained by density functional theory (DFT) calculations at the B3LYP/6-31G level with the Gaussian 09W program package. Single crystal of **P1** was obtained by slowing solvent evaporation in mixture of DCM and ethanol, and selected for X-ray diffraction analysis in a Rigaku RAXIS-RAPID diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The crystal was kept at room temperature during data collection. The structure was solved by the direct methods and refined on F2 by full-matrix least-square using the SHELXTL-97 program. The C, N, O and H atoms were easily placed from subsequent Fourier-difference maps and refined anisotropically. CCDC 1518082. DMF was dried over phosphorus pentoxide. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. The other chemicals and reagents were used as received without further purification.

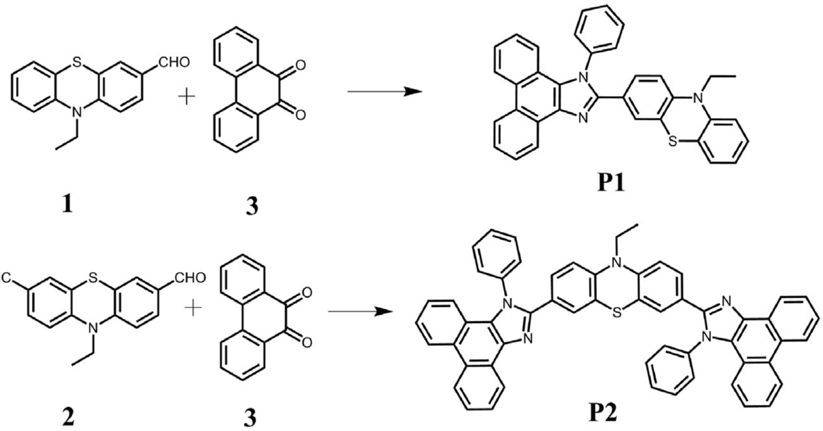
2.2. Preparation of the samples for piezofluorochromism study

The powders were prepared by grinding the crystals with a pestle in the mortar. The fumed samples were obtained by fuming the powders with DCM for 30 s.

2.3. Synthetic procedures and characterizations

2.3.1. 10-Ethyl-3-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-10H-phenothi-azine (*P1*)

A mixture of 9,10-phenanthrenequinone (0.81 g, 3.91 mmol),10-ethyl-10*H*-phenothiazine-3-carbaldehyde (1.0 g, 3.91 mmol), aniline (0.54 mL, 5.87 mmol) and ammonium acetate (3.0 g, 39.1 mmol) was added into glacial acetic acid (50 mL) under N_2 atmosphere. The mixture was refluxed for 4 h, and then was cooled to room temperature, followed by poured into water (300 mL) with stirring. The separated solid was filtered off, washed with 20 mL methanol. The crude product was purified by column chromatogram (silica gel, petroleum ether/dichloromethane, v/v = 1/1), and then was recrystallized from petroleum ether and dichloromethane



Scheme 1. The synthetic routes for the phenothiazine substituted phenanthroimidazoles **P1** and **P2**. Reagent and conditions: Aniline, ammonium acetate, 10-ethyl-10*H*-phenothiazine-3-carbaldehyde (for **P1**)/10-ethyl-10*H*-phenothiazine-3,7-dicarbaldehyde (for **P2**), acetic acid, reflux.