

Mechanofluorochromism of D-A typed phenothiazine derivative

Junhui Jia^{a,*}, Huijuan Zhang^{b,1}

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

^b College of Physics and Electronic Information, Shanxi Normal University, Linfen, 041000, China



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ABSTRACT

A D-A typed phenothiazine derivative **MPTPM** has been designed and synthesized via a Friedel-Crafts reaction, which contains two benzoyl groups. It was found that **MPTPM** gave strong emission in solution and in solid state, and the solid fluorescence quantum yield was as high as 0.60. Moreover, an excellent reversible mechanofluorochromic behavior was realized upon the treatment of grinding/fuming with CH₂Cl₂ or heating in spite of a very simple molecular structure. The emission color of **MPTPM** changed from green to orange-yellow after grinding and could be restored via fuming with CH₂Cl₂ or heating with a spectra shift of ~63 nm. Photophysical, XRD, DSC studies indicated the mechanofluorochromic properties of **MPTPM** originating from the transformation between crystalline phase and amorphous phase.

1. Introduction

Recently, fluorescent organic materials have been received more attention due to their unique properties and potential applications in organic light-emitting diodes, solar cells, bio-imaging, chemical-sensors and so on [1–7]. Among them, mechanofluorochromism (MFC) involving a physical change in the aggregate morphology instead of chemical alteration in the molecular structure has sparked tremendous interest because of their potential for various applications in the fields of sensors, memory devices, security ink and optical displays [8–14]. As is well known, nonplanar π -conjugated fluorescent organic molecules, such as tetraphenylethene derivatives, cyano-substituted diarylethene derivatives, cyano-substituted diphenylethene derivatives, difluoroboron- β -diketones and 9, 10-divinylanthracene derivatives are preferentially considered to act as MFC materials [15–19]. Harima and co-workers demonstrated that the D-A structure was important for the organic dyes to show MFC behaviors [20–21] and some D-A typed molecules always contribute to the realization of fluorescence change under mechanical stimuli. It is worth mentioning that the nonplanar, bowl-shaped configuration of phenothiazine usually induces the loose molecular stacking in the solid states, so that the solid emission of the phenothiazine-based dyes would be affected by external forces and recently some studies have found that it can be introduced into molecular structures to obtain MFC-active fluorescent molecules. Although lots of mechanofluorochromic materials have been synthesized, the design of smart luminophores with excellent performance in

mechanofluorochromism as well as with high fluorescence quantum yields in solid states still remains a great challenge. With these in mind, phenothiazine was selected as a building block in target molecule, which was functionalized with benzoyl groups to form a D-A typed molecule **MPTPM** (Scheme 1). It was found that **MPTPM** gave strong emission in solution and in solid-state, and the solid fluorescence yield was as high as 0.60. Meanwhile, reversible mechanofluorochromic behavior of **MPTPM** realized upon the treatment of grinding/fuming with CH₂Cl₂, and the emission color of **MPTPM** changed from green to orange-yellow after grinding. Power X-ray diffraction analysis showed that the mechanofluorochromic nature was generated through crystalline-amorphous phase transformation under external pressure.

2. Experimental section

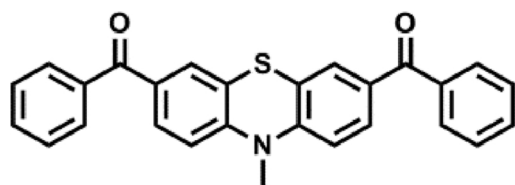
2.1. Measurements

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 ¹³C NMR spectra were recorded with a Mercury Plus instrument at 600 MHz and 151 MHz by using CDCl₃ as the solvent in all cases. 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

* Corresponding author.

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

¹ The two authors contributed equally.

**MPTPM**

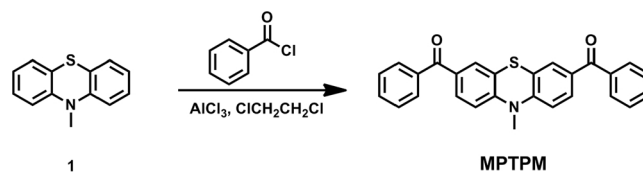
Scheme 1. The structure of MPTPM.

quantum yields of target molecules in various solvents were measured by comparing with a standard (9, 10-diphenylanthracene in benzene, $\Phi_F = 0.85$) and the excitation wavelength was 390 nm. The solid fluorescence quantum yields were measured using an Edinburgh Instrument FLS920 with integrating cavity scanning (ICS) method. 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 Cu K α 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 60. 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 MPTPM was pressed with a pestle or spatula on weighing paper at room temperature. Solvent-fuming experiment: The ground sample was placed above the dichloromethane level and was exposed to the vapor at room temperature. The molecular configuration was used to obtain the frontier orbitals of MPTPM by density functional theory (DFT) calculations at the B3LYP/6-31 G (d, p) level with the Gaussian 09 W program package.

2.2. Synthesis, procedures, and characterization

(10-methyl-10H-phenothiazine-3,7-diyl)bis(phenylmethanone) (MPTPM)

10-methylphenothiazine (2.13 g, 10 mmol), AlCl_3 (3.34 g, 25 mmol) and $\text{ClCH}_2\text{CH}_2\text{Cl}$ (15 mL) were mixed in 100 mL three-necked flask, benzyl chloride (2.59 mL, 22.01 mmol) dissolved in 1, 2-dichloroethane (10 mL) was added dropwise under ice-water bath, After being stirred for 20 min, the reaction mixture was warmed to room temperature and then heated to reflux for 10 h. The reaction mixture was cooled to room temperature and poured into 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 crystals were obtained after recrystallization from petroleum ether/dichloromethane. Yield: 2.95 g, 70.1%. mp: $>280^\circ \text{C}$. IR (KBr, cm^{-1}): 3430, 3281, 3058, 2992, 2932, 2875, 2603, 1963, 1901, 1814, 1776, 1720, 1651, 1597, 1572, 1466, 1448, 1396, 1361, 1315, 1269, 1159, 1134, 1107, 1074, 1053, 1000, 966, 927, 903. $^1\text{H NMR}$ (600 MHz, CDCl_3) $\delta = 7.77\text{--}7.73$ (m, 4H), 7.70 (d, $J = 1.9 \text{ Hz}$, 1H), 7.69 (d, $J = 2.0 \text{ Hz}$, 1H), 7.61 (d, $J = 1.9 \text{ Hz}$, 2H), 7.58 (t, $J = 7.4 \text{ Hz}$, 2H), 7.49 (t, $J = 7.7 \text{ Hz}$, 4H), 3.50 (s, 3H). (Fig.S1) $^{13}\text{C NMR}$ (151 MHz, CDCl_3) $\delta = 194.69, 148.30, 137.81, 132.46, 132.21, 130.76, 129.70, 129.23, 128.34, 122.75, 113.85, 36.04$. (Fig.S2) Anal. Calcd. (%) for $\text{C}_{22}\text{H}_{19}\text{NO}_2\text{S}$: C, 76.93; H, 4.54; N, 3.32. Found (%): C, 77.02; H, 4.51; N, 3.37.



Scheme 2. Synthetic routes of phenothiazine derivative MPTPM.

3. Results and discussion

3.1. Synthesis of MPTPM

The synthetic routes for phenothiazine derivative MPTPM are shown in Scheme 2. Firstly, 10-methyl-10H-phenothiazine was synthesized according to the reported procedures [17,19]. The Friedel-Crafts reaction between 10-ethyl-10H-phenothiazine and benzoyl chloride yield MPTPM in a yield of 70.1%. The target molecule was characterized by $^1\text{H NMR}$, $^{13}\text{C NMR}$, C, H, and N elemental analyses and FT-IR spectrum. Additionally, MPTPM could be dissolved in most organic solvents, such as CH_2Cl_2 , THF, toluene, DMF, and so on.

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

The UV-vis absorption spectra of MPTPM in different solvents were recorded and the data were summarized in Table. S1. As shown in Fig. 1a, MPTPM exhibited two obvious absorption bands located at ca. 295 nm and ca. 390 nm, respectively, in cyclohexane ($1.0 \times 10^{-6} \text{ M}$). The former one was attributed to $\pi\text{-}\pi^*$ transition and the later one was ascribed to the intermolecular charge transfer (ICT) transition [17]. In toluene, the absorption at 390 nm shifted to 405 nm, further increase in solvent polarity did not result in further red-shift of absorption spectra. However, the fluorescence spectra of MPTPM were strongly dependent on the solvent polarity (Fig. 1b). It had a vibrational structure emission band with emission peak at 499 nm and a shoulder peak at ca. 528 nm in cyclohexane solution. The fluorescence quantum yield was 0.43. Moreover, this emission band became wide, and the maximum peak shifted to 526 nm in toluene. In polar DMF, the emission peak was located at $\sim 555 \text{ nm}$ with the fluorescence quantum yields decreased to 0.18. Such large red shift of fluorescence spectra in polar solvents indicated that the molecule MPTPM had a larger polarity in the excited state than in the ground state. And quantum chemical calculations were performed by time-dependent density functional theory (TDDFT) calculations at the B3LYP/6-31 G (d, p) level and the calculate dipole moment was 4.7875 D, which indicated it had a large molecular polarity. Moreover, the optimized geometries of MPTPM indicated that it gave a nonplanar configuration (Fig. S3). Quantum chemical calculation was performed to understand the further change in solvent-dependent fluorescence, based on the ground-state optimized geometry, the stimulated electron transitions were obtained through time-dependent density functional theory calculation. The results are listed in Table S2, and the stimulated absorption spectra are shown in Fig. S4. The transition energy of MPTPM from S_0 to S_1 reached 2.95 eV, which corresponded to 419.9 nm and was mainly ascribed to the transition from the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). As shown in Fig. 2, the HOMO density of MPTPM was mainly distributed at phenothiazine group, whereas LUMO density was mainly observed at benzoyl moieties and the phenyl groups of phenothiazine. Thus, light excitation would lead to intramolecular charge transfer from the donor unit to the acceptor unit and increase the polarity of the molecule in the excited state. To better evaluate the effects of solvents on the emission features, the relationship between the solvent polarity parameter and the Stokes shift according to the Lippert-Mataga equation [22] was investigated.

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