



Systemic study on fluorescent switching systems composed of naphthopyran and benzimidazole in solution and film forms



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ABSTRACT

The fluorescent photo-switching systems were prepared based on fluorescent benzimidazole and photochromic naphthopyran. Naphthopyran in this systems displayed excellent photochromic performance in tetrahydrofuran solutions and in PMMA films. The fluorescent emission of benzimidazole was modulated between “on” and “off” via the photoisomerization of naphthopyran in high-contrast due to the photoinduced energy transfer from benzimidazole to the open-form naphthopyran. Both the fluorescent photoswitching and the photochromism of benzimidazole–naphthopyran dyads in solutions and films displayed excellent fatigue resistance. The spaces between benzimidazole and naphthopyran affect the absorbance and fluorescence spectra of benzimidazole–naphthopyran dyads. The non-destructive readout ability of synthesized dyads in doped PMMA film was achieved.

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1. Introduction

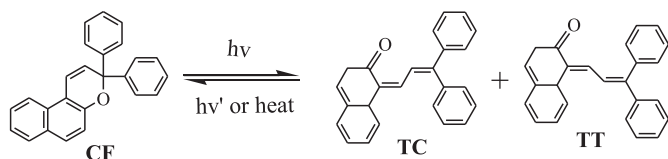
Fluorescence switchings have attracted increasing interest due to their potential applications in molecular switches, optical data storage, fluorescent biological markers and other molecular electronic and photonic devices [1–5]. The photochromic fluorescence switching is one important kind of fluorescence switching and received more and more research interesting. In photochromic fluorescence switching systems, the fluorescent emission of fluorophore can be modulated between “on” and “off” via the photochromic reaction of photochromic moieties under irradiation of different wavelength lights or thermal effect. In most cases, the fluorescence quenching is due to the intramolecular energy transfer and/or electron transfer [6,7]. Most of photochromic fluorescence switchings are usual prepared in the following three formations: the fluorescent units and photochromic groups are combined to be organic dyad or in copolymer or doped in polymeric matrices. Diarylethene, spiropyran, spirooxazine, azobenzene derivatives and other photochromic unit are often used as photochromic units to prepare the photochromic fluorescence switchings [8–11]. Naphthopyran (NP) derivatives are an important

class of photochromic dyes due to their breadth of color generated, absence of background color, good thermal reversibility, fine control over fading kinetics and good resistance to photochemical fatigue [12,13]. Under UV light irradiation, the uncolored naphthopyran undergoes an electrocyclic pyran-ring opening with cleavage of the C (sp³)-O bond and a subsequent structural reorganization to be more planar structures (the so called ‘open form’, OF) with greater conjugation, which is responsible for the increased absorption in the visible part of the spectrum, their molecular structures are shown in Scheme 1 [14–16]. The OF is constituted by a set of colored stereoisomers, with similar absorption characteristics but with diverse thermal stabilities. Under continuous UV irradiation, a photostationary equilibrium is attained between the uncolored ‘closed form’ (CF) and the colored OF form. This isomerization process is accompanied by color change of the system. Up to now, only our group has reported on naphthopyran as photochromic unit to be used in fluorescence switching [17–20].

In the paper [18], we fabricated the fluorescence photoswitching using naphthopyran as photochromic unit and benzimidazole as fluorophore. In this switching molecule, the naphthopyran connected with benzimidazole via ester bond on the nitrogen atom of imidazole ring and benzimidazole connected with a pyridine ring, but its shortcoming is the large degradation of fluorescent intensity after first fluorescent switch. Compared to the above report, the connect manner of naphthopyran with benzimidazole is not same

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Scheme 1. The photochromic reaction of naphthopyran molecule.

in this paper. In this system, we designed a systematic naphthopyran-benzimidazole fluorescence switching, the spaces between naphthopyran and benzimidazole were ester bond, two-carbon chain and six-carbon chain, respectively. In addition, the linked atom on the benzimidazole is oxygen atom of hydroxy on benzene ring but not nitrogen of imidazole ring. Their molecular structures and synthetic routes are shown in [Scheme 2](#). The performance of their fluorescent switching in solutions and films were investigated and compared, the effect of spaces between naphthopyran and benzimidazole on the photophysical properties were also studied.

2. Experimental

2.1. Materials and characterization

4-dimethylaminopyridine (DMAP), 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide (EDC), 6-hydroxy-2-naphthoic acid and 2,6-dihydroxynaphthalene were purchased from Aldrich. The other materials were commercial products and used without further purification. Solvents were purified by normal procedures and handled under moisture free atmosphere. All chromatography examinations were performed using silica gel, and TLC was performed on silica plates (made in China).

^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova Spectrometer at room temperature using *d*-chloroform and dimethylsulfoxide- d_6 as solvent. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. Fluorescence and UV–Vis absorbance spectra were measured on Cary Eclipse Fluorescence Spectrophotometer and Varian Cary 500 spectrophotometer, respectively. Photochromic performances of the films were examined using a Varian Cary 500 UV–vis–NIR spectrophotometer. The ultraviolet source for irradiation was CHF-XM35 parallel light system (Beijing Changming Technology Co. Ltd) with a 500 W xenon lamp and monochromatic filter (360 nm). The irradiating light

reached to the samples was parallel and its intensity was about 5 mW/cm^2 .

2.2. Synthesis

2.2.1. Compound 1, 2 and 5 was synthesized according to our previous reports [\[18,21\]](#)

2.2.2. Synthesis of PBI.

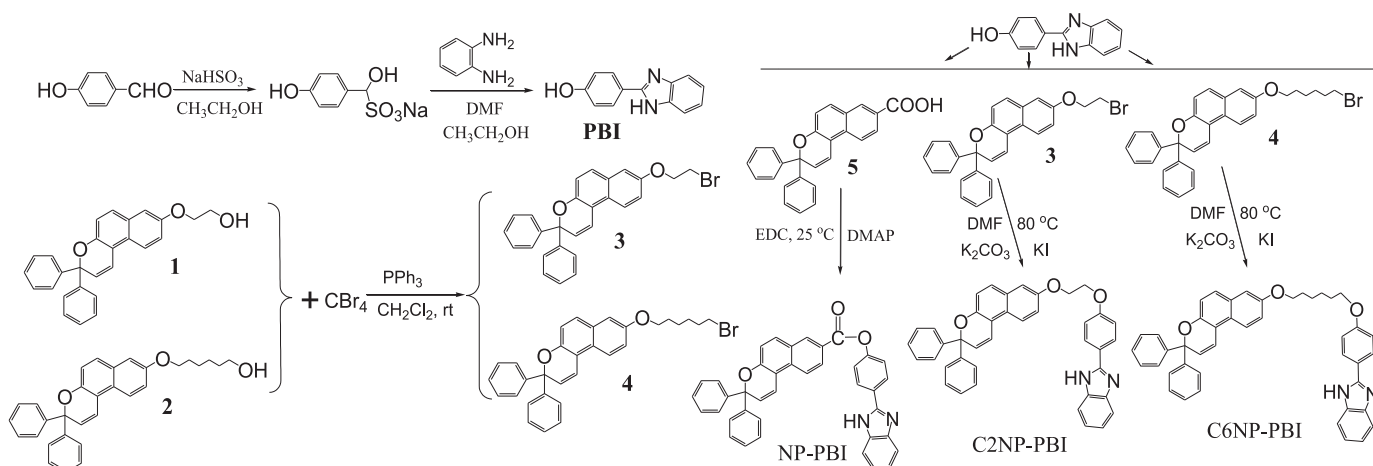
After the mixture of *p*-hydroxybenzaldehyde (6.1 g, 50 mmol), sodium bisulfite (5.2 g, 50 mmol) and anhydrous ethanol (30 mL) was stirred at room temperature for 4 h, the solution of *o*-diaminobenzene (5.4 g, 50 mmol) in DMF (30 mL) was added and the reaction mixture was then stirred at 120°C for 3 h. After cooling down to room temperature, the reaction mixture was poured into 300 mL water and the precipitate was obtained by filtering. The pure product was obtained by recrystallization in ethanol, faint yellow solid, 9.42 g, yield 89.7%. ^1H NMR (400 MHz, DMSO- d_6) δ ppm: 12.63 (s, 1H), 9.99 (s, 1H), 8.02–8.00 (t, 2H, $J = 7.0$), 7.55–7.53 (dd, 2H, $J = 3.0, 5.6$ Hz), 7.18–7.14 (m, 2H), 6.94–6.91 (t, 2H, $J = 6.5$).

2.2.3. Synthesis of compound 3 and 4.

Compound **3** and **4** were synthesized by the following procedure.

For compound **3**: Compound **1** (2.0 g, 5 mmol), carbon tetrabromide (2.7 g, 8 mmol) and triphenylphosphine (2.1 g, 8 mmol) were dissolved in purified CH_2Cl_2 (30 mL) and stirred for 24 h at room temperature. The reaction mixture was poured into 50 mL water and the product was extracted with CH_2Cl_2 (30 mL \times 3). The organic phase was dried with anhydrous sodium sulfate, the purified compound **3** was obtained by column chromatography on silica gel (eluent: petroleum ether: $\text{CH}_2\text{Cl}_2 = 3:1$) to give white powder, 1.91 g, yield 83.6%. ^1H NMR (CDCl_3 , 500 MHz) δ ppm: 7.88–7.86 (d, 1H, $J = 11.5$ Hz), 7.54–7.52 (d, 1H, $J = 9.0$ Hz), 7.48–7.46 (d, 4H, $J = 9.0$ Hz), 7.33–7.15 (m, 9H), 7.04–7.03 (d, 1H, $J = 3.0$ Hz), 6.29–6.26 (d, 1H, $J = 10.0$ Hz), 4.41–4.32 (t, 2H, $J = 7.5$ Hz), 3.68–3.63 (m, 2H, $J = 7.5$ Hz).

For compound **4**: White powder, yield 87.2%. ^1H NMR (CDCl_3 , 500 MHz) δ ppm: 7.86–7.84 (d, 1H, $J = 9.0$ Hz), 7.54–7.51 (d, 1H, $J = 9.0$ Hz), 7.49–7.47 (d, 4H, $J = 9.0$ Hz), 7.32–7.12 (m, 9H), 7.01–7.03 (d, 1H, $J = 2.0$ Hz), 6.28–6.25 (t, 1H, $J = 10.0$ Hz), 4.0–4.01 (t, 2H, $J = 7.0$ Hz), 3.45–3.41 (t, 2H, $J = 7.0$ Hz), 1.91–1.82 (m, 4H), 1.56–1.52 (m, 4H).



Scheme 2. The synthetic route of the systematic photochromic fluorescent switching.

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