



Study on fluorescent switching of naphthopyran and pyrene-containing dyad and copolymer in solutions and films



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ARTICLE INFO

Article history:

Received 11 September 2013

Received in revised form

20 October 2013

Accepted 30 October 2013

Available online 7 November 2013

Keywords:

Fluorescence switching

Photochromism

Pyrene

Naphthopyran

Photoinduced energy transfer

High-degree modulation

ABSTRACT

The fluorescent photo-switching systems were prepared based on fluorescent pyrene and photochromic naphthopyran in the forms of organic dyad and copolymer. Naphthopyran in two systems displayed excellent photochromic performance, especially in tetrahydrofuran solution. The fluorescent emission was modulated between “on” and “off” via the photoisomerization of naphthopyran in high-degree, especially in polymer (>90%) due to the photoinduced energy transfer from pyrene excimers to the open-form naphthopyran. Both the fluorescence photoswitching and the photochromism of polymer in solution displayed excellent fatigue resistance. The fluorescent image shows the patterned irradiation of the polymer-doped polymethylmethacrylate film can be recorded by fluorescent pattern on the sample. The non-destructive readout ability of polymer-doped polymethylmethacrylate film was achieved.

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1. Introduction

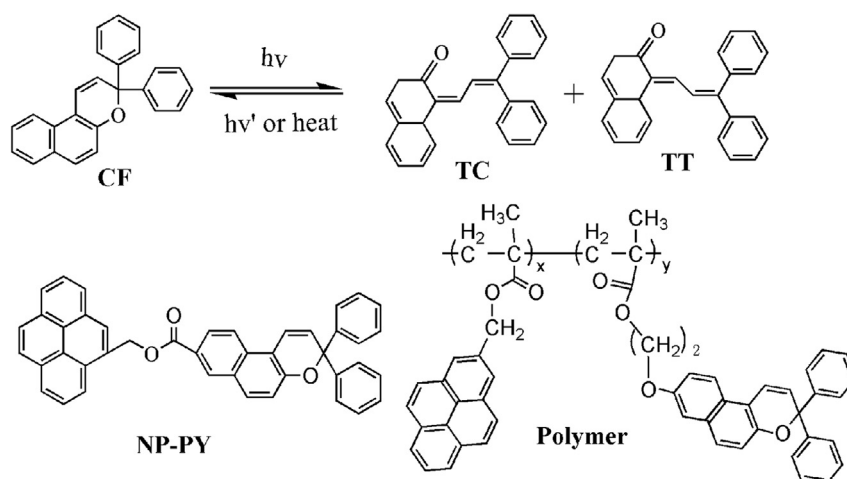
Fluorescent switches have attracted increasing interest due to their potential applications in molecular switches, optical data storage, fluorescent biological markers and other molecular electronic and photonic devices [1–8]. The photochromic fluorescence switching is one important kind of fluorescent switching and received more and more research interesting. In such fluorescent switching systems, the fluorescence can be modulated between “on” and “off” via the photochromic reaction of photochromic moieties under irradiation of different wavelength lights or thermal effect. Under these conditions, both intramolecular energy transfer and electron transfer can be employed as the fluorescence quenching mechanism [9–11]. Most of photochromic fluorescent switching is 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. The most of photochromic units in the reported photochromic fluorescent switching are diarylethene derivatives [12–17], the spiropyran, spirooxazine and azobenzene derivatives [18] are also used to prepare the photochromic fluorescent switching.

Naphthopyran 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 [19]. 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 allowing the photogenerated species to adopt 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 [20–24]. 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 OF leading to a color change of the system. However, the reports about photochromic fluorescent switching with naphthopyran as photochromic unit are few, only our group has reported on naphthopyran to be used in fluorescent switching [25,26]. However, there are some shortages in our reported fluorescent switching, such as low-degree modulation efficiency and poor fatigue resistance.

To explore new excellent fluorescent switching with naphthopyran as photochromic group, we selected pyrene as fluorescent unit to fabricate fluorescent switching with naphthopyran. This is based on the following points: our previous studies demonstrated

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Scheme 1. The photochromism of naphthopyran and the molecular structures of synthesized naphthopyran-containing organic molecule and polymer.

that naphthopyran possesses the ability to modulate the fluorescence of fluorophore via its reversible photochromic isomerization; pyrene is one excellent fluorescent emitting materials and has high quantum efficiency; the absorbance band of open-form naphthopyran overlaps well with the emission spectra of pyrene, especial with that of pyrene excimers. In this paper, we present the systematic studies on the fluorescent switching composed of naphthopyran and pyrene in the forms of the organic dyad and copolymer, their molecular structures and synthetic routes are shown in [Scheme 1](#) and [Scheme 2](#), respectively. The potential application in non-destructive readout was investigated, and the write, read, and erase cycles could be carried out independently with photons of different wavelengths.

2. Experimental

2.1. Materials

Polymethylmethacrylate (PMMA) and 1,1-diphenyl-2-propyn-1-ol were purchased from Aldrich Chemical Co and used without further purification. Dichloromethane and tetrahydrofuran were distilled after refluxed with CaH_2 and sodium, respectively. *p*-toluenesulphonic acid was purified by recrystallization from ethanol. All other reagents were purchased to be used without further purification.

2.2. ^1H and ^{13}C NMR spectroscopy IR spectra

^1H NMR spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) at room temperature using *d*-chloroform and dimethylsulfoxide- d_6 as solvent. The IR spectra were obtained on a Nicolet 6700 Fourier Transform Infrared Spectrometer.

2.3. Optical instrumentations

The fluorescence spectra and UV–Vis spectra were recorded on a FLSP920 Edinburgh Fluorescence Spectrophotometer and a Varian Cary 500 spectrophotometer, respectively. The ultraviolet irradiation source was CHF-XM35 parallel light system with a 500 W xenon lamp and monochromatic filters. The intensity of irradiating UV and visible light on the surface of samples was about 8 mW cm^{-2} .

2.4. Fluorescence microscopy

Fluorescence images of the polymer-doped PMMA films were recorded with an Olympus FluoView 1000-Confocal laser scanning microscope providing superior linear spectra and images. This apparatus is equipped with SIM Scanner (while one laser stimulates, the second laser simultaneously offers high-resolution image) and IX81 inverted microscope.

2.5. Synthesis of fluorescent photoswitching compound NP–PY and polymer

The synthetic routes of compound NP–PY and polymer are illustrated in the following [Scheme 2](#).

2.5.1. 3,3-Diphenyl-[3H]naphtho[2,1-b]pyran-8-carboxylic acid (DNPA)

A solution of 6-hydroxynaphthalene-2-carboxylic acid (0.98 g, 5 mmol) and 1,1-diphenyl-2-propyn-1-ol (1.14 g, 5 mmol) in dichloromethane (CH_2Cl_2 , 70 mL) at 35°C was stirred well under nitrogen atmosphere. Then a catalytic amount of *p*-toluenesulphonic acid (PTSA, 100 mg) was added and the reaction mixture was stirred for 2 days. The crude product was collected by filter and the purified product was obtained by flash column chromatograph (dichloromethane:ethyl acetate = 8:2), white powder 1.52 g, yield 79%. ^1H NMR (500 MHz, CDCl_3): δ 8.49 (1H, s), 8.18 (1H, d, $J = 8.5$ Hz), 7.98 (1H, d, $J = 24.5$ Hz), 7.50 (1H, d, $J = 9$ Hz), 7.52–7.49 (5H, m), 7.41–7.34 (5H, m), 7.26 (2H, m), 6.64 (1H, d, $J = 10$ Hz).

2.5.2. 1-Pyrenemethanol

1-Pyrenecarboxaldehyde (2.8 g, 12.2 mmol) was taken into 100 mL of dry MeOH under nitrogen atmosphere. NaBH_4 (0.68 g, 18.1 mmol) was added into the above solution in portions at 0°C and the reaction mixture was stirred at room temperature for 30 min. The mixture was heated to reflux for 6 h. After the reaction was cooled down to room temperature, the reaction mixture was diluted with 150 mL of 5% HCl and the white precipitate separated out. The white precipitate was collected by filter and dissolved into ethyl acetate, the organic solution was washed with brine, dried with Na_2SO_4 and finally used vacuum rotary evaporation to get the solid product, 2.58 g (yield, 91%, mp = 126 – 128°C), ^1H NMR (500 MHz, CDCl_3): δ 8.05–8.38 (9H, m, Ar–H), 5.41 (2H, s, Ar CH_2).

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