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Solvent-dependent fluorescence enhancement and piezochromism of a carbazole-substituted naphthopyran

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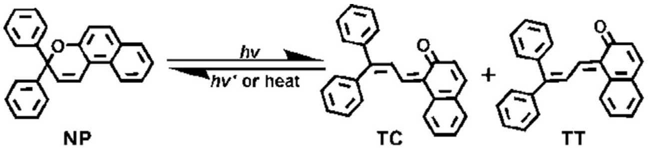
ABSTRACT

A novel carbazole-substituted naphthopyran, 3,3-bis-(4-carbazolylphenyl)-[3H]-naphtho[2,1-b]pyran (CzNP) was designed and synthesized. The new compound exhibited normal photochromism in dichloromethane solution and the UV irradiation did not influence its fluorescence. On the contrary, the fluorescence of CzNP in N,N-dimethylformamide (DMF) was intensively enhanced to 29 times after 60 min of the UV irradiation and this enhanced fluorescence can be quenched by addition of triethylamine (TEA). The study of enhanced extent of fluorescence of CzNP in solvents with different polarities and in mixed solvents demonstrated that the enhanced fluorescence is dependent on the polarity of solvents. The larger the polarity of solvent was, the stronger was the fluorescence of CzNP. CzNP also exhibited piezochromic performance and the pressure led to the cleavage of the C–O bond of pyran ring.

1. Introduction

Photochromism refers to the photoinduced reversible transformation of chemical species between two electronic states characterized by different absorption spectra [1]. Photochromic materials change their color under light irradiation. In most situations, a colorless state transforms into a colored one under ultraviolet irradiation and reverts back by thermal effect or upon visible irradiation. The reversible conversion accompanied by modifications of molecular structures and electron states often alters the ability of photochromic compound to emit light [2]. Therefore, attaching covalently the fluorescent group can effectively be implemented to modulate the fluorescence emission, especially, photo-responsive modulation of fluorescence emission [3]. Among various photochromic systems, naphthopyrans (NP) are well known due to their breadth of generated color, absence of background color, good thermal reversibility, fine control over fading kinetics, and good resistance to photochemical fatigue [4,5].



Scheme 1. The photochromic reaction of naphthopyran molecule.

Photochromic fluorescent molecules have attracted increasing interests due to their potential applications in molecular switches, optical data storage, fluorescent biological markers and other molecular electronic and photonic device [6–10]. So far, diarylethene, spiropyran and spirooxazine derivatives have been extensively studied for constructing fluorescence-photochromism switches, whereas less attention has been paid to NP unit [11–14]. Up to now, only a few examples using photochromism of naphopyran to modulate the fluorescence via different ways, such as the binding of metal ion and protonation, photoinduced energy and electron transfer have been reported [15–18]. The photochromic reaction of naphthopyran molecule is illustrated in Scheme 1.

Recently, our group reported the photochromic fluorescence switching adopting NP as photochromic unit and benzimidazole as fluorescent moiety [17–20]. Reversible modulation of fluorescence intensity was implemented by the photochromism of NP unit.

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However, further research on the synthesis of new photochromic fluorescent switching materials with better performance is still indispensable because of the low fluorescent modulation efficiency obtained in the previous reports. In this work we did not follow the normal molecular principle of fluorophore-space-photochrome to design fluorescent switching molecule. Alternatively, we prepared a new naphthopyran–carbazole dye denoted as CzNP via direct combination of NP and carbazole (Cz) as fluorescent moiety (Scheme 2). To the best of our knowledge, Cz derivatives are excellent fluorescent chromophores because of their good photostability and high fluorescent quantum yield [21–24]. Thus, two Cz units were directly combined with NP unit to form a large conjugation system, and it was found that the photochromic species of NP can remarkably affect the fluorescence of carbazole units in more polar solvents. The molecular structure and synthetic route of CzNP are shown in Scheme 2.

2. Experimental

2.1. Materials and equipments

Carbazole, t-BuOK, bis(4-fluorophenyl)methanone, n-butyllithium, trimethylsilylacetylene, and 2-naphthol in analytical purity were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further treatment. p-Toluenesulfonic acid (PTSA) was recrystallized from ethanol. All solvents were refined prior to use.

^{1}H and ^{13}C NMR spectra were obtained using a Varian Unity Inova Spectrometer at room temperature using D-chloroform as solvent and tetramethylsilane (TMS) as internal standard. Mass spectrum was recorded on BRUKER autoflex III Smartbeam MALDI-TOF/TOF MS-spectrometer. Fluorescence and UV–vis absorption spectra were measured on Cary Eclipse Fluorescence Spectrophotometer and Varian Cary 500 spectrophotometer, respectively. The absorption spectra of solid samples were obtained by means of a Cary 500 UV–vis–NIR Spectrophotometer. The IR spectra were recorded on a Nicolet 6700 Fourier Transform Infrared Spectrometer (FT-IR). 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 and 550 nm). The irradiating light that reached the samples was parallel and its intensity was 8 mW/cm^2. Single-crystal X-ray diffraction data for compound CzNP were taken using a Bruker Apex II CCD diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71073 Å) at 293 K. Absorption corrections were applied using a multi-scan technique. The structure was solved by direct method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX [25–27]. Piezochromic experiments were carried out on a CARL-ZEISS infrared tablet machine.

2.2. Synthesis of 3, 3-bis-(4-carbazolylphenyl)-[3H]-naphtho[2, 1–b] pyran, CzNP

2.2.1. Synthesis of bis(4-(9H-carbazol-9-yl)phenyl)methanone 1

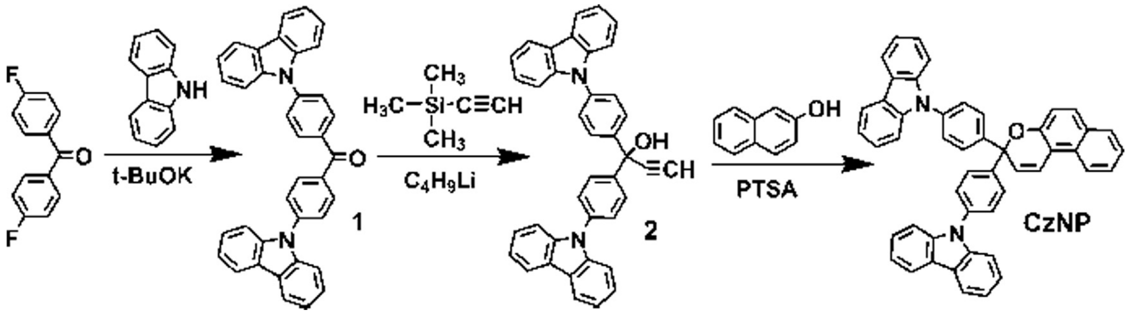
A mixture of carbazole (16.7 g, 100 mmol) and t-BuOK (11.8 g, 105 mmol) in anhydrous DMF (150 mL) was stirred at 65 °C for 10 min, before bis(4-fluorophenyl)methanone (10.9 g, 50 mmol) was added. The reaction mixture was then heated to 110 °C for 12 h. The resulting mixture was cooled to room temperature, poured into water and filtered. The crude product was recrystallized from acetone. The title compound 1 was obtained as a white powder (24.1 g, 94.3%). ^{1}H NMR (500 MHz, CDCl$_3$, δ) 8.19–8.16 (m, 8H, Ar–H), 7.81–7.79 (m, 4H, Ar–H), 7.56 (d, 4H, *J*=8 Hz, Ar–H), 7.47–7.44 (m, 4H, Ar–H), 7.35–7.32 (m, 4H, Ar–H).

2.2.2. Synthesis of 1, 1-bis-(4-carbazolylphenyl)-propyn-1-ol 2

Anhydrous THF (10 mL) was cooled in the ice bath under nitrogen atmosphere. The solutions of n-butyllithium (2.5 M) in hexanes (4.8 mL, 12 mmol) and trimethylsilylacetylene (1.8 mL, 12 mmol) were added via syringe. After stirring for 1 h, compound 1 (5.12 g, 10 mmol) was added and the reaction mixture was stirred for another 3 h. A methanol solution (2 mL) of KOH (0.818 g, 12 mmol) was added in a single portion. The cooling bath was then removed and the mixture warmed to room temperature for 0.5 h. After adding water (40 mL) into the reaction mixture, the product was extracted with dichloromethane. The organic solution was washed with brine and dried with anhydrous sodium sulfate. The purified product was obtained by column chromatography on silica gel (ethyl acetate:dichloromethane=1:1) to give the title compound as a white powder (3.84 g, 71.6%). M.p. 208–209 °C. 1H NMR (500 MHz, CDCl$_3$, δ) 8.15 (d, 4H, *J*=7.5 Hz, Ar–H) 7.96 (d, 4H, *J*=9 Hz, Ar–H), 7.63 (d, 4H, *J*=9 Hz, Ar–H), 7.48 (d, 4H, *J*=8 Hz, Ar–H) 7.43–7.40 (m, 4H, Ar–H), 7.31–7.28 (m, 4H, Ar–H), 3.06 (s, 1H, –C≡H), 3.05 (s, 1H, –OH).

2.2.3. Synthesis of 3, 3-bis-(4-carbazolylphenyl)-[3H]-naphtho[2, 1–b]pyran CzNP

A mixture of compound 2 (0.539 g, 1 mmol), 2-naphthol (0.144 g, 1 mmol), and PTSA (0.02 g) in dry CH$_2$Cl$_2$ (10 mL) was stirred at room temperature under nitrogen atmosphere for 48 h. PTSA was extracted off with water and the organic solution was dried with anhydrous sodium sulfate. The purified product was obtained by column chromatography on silica gel (ethyl acetate: dichloromethane=3:5) to give the title compound as a white powder (4.3 g, 65.4%). M.p. 291–293 °C. ^{1}H NMR (500 MHz, CDCl$_3$, δ): 8.06 (d, 4H, *J*=8 Hz, Ar–H), 7.99 (d, 1H, *J*=9 Hz, –O–C–CH=CH–C–), 7.75–7.73 (m, 4H, Ar–H), 7.71–7.69 (m, 2H, Ar–H), 7.53 (d, 4H, *J*=8.5 Hz, Ar–H), 7.47 (m, 1H, Ar–H), 7.40-7.38 (m, 5H, Ar–H), 7.34–7.30 (m, 5H, Ar–H), 7.26 (d, 1H, *J*=8.5 Hz, Ar–H), 7.22–7.19 (m, 4H, Ar–H), 6.37 (d, 1H, *J*=9.5 Hz, –O–C–CH=CH–C–); 13C NMR (125 MHz, CDCl3, δ): 150.4, 143.7, 140.6, 137.2, 130.3, 128.6, 128.5,



Scheme 2. Molecular structure and synthetic route of CzNP.