



Synthesis and photochromic properties of a bis(diarylethene)-naphthopyran hybrid



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ABSTRACT

The synthesis and photochromic properties of a triphotochromic molecule consisting of one naphthopyran flanked by two diarylethene units investigated by UV–Visible and Nuclear Magnetic Resonance spectroscopies are reported. Six different states resulting from the open/closed naphthopyran associated with one or two open/cyclized diarylethenes have been characterized. The photochemical and thermal interconversion between the six states of the triphotochromic target was followed allowing to determine the existing pathways upon irradiation with 313 and 365 nm light excitation, and during thermal evolution. Switching of the naphthopyran group is possible, independently of the state of the diarylethene groups. However, the diarylethene groups cannot be closed if the naphthopyran group is open.

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1. Introduction

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two isomeric states, A and B, having different absorption spectra [1]. Usually the thermodynamically stable state A is transformed by irradiation with UV light into state B. The back reaction can occur thermally (photochromism of type T) or photochemically with visible light (photochromism of type P). The two isomers differ from one another not only in the absorption spectra but also in various physical and chemical properties, such as refractive indices, dielectric constants, oxidation–reduction potentials, geometrical structure, conductivity and dipole moment [2].

Application of photochromic compounds to devices such as optical memory media and photoswitches requires thermal stability of the two isomers, fatigue-resistant property, high sensitivity and a rapid response. Diarylethenes fulfill all the above requirements simultaneously [3,4]. Naphthopyrans represent another family of photochromic compounds which exhibit excellent photochromic properties and are successfully applied in ophthalmic glasses as T-type compounds [5].

As the demand for optical memories with high memory density, large storage capacity and high data process/transfer rate is increasing, multi-wavelength (or multi-frequency) optical storage is one of the promising approaches to increase the recording density and data capacity [6]. In two-state photochromic systems, interconversion is possible between only two states. On the other hand, multicomponent systems can result in reversible multimode switching between the states [7]. N-wavelength memory can increase the recording density by N times of that of single-wavelength memory [8]. Multi-color systems can be achieved by mixing photochromic compounds with different colors in solution [8,9], in polymer matrices [10], in single crystals [11] and by incorporating two or more photochromic units in one molecule. The latter is referred as single molecule multiphotochromism [12]. Some advantages of a single-molecule system over mixture systems are high image resolution arising from local homogeneity, constant color balance in a large area, and long term storage stability [6,13]. Multi-frequency optical memories in hybrid systems consisting of photochromic units of different kinds have a potential advantage in the ease of selecting and designing photochromic moieties with different absorption bands [14]. In this regard, hybrid systems between dihydroazulene and diarylethene [15], phenoxynaphthacene–diarylethene [16], spirooxazine–naphthopyran [17] have been reported. Association of diarylethene and

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naphthopyran units was first introduced by Frigoli and Mehl and then extended to two naphthopyrans connected via a diarylethene group, leading to the formation of four and six different states respectively [18–20]. The most extensively studied class of multi-photochromic materials consists of linked diarylethene based systems [12]. For covalently bound electronically disconnected diarylethene systems, sequential closing has been confirmed [21,22] as well as for supramolecular arrays [23]. For materials where the diarylethene groups are electronically connected, the current data does not yet allow to identify an overall trend. On the one hand, there are a number of clear and unambiguous reports for linear molecules, showing that the closing of one diarylethene group results in ring-opening of the adjacent system [24,25], allowing for the rational design of multicolor diarylethene systems [13]. At the other hand, there are reports showing that in almost similar chemical structures [26] or in stable organic radicals containing diarylethene dimers [27], all the diarylethene groups can be closed. Results for a star shaped hexameric systems [28,29] suggest that a combination of electronic effects such as energy transfer between diarylethenes or steric effects, such as ring twists determine the switching behavior in multi-diarylethene systems.

Considering the technological and scientific importance of this class of molecules and the effect of conjugation and molecular linearity on their properties, we decided to explore the issue for photoreactivity in multiphotochromic systems systematically. In this contribution we report on the investigation of a triphotochromic system (**OD-CN-OD**, Chart 1) where two diarylethenes (**OD** as Open Diarylethene) are linked to a naphthopyran (**CN** as Closed Naphthopyran) group. The linkage is selected in such a manner that in the closed naphthopyran, the two diarylethenes are separated by an sp^3 hybridized carbon. In the open naphthopyran, this carbon is sp^2 hybridized and conjugated and each of the diarylethene units are linked to the naphthopyran moiety by π -conjugation, though the linkage between the diarylethene restricts their electronic communication to a certain degree. The aim is here to investigate and characterize the six different states which are theoretically expected upon irradiation under suitable conditions of these three electronically linked photochromic units. Crucially, some of the states involve two electronically linked diarylethene groups. Using a construction where the two diarylethenes are electronically separated, when the naphthopyran group is closed; or linked, when

it is open, the optical linking of the conjugation of multiple diarylethene groups is explored.

The photochromic behavior of the synthesized system was investigated by UV–Vis Spectroscopy and NMR spectroscopy. As open naphthopyrans are thermally unstable at ambient temperature while cyclized diarylethenes are thermally stable, we first studied the photocyclization of diarylethene units upon excitation with 313 nm irradiation at room temperature. Then the photochemical ring opening of the naphthopyran moiety was investigated by irradiating with 365-nm light at rt by UV–visible spectroscopy and at low temperature by NMR spectroscopy.

2. Experimental

2.1. Equipment

Unless otherwise stated, reagents were used as supplied. UV–visible spectra were recorded for spectroscopic grade toluene solutions of the sample (10 mm pathlength quartz cuvette, ca. 5×10^{-5} mol l^{-1}) using a Cary 50 Probe spectrophotometer. NMR spectra of target compound OD-CN-OD were recorded on a Bruker Avance 500 MHz instrument (1H NMR 500 MHz, ^{13}C NMR 125 MHz) equipped with a TXI probe for sample solutions in toluene- d_6 . Irradiation for UV–visible was provided by a 200 W high pressure Hg/Xe lamp. Irradiation for NMR measurements was carried out directly into the NMR tube in a home-built thermoregulated (295, 243, 233, 223 and 213 K) apparatus with a 1000 W high-pressure Hg – Xe lamp. Monochromatic UV (313 or 365 nm) or visible light (577 nm) was obtained by passing the light through a first filter to select UV or visible band, then through an interferential one. When required, NMR experiments were carried at various low temperatures using a N_2 cooling setup connected to the 500 MHz spectrometer.

Elemental analyses of products were carried out using an EA 1108 CHNS analyzer. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm silica gel plates (60F-254). Column chromatography was performed on silica gel (35–70 μ 60 A). The purity of all final compounds were checked by GLC analysis using a 9001 capillary gas chromatograph fitted with a fused silica column (CP-Sil5 CB 0.12 m, 10 m long, 0.25 mm internal diameter) and using nitrogen as the carried gas and by HPLC analysis using a system fitted with a 5 μ m silica column (25 cm long, 4.6 mm internal diameter) and were found to be >99.5%. 1H and ^{13}C NMR spectra of intermediate compounds in chloroform- d_1 were recorded at 400 and 100 MHz, respectively, for 1H and ^{13}C . Mass spectrum was recorded on Autoflex Speed MALDI TOF/TOF MSMS instrument using 3,5-dimethoxy-4-hydroxycinnamic acid as matrix.

2.2. Preparation of intermediate compounds

2.2.1. Reagents

All reagents used were of analytical grade and were purchased from Sigma Aldrich (most of them) and Fluorochem (octafluorocyclopentene). The THF was dried by distillation on Na/benzophenone. The other solvents were used without further purification other than drying over molecular sieves. The intermediate 4-bromo-5-methyl-2-thienylboronic acid (**5**) and 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene (**7**) were obtained following the procedure described previously ((**5**) [30–32]; (**7**) [32,33]).

2.2.2. Bis(4-bromophenyl)methanone (1)

A mixture of 4-bromobenzoyl chloride (6.58 g, 30 mmol) in bromobenzene (25 mL) was added to a solution of $AlCl_3$ (4 g, 30 mmol) in bromobenzene (26 mL) under nitrogen. The mixture was stirred at 55 °C for 3 days and then, 100 g ice and 50 mL HCl

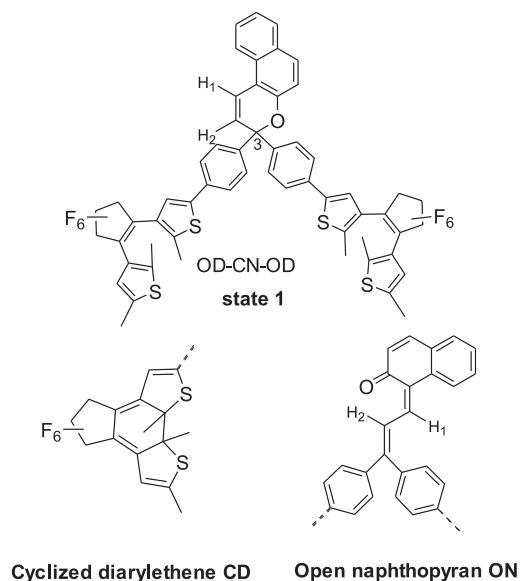


Chart 1. Structure of the target compound.

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