

Synthesis and Photochromic properties of a bis(Diarylethene)-Naphthopyran Hybrid

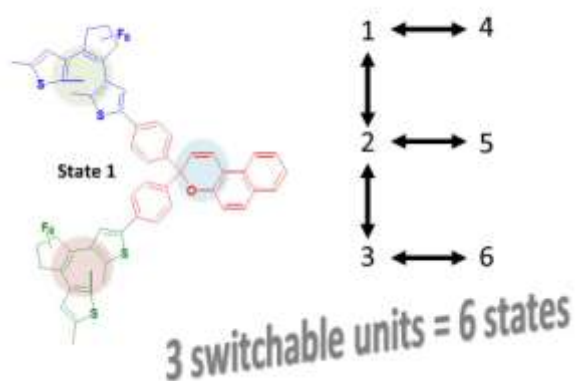
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Abstract

The synthesis and photochromic properties of a triphotochromic molecule consisting of one naphthopyran flanked by two diarylethene units investigated by UV-Visible and NMR spectroscopies are reported. Six different states resulting from the open/closed naphthopyran associated with one or two open/cyclized diarylethenes have been characterized. Switching of the naphthopyran group is possible, independently of the state of the diarylethene groups, permitting the controlled generation of electronically connected diarylethene groups. However, the diarylethene groups cannot be closed if the naphthopyran group is open.

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 photoswitching requires thermal stability of the two isomers, fatigue-resistant property, high sensitivity, 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 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 multiphotochromic 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 [26]. At the other hand, there are reports showing that in almost similar chemical structures [25], in stable organic radicals containing diarylethene dimers [27] as well as in a star shaped trimeric material, all the diarylethene groups can be

closed, even though conjugation through the connecting aromatic central core and bridged ethynyl groups is possible [28]. Results for a star shaped hexameric systems [29-30] 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) 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 a sp³ hybridized carbon. In the open naphthopyran, this carbon is sp² hybridized and conjugated and each diarylethene unit is linked to the central naphthopyran moiety by pi-conjugation. ~~though the linkage between the diarylethene are the cross-conjugation which 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. To do this unambiguously, UV-visible and NMR techniques are employed. 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 diarylethenes are thermally stable, we first studied the photocyclization of diarylethene units upon irradiation with 313 nm 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.

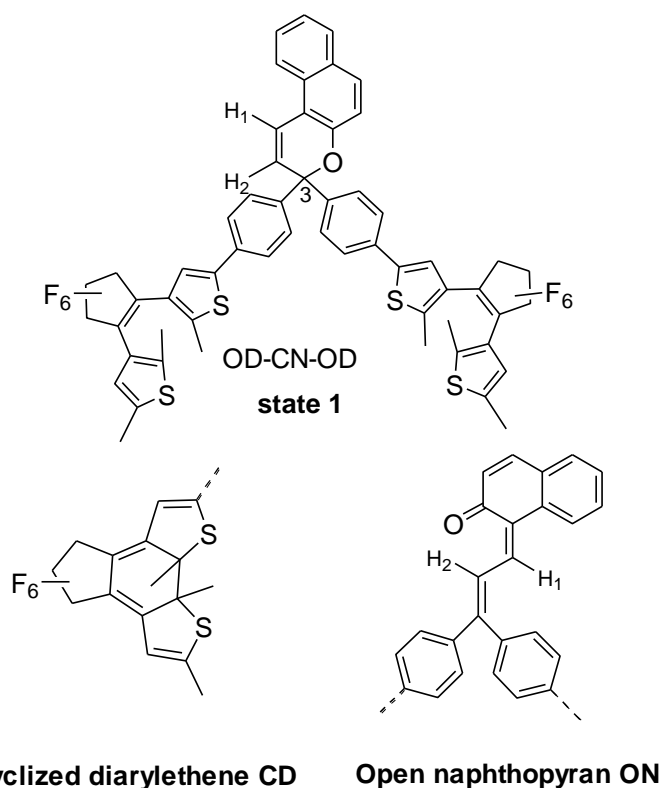


Chart1: Structure of the target compound

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, ¹³C NMR 125 MHz) equipped with a TXI probe for sample solutions in toluene-d₈. 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 213K) apparatus with a 1000W high-pressure Hg – Xe lamp. Monochromatic UV (313 or 365nm) or visible light (577 nm) was obtained by passing the light through a first filter, then through an interferential one. When required, NMR experiments were carried at various low temperatures using a N₂ cooling setup connected to the 500MHz 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 (35-70u 60A). 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 5µm silica column (25 cm long, 4.6 mm internal diameter) and were found to be > 99.5 %. ¹H and ¹³C NMR spectra of intermediate compounds in chloroform-d₁ were recorded at 400 and 100 MHz, respectively, for ¹H and ¹³C. 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-2thienylboronic acid (**5**) and 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene (**7**) were obtained following the procedure described previously (**5**) [31-33]; (**7**) [33, 36]).

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 at a solution of AlCl₃ (4 g, 30 mmol) in bromobenzene (26 ml) under nitrogen. The mixture was stirred at 55 °C for 3 days and after it was added 100 g ice and 50 ml HCl conc. The resulting mixture was extracted twice with diethyl ether washed with aqueous NaOH 5% and then with water, dried over magnesium sulfate, then concentrated under vacuum. The crude product recrystallized from methanol gave white powder (8.45 g, 83 %). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.6 (s, 8H); ¹³C-NMR (CDCl₃): 135.8, 131.7, 131.4, 127.8, 194.2; Elemental analysis calcd. (%) for C₁₃H₈Br₂O: C 45.92, H 2.37; found C 45.84, H 2.26.

2.2.3 1,1-bis(4-bromophenyl)prop-2-yn-1-ol (**2**).

A solution of bis(4-bromophenyl)methanone (**1**) (5.1 g, 15 mmol) in dry THF (100 ml) was added to a solution of lithium acetylide-ethylenediamine (13.8 g, 150 mmol) in dry THF (60 ml) under nitrogen at 5 °C. The mixture was stirred at room temperature for 23h and then a solution KOH

(10 g) in ethanol (125 ml) was added. The mixture was stirred at r.t. for 15 min. The acetic acid glacial was added until pH = 7. Water (400 ml) was added and the organic compound was extracted with diethyl ether three times and dried over MgSO₄. The crude product was obtained by remove the solvent under pressure. Column chromatography (silica, CH₂Cl₂) gave white liquid (2.25 g, 41 %). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.45 (s, 8H, Har), 2.90 (s, 1H, C≡CH), 2.80 (s, 1H, -OH); Elemental analysis calcd. (%) for C₁₅H₁₀Br₂O: C 49.22, H 2.75; found C 49.34, H 2.69.

2.2.4 3,3-Bis(4-bromophenyl)-3H-benzo[f]chromene (3).

A mixture of 2-naphthol (2.0 g, 0.014 mol) and the 1,1-bis(4-bromophenyl)prop-2-yn-1-ol (**2**) (5.0 g, 0.014 mol) in CH₂Cl₂ (30 ml) in the presence of PPTS catalytic amount, trimethylorthoformate (20 ml) was refluxed for 24 h. The solvent was removed and the crude product was purified by column chromatography (silica, CH₂Cl₂); yield 45 % (3.1 g). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.94 (d, 1H, J = 8.0), 7.71 (dd, 1H, J = 8.8), 7.66 (d, 1H, J = 8.8), 7.45 (m, 1H), 7.43 (m, 4H), 7.31-7.36 (m, 6H), 7.15 (dd, 1H, J = 8.8), 6.13 (d, 1H, J = 9.9), ¹³C-NMR (CDCl₃, 100 MHz): 150.0, 143.3, 131.3, 130.2, 129.4, 128.7, 128.5, 126.9, 126.5, 123.9, 121.9, 121.3, 120.4, 118.1, 114.2, 82.4. Elemental analysis calcd. (%) for C₂₅H₁₆Br₂O: C 60.01, H 3.28; found C 59.87, H 3.19.

2.2.5 3,3-Bis(4-(4-bromo-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (6).

Compound 3,3-bis(4-bromophenyl)-3H-benzo[f]chromene (**3**) (1.47 g, 3 mmol) was dissolved in THF (12 ml) and after addition of Pd(PPh₃)₄ (23x10⁻² g, 0.2 mmol), the solution was stirred at r. t. for 15 min. Aqueous Na₂CO₃ (5.3 g in 25 ml H₂O) and 6 drops of ethylene glycol were then

added, and the resulting two phase system was heated until reflux. A solution of 5-bromo-2-methylthiophen-3-yl-3-boronic acid (**5**) (1.54 g, 7 mmol) in THF (15 ml) was added drop wise. After the addition was complete, the reaction mixture was refluxed for 8 h and then allowed to cool down at r. t.. 25 ml of water were added and the crude product was extracted by diethyl ether (3 X 25 ml) and dried over MgSO₄. Evaporating the solvent, the crude product was purified on the column (silica, hexane for 30 min. and then hexane/CH₂Cl₂, 9/1). Recrystallization from ethyl acetate gave a white powder with yield of 30 % (0.6 g). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.95 (d, 1H, J = 8.2), 7.71 (d, 1H, J = 8.1), 7.67 (d, 1H, J = 8.8), 7.21-7.50 (m, 9H), 7.30-7.37 (m, 2H), 7.20 (d, 1H, J = 8.8), 7.05 (s, 2H), 6.24 (d, 1H, J = 9.9), 2.39 (s, 6H); Elemental analysis calcd. (%) for C₃₅H₂₄Br₂OS₂: C 61.41, H 3.53, S 9.37; found C 61.72, H 3.17, S 9.4

2.2.6 3,3-Bis(4-(4-(3,3,4,4,5,5,-hexafluoro-2-(2,5-dimethylthiophene-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (OD-CN-OD).

To a solution of compound 3,3-bis(4-(4-bromo-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (**6**) (200 mg, 0.293 mmol) in dry THF (15 ml) was added *n*-BuLi (0.4 ml of 1.6 M solution in hexane, 0.586 mmol) under nitrogen at -78 °C. This solution was stirred 1 h and then compound 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene (**7**) (178.3 mg, 0.586 mmol) was added in one portion. The mixture was stirred at -78 C for 1 h, and then allowed to warm-up to r. t. After stirring for additional 12h, diethyl ether (20 ml) was added, and the mixture was washed with water. The organic layer was dried over MgSO₄ and solvent evaporated. The crude product was purified by 2 columns (silica, CH₂Cl₂/hexane, 7/3; silica, CH₂Cl₂/hexane, 0.5/9.5) and afforded 115.5 mg (36%) finale compound.

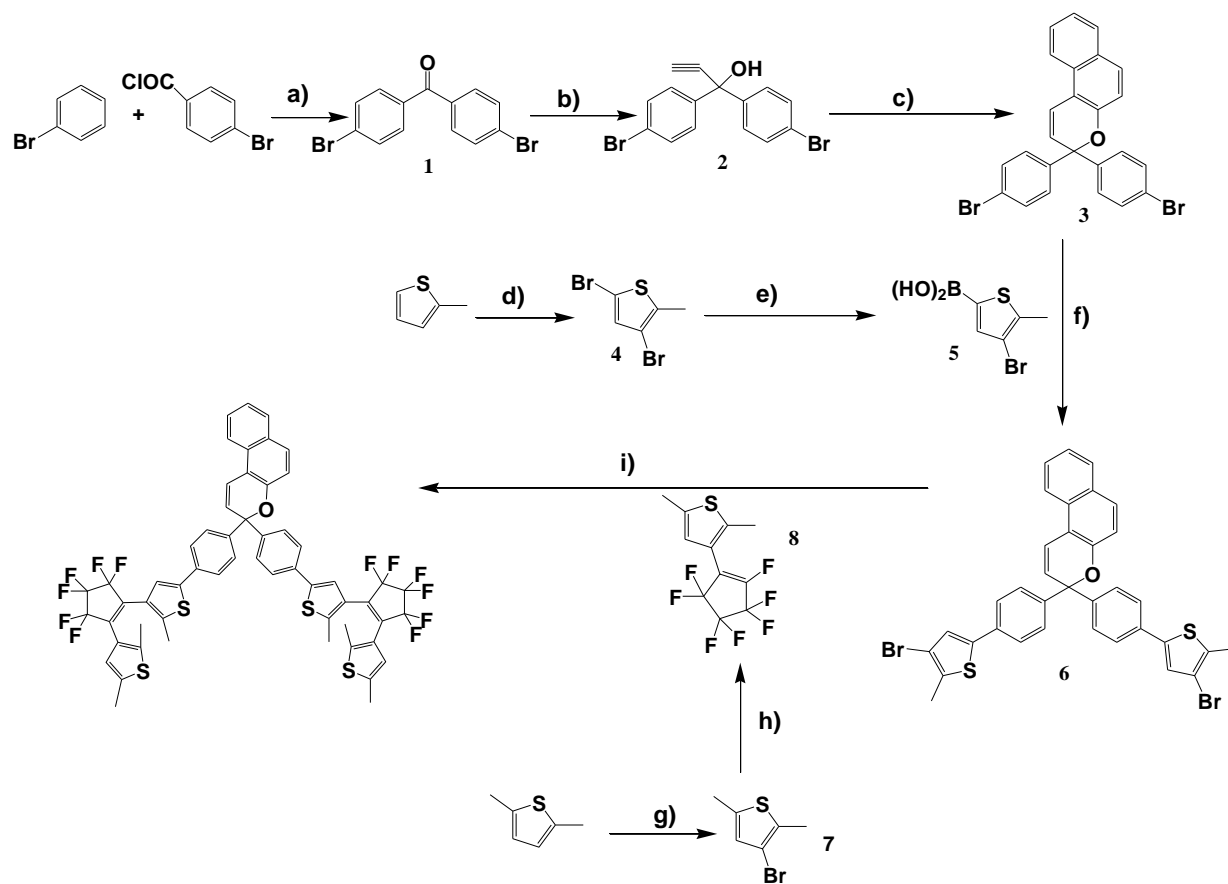
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ [ppm]): 7.96 (d, 1H, H^{10} , $J = 8.3$), 7.72 (d, 1H, H^7 , $J = 8.1$), 7.68 (d, 1H, H^6 , $J = 8.8$), 7.46-7.54 (m, 9H, $\text{H}^{1,2,9}$), 7.30-7.37 (m, 2H, $\text{H}^{5,8}$), 7.21 (s, 2H, H^{11}), 7.20 (d, 1H, H^4 , $J = 8.8$), 6.71 (m, 2H, H^{13}), 6.25 (d, 1H, H^3 , $J = 9.9$), 2.40 (s, 6H, H^{14}), 1.89 (s, 6H, H^{12}) 2.81 (s, 6H, H^{15}). Elemental analysis calcd. (%) for $\text{C}_{57}\text{H}_{38}\text{F}_{12}\text{OS}_4$: C 62.51, H 3.50, S 11.71; found C 62.68, H 3.46, S 11.57. $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): 150.5, 144.3, 141.5, 141.4, 139.9, 132.8, 130.2, 129.9, 129.5, 128.7, 127.7, 127.1, 126.9, 126.1, 125.5, 124.7, 124.6, 123.9, 122.8, 121.4, 120.4, 118.3, 116.3, 115.6, 114.2, 113.6, 11.1, 82.1, 15.2, 14.5, 14.4. Mass spectrum: m/z 1095.49.

HPLC (MeCN/DCM = 9/1) BI-before irradiation; AI-after irradiation with 365 nm

	Before irradiation		After irradiation with 365 nm		Photo-stationary state after irradiation with 365 nm	
	Retention time	Area %	Retention time	Area %	Retention time	Area %
Peak after irradiation			10.05	1.03		
Peak initial	10.82	2.55	10.62	2.35		
Peak after irradiation			12.09	0.60		
Peak after irradiation			14.15	0.83		
Peak initial	19.06	95.44	18.65	71.27	18.76	11.55
Peak initial	21.03	2.01	21.22	26.76	21.35	48.11
Peak after irradiation			24.02	2.83	24.23	40.31

HPL experiments proved a purity of 97.45 of triphotochromic compound. In my opinion the peak with retention time around 19 is OD-CN-OD, the peak from 21 is CD-CN-OD and from 24 is CD-CN-CD. (The result from HPLC are not in agreement with the results from NMR or my interpretation from HPLC is not good).

3. Synthesis of target compound OD-CN-OD



*Scheme 1. Synthesis of the triphotochromic hybrid OD-CN-OD; Reagent and conditions: a) AlCl₃; b) lithium acetylide-ethylenediamine, THF; c) 2-naphthol, pyridinium *p*-toluenesulfonic acid (PPTS), CH(OCH₃)₃, CH₂Cl₂; d) Br₂, acetic acid; e) *n*-BuLi, THF, B(OCH₃)₃; f) Pd(PPh₃)₄, Na₂CO₃, THF; g) Br₂, CHCl₃; h) *n*-BuLi, THF, 3 eq of octafluorocyclopentene; i) *n*-BuLi, THF.*

The preparation of triphotochromic system was carried out in a nine step synthesis. The synthetic path to this new molecule is outlined in Scheme 1. The synthesis started with the preparation of ketone **(1)** which was obtained (yield: 83 %) from the reaction of bromobenzene with 4-bromobenzoyl chloride in the presence of AlCl₃. The subsequent condensation of lithium acetylide-ethylenediamine with **(1)** resulted in the corresponding propargylic alcohol **(2)** (41 %

yield). The intermediate naphthopyran **(3)** was obtained by a “one-pot reaction” of **(2)** and 2-naphthol in the presence of a catalytic amount of pyridinium p-toluenesulfonic acid and trimethyl orthoformate as desiccating agent (**(3)**, 45 % yield). The intermediate 4-bromo-5-methylthiophen-2-yl-2-boronic acid **(5)** was obtained in a 72 % yield from 2-methyl-thiophene by using bromine in acetic acid followed by the addition of trimethoxy borate, according to the procedure described in the literature [31-33]. The intermediate naphthopyran **(6)** was obtained by a Suzuki coupling reaction between **(3)** and **(5)** in the presence of highly active palladium catalyst which afforded the naphthopyran **(6)** (30 % yield). ~~The formation of an asymmetrical product in the metathesis reaction of **(3)** is responsible for the moderate yield observed.~~ The intermediate 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene **(8)** was obtained in three steps. The reaction sequence started with the bromination in the 3-position using bromine in chloroform, resulting in 3-bromo-2,5-dimethylthiophene **(7)**. This introduces the functionality required for the assembly of the photochromic skeleton. The treatment of **(7)** in THF with n-butyllithium at -78°C , followed by the addition of three equivalents of hexafluorocyclopentene yields the compound **(8)** (53 % yield). Lithiation of the intermediate naphthopyran **(6)** by bromine/lithium exchange using n-BuLi in THF at -78°C , follow by the addition of the intermediate **(8)** afforded the symmetrical triphotochrome system (OD-CN-OD, 36 % yield).

4. Photochemical and thermal reactions

4.1 UV-visible spectroscopy investigations

4.1.1 Irradiation at 313 nm

Upon irradiation at 313 nm, the toluene solution of **OD-CN-OD** (state **1**) turned from colorless to deep purple characterized by an absorption band located at $\lambda_{max} = 559$ nm (Figure 1a) which is thermally stable. Complete photobleaching is achieved upon irradiation with 577 nm light (Figure 1b). The observed maximal absorption wavelength, the thermal stability and the photochemical bleaching with visible light are characteristic of the cyclized diarylethene. However, as **OD-CN-OD** is constituted by two diarylethene units, it is not possible to conclude if one or two underwent ring closure.

4.1.2 Irradiation with 365 nm

Upon irradiation at 365 nm at room temperature, one absorption bands appears at 471 nm with a shoulder at 580 nm (Figure 1c). The band at 480 nm thermally decreased when the light is off, while the band at 580 nm persisted throughout thermal relaxation, although with a shift toward 559 nm, and was completely bleached with visible light (577 nm). Thus, the appearance of an absorption band at 480 nm that relaxes thermally is an indication of the naphthopyran opening and the thermally stable second band characterize the diarylethene closing. Its shifts corresponds to the pathways $5 \rightarrow 2$ and $6 \rightarrow 3$.

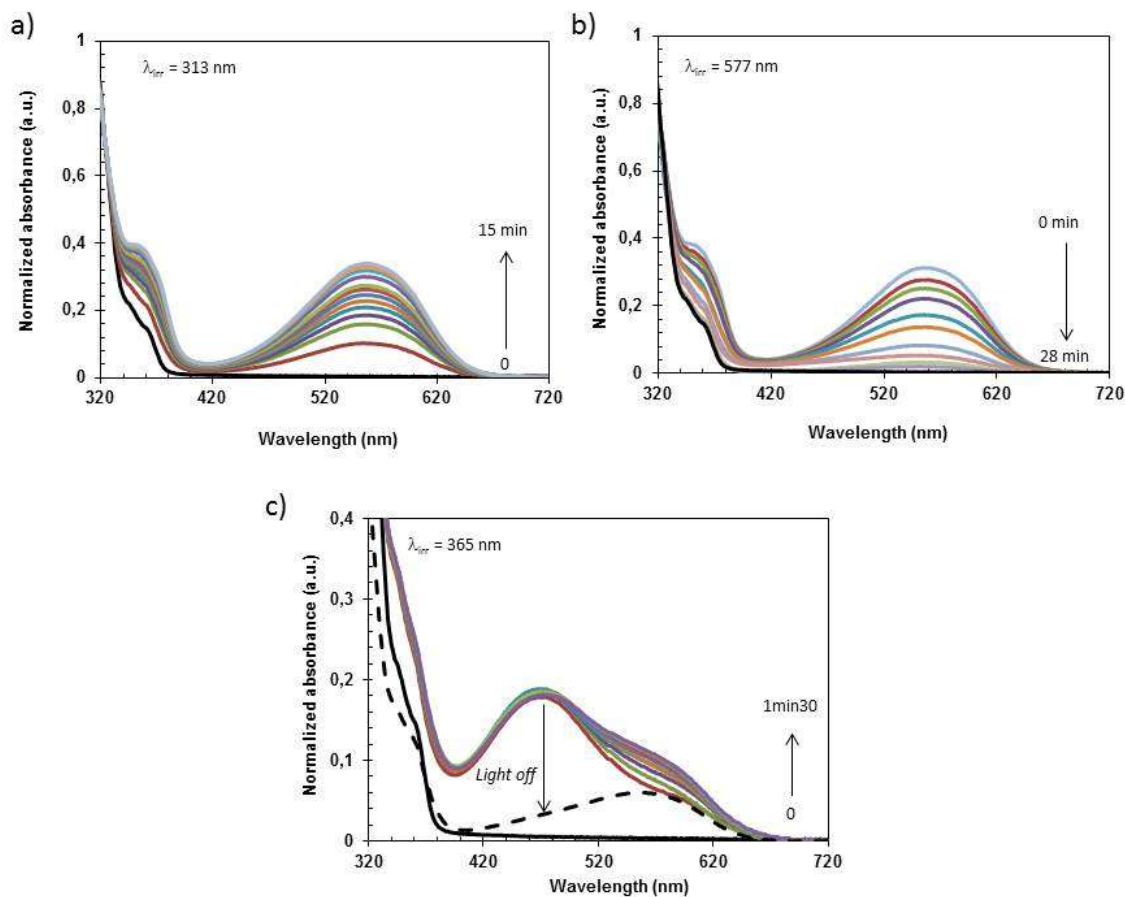


Figure 1: UV-Vis absorption spectra (295 K, toluene, 5×10^{-5} M) of state **1** a) upon irradiation at 313 nm, b) followed by irradiation with 577 nm; c) upon irradiation with 365 nm (black line : before irradiation ; dashed line in c) : light is off)

As **OD-CN-OD** is constituted of three photochromic entities, UV-visible studies did not allow for distinguishing if one or two diarylethenes underwent ring closure, and if the opening of naphthopyran is associated with diarylethene being cyclized or not. Consequently, the studies were carried out by NMR spectroscopy to determine if it is possible to reach each of the six possible states.

4.2 NMR investigations

4.2.1 Irradiation with 313 nm at room temperature

A fresh solution of **OD-CN-OD** (state **1**) in toluene (Figure 2a) was subjected to irradiation at room temperature with 313-nm light and ^1H NMR spectra were recorded after each period of irradiation. New signals which are thermally stable are observed (Figure 2b). More particularly, we observed the appearance of a 'doublet of doublets' like signal at 6.00 ppm and a 'doublet of triplet' like signal at 5.97 ppm. Such chemical shifts are typical of the H-2 in closed naphthopyrans, which is expected to be a doublet signal with a vicinal coupling constant of 9.9 Hz. The observed multiplicity at 6.00 and 5.97 ppm is explained by the formation of diastereomers, as reported for previously investigated diarylethene-naphthopyran hybrid photochromic systems [19-20]. The sp^3 carbon C-3 of the closed naphthopyran is either in the R or S configuration when one diarylethene is closed. The closing of diarylethene is itself in RR or SS configuration. Then, this results in two possible diastereomers (RR-R/SS-S, RR-S/SS-R). Here, they are associated with the two doublets at 6.00 ppm (state **2**). Similarly, the cyclization of both diarylethenes leads to the possible formation of four couples of diastereomers : RR-R-RR/SS-S-SS, SS-R-SS/RR-S-RR, SS-R-RR/RR-S-SS and RR-R-SS/SS-S-RR. The latter two are the identical sets. Hence, it results in the three doublets observed at 5.97 ppm, one being twice intense. Consequently, irradiation with 313-nm light induces the cyclization of one diarylethene unit, producing the state **2** = **CD-CN-OD**, and the cyclization of both diarylethene units forming the state **3** = **CD-CN-CD** (Scheme 2). This cyclization process was followed by irradiating the sample by successive periods, thus allowing to get the time-evolution of concentrations (Figure 3a). The

first periods of irradiation generate state **2**, and state **3** could be detected only when irradiation is prolonged. Also, it can be observed that the concentration of state **2** reaches a plateau, while that of state **3** is always increased. When the light source is replaced with visible light at 577 nm, the photobleaching of the solution is observed (Figure 3b). State **3** decreased following a mono-exponential decay, whereas state **2** is characterized by a bi-exponential evolution. Thus, the kinetic behavior upon UV and upon visible irradiation is a clear indication of the pathways from state **1** to state **3** by the intermediary of state **2**. In other words, UV light induced the cyclization of one diarylethene from initial OD-CN-OD (**1**) into CD-CN-OD (**2**). This latter absorbs UV light and the cyclization of its second diarylethene unit occurs to form CD-CN-CD (**3**). The reverse processes, decyclization of one diarylethene of CD-CN-CD (**3**) to produce CD-CN-OD (**2**), followed by the ring-opening of the second diarylethene unit of CD-CN-OD towards the initial state **1**, are fully achieved with visible light irradiation. Thus, at room temperature, the photochromic reaction of diarylethene has been underlined, with a high conversion of cyclization, as 90 % of cyclized structures has been measured.

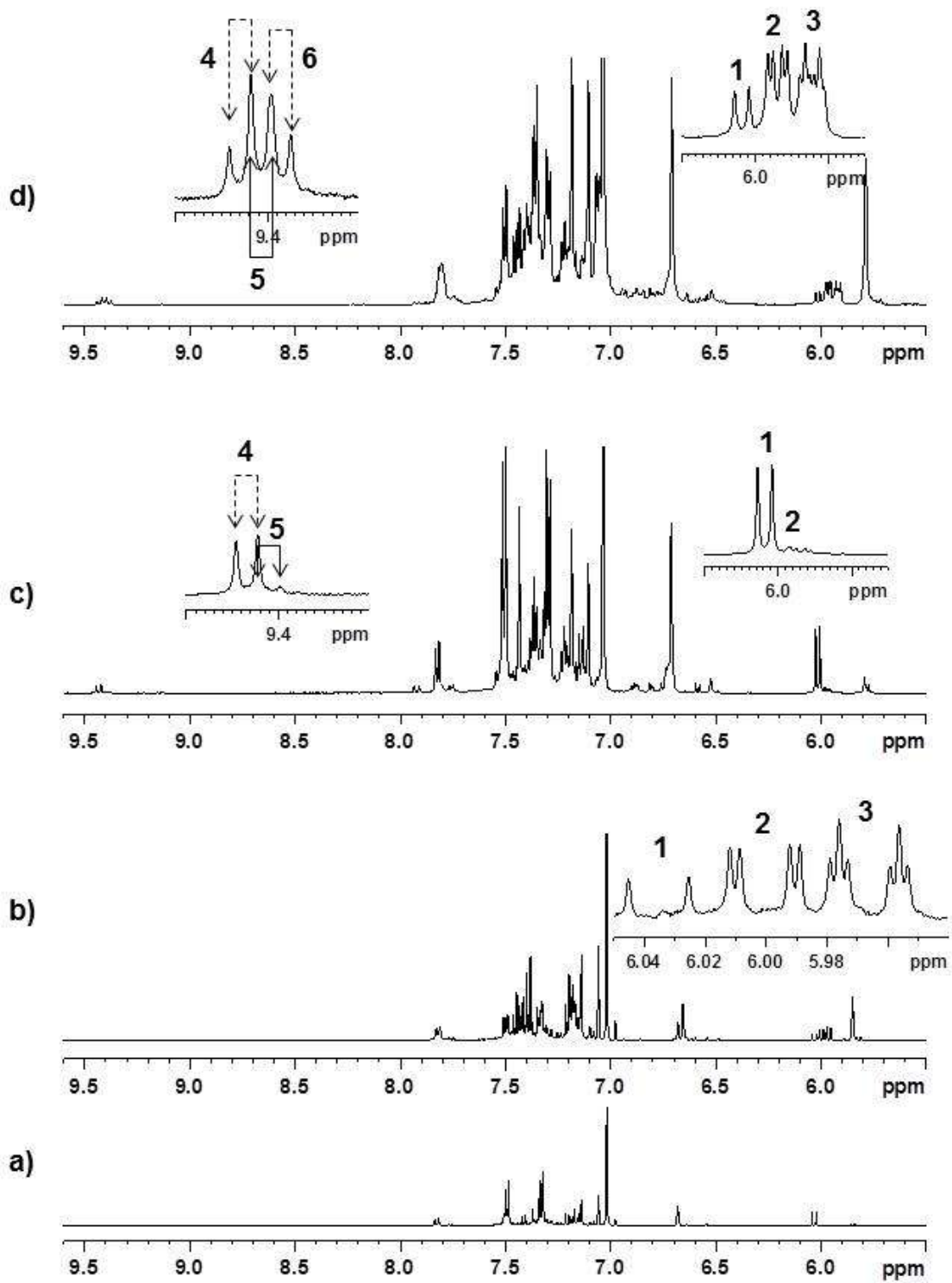


Figure 2: ^1H NMR Spectra of **1** (1 mM in toluene) a) at rt, b) after irradiation with 313 nm at rt, c) after irradiation with 365 nm at 223K, d) after irradiation with 313 nm at rt + 365 nm at 223K

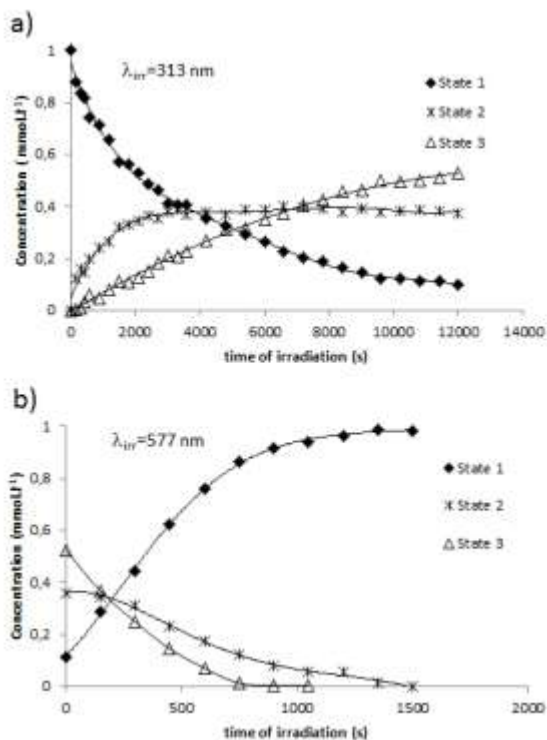


Figure 3: Time-evolution of concentrations of the states, **1**, **2** and **3** followed by ^1H NMR during irradiation (a) with 313 nm and (b) with 577 nm light at 295 K in toluene- d_8

4.2.2 Irradiation with 365 nm at low temperature

Irradiation with 365-nm light was applied to a fresh solution of **1** cooled at 223 K. As displayed in Figure 2c, new signals are detected and among them, the emergence of one doublet signal is observed at 9.43 ppm with a coupling constant of 11.9 Hz, which is characteristic of H2 proton in Transoid-Cis photomerocyanine [34]. The time-evolution of solution underlined its thermal

conversion into the initial state **1**, with a rate constant of relaxation ($^{223}k_{\Delta} = 1.2 \times 10^{-5} \text{ s}^{-1}$) similar to values generally reported for TC-isomer [35]. Consequently, the state **4** was here proved to be produced from 365-nm light irradiation of state **1**. However, it must be noted that the conversion is low, as no more than 16% of open naphthopyran could be produced. In addition, another very low-intense doublet signal (less than 3%) at 9.41 ppm with $^3J=11.9 \text{ Hz}$ is also present. Its thermal evolution was also followed and the signal decreased in intensity while that of the doublet at 6.01 ppm (state **2**) increased. A relaxation rate, $^{223}k_{\Delta} = 1.2 \times 10^{-5} \text{ s}^{-1}$, equal to that measured for **4**→**1** was extracted. Therefore, this indicates that cyclization of one diarylethene can be induced with 365 nm light, as it was observed with UV-visible spectroscopy, The doublet at 9.41 ppm is therefore assigned to the state **5**, corresponding to the opening of naphthopyran from state **2** and thermally converting into state **2**. Experiments were repeated at 233 and 243K. The same phenomenon was observed, ie, photochemical formation of state 4 from 1, and state 5 from 2, by the intermediary of 1. Thermal relaxation resulted again in equal rate constants: $^{233}k_{\Delta} = 6.5 \times 10^{-5} \text{ s}^{-1}$ and $^{243}k_{\Delta} = 3.4 \times 10^{-4} \text{ s}^{-1}$ for **4**→**1** and **5**→**2**. This means that the thermal closing of photomerocyanine is not affected by the status, open or cyclized, of diarylethene.

Finally, irradiation with 365 nm light at 223K was carried out with a fresh sample and instead of recording the thermal relaxation, irradiation with 313 nm light was applied to check if conversion **4**→**5**, ie the closing of diarylethene unit when naphthopyran is already open, is possible. However, no change was observed, thus, there is no cyclization of diarylethene observed when naphthopyran is in open configuration.

4.2.3 Irradiation of mixture of states **1**, **2** and **3** with 365 nm at low temperature

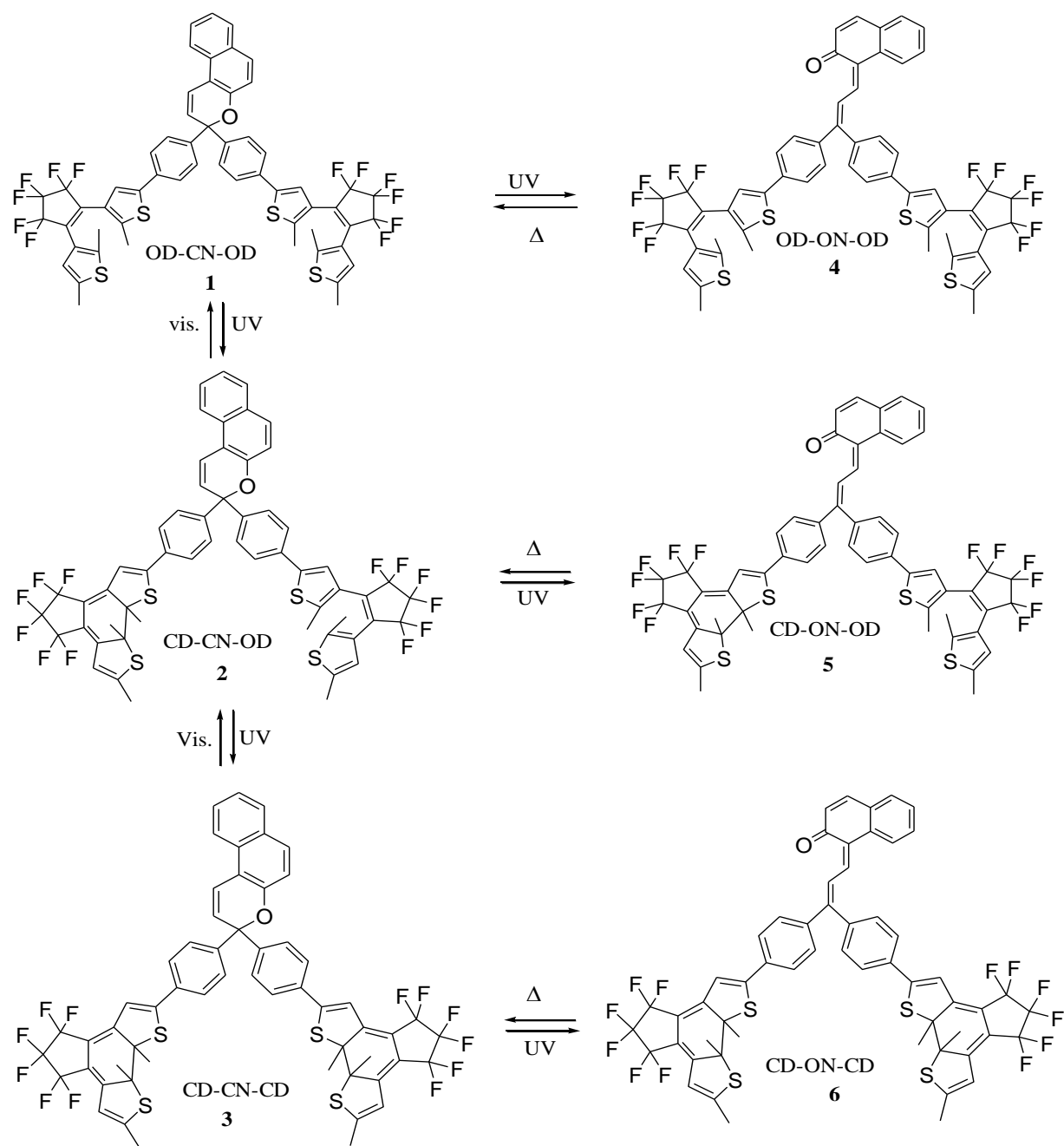
Irradiation with 365 nm-light at low temperature was applied to a sample previously irradiated at room temperature with 313 nm to investigate the possible opening of naphthopyrans **2**→**5** and **3**→**6**. Irradiation at room temperature with 313nm allowed to get a sample containing 46% **CD-CN-CD** (**3**), 41% **CD-CN-OD** (**2**) and the remaining 13% **OD-CN-OD** (**1**). This sample was cooled at 223K and submitted to irradiation with 365 nm light. In the ¹H NMR spectrum (Fig. 2d), the total conversion is less than 20% and could not be improved even when increasing the duration of irradiation. The concentrations of the three initial states are 8% (**1**); 35% (**2**) and 38% (**3**). In addition, three superimposed doublet signals around 9.4 ppm, with the characteristic coupling constant of 11.9 Hz, are detected. They are straightforwardly attributed to H2 proton in Transoid-Cis photomerocyanine. The signals at 9.43 ppm (5%) and 9.41 ppm (6%) were previously identified as H2 in state **4** and state **5**, respectively. The third doublet at 9.38 ppm (8%) is assumed to be H2 in state **6**. This was fully confirmed by recording thermal evolution, these signals decreased in intensity while the signals of H2 for the closed configuration of naphthopyran increased. Hence it is possible to associate them in pairs, the doublets at 9.43 ppm (H-2 in state **4**) and 6.03 ppm (H-2 in state **1**); the doublets at 9.41 ppm and 5.96 ppm (H-2 in state **2**); and the doublets at 9.38 ppm and 5.92 ppm (H-2 in state **3**). Therefore, signals at 9.41 and 9.38 ppm are characteristic of the formation, upon irradiation, of states **5** and **6** respectively, underlining the opening of naphthopyrans upon irradiation. Also, it should be noted that the three states with open naphthopyrans, namely, **4**, **5** and **6** evolved thermally with the same rate constant of relaxation ($^{223}k_{\Delta} = 1.2 \times 10^{-5} \text{ s}^{-1}$), thus indicating again

that the status of diarylethene (open or closed) has no effect on the thermal stability of open naphthopyrans.

5. Discussion

Combining all the experiments performed, the overall mode of action of **OD-CN-OD** is outlined in Scheme 2. Six different states resulting from the open/closed naphthopyran associated with one or two open/cyclized diarylethenes have been structurally identified by ^1H NMR spectroscopy. The cyclization of diarylethene with 313 nm light and at room temperature could be reached with more than 90%. The irradiation time to get such conversion is high (3 hours) but it concerns a sample with a concentration of 5 mM for NMR spectroscopy. We could observe the formation of state **2**, followed by the formation of state **3**. This means that the cyclization of each diarylethene unit can be achieved with 313 nm light. When investigation of the same process is performed by UV-Visible spectroscopy with a sample at $5 \times 10^{-5}\text{M}$, the photostationary state was reached in 15 minutes. Using the percent of conversion (90%) measured in NMR spectrum, it is possible to estimate the molar extinction coefficient at $\lambda_{\text{max}} = 559\text{nm}$ of states **2** and **3** at *ca* $9000 \text{ l}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Then, the presence of naphthopyran has no effect on the photochromic response of diarylethene, as the values are very close to that reported for 1,2-bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentene in hexane by Irie et al. [ref Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. J. Org. Chem. 1995, 60, 8305]. The reverse decyclization is achieved with visible light irradiation. Irradiation with 365 nm, followed by UV-visible spectroscopy allowed to detect the formation of photomerocyanine and cyclization of diarylethene, but switch off the light leads to fast relaxation of open form of

naphthopyran as expected, due to their poor thermal stability. Repeating this experiment with NMR spectroscopy at low temperature enabled to produce and stabilize photomerocyanines. According to the initial composition of sample (state **1** or mixture of states **1**, **2** and **3**), it was possible to observe the formation with 365nm light of the corresponding states with open naphthopyran (State **4**, **5** and **6**). From a general overview, they behave similarly as they are all formed with relatively low conversion, and they all decreased thermally with the same rate constant of relaxation. The thermal relaxation processes were followed at 223, 233 and 243K, from which the values of k was deduced and used to determine using Arrhenius plot, an activation energy equal to 75 kJ.mol^{-1} . Such results indicate that the status of the diarylethene unit (open or cyclized) has no effect on the thermal stability of photomerocyanines, and activation energy determined for the closing of naphthopyrans is in complete agreement with values generally reported [ref].



Scheme 2: Photochemical and thermal interconversion of the six states of triphotochromic OD-CN-OD

6. Conclusions

The synthesis and photochromic properties of a triphotochromic molecule consisting in one naphthopyran flanked by two diarylethene units have been described in detail. The results show unambiguously that it is possible to generate species where both ring closed diarylethenes are linked **by cross conjugation**. The cyclisation of the diarylethene at 313 nm and the reverse process with visible light does only occur when the linking naphthopyran is in the closed configuration. The naphthopyran moiety can generate photomerocyanine species both with open or closed diarylethene groups and the states with open naphthopyrans (**4**, **5** and **6**) have very similar thermal stability. In other words, switching of the naphthopyran group is possible, independently of the state of the diarylethene groups. However, the diarylethene group cannot be closed if the naphthopyran group is open. **As the phenyl groups in the naphthopyran group, forming the link to the diarylethene group are free to rotate, this suggests that subtle electronic effects, such as an energy transfer from the open naphthopyran group, not steric crowding are in the main responsible for the gating of the photoswitching. More generally, the results open the perspective of multi- or poly-diarylethene–naphthopyran species where the open and flexible diarylethene can be ring closed and rigidified, and full planarization of the species can be achieved by ring opening of the naphthopyran groups.**

7. Experimental Section

General. ¹H and ¹³C NMR spectra were recorded at 400 or 500 and 100 or 125 MHz, respectively, for ¹H and ¹³C. UV-visible spectra were recorded on a diode array

spectrophotometer. 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 nm silica gel plates (60F-254). Column chromatography was performed on silica gel (35-70u 60A). 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 %. The identification of previously reported compounds was made by ¹H and ¹³C NMR by comparison with literature data. Mass spectrum was recorded on Autoflex Speed MALDI TOF/TOF MSMS instrument using 3,5-dimethoxy-4-hydroxycinnamic acid as matrix.

Photochemical measurements: A 200 W high pressure Hg/Xe lamp was used for irradiation the solutions for UV Visible measurements.

Photoirradiation for NMR measurements was carried out directly into the NMR tube in a home-built apparatus with a 1000W high-pressure Hg – Xe lamp equipped with filters. Monochromatic UV (313 or 365nm) or visible light (546 or 577 nm) was obtained by passing the light through a first filter, then through an interferential one. Samples are dissolved in acetonitrile-d₃ in NMR tubes. When required, NMR experiments were carried at various low temperatures using a N₂ cooling setup connected to the 500MHz spectrometer.

Reagents. All reagents used were of analytical grade and were purchased. 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-2thienylboronic

acid **(5)** and 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene **(7)** were obtained following the procedure described previously (**(5)** [31-33]; **(7)** [33, 36]).

Bis(4-bromophenyl)methanone (1). A mixture of 4-bromobenzoyl chloride (6.58 g, 30 mmol) in bromobenzene (25 ml) was added at a solution of AlCl₃ (4 g, 30 mmol) in bromobenzene (26 ml) under nitrogen. The mixture was stirred at 55 °C for 3 days and after it was added 100 g ice and 50 ml HCl conc. The resulting mixture was extracted twice with diethyl, washed with aq NaOH 5% and then with water, dried over magnesium sulfate, then concentrated under vacuum. The crude product recrystallized from methanol gave white powder (8.45 g, 83 %). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.6 (s, 8H); ¹³C-NMR (CDCl₃): 135.8, 131.7, 131.4, 127.8, 194.2; Elemental analysis calcd. (%) for C₁₃H₈Br₂O: C 45.92, H 2.37; found C 45.84, H 2.26.

1,1-bis(4-bromophenyl)prop-2-yn-1-ol (2). A solution of bis(4-bromophenyl)methanone **(1)** (5.1 g, 15 mmol) in dry THF (100 ml) was added at a solution of lithium acetylide-ethylenediamine (13.8 g, 150 mmol) in dry THF (60 ml) under nitrogen at 5 °C. The mixture was stirred at room temperature 23h and then was cooled and a solution KOH (10g) in ethanol (125 ml) was added. The mixture was stirred at r.t. for 15 min. The acetic acid glacial was added until pH = 7. Water (400 ml) was added and the organic compound was extracted with ether 2-3 times and dried over MgSO₄. The crude product was obtained by remove the solvent under pressure. Column chromatography (silica, CH₂Cl₂/hexane, 8/2) gave white liquid (2.25 g, 41 %). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.45 (d, 8H, Har, J = 0.7), 2.90 (s, 1H, C≡CH), 2.80 (s, 1H, -OH); Elemental analysis calcd. (%) for C₁₅H₁₀Br₂O: C 49.22, H 2.75; found C 49.34, H 2.69.

3,3-Bis(4-bromophenyl)-3H-benzo[f]chromene (3). A mixture of 2-naphtol (2.02 g, 0.014 mol) and the 1,1-bis(4-bromophenyl)prop-2-yn-1-ol (**2**) (5 g, 0.014 mol) in CH₂Cl₂ (30 ml) in the presence of PPTS catalytic amount, trimethylorthoformate (20 ml) was refluxed for 24 h. The solvent was removed and the crude product was purified by column chromatography (silica, CH₂Cl₂); yield 45 % (3.1 g). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm], see SI for numbering): 7.94 (d, 1H), 7.71 (dd, 1H), 7.66 (d, 1H), 7.45 (m, 1H), 7.43 (m, 4H), 7.31-7.36 (m, 6H), 7.15 (dd, 1H), 6.13 (d, 1H). Elemental analysis calcd. (%) for C₂₅H₁₆Br₂O: C 61.01, H 3.28; found C 59.87, H 3.19.

3,3-Bis(4-(4-bromo-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (6). Compound 3,3-bis(4-bromophenyl)-3H-benzo[f]chromene (**3**) (1.47 g, 3 mmol) was dissolved in THF (12 ml) and after addition of Pd(PPh₃)₄ (0.23 g, 2 · 10⁻⁴ mol), the solution was stirred at r. t. for 15 min.. Aq. Na₂CO₃ (5.3 g in 25 ml H₂O) and 6 drops of ethylene glycol were then added, and the resulting two phase system was heated until reflux. A solution of 5-bromo-2-methylthiophen-3-yl-3-boronic acid (**5**) (1.54 g, 7 mmol) in THF (15 ml) was added drop wise. After the addition was complete, the reaction mixture was refluxed for 8 h and then allowed to cool down at r. t. Diethyl ether and water were added and the organic layer was collected and dried over MgSO₄. Evaporating the solvent, the crude product was purified on the column (silica, hexane for 30 min. and then hexane/CH₂Cl₂, 9/1). White powder was obtained with yield of 30 % (0.6 g). ¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.95 (d, 1H, H¹⁰), 7.71 (d, 1H, H⁷), 7.67 (d, 1H, H⁶), 7.21-7.50 (m, 9H, H^{1,2,9}), 7.30-7.37 (m, 2H, H^{5,8}), 7.20 (d, 1H, H⁴), 7.05 (s, 2H, H¹¹), 6.24 (d, 1H, H³), 2.39 (s, 6H, H¹²); Elemental analysis calcd. (%) for C₃₅H₂₄Br₂OS₂: C 61.41, H 3.53, S 9.37; found C 61.72, H 3.17, S 9.4

3,3-Bis(4-(4-(3,3,4,4,5,5-hexafluoro-2-(2,5-dimethylthiophene-3-yl)cyclopent-1-enyl)-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (OD-CN-OD). To a solution of compound 3,3-bis(4-(4-bromo-5-methylthiophen-2-yl)phenyl)-3H-benzo[f]chromene (**6**) (200mg, 0.293 mmol) in dry THF (15 ml) was added *n*-BuLi (0.4 ml of 1.6 M solution in hexane, 0.586 mmol) under nitrogen at -78 °C. This solution was stirred 1 h and then compound 2,5-dimethyl-3-(perfluorocyclopent-1-enyl)thiophene (**7**) (178.32 mg, 0.586 mmol) was added in one portion. The mixture was stirred at -78 C for 1 h, and then allowed to warm-up to r. t. After stirring for additional 12h, diethyl ether (20 ml) was added, and the mixture was washed with water. The organic layer was dried over MgSO₄ and solvent evaporated. The crude product was purified by 2 columns (silica, CH₂Cl₂/hexane, 7/3; silica, CH₂Cl₂/hexane, 0.5/9.5) and afforded 115.5 mg (36%) finale compound.

¹H-NMR (CDCl₃, 400 MHz, δ [ppm]): 7.96 (d, 1H, H¹⁰), 7.72 (d, 1H, H⁷), 7.68 (d, 1H, H⁶), 7.46-7.54 (m, 9H, H^{1,2,9}), 7.30 (d, 1H, H⁵), 7.34 (m, 1H, H⁸), 7.21 (s, 2H, H¹¹), 7.20 (d, 1H, H⁴), 6.71 (m, 2H, H¹³), 6.25 (d, 1H, H³), 2.40 (s, 6H, H¹⁴), 1.89 (s, 6H, H¹²) 2.81 (s, 6H, H¹⁵). Elemental analysis calcd. (%) for C₅₇H₃₈F₁₂OS₄: C 62.51, H 3.50, S 11.71; found C 62.68, H 3.46, S 11.57. Mass spectrum: *m/z* 1095.49.

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Supporting Information

^1H NMR spectrum for precursor **6**; ^1H , ^{13}C NMR and MS spectra for target compound ODCN-OD.

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