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Bridging the Visible: The Modulation of the Absorption by More than 450 nm

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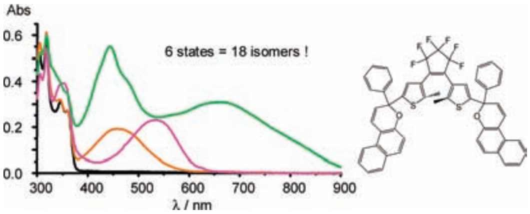
ABSTRACT



The coexistence of 18 isomers, identified by NMR spectroscopy and gathered into six states with very different absorption properties, is observed upon irradiation with selective wavelengths of a triphotochromic system joining two naphthopyran entities through a dithienylethene bridge. The sequential electronic coupling of photochromic groups resulted in an absorption behavior reaching far into NIR.

The efficient modulation of the absorption spectra of organic materials is a challenge involving a wide spectrum of interests, ranging form the design and application of dyes to the use of panchromatic materials as sensitivity enhancers for solar cells and to fundamental studies focused on understanding the electronic parameters responsible for the extension of the absorption.[1] For photochromic materials where irradiation, typically in the UV range, leads to reversible transformations, resulting in colored forms with absorption maxima in the visible region,[2] the extension of the absorption far into the NIR has not yet been much in the focus of research. However, the increase in the length of the π-conjugation is expected to generate systems absorbing in the red-end of the visible spectrum or even with infrared-absorbing properties, paving the way to develop applications as materials for write-once and erasable memories.[3] To achieve this goal, several strategies of connecting two or more photochromic groups to prepare multiphotochromic switches have been reported.[4]

Usually, UV/vis spectroscopy, as a relatively fast technique, is employed to record changes. However, no detailed information can be gained concerning the structures of the species formed. This makes NMR investigations invaluable, even though this technique is slower and requires a higher concentration of samples.[5] Moreover, when multiple species are formed through irradiation and a number of potential reaction pathways become possible, only an unambiguous identification of species can clarify the processes actually

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(1) (a) Sreejith, S.; Carol, P.; Chithra, P.; Ajayaghosh, A. *J. Mater. Chem.* **2008**, *18*, 264–274. (b) Son, H.-J.; Han, W.-S.; Yoo, D.-H.; Min, K.-T.; Kwon, S.-N.; Ko, J.; Ook Kang, S. *J. Org. Chem.* **2009**, *74*, 3175–3178.

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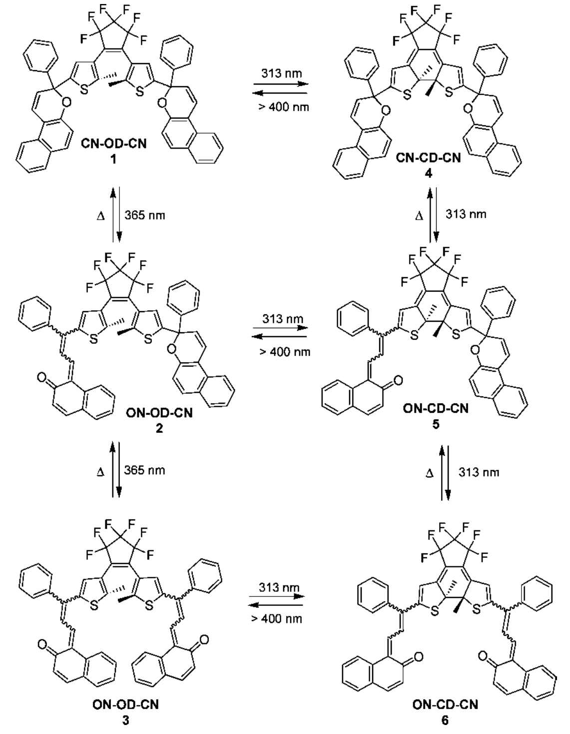
occurring. This is essential for the design of materials with improved properties.

Recently, we investigated the behavior of a biphotochromic system, consisting of connected naphthopyran and dithienylethene entities. Under UV irradiation, four different states were identified by UV−vis spectroscopy, characterized by very different absorption properties.[6] These were unambiguously identified by NMR spectroscopy as the coexistence of seven different isomers.[7,8] Notable was the extension of the absorption in excess of 700 nm, giving rise to the question of whether a triphotochromic system would extend the absorption further in the NIR and how many species occur and which reaction pathways are possible. Therefore the triphotochromic hybrid **CN-OD-CN**, shown in Scheme 1, was synthesized[9] and investigated.

Scheme 1. Principal Mode of Action of the Multifunctional Photochromic System **CN-OD-CN**



The principal and expected mode of action of the multifunctional photochromic system **CN-OD-CN** (state **1**) is illustrated in Scheme 1. To check this hypothesis, the switching properties were investigated by a series of steady-state experiments in which light was switched on or off and spectra were recorded until a photostationary state (PS) was obtained. The sequential approach along with the experimental setup led to the observation of four PS which correspond to single and/or combined absorption behaviors of six different states.

Irradiation with light at wavelengths above 350 nm triggers selectively the reactions outlined in the left pathway of Scheme 1. Monitoring the spectral modifications[10] shows a change from colorless to orange ($\lambda_{\max}$ = 456 nm (2.96 × 10^{-5} mol•L^{-1}) states **2** and **3**, Figure 1), which is anticipated for the opening of naphthopyrans. A return to the colorless form **1** in the dark typical for naphthopyrans occurs.

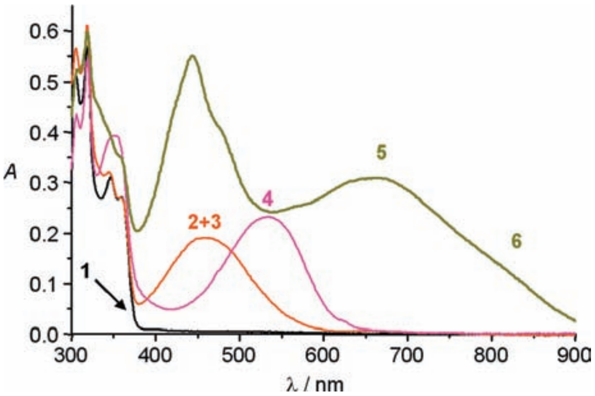


Figure 1. Absorption spectra of toluene solution **1** (2.96 × 10^{-5} mol•.L^{-1}) before irradiation (black), upon irradiation with 365 nm (orange), upon irradiation with 313 nm light (green), and after irradiation with 313 nm and thermal bleaching (pink).

Detailed NMR experiments at 227 K of more concentrated solutions (10^{-3} M) to take into account the different sensitivities of NMR and UV/vis spectrometers were carried out. In the ^{1}H NMR spectra recorded before irradiation (Figure 2a), all signals of **CN-OD-CN** are split, and peak-intensities measurements made it possible to correlate them with the two parallel/antiparallel[11] conformers (55−45%) expected for dithienyl-based photochromes. Upon irradiation at 365 nm, partial conversion of **1** into six different thermoreversible forms occurs (Figure 2b). Not only species where one of the naphthopyran groups is opened (state **2**), such as **CTC-OD-CN**, **TTC-OD-CN**, or **TTT-OD-CN**, but also forms where both groups are activated could be detected, such as **CTC-OD-CTC**, **TTC-OD-TTC**, and **TTC-OD-CTC** (state **3**). These photoproducts have been characterized on the basis of specific chemical shifts,[12] peak-intensities measurements and constants of thermal relaxation. The associated thermally reverse pathways are at 227 K: 1) **CTC-OD-CTC** (7 × 10^{-4} s^{-1}) → **CTC-OD-CN** (8 × 10^{-5} s^{-1}) → **CN-OD-CN**, 2) **TTC-OD-CTC** (3 × 10^{-4} s^{-1}) and **TTC-OD-TTC** (3 × 10^{-5} s^{-1}) and **TTT-OD-CN** (very slow) → **TTC-OD-CN** (1 × 10^{-5} s^{-1}) → **CN-OD-CN**.

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(9) The synthesis is reported in the Supporting Information.

(10) UV−vis spectra are displayed in the Supporting Information.

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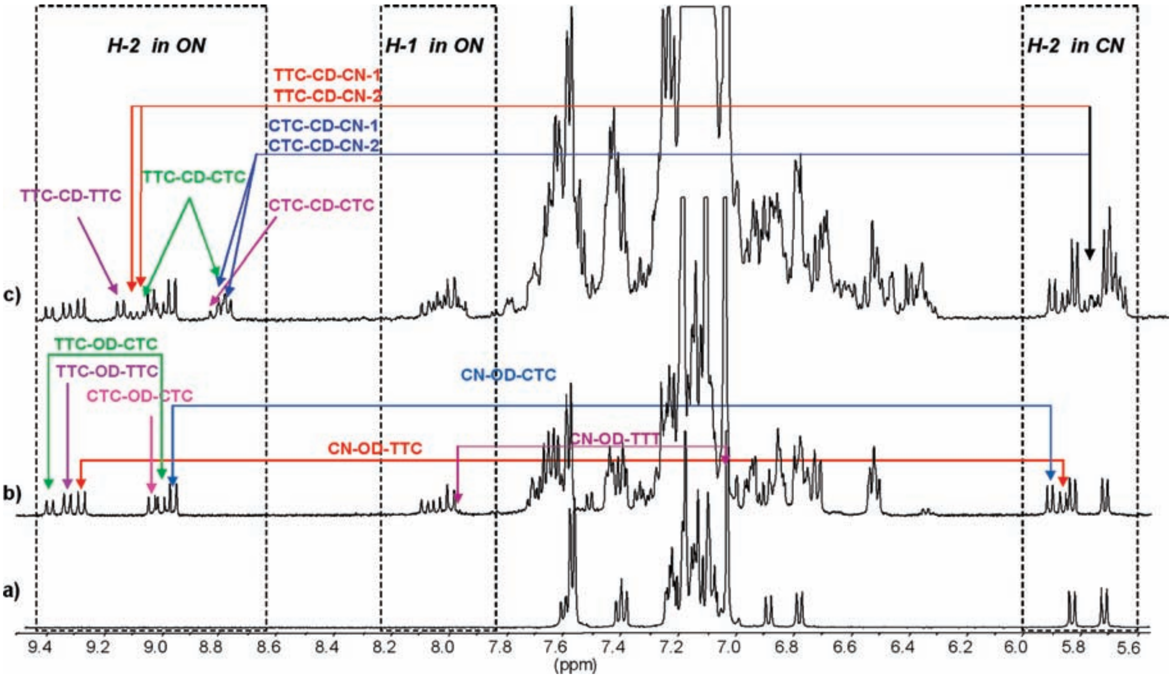


Figure 2. ^{1}H NMR aromatic part of toluene solution of **CN-OD-CN** (10^{-3} mol·L^{-1}) at 227 K (a) before, (b) after irradiation with 365 nm, and (c) after irradiation with 313 nm.

These measurements confirm that both naphthopyran groups react, an experimental observation which is not possible directly from steady-state UV/vis measurements. It is also noted that although π-conjugation of the open diarylethene group has been extended through conjugation with the opened naphthopyran groups so that the molecules do absorb at 365 nm, no electrocyclization of the diarylethene moiety occurs.

Irradiation of **1** at 313 nm has the potential to transform all photochromic groups, schematically shown in the middle and right paths of Scheme 1. In a steady-state UV/vis experiment with time, an absorption reaching from the UV through the visible into the NIR can be detected, as shown in Figure 1. This is associated with the initial colorless solution of **1** turning into a very dark solution on irradiation. This very dark solution turns red in the dark. Irradiation with visible light turns this red solution colorless, irradiation in the UV (313 nm) returns the previously observed dark color whose absorption reaches up to ~850 nm. The kinetics of fading at selected wavelengths (658 nm: 9.57×10^{-4} s^{-1}, 700 nm: 11.10×10^{-4} s^{-1} and 840 nm: 32.89×10^{-4} s^{-1}) allow fitting to a monoexponential function. On the other hand, for 750 nm (9.75×10^{-4} s^{-1} (47%), 30.67×10^{-4} s^{-1} (53%)] and for 800 nm (10.24×10^{-4} s^{-1} (19%), 34.48×10^{-4} s^{-1} (81%)), the best fading fits are obtained with a biexponential function. This suggests that the fully conjugated systems involving the electronic participation of all three groups are the only absorbing species above 820 nm. However, the fading characteristics of the species present at 658 nm species can be explained by two groups electronically connected of the type CD-ON.

Here NMR investigations are crucial. Irradiation of **1** at 293 K with 313-nm light reveals the partial conversion of state **1** into three photoproducts resulting from cyclization in dithienylethene part (Figure 3). As the naphthopyrans are either *l* or *d* and the conrotatory photocyclization of dithienylethene produces two enantiomeric closed-ring isomers *R*,*R* and *S*,*S* originating from asymmetric carbon atoms, these three are identified to be the three possible diastereomers, being arbitrary designed as *d-R*,*R-d* (= *l-S*,*S-l*) and *d-S*,*S-d* (= *l-R*,*R-l*) for signals 2 and signals 3, respectively, and *d-R*,*R-l* (= *l-S*,*S-d*) for lines 1 and 4.

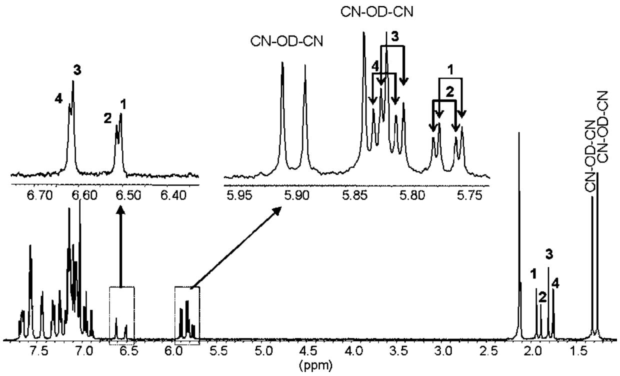


Figure 3. ^{1}H NMR spectrum of toluene solution of **CN-OD-CN** (10^{-3} mol·L^{-1}) after irradiation with 313 nm light at 293 K.

Repeating the NMR experiments at 227 K with 313 nm light (Figure 1c) allows the identification of the structures

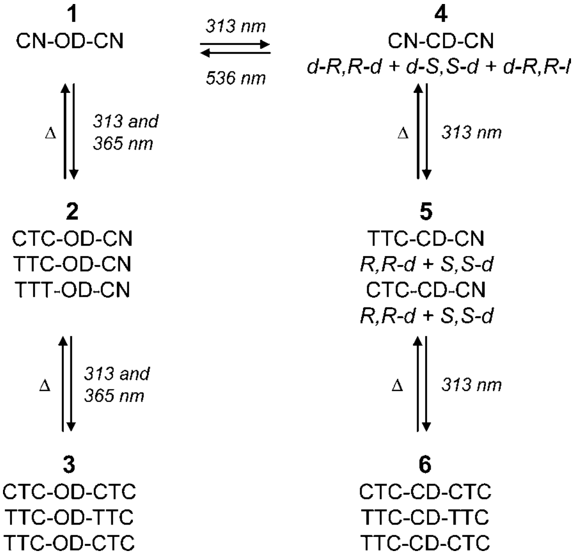
CN-CD-CN (state **4**), **CTC-CD-CN**, **TTC-CD-CN** (state **5**), where both the diarylethene group (closed) and one naphthopyran group are involved. As previously noticed for state **4**, **CTC-CD-CN** and **TTC-CD-CN** both exist under two couples of diastereomeric forms being arbitrary designed as *R*,*R*-*d* (= *S*,*S*-*l*) and *S*,*S*-*d* (= *R*,*R*-*l*).

Additionally, the structures **CTC-CD-CTC**, **TTC-CD-TTC**, and **CTC-CD-TTC** (state **6**) were detected. Monitoring of the fading kinetics indicates unambiguously a process where first one of the two open naphthopyrans is closed and then the other one. Although the accurate measurement of peak intensities is difficult because of superimposed lines and low concentrations of species, the thermal relaxation has been monitored at different temperatures to estimate the stability. At 227 K, **CTC-CD-CTC** bleaches (9.0×10^{-5} s^{-1}) into **CTC-CD-CN** ($0.85-1.4 \times 10^{-5}$ s^{-1}). Both exhibit, however, a higher stability than their homologous structures without cyclization (**CTC-OD-CTC** and **CTC-OD-CN**). More remarkable is the thermal stability of structures **TTC-CD-TTC** and **TTC-CD-CN** at 227 K. A significant value of the rate constant of bleaching has been estimated at 254 K for **TTC-OD-TTC** (3×10^{-5} s^{-1}) → **TTC-OD-CN**. This latter evolves toward **CN-OD-CN** at 273K (9.4×10^{-5} s^{-1}).

Finally, a fresh sample was preliminarily irradiated with 365 nm light to produce states **2** and **3** and then irradiated with 313 nm. No cyclization of the molecules identified by the states **2** and **3** into states **5** and **6** was observed. This clearly indicates that no photocyclization occurs when the naphthopyran is in an open configuration, or in other words, it means no pathways **2** → **5** or **3** → **6** are open to the system. In the same way, no reverse thermal opening of diarylethene was detected.

To conclude, the present work reports on the coexistence of 18 isomers gathered into six different states (Scheme 2). This system provides useful lessons for the design of future systems. The sequential electronic coupling of photochromic groups allows for the design of materials whose absorption reaches far into NIR, beyond the absorption of the individual photochromes. The relatively large bathochromic shift change in the absorption maxima, moving from two (**OD-CN**) to three (**CN-OD-CN**) active groups of about 100 nm, suggests that this approach is well below some limit. Additionally, the results show that switching of the naphthopyran group is possible, independent of the state of the diarylethene group. However, the diarylethene group cannot be closed if a naphthopyran group is open. It was found that the open naphthopyran groups are thermally more stable if the diarylethene is closed.

Scheme 2. Summary of Reactions of the Six Photochromic States Corresponding to the 18 Identified Structures



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Supporting Information Available: Details of irradiation techniques, UV−vis experiments, and NMR experiments. X-ray crystal structure of **1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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