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Controlled Conversion of Isomers in a Hybrid Biphotochromic System

Stéphanie Delbaere,* Gaston Vermeersch, Michel Frigoli,[†,‡] and Georg H. Mehl[†]

CNRS UMR 8009, Laboratoire de Physique, Faculté de Pharmacie, Université de Lille 2, F-59006 Lille Cedex, France

stephanie.delbaere@univ-lille2.fr

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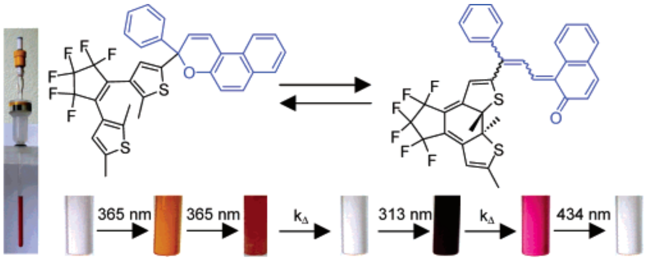
ABSTRACT



The photochromic performance of a hybrid system connecting naphthopyran and dithienylethene was investigated, and the photochemistry of eight different isomers was explored by choosing an appropriate wavelength of light.

Reversible light-induced transformation between several states allows the exploration of fundamental relationships of electromagnetic radiation with organic matter and the elucidation of correlations between chemical structure, electronic properties, reactivity and the controlled interconversion of species.[1] Naphthopyrans[2] whose photochromism is based on the ring opening of a pyran group have been intensively investigated as a result of their high colorability, rapid thermal relaxation and fatigue resistance, properties relevant to applications in the optical glass industry[3] and optoelectronics.[4] More recently, the thermally irreversible photocyclization reactions of 1,2-dithienylethenes, materials that can be tuned to very high photoconversion quantum yields and whose absorption spectra can be modulated rationally by suitable chemical construction, are becoming increasingly significant.[5] Multiphotochromic systems incorporating a dithienylethene moiety are in the focus of research, as the controlled sequential interaction of photons promises synergies in the design of such materials and their electronic properties.[6] Furthermore, ultrahigh information data storage systems might be obtainable as a result of the information density inherent in such materials. Information could be encoded according to the multispectral properties of such compounds either in their bistable mode or for time-resolved read-out.[7] It is crucial, however, that the interaction of the "read-out beam" with the information carrying species can be controlled, to deal with the issue of data erasure during read-out.

Recently, some of us reported the synthesis and photochromic properties of a hybrid system, OD-CN: 3-(1,2-bis-(2,5-dimethyl-3-thienyl)perfluorocyclopentene) 3-phenyl-

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[†] Department of Chemistry, University of Hull, Hull HU6 7RX, UK.

[‡] Current address: University of Versailles, Lavoisier Institute, France.

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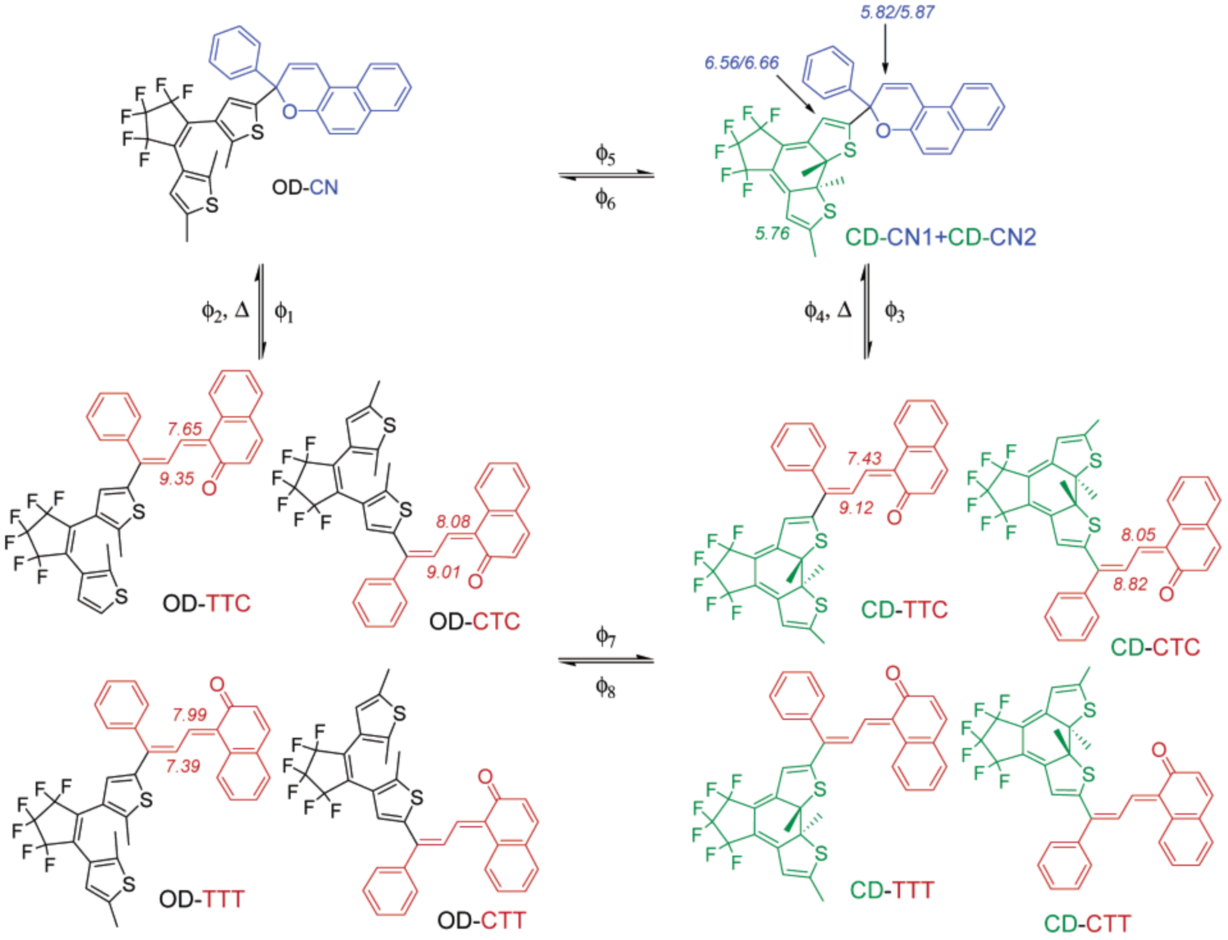

Figure 1. General photochromic reaction of OD-CN (OD, open dithienylethene; CD, cyclized dithienylethene; ON, open naphthopyrans; CN, closed naphthopyrans; TTC, trans-transoid-cis; CTC, cis-transoid-cis; TTT, trans-transoid-trans; CTT, cis-transoid-trans); numbers refer to ^{1}H chemical shifts (ppm) of selected protons.

naphthopyran.[8] Four different states were detected by UV−vis spectroscopy. However, as the individual photochromes form isomers, such a system consisting of a dithienylethene group (termed OD/CD, as open/cyclized dithienylethene) and a naphthopyran group (here named CN/ON for closed/open naphthopyran) consists of at least 10 colored states (Figure 1). Provided that these isomers are identifiable and addressable, an isomer density of approximately 10 states per nm^3 can be estimated, leading in turn to a system with potentially 10^{19} states (theoretically addressable isomers) per cm^3 in the solid state.[9] For the investigation of this switching behavior the initial challenge is the identification of the species formed, the selective and controlled addressing of individual photochromic units, and the conversion of the system in the photon mode. To achieve this, NMR spectroscopy of samples irradiated under controlled conditions is uniquely suitable, as this technique measures directly and quantitatively the concentration of different species (isomers).[10]

In initial experiments, the structures of the species formed on irradiation were identified; in a second series of experiments, the interconversion of species was monitored. Irradiation of a solution of OD-CN at 313 nm at 293 K allows the monitoring of the cyclization of the dithienylethene group (a colorless solution turns pink). At this temperature, the open forms of naphthopyran are not accumulated sufficiently to be detected by NMR because of their low thermal stability. In ^{1}H NMR spectra, peaks appear at 5.82 (24%) and 5.87 (33%) ppm (each with doublet multiplicity, $^3J = 9$ Hz), at 5.76 (57%) ppm (multiplet with $^5J = 1.2$ Hz), and at 6.56 (24%) and 6.66 (33%) ppm (singlet resonances). On the basis

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[9] $V_m = M_w/\rho N_A$; $\rho = 103$ kg m^{-3}; $M_w = 628, 92$; $V_m = 1.04$ nm^3. As the molecular volume does not change, this results in 10 theoretical states per nm. It is noted that this is only a theoretical number, unlikely to be achieved in practice.

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of 1D and 2D NMR experiments, the two photoproducts were assigned to the possible two diastereomers (formed as racemates) for a cyclized dithienylethene and closed naphthopyran, CD-CN1 and CD-CN2. Indeed, the photogenerated closed-ring form (CD) has either *SS* or *RR* asymmetric structure,[5a] and the stereochemistry at the sp^3 carbon in CN is either R or S. Consequently, the two couples of enantiomers (*RR*-R=*SS*-S and *RR*-S=*SS*-R) can be distinguished by NMR.

Irradiation of a solution (1.8 mM of OD-CN) at 365 nm at 227 K (the colorless solution turns red via orange) revealed the partial conversion of OD-CN into three photoproducts, which displayed resonances at δ 9.35, 9.01 and 7.99 ppm (each with doublet multiplicity, $^3J \approx 12$ Hz). Thermal evolution in the dark indicated conversion toward the initial form OD-CN with different rates ($^{227}k_\Delta$ (δ 9.35 ppm) $= 9 \times 10^{-6}$ s^{-1}; $^{227}k_\Delta$ (δ 9.01 ppm) $= 1.5 \times 10^{-4}$ s^{-1}; $^{227}k_\Delta$ (δ 7.99 ppm) = very slow). Such rate constants and 2D NMR experiments allowed unambiguous attribution of these three forms to open diarylethene with open naphthopyran groups (OD-TTC, OD-CTC, and OD-TTT). Irradiation of OD-CN at 227 K at 313 nm (the solution turns brown via orange/red) allowed the observation of the five previously assigned photoproducts: CD-CN1, CD-CN2, OD-TTC, OD-CTC, and OD-TTT. In addition, new intense doublet signals ($^3J = 12$ Hz) at 9.12 and 8.82 ppm, correlated in concentration with singlet resonances at 5.75 and 5.76 ppm were detected. Both were thermally unstable ($^{227}k_\Delta$ (δ 9.12 ppm) $= 5 \times 10^{-6}$ s^{-1} and $^{227}k_\Delta$ (δ 8.82 ppm) $= 2.1 \times 10^{-5}$ s^{-1}). Chemical shifts, multiplicity, and thermal rate constants were used to assign both structures to CD-TTC and CD-CTC, respectively.

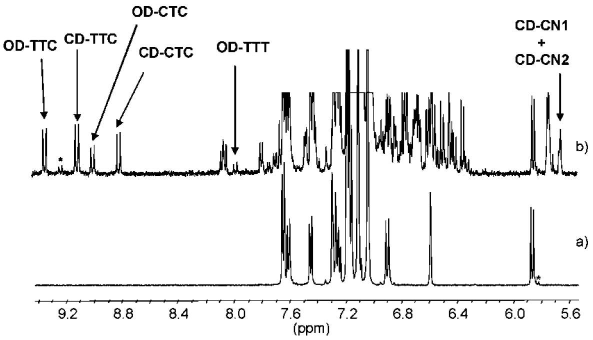

Figure 2. Typical ^{1}H NMR spectra of ODCN (a) and mixture after irradiation at 313 nm (b).

To estimate the pathways for photocyclization of dithienylethene moiety and photo-opening of the naphthopyran part in more detail, a sample of OD-CN was subjected to 20 periods of 120 s of irradiation with 313 nm light and the spectra were recorded at 227 K (Figure 3). After irradiation of OD-CN at 313 nm for 120s, 13% of the material converted into a ~1:1:1 mixture of OD-TTC, OD-CTC, and CD-CN (= CD-CN1 + CD-CN2). After 240 s of photolysis, the ratio changed to favor OD-CTC and CD-CN (1:2:2) and signals for OD-TTT, CD-TTC and CD-CTC were also observed. At the end of cumulative irradiation (2400 s), about 30% of structures with open dithienylethene and open naphthopyran groups were obtained (17%, 9%, and 4% of OD-TTC, OD-CTC, and OD-TTT, respectively), and compounds with cyclized dithienylethene represented 47% of the solution (17%, 20%, and 10% of CD-CN, CD-TTC, and CD-CTC, respectively).

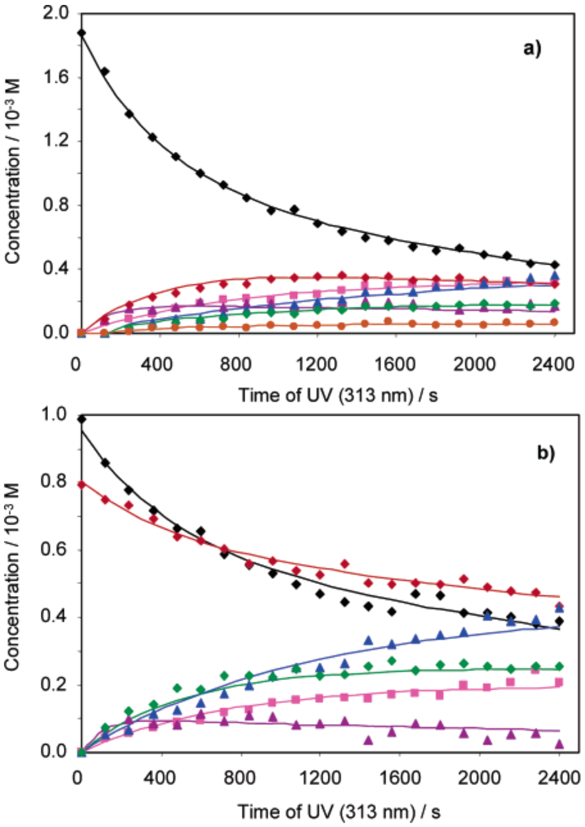

Figure 3. Time−evolution concentrations at 227 K under 313 nm light of OD-CN (black), OD-TTC (pink), OD-CTC (purple), OD-TTT (orange), CD-CN1 + CD-CN2 (red), CD-TTC (blue), CD-CTC (green). (a) [OD-CN]$_0$ = 100%, (b) [OD-CN]$_0$/[CD-CN]$_0$ = 54%/46%.

A similar experiment was repeated but with preliminary irradiation of the sample with 313 nm light at 293 K to generate a mixture of OD-CN and CD-CN (54%:46%). Irradiation (120s) generated OD-TTC and CD-TTC (ratio ~1:1) and OD-CTC and CD-CTC (ratio ~1:1), but concentrations of CTC were twice as high as those of TTC. At the end of cumulative photolysis, the conversion to OD-ON was similar to the previous experiment (17% corresponding to ~30% of initial OD-CN), while higher for the formation of CD-ON structures (~40%), indicating that they were formed mainly from CD-CN.

To confirm the prevalent process at low temperatures, irradiation of a solution of OD-CN at 227 K at 313 nm for 1 h was performed, and this resulted in a mixture containing ~17% of OD-CN, ~52% of OD-ON isomers, ~7% of CD-CN isomers, and 24% of CD-ON isomers. The accumulation of photoproducts “OD-ON” identifies the naphthopyran group as the most active group under these conditions.

The effect of photobleaching in the visible was investigated for a sample preirradiated at 313 nm in irradiation intervals (434 nm) of 15 min. All of the photoproducts decreased along monoexponential-type curves from which pseudo rates have been extracted. The faster rate corresponded to the decrease in CD-CN ($5.5\ 10^{-4}\ s^{-1}$), while rates for OD-CTC and CD-TTC were about three times lower and those for OD-TTT and OD-TTC were five times lower.

In summary, the photochromic performance of a linked naphthopyran-dithienylethene system was investigated, and the photochemistry of eight different isomers was explored. Irradiation with 365 nm light gives rise to the thermally reversible opening of naphthopyran ring. Irradiation at 313 nm leads to the closure of the dithienylethene moiety and the opening of the naphthopyran group, generating seven different structures in different concentrations. The enrichment of the closed dithienylethene is achieved more optimally at higher temperatures. The structures CD-ON are thermally reversible but with rate constants for bleaching considerably lower than those of their corresponding OD-ON forms.

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Supporting Information Available: Details of irradiation techniques and NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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