Photochemistry

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Multiple Addressing in a Hybrid Biphotochromic System

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Addressing the optical and electronic properties of organic materials by light is currently a very active research area and such systems are expected to be of great importance for optical computing—as logic gates, as the optical equivalent of field-effect transistors, as high density (3D) data storage systems, as well as for light rectification and harvesting.[1–3] The goal is a miniaturization of functional elements down to the molecular level, or at least close to that, which could result in a markedly increased performance as a consequence of the higher volume density of the functional elements compared to that of current devices.

Irradiation of photochromic systems at selected wavelengths leads to the reversible formation of colored forms as a result of a change of the structure of conjugated π systems. Bistable materials or systems that are dependent on continuous irradiation to maintain the colored (high-energy) form are suitable candidates for such applications. Nanostructured crystalline systems, high-density photochromic polymers, and a range of systems which form anisotropic fluids either as mixtures or as molecular materials in the condensed state, have been reported recently.[4,5]

In this context, biphotochromic systems are particularly attractive, as the controlled sequential interaction of photons in one molecular system promises synergies in the design and electronic properties (for example, a sequential change of the electronic properties would be a precondition for a fully photonic molecular logic gate).[2a,g,3g] Investigations on biphotochromes based on naphthacene–diarylethene, interconnected diarylethenes, and diarylethene–dihydroazulene systems have been reported recently.[6–8] The challenge with biphotochromic systems is both the selective and controlled addressing of individual photochromic units and the conversion of the combined system. In this context, the combination of naphthopyrans and photochemically bistable and very fatigue resistant diarylethene groups (Scheme 1) are particularly interesting, and as yet not investigated.[2b]

Naphthopyrans are currently the most important class of photochromes commercially as a result of their high stability, fatigue resistance, and addressable bleaching kinetics.[9] Herein we report the synthesis and investigation of the photochromic properties of a combined system consisting of a

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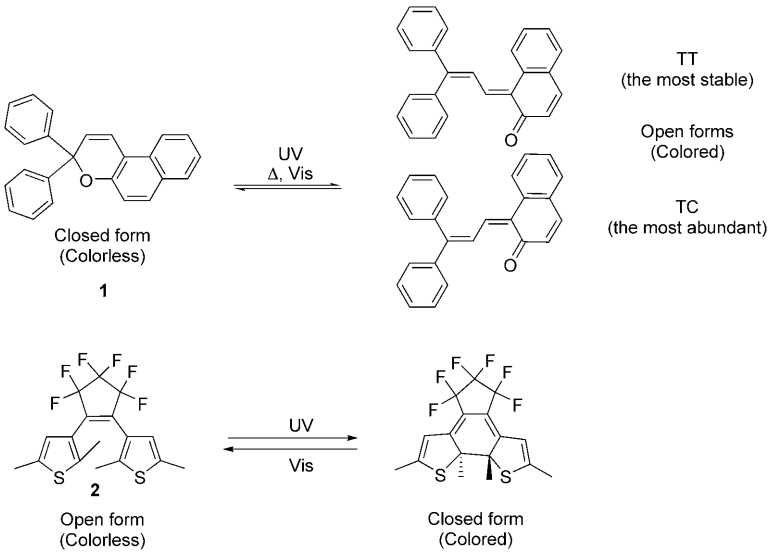
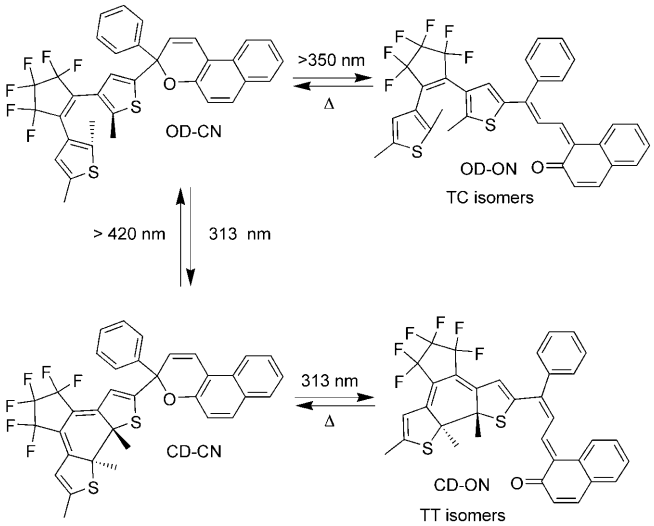


Scheme 1. Photochemical interconversion in the [3*H*]-naphthopyran and dithienylethene series; TT = transoid,*trans*; TC = transoid,*cis*.

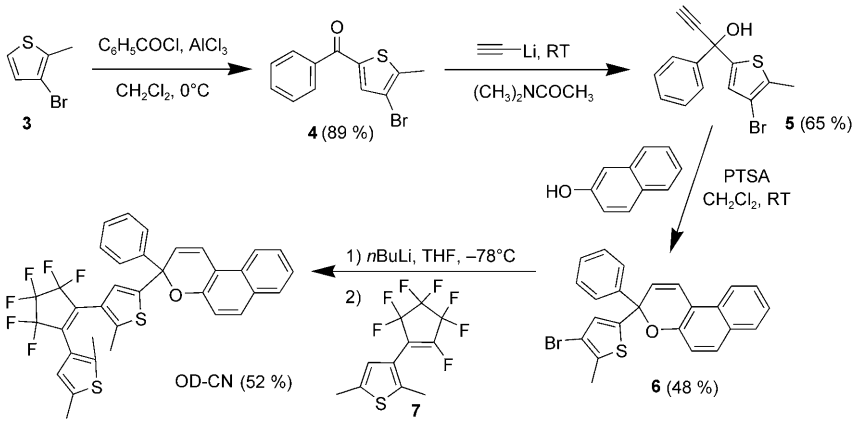
naphthopyran unit and a diarylethene group. An important feature in the design of this system is the different absorption behaviors of the naphthopyran (CN) and the diarylethene (OD) groups which are connected through a sp^3-hybrdized carbon center. Only the conversion of the closed naphthopyran (CN) into the open form (ON) leads to conjugation and an electronic connection. Closure of the open diarylethene system (OD to CD) extends the π-electron system over the whole molecule. The different behavior of these two photochromes—diarylethenes are essentially bistable and naphthopyrans open on irradiation to a number of isomers, most of which revert back thermally to the closed forms in the dark—results in a multiaddressable hybrid photochrome.

The synthesis of OD-CN (Scheme 2) starts with the preparation of ketone **4**, which was obtained (89% yield) from the reaction of 2-methyl-3-bromothiophene with benzoyl chloride in the presence of $AlCl_3$. The subsequent condensation of the lithium acetylide diamine complex with **4** resulted in the corresponding propargylic alcohol **5** (65% yield).[10] The intermediate chromene **6** was obtained by a "one-pot reaction" of **5** and 2-naphthol in the presence of a catalytic amount of *para*-toluenesulfonic acid (PTSA; yield 48%).[11] Lithiation of the chromene **6** by bromine/lithium exchange using *n*BuLi in THF at −78°C, followed by quenching of the reaction mixture with **7** afforded the hybrid biphotochrome OD-CN (52% yield).[12a]

The mode of action of the multiaddressable photochromic system OD-CN is illustrated in Scheme 3. The path from OD-CN to CD-ON requires the interaction of OD-CN with two photons. The photochromic properties were investigated by a series of steady-state experiments in which light was either switched on or off (input: 0,1) and spectra were recorded until a photostationary state (PS) was obtained. This sequential approach revealed the formation of four different states with entirely different absorption behaviors, and five addressing modes were investigated.[12b]



Scheme 3. Photochemical reactions of the hybrid OD-CN showing all four photochromic states.



Scheme 2. Synthesis of the biphotochromic hybrid OD-CN.

The associated investigated reaction pathways are: 1) OD-CN→OD-ON, 2) OD-CN→CD-ON (via CD-CN), 3) CD-ON→CD-CN, 4) CD-CN→CD-ON, 5) CD-CN→OD-CN. Our experimental set-up did not allow for the investigation of the potential direct path from OD-ON to CD-ON. Two of the states, OD-CN and CD-CN, are bistable, while OD-ON and CD-ON have to be triggered by irradiation. The absorption spectra of all four forms are shown in Figure 1 and the colored solutions are shown in Figure 2.

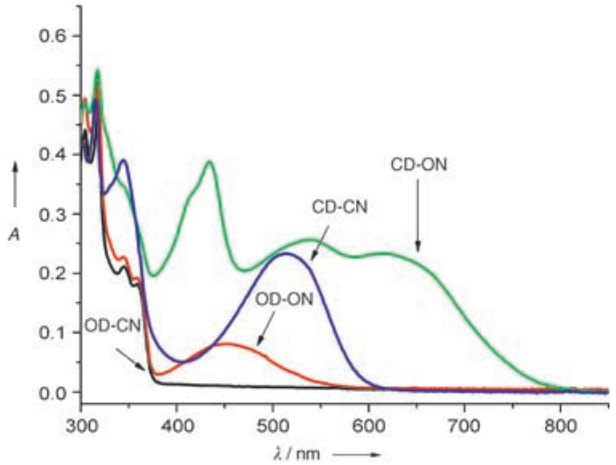


Figure 1. UV/Vis absorption spectra (cylohexane solution, 3.33×10^{-5} M) of the four photochromic states of the system OD-CN, before irradiation (OD-CN), with irradiation at 366 nm (OD-ON), with irradiation at 313 nm (CD-ON), after irradiation at 313 nm then left in the dark (CD-CN).

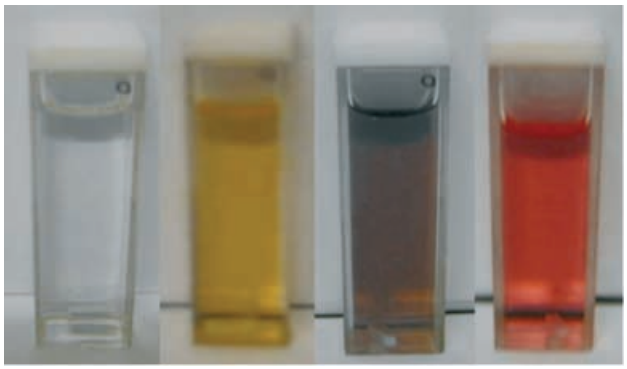


Figure 2. Colors obtained for each stationary state: OD-CN (initial state, colorless), OD-ON (after irradiation at 366 nm, yellow), CD-ON (after irradiation of OD-CN or CD-CN at 313 nm, brown), and CD-CN (from thermal bleaching of OD-ON in the dark, red/pink).

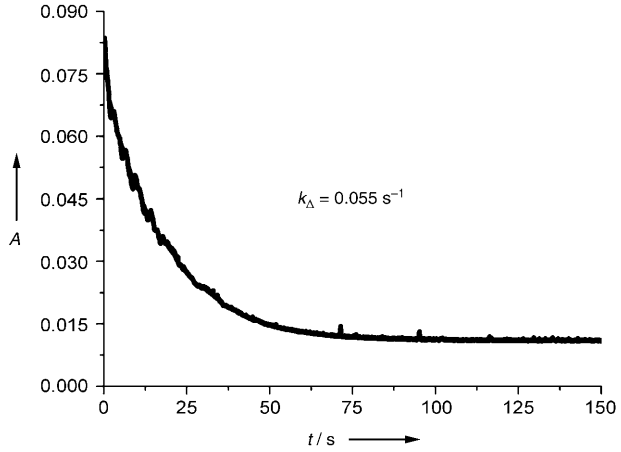


Figure 3. Thermal bleaching of OD-ON monitored at 456 nm.

An interesting feature of the OD-CN system is the electronic decoupling of the two photochromic groups connected through a sp^3-hybridized carbon atom. Irradiation above 350 nm transforms the naphthopyran group selectively from the closed (colorless) form of OD-CN to the open form (orange, $\lambda_{max}=456$ nm) of OD-ON (path 1; Figure 1). The thermal bleaching kinetics of the majority of the photoproducts (ca. 81%) can be described with a monoexponential function ($k_\Delta=0.055\ s^{-1}$; Figure 3), with a value for the closure rate similar to that observed for other chromene systems.[13] The residual absorption (ca. 19%) in the visible region is typical for 2*H*-chromenes and is attributed to the presence of stable isomers; such isomers have been observed with other naphthopyrans.[14] These forms can be converted fully into the closed form by irradiation above 400 nm. In other words, this system has a read-out window between 350 and 380 nm, where the naphthopyran group can be switched selectively without affecting the diarylethene moiety.

Irradiation of OD-CN at 313 nm triggers both the ring-opening reaction of the naphthopyran and also the ring-closing reaction of the diarylethene, as the electronic properties of the ground states of the two photochromic moieties overlap between 300 and 350 nm, which leads initially to the formation of OD-ON and CD-CN. After irradiation for one minute the absorption is centered at 539 nm with a shoulder at 434 nm and also with absorption above 600 nm (Figure 4a). This is, however, not an equilibrium, CD-CN is bistable while OD-ON is not and reverts to OD-CN. Continuing the irradiation leads to an enrichment of CD-CN in the mixture, which is subsequently converted into CD-ON on further irradiation (path 2). The initially colorless solution turns brown, and the UV/Vis spectrum shows absorption up to 800 nm with three absorption maxima at 434, 539, and 618 nm.

When the irradiation is stopped, the open forms of the naphthopyran revert back to the closed form CD-CN (see Figure 4b) and the solution turns slowly from brown to pink (the maxima at 434 and 618 nm decrease and a new maximum at 516 nm is observed; path 3). Monitoring the kinetics of the conversion of CD-ON into CD-CN at 680 nm, where only the fully conjugated system absorbs, gives a bleaching rate constant of $1.95\times10^{-3}\ s^{-1}$ (monoexponential; Figure 4d). This comparatively high value indicates that the extension of the π conjugation in the CD-ON isomer stabilizes the open naphthopyran moiety to a large extent.[15]

Two photopathways are possible from the stationary state of CD-CN. Ring opening of the diarylethene to recover the OD-CN starting material (path 4) can be effected quantitatively from CD-CN with visible light (> 420 nm), a behavior typical of dithienylethenes. Irradiation of CD-CN (path 5) at 313 nm (OD-CN and CD-CN have a similar absorption at 313 nm; see Figure 1) induces the formation of CD-ON. The photostationary state (CD-ON) is reached faster from CD-CN than starting from OD-CN (Figure 4c).

The absorption characteristics of CD-ON are the same, regardless of whether the conversion is from OD-CN or CD-CN, which indicates that the naphthopyran group can be selectively opened and closed using UV light without affecting the diarylethene moiety.

In summary, we have investigated a hybrid biphotochromic system based on the thermally reversible naphthopyran

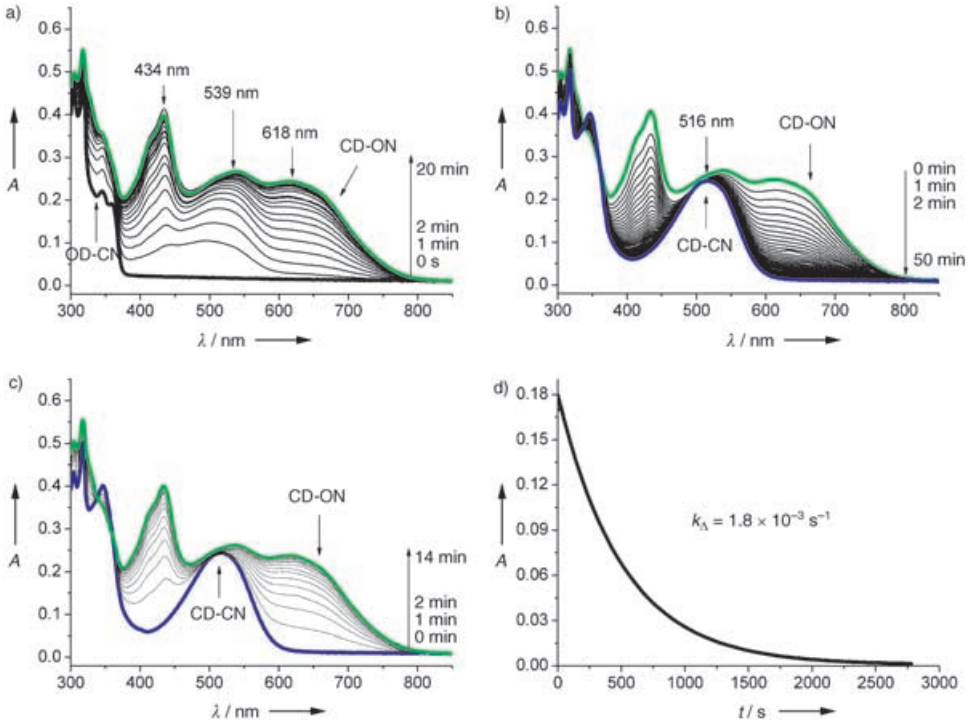


Figure 4. a) Time-dependent absorption spectra of a solution of OD-CN in cyclohexane (3.33×10^{-5} M) upon irradiation at 313 nm; b) fading of CD-ON after irradiation at 313 nm; c) time-dependent absorption spectra of CD-CN upon irradiation at 313 nm; d) thermal bleaching of CD-ON monitored at 680 nm.

and photochemically bistable dithienyl groups. Four different states were detected in this system, which are characterized by very different absorption properties and which can be addressed in the photon mode.

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[11] M. Frigoli, C. Moustrou, A. Samat, R. Guglielmetti, *Eur. J. Org. Chem.* **2003**, 2799.
[12] a) A solution of *n*BuLi in hexane (2.5 M, 0.53 mL) was added dropwise to a solution of **6** (0.52 g, 1.20 mmol) in dry THF (20 mL) at −78 °C. After the mixture had been stirred for 1 h at this temperature, a solution of **7** (0.36 g, 1.20 mmol) in dry THF (5 mL) was added dropwise. The reaction mixture was allowed to warm up to room temperature and then an aqueous solution of NH_4Cl was added. The resulting mixture was extracted twice with diethyl ether, washed with water, dried over magnesium sulfate, then concentrated under vacuum. Column chromatography (silica, hexane/CH_2Cl_2, 70/30) gave OD-CN as a slightly orange pure product (0.4 g, 52%). M.p. 67.5–68.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H), 1.84 (s, 3H), 2.33 (s, 3H), 6.17 (d, $J = 9.8$ Hz, 1H,), 6.60 (s, 1H), 6.85 (s, 1H), 7.16 (d, $J = 9.0$ Hz, 1H), 7.29–7.58 (m, 8H), 7.68 (d, $J = 9.0$ Hz, 1H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.96 ppm (d, $J = 8.4$ Hz, 1H). Elemental analysis calcd (%) for $C_{35}H_{24}F_6OS_2$: C 65.82, H 3.79; found: C 65.98, H 3.67; b) the experimental set-up for the photochemical measurements is described in ref. [4d, g].
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[14] a) F. Ortica, P. Smimmo, G. Favaro, U. Mazzucato, S. Delbaere, D. Venec, G. Vermeersch, M. Frigoli, C. Moustrou, A. Samat, *Photochem. Photobiol. Sci.* **2004**, *3*, 878; b) S. Delbaere, J.-C. Micheau, G. Vermeersch, *J. Org. Chem.* **2003**, *68*, 8968; c) note: this is typical for 2*H*-chromenes and indicates, in principle, the presence of four photoproducts (CTC, TTC, TTT, and CTC). The isomers differ only in the configuration at the double bond attached to the naphthalene ring and at the position of the aryl group at the terminal double bond. The isomers CTC and TTC are thermoreversible whereas the other two are thermally stable and bleach on exposure to visible light. (TTT = *trans*,transoid, *trans*, CTT = *cis*,transoid,*trans*).
[15] Note: The thermal stability of CD-ON increased about 28 times relative to OD-ON. This result, together with monoexponential bleaching kinetics, might indicate that TT isomers, whose formation is selectively photoinduced by the extended π conjugation throughout the molecule, are formed preferentially.

