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Signaling and Expression of Electronic Effects by Dihydroazulene-Vinylheptafulvene Photochromism

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Dihydroazulene(DHA)/vinylheptafulvene(VHF) equilibration is based on photochemical ring opening and thermal cyclization. Optical and non-linear optical properties of DHA/VHF are reported. Multimode switching, comprising both photo-redox and off/on-fluorescence switching, are investigated. DHA covalently attached to cellulose shows multifold switching. A concept for cyclic multistate switching is proposed based on biphotochromic compounds.

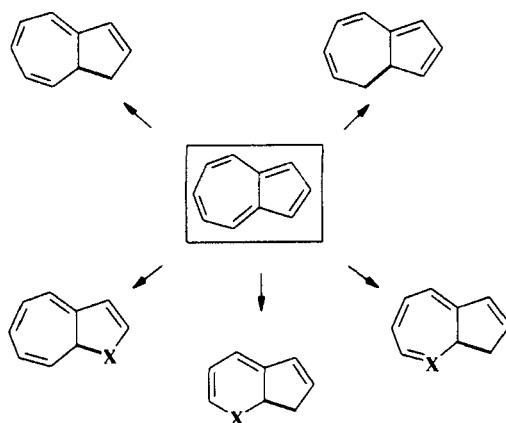
Keywords: photochromism; biphotochromism; photo-redox-switching; optical and nonlinear optical properties; dye modified cellulose

In recent years the most studied photochromic systems were cyclic and heterocyclic compounds such as spiropyrans, spirooxazines, spirodihydroindolizines, benzo- and naphthopyranes (chromenes), fulgides, and diarylethenes. A comprehensive survey of various families and their potential applications in optical information storage and related areas is available in recent literature.^[1] A common feature of the above photochromism is six-electron-interconversion. The equilibration may either be purely photochemical or split into a photochemical and a

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thermal process. The well-known diarylethene/dihydrobenzodiarene isomerization represents a subclass of the $(4n+2)$ -electron processes ($n = 0, 1, 2, \dots$).^[2] Another interesting group of compounds can be derived from ten-electron isomerization ($n = 2$) as in the case of naphthalene or azulene derivatives. We considered photochromic systems derived from azulenes (scheme 1) to be of special interest due to their unique electronic configuration.

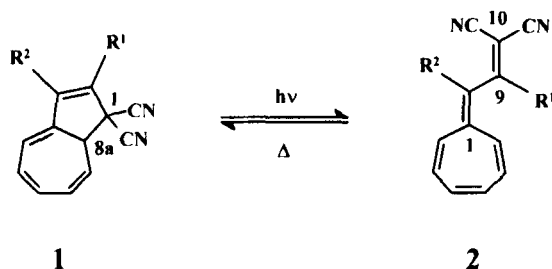


SCHEME 1 Basic structures of potential photochromic compounds derived from azulene (X: heteroatom).

There are several ways to structurally modify azulene in order to achieve photochromism. One necessary requirement is to replace a double bond with a single bond leading to vicinal dihydro forms. Also methine carbons or the residual double bonds can be replaced with heteroatoms such as nitrogen.

Combinatorial approaches to alter the structural pattern led to optimize the ring-opening/cyclization processes. Although several strategies were pursued, the incidentally discovered 1,8a-dihydro-1,1-azulenedicarbonitrile **1** ($R^1 = \text{aryl/alkyl}$; $R^2 = \text{H/alkyl/aryl}$) proved to be

the most versatile compound till today^[3]. Compound **1** photochemically rearranges to the deeply coloured 10,10-dicyanovinylheptafulvene **2**.



SCHEME 2 The dihydroazulene (DHA)/vinylheptafulvene (VHF) equilibrium.

These dicyanovinylheptafulvenes **2** are photochemically non-active but can be thermally cyclized to the corresponding DHA forms (scheme 2, figure 1).

The difference of the maxima of the longest wavelength absorptions of the dihydroazulenes **1** and the vinylheptafulvenes **2** amounts up to about 160 nm depending on the substituents R^1 and R^2 . As a representative example the photochromism of the phenol ether derivative **1a** is shown in Figure 1.^[4] The effects of the substituents are more pronounced in the vinylheptafulvene forms. In addition, these nonalternant isomers show positive solvatochromism, whereas the absorption spectra of the dihydroazulenes are little affected by the solvent polarity. This is also in agreement with the findings on the nonlinear optical properties, which give higher β -values for the vinylheptafulvenes compared with the dihydroazulene forms.^[5] The DHA/VHF system may therefore be useful in photochemically driven switching of nonlinear optical properties.

The photoreaction occurs on the S_1 surface. At room temperature the quantum yields of the photoreactions $[\phi_{DHA \rightarrow VHF}]$ vary between 0.6 and <0.004 depending on the substituents. The quantum

yields of photoreaction and fluorescence strongly depend on temperature (the fluorescence quantum yields ϕ_F can be as high as 0.8 at $-196\text{ }^\circ\text{C}$).^[3i,j] The thermal back reaction $\text{VHF} \rightarrow \text{DHA}$ is exothermic, as shown by differential thermoanalysis, and obeys first-order kinetics with energies of activation (E_a) of about 20 kcal/mol at ambient temperature. Again the thermal back reaction depends on solvent polarity and substituents, respectively. Electron withdrawing substituents R^1 increase the rate of the thermal process. The same is true for solvents having a high dielectric constant.

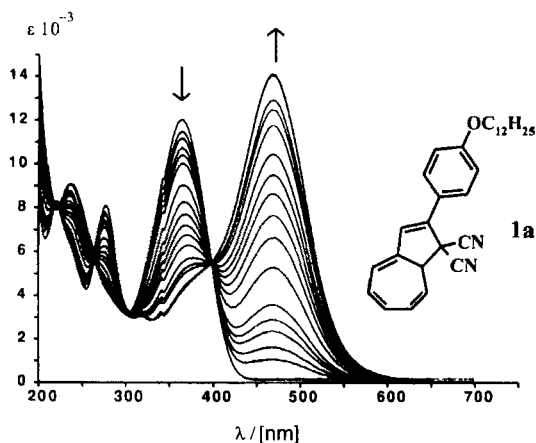


FIGURE 1 Changes of the UV/VIS absorption spectra of dihydroazulene **1a** on irradiation in acetonitrile at room temperature using an incandescent lamp (500 Watt OSRAM HWLS 500).

Unlike the dihydroazulenes **1** the vinylheptafulvenes **2** are non-fluorescent at room temperature. By the use of fluorophores as substituents efficient on/off switching of emission can be observed.^[3k, 6]

Figure 2 visualizes the on/off-switching of fluorescence of the yet unpublished hydroquinoid derivative **1b**.^[7]

The topology of DHA **1** and VHF **2** (alternant vs nonalternant hydrocarbons) leads to substituent effects which can be used in dual-mode switching as for example demonstrated by the *p*-cyanophenyl derivative **1c/2c** (Figure 3).^[3f] The DHA form **1c** is reduced at higher negative potential compared with the VHF form **2c**. Photomodulated amperometry, a technique which measures the current response on light-pulse treatment, if a bias voltage is set in between the two reduction waves, gives a current/time curvature as shown in Figure 3/bottom.^[3e,f, 8]

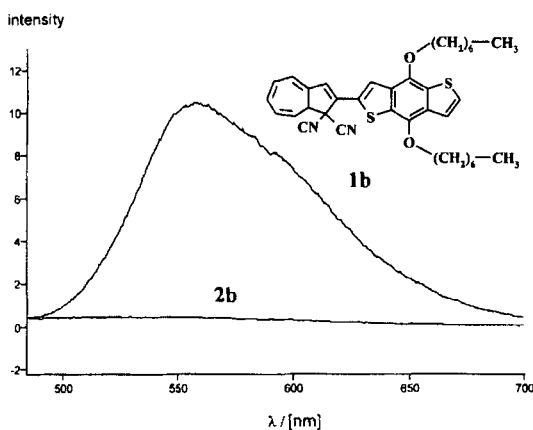


FIGURE 2 On/off switching of luminescence by **1b/2b** equilibration.

We also started to investigate the photochromic behaviour in multiple functionalized high molecular weight materials such as cellulose.^[9] By esterification, the photochromic groups were regioselectively linked at C-6 of the anhydroglucose subunits leading to the formation of chemically modified cellulose **1d**. As starting material

we used Avicel, a microcrystalline cellulose with a degree of polymerization (DP) of about 200 glucose units. The degree of substitution (DS) was found to be 0.25 indicating that around 50 dihydroazulene units are covalently linked at one chain of cellulose. Due to the fact that the dihydroazulene groups occupy different local environment within a chain, the photochemical transformation of the DHA into VHF lead to randomly distributed isosbestic points (Figure 4).

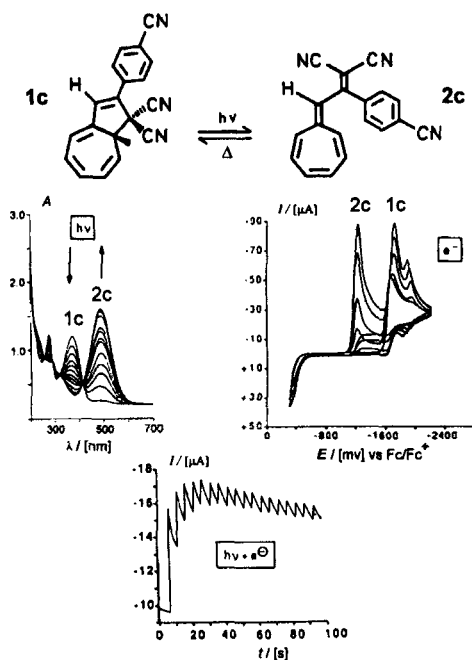


FIGURE 3 Photochromism, cyclic voltammetry, and photomodulated amperometry of 1c/2c. Middle left: change of absorption spectra on irradiation; middle right: cyclic voltammograms of the DHA and VHF forms; bottom: response signal (current vs time) resulting from light-pulse irradiation.

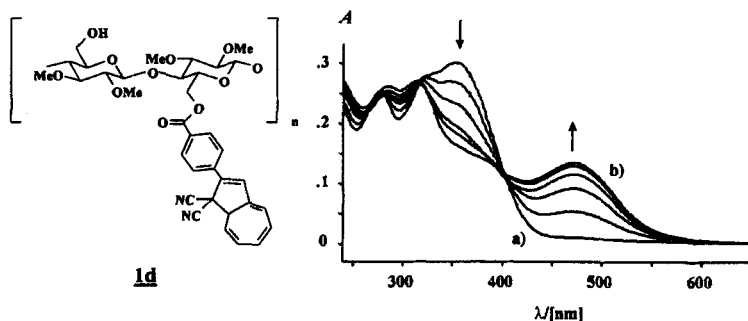


FIGURE 4 Photochromic switching of cellulose **1d**. Right: spectral changes on irradiation for 200 s, in tetrahydrofuran at room temperature using an incandescent lamp (500 Watt OSRAM HWLS 500); trace a: DHA **1d**; trace b: VHF **2d**.

By purpose-oriented functionalization, DHA/VHF photochromism can also be employed for three-mode switching which combines photochromism, redox switching and proton transfer (Figure 5).^[3g] It is found that photochromism occurs on the quinoid stage **1e** but is only scarcely active on the hydroquinone stage **1f**. System **1e-f/2e-f** therefore represents a logic module with yes/no and lock functions.^[3i] Recently, an interesting system of a three-mode molecular switching device based on DHA/VHF photochromism was also reported, employing twofold-photochromism and proton transfer.^[10]

New work^[11] in our group deals with the concept of cyclic-multistate switching as shown in Figure 6. Similar multistep processes dealing with unidirectional molecular rotors have been reported in two recent papers.^[12] It also reminds of the light-driven cyclic multistep events in nature as for example bacterial light-harvesting or the visual process in which photonic and thermal processes both occur. The final goal is to achieve a directional circular switching by utilizing gated photochemical and thermal steps. The biphotochromic compounds **3** can

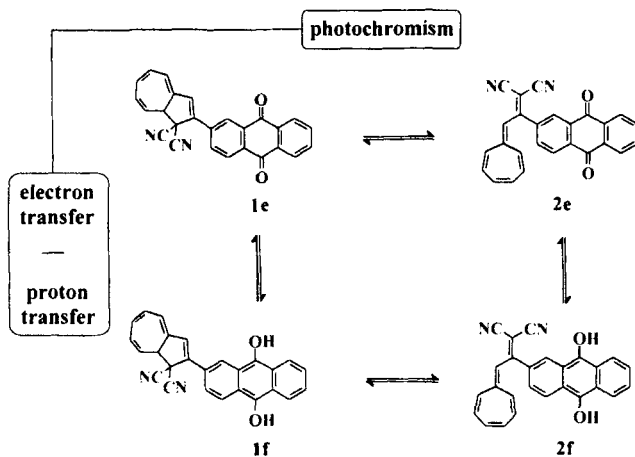


FIGURE 5 Multimode switching of quinoid derivatives **1e/2e** comprising photochromic, electron transfer, and proton transfer processes.

either undergo DHA/VHF photochromism or dithienyl-ethene/dihydrobenzodithiophene (DTE/DHB) photochromism. At the present stage of investigation switching between the forms **a**, **b** and **d** is identified ($R^1 = R^2 = \text{Me}$). Attractive target molecules are expected to be donor/acceptor functionalized compounds **3** ($R^1 = \text{acceptor group}$; $R^2 = \text{donor group}$) which may allow to stabilize the yet unknown dipolar species **3c**.

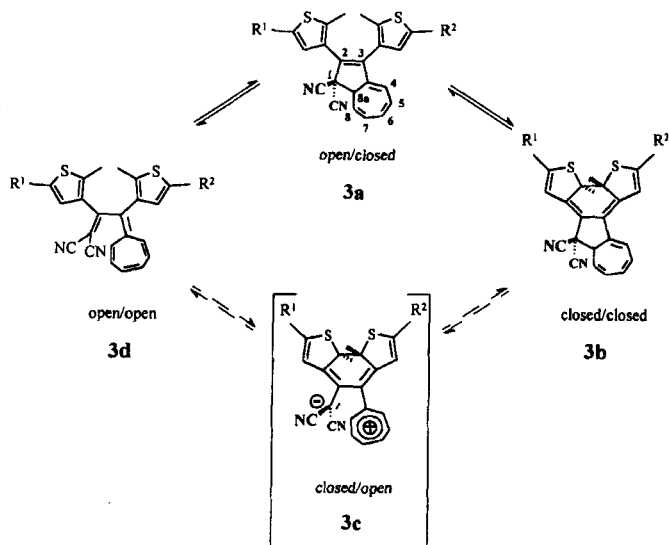


FIGURE 6 Concept of a biphotochromic system 3 based on the DHA/VHF- and DTE/DHB-system.

Acknowledgement

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