Molecular Switches

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Toward Fluorescent Memories with Nondestructive Readout: Photoswitching of Fluorescence by Intramolecular Electron Transfer in a Diaryl Ethene-Perylene Bisimide Photochromic System**

Martin Berberich, Ana-Maria Krause, Michele Orlandi, Franco Scandola, and Frank Würthner**

Photochromic compounds change their optical and electronic properties by reversible photochemical reactions upon irradiation and are therefore suitable for many tasks.[1] Very recently, the application of photochromic compounds to the imaging of living cells by single-molecule photoswitching has been demonstrated.[2] In the last few years diaryl ethenes (DAEs) have evolved as highly promising photochromic molecules for optical data storage because of their durable persistency and the thermal irreversibility of their closed and open forms.[3]

Fluorescence photoswitching of DAEs linked to fluorescent dyes has been demonstrated even at the single-molecule level.[4] In these systems, the readout is based on the observed fluorescence of the open form of diaryl ethene (DAE$_O$), whilst fluorescence quenching from the excited dye to the closed form of the diaryl ethene (DAE$_C$) takes place by an intramolecular Förster resonance energy transfer (FRET). The drawback of such energy-transfer-based memory systems is that FRET induces photochromic cycloreversion during the readout step, and thus destroys the memory.

Such destructive readout may be circumvented by fluorescence switching through intramolecular photoinduced electron transfer (PET)[5] if the open and closed forms of the photochromic moieties were to possess different redox properties.[6] The optimal case would be if the electron transfer involves oxidation of the dye and reduction of the DAE[7,8] and the solvent-dependent driving force for PET is exergonic for the DAE$_C^-$–dye$^+$ but not for the DAE$_O^-$–dye$^+$ charge transfer (CT) state (Figure 1). Furthermore, the emission spectrum of the dye should not overlap with the absorption spectrum of any isomer of the DAE, as in FRET-based systems, but needs to be at a higher wavelength.[9] This would facilitate writing, erasing, and reading data with light sources of three different wavelengths without destructive readout.

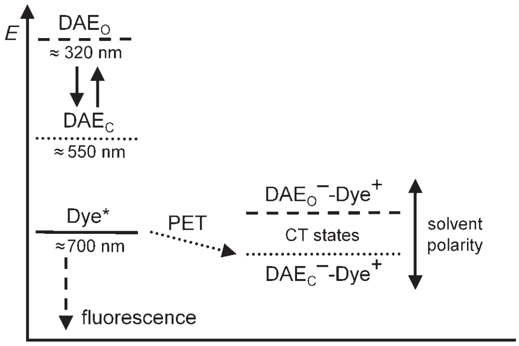
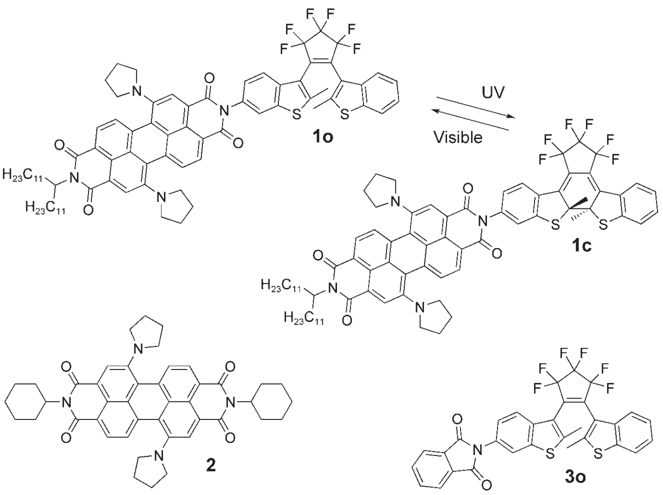


Figure 1. Schematic energy diagram for the fluorescent open form (dashed line) and the nonfluorescent closed form (dotted line) of a DAE and CT states of the DAE–dye conjugate.

A photochromic DAE system based on the above-mentioned optimized concept is, to the best of our knowledge, unknown.[10] Thus, we have designed the photochromic system **1o** based on a perfluorinated DAE derivative and a bay-substituted perylene bisimide (PBI) dye (Scheme 1). The fluorescent 1,7-dipyrrolidinylperylene bisimide was chosen because of its low oxidation potential and its absorption maximum in the NIR region (around 700 nm).[11] The photochromic compound **1o** was synthesized by imidization of the



Scheme 1. Photochromic compounds **1o** and **1c**, and reference compounds **2** (perylene bisimide dye) and **3o** (DAE).

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[*] M. Berberich, A.-M. Krause, Prof. Dr. F. Würthner
Universität Würzburg, Institut für Organische Chemie
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4756
E-mail: wuerthner@chemie.uni-wuerzburg.de
M. Orlandi, Prof. Dr. F. Scandola
Università di Ferrara, Dipartimento di Chimica
44100 Ferrara (Italy)
Fax: (+39) 0532-240-709
E-mail: snf@unife.it

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respective amino-substituted diaryl ethene with 1,7-dipyrrolidinylperylene monoanhydride monoimide (see the Supporting Information for details). Compound **1o** can be switched between two photostationary states. Upon irradiation with UV light ($\lambda_{max} = 350$ nm) a photostationary state containing 66% of the closed form of the PBI–DAE conjugate **1c** (Scheme 1) was obtained,[12] which could be isolated by column chromatography. The open form can be regenerated almost quantitatively (99%) by irradiation of a solution of the closed form with visible light ($\lambda > 400$ nm).

The fluorescence quantum yields for **1o** and **1c** were determined in a series of solvents of different polarity, with dielectric constants (ε_r) ranging from 2.24 (tetrachloromethane) to 36.71 (dimethylformamide). These values, divided by the quantum yield of the reference PBI **2** (without a DAE moiety), are shown as a function of the ε_r values of the solvents in Figure 2 (see also Table S1 in the Supporting Information). In low-polarity solvents such as chloroform ($\varepsilon_r = 4.89$), the quantum yields of **1o** and **1c** are nearly identical to that of the reference dye **2**, which indicates that no fluorescence quenching by the DAE$_C$ or DAE$_O$ moieties occurs. Interestingly, the quantum yields of **1o** and **1c** differ significantly at higher solvent polarity, and in dimethylformamide (highly polar) almost complete quenching of the closed form **1c** is observed. Fluorescence quenching by FRET from the excited dye to the closed form of the DAE can be excluded as a deactivation path. Thus, the increase in the fluorescence quenching of **1c** as the solvent polarity increases is highly indicative of a preferential PET from the dye to the closed form of DAE.

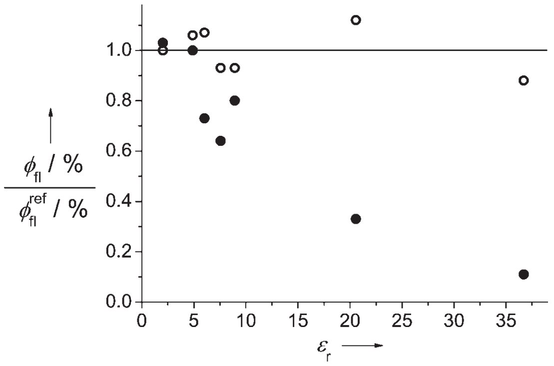

Figure 2. Fluorescence quantum yields of **1o** and **1c** (ϕ_{fl}) divided by the quantum yield of the reference perylene bisimide **2** (ϕ_{fl}^{ref}) without the DAE moiety as a function of dielectric constants of solvents; open form (○), closed form (●).

The Gibbs free energy (ΔG°) for an intramolecular charge-separated state of a covalently bound donor–acceptor system in a given solvent can be estimated using the Rehm–Weller Equation (1).

$$\Delta G^\circ = e[E_{ox}(\mathrm{D}) - E_{red}(\mathrm{A})] - E_{00} - \frac{e^2}{4\pi\varepsilon_0\varepsilon_S R_{cc}} - \frac{e^2}{8\pi\varepsilon_0}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)\left(\frac{1}{\varepsilon_{ref}}-\frac{1}{\varepsilon_S}\right) \qquad (1)$$

Rehm – Weller equation

E_{ox}(D) and E_{red}(A) are the first oxidation potential of the donor perylene bisimide and first reduction potential of the acceptor DAE, respectively. E_{00} signifies the spectroscopic excited state energy, while R_{CC} is the distance between the centers of the donor and acceptor moieties. The effective ionic radii of the donor radical cation and acceptor radical anion are labeled as r^+ and r^-, respectively. The dielectric constant of the reference solvent used in electrochemistry is denoted as ε_{ref}, while ε_S is the dielectric constant of the given solvent.[13]

Compounds **1o** and **1c** exhibit the characteristic UV/Vis spectra of 1,7-dipyrrolidinylperylene bisimides, with an absorption maximum at around 700 nm. The spectrum of **1c** displays some additional bands (in particular, a broadened absorption band between 450 and 550 nm, see Figure 3) that are attributed to the closed form of DAE. From the UV/Vis and fluorescence spectra recorded in dichloromethane an S$_0$–S$_1$ excitation energy of 1.71 eV was estimated for **1o** and **1c**.

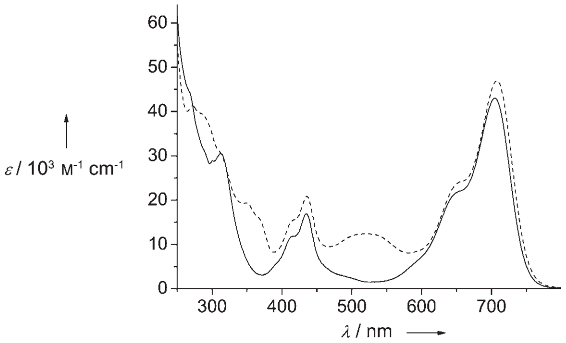

Figure 3. UV/Vis spectra of **1o** (solid line) and **1c** (dashed line) in dichloromethane.

The redox potentials of **1o** and **1c** and the reference compounds (see Table S2 in the Supporting Information) were obtained by cyclic voltammetry measurements in dichloromethane, with ferrocene used as an internal reference (Figure 4). The cyclic voltammogram of **1o** is identical to that of the reference dye **2** (see Figure S1 in the Supporting Information). Thus, additional redox processes associated with the DAE$_O$ moiety are apparently not observable within the available potential window. The first half-wave oxidation potentials of the PBI moiety were observed at 0.22 V and 0.21 V for **1o** and **1c**, respectively. The closed form **1c** showed additional waves for the DAE moiety at −1.60 V and 1.00 V, in agreement with the reference DAE compound **3c** bearing a phthalic imide residue (see Figure S3 in the Supporting Information). The first reduction potential of **3o** was observed at −1.98 V while the respective wave for **1o** was not observable within the available potential range (up to ca. −2.0 V). Donor–acceptor distances of 1.32 nm and 1.24 nm were estimated from the optimized geometries of **1o** and **1c** conjugates, respectively.

Since all experimental values were determined in dichloromethane, the solvent-related term in the Rehm–Weller equation can be neglected in the present case, and by

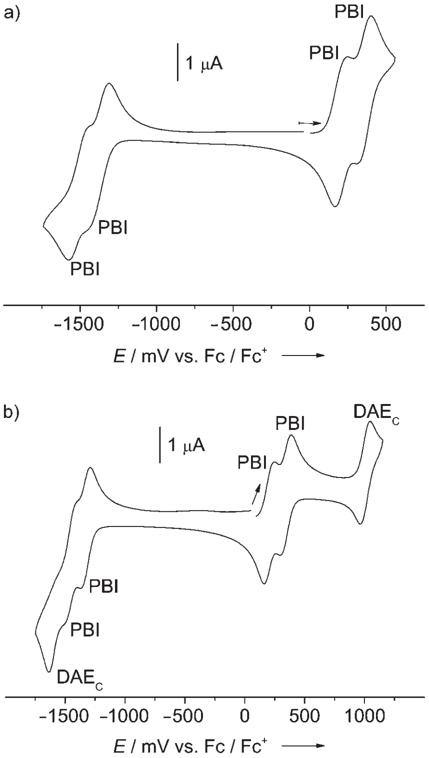

Figure 4. Cyclic voltammograms of a) **1o** (2.7×10^{-4} M) and b) **1c** (3.8×10^{-4} M) in dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, scan rate 100 mV s^{-1}. Fc/Fc^{+} = ferrocene/ferrocenium couple.

applying the obtained data in this equation, a $\Delta G°$ value of 0.37 eV for **1o** and a slightly exergonic value of −0.03 eV for **1c** in dichloromethane can be calculated. These energy values imply that the electron-transfer process, clearly endergonic for the open form, is thermodynamically feasible only for the closed form in dichloromethane. In more polar solvents such as dimethyl sulfoxide ($\varepsilon_r = 46.68$), the CT state for **1c** (DAE_C^{-}–PBI^{+}) becomes more stable[14] and PET is more likely to take place (Figure 2). Fluorescence lifetime measurements in dimethyl sulfoxide solution provided values of 1.9 ns for **1o** and 0.23 ns for **1c**, thus indicating that the excited fluorophore is subject to an additional quenching process when the photochrome is in its closed form (see Table S3 in the Supporting Information).

Photochromic compounds **1o** and **1c** were also investigated by femtosecond transient absorption spectroscopy in dimethyl sulfoxide by excitation at 680 nm (the $S_0 \rightarrow S_1$ transition of the perylene bisimide dye). An intense bleaching between 650 and 770 nm that arises from the depopulation of the ground-state molecules and the stimulated emission between 770 and 800 nm is observed as a combined negative signal in the spectrum of **1o** (Figure 5a) that decays with a lifetime of approximately 1.5 ns. Compound **1c** shows the same qualitative behavior (Figure 5b), but with a greatly reduced lifetime of 230 ps. The fact that the quenching of the dye S_1 state is not accompanied by a distinctive accumulation of a transient charge-separated species suggests that charge separation is slower than charge recombination and the former is the rate-determining step in *PBI–DAE_C deactivation. Clear evidence for the occurrence of photoinduced electron transfer is obtained from femtosecond transient absorption experiments by excitation at 400 nm (the $S_0 \rightarrow S_2$ transition of the dye). In this case, while the behavior of **1o** is virtually identical to that observed upon excitation at 680 nm (see Figure S4 in the Supporting Information), an additional short-lived positive absorption band with a maximum centered at 613 nm is observed for **1c** (Figure 6). The latter can be assigned to the radical cation of the 1,7-pyrrolidinylperylene bisimide moiety,[15] which was verified by spectroelectrochemistry (see Figure S5 in the Supporting Information). In this case, population of the DAE_C^{-}–PBI^{+} state from the upper S_2 state of the dye, rather than from the S_1 state, is fast

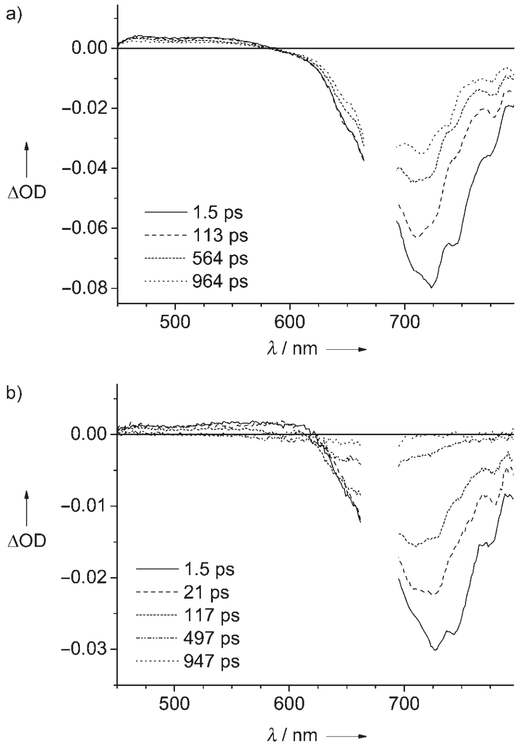

Figure 5. Ultrafast transient absorption spectra of a) **1o** and b) **1c** in dimethyl sulfoxide; $\lambda_{ex} = 680$ nm.

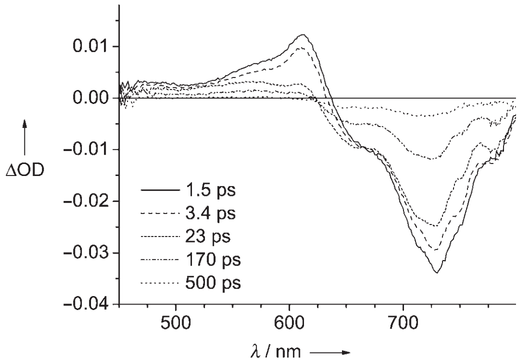

Figure 6. Ultrafast transient absorption spectra of **1c** in dimethyl sulfoxide; $\lambda_{ex} = 400$ nm.

enough to lead to appreciable transient accumulation of the charge-separated product.

In summary, this new design of photoswitch is effective in a polar environment where an intramolecular electron transfer from the excited PBI dye to the closed form, but not to the open form of the DAE takes place, leading to fluorescence quenching by a PET mechanism. Thus, a prototype photochromic switch for nondestructive readout optical memory systems has been introduced.

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[1] For reviews see: a) M. Irie, T. Mrozek, J. Daub, A. Ajayaghosh, Y. Yokoyama in *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, **2001**, pp. 37–121; b) *Photochromism: Molecules and Systems* (Eds.: H. Dürr, H. Bouas-Laurent), Elsevier, New York, **1990**; c) *Molecular Devices and Machines: A journey into the Nano World* (Eds.: V. Balzani, A. Credi, M. Venturi), Wiley-VCH, Weinheim, **2003**; d) B. L. Feringa, *J. Org. Chem.* **2007**, *72*, 6635–6652.

[2] J. Fölling, V. Belov, R. Kunetsky, R. Medda, A. Schönle, A. Egner, C. Eggeling, M. Bossi, S. W. Hell, *Angew. Chem.* **2007**, *119*, 6382–6386; *Angew. Chem. Int. Ed.* **2007**, *46*, 6266–6270.

[3] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; b) H. Tian, S. J. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97; c) H. Tian, S. Wang, *Chem. Commun.* **2007**, 781–792.

[4] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759–760; b) T. Fukaminato, T. Sasaki, T. Kawai, N. Tamai, M. Irie, *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849; c) T. A. Golovkova, D. V. Kozlov, D. C. Neckers, *J. Org. Chem.* **2005**, *70*, 5545–5549; d) G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian, D. Zhu, *Chem. Mater.* **2006**, *18*, 235–237; e) J. H. Hurenkamp, J. J. D. de Jong, W. R. Browne, J. H. van Esch, B. L. Feringa, *Org. Biomol. Chem.* **2008**, *6*, 1268–1277.

[5] a) *Supramolecular Photochemistry* (Eds. V. Balzani, F. Scandola), Ellis Horwood, New York, **1991**; b) *Electron Transfer in Chemistry* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2001**; c) *Fundamentals of Photoinduced Electron Transfer* (Ed. G. J. Kavarnos), VCH Publishers, New York, **1993**; d) N. Mataga, H. Chosrowjan, S. Taniguchi, *J. Photochem. Photobiol. C* **2005**, *6*, 37–79; e) D. M. Guldi, *Chem. Soc. Rev.* **2002**, *31*, 22–36; f) J. M. Endtner, F. Effenberger, A. Hartschuh, H. Port, *J. Am. Chem. Soc.* **2000**, *122*, 3037–3046.

[6] a) A. J. Myles, N. R. Branda, *J. Am. Chem. Soc.* **2001**, *123*, 177–178; b) Y. Terazono, G. Kodis, J. Andréasson, G. Jeong, A. Brune, T. Hartmann, H. Dürr, T. A. Moore, A. L. Moore, D. Gust, *J. Phys. Chem. B* **2004**, *108*, 1812–1814; c) F. M. Raymo, M. Tomasulo, *Chem. Soc. Rev.* **2005**, *34*, 327–336.

[7] Electrochemically induced ring opening/closure has been reported to occur upon oxidation of diaryl ethenes.[8] In principle, therefore, destructive readout could not be ruled out with this type of electron-transfer quenching.

[8] a) T. Koshido, T. Kawai, K. Yoshino, *J. Phys. Chem.* **1995**, *99*, 6110–6114; b) A. Peters, N. R. Branda, *J. Am. Chem. Soc.* **2003**, *125*, 3404–3405; c) A. Peters, N. R. Branda, *Chem. Commun.* **2003**, 954–955; d) B. Gorodetsky, H. D. Samachetty, R. L. Donkers, M. S. Workentin, N. R. Branda, *Angew. Chem.* **2004**, *116*, 2872–2875; *Angew. Chem. Int. Ed.* **2004**, *43*, 2812–2815; e) S. Fraysse, C. Coudret, J. P. Launay, *Eur. J. Inorg. Chem.* **2000**, 1581–1590; f) X. H. Zhou, F. S. Zhang, P. Yuan, F. Sun, S. Z. Pu, F. Q. Zhao, C. H. Tung, *Chem. Lett.* **2004**, *33*, 1006–1007; g) W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch, B. L. Feringa, *Chem. Eur. J.* **2005**, *11*, 6414–6429; h) W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch, B. L. Feringa, *Chem. Eur. J.* **2005**, *11*, 6430–6441; i) G. Guirado, C. Coudret, M. Hliwa, J. P. Launay, *J. Phys. Chem. B* **2005**, *109*, 17445–17459; j) Y. Moriyama, K. Matsuda, N. Tanifuji, S. Irie, M. Irie, *Org. Lett.* **2005**, *7*, 3315–3318.

[9] The requirement that forbids energy transfer from the excited dye to both forms of the diaryl ethene implies, on the other hand, that the reverse energy-transfer processes are thermodynamically allowed. In practice, however, energy transfer to the dye is not expected to compete effectively with the ultrafast (a few ps) ring closure/opening processes of the diaryl ethene excited state.

[10] The concept has recently been suggested by Y. Odo, T. Fukaminato, M. Irie, *Chem. Lett.* **2007**, *36*, 240–241, and by us: M. Berberich, Masters Thesis, University of Würzburg, Würzburg (Germany), **2007**.

[11] F. Würthner, *Chem. Commun.* **2004**, 1564–1579.

[12] The quantum yield for the photocyclization of the open form PBI–DAE **1o** at 350 nm in dichloromethane is estimated to be 0.017.

[13] A. Z. Weller, *Z. Phys. Chem.* **1982**, *133*, 93–98.

[14] An approximate value for the driving force, calculated with average molecular radii of ca. 7 Å in the Rehm–Weller equation, is ca. −0.15 eV.

[15] a) A. S. Lukas, Y. Zhao, S. E. Miller, M. R. Wasielewski, *J. Phys. Chem. B* **2002**, *106*, 1299–1306; b) M. J. Ahrens, M. J. Tauber, M. R. Wasielewski, *J. Org. Chem.* **2006**, *71*, 2107–2114.