Optical Switches

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Multiple Switching and Photogated Electrochemiluminescence Expressed by a Dihydroazulene/Boron Dipyrromethene Dyad**

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Optical signal generation, control, and transduction are key processes in natural and technological systems that essentially rely on fast and efficient processing of information.^[1]

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Prominent examples in nature are the vision process, phototropism, photomorphogenesis, and circadian rhythms where the response to light is realized by a variety of enzymatic photoreceptors, including rhodopsins, phototropins, phytochromes, cryptochromes, and BLUF domains.^[2] All of these photoreceptors rely on a functional chromophore as the photoactive element, which initiates a highly sophisticated signaling cascade with, for example, an electron transfer or a photochromic reaction as the primary step after light absorption.

In studying these biological systems chemists have recognized the superiority of signal processing by light in terms of velocity and efficiency, and they have strived to use lightdriven and -controlled processes in artificial chromophoric ensembles at the molecular level for technological purposes such as molecular electronics and photonics, and artificial photosynthesis. Especially photochromic compounds have gained strong popularity here, for instance, in high-density optical data storage and multimode photoswitching.^[3] Using light as a trigger medium and as a tool for readout, the latter typically by fluorescence, offers the advantages of the nondestructive control and processing of information. However, up to now, only a few systems that show photochromically modulated luminescence have been realized, and the efficiency of the modulation and the overall brightness of the systems is often rather poor.^[4] Furthermore, to our knowledge, a photochromic ensemble in which the switching states are photocontrolled but the luminescence readout signal can be sampled by either optical or electrochemical excitation, i.e., by photo- or electrochemiluminescence (ECL), has not yet been reported. The latter feature would be a key link between OLEDs (organic light-emitting diodes) and conventional optical-gate technologies.

We realized our aim of a bright photochromic luminescent switch that can be either photo- or electrochemically excited by combining the photochromic system dihydroazulene/vinylheptafulvene (DHA/VHF; Scheme 1 a) with the boron dipyrromethene (BDP) fluorophore in dvad 1 (Scheme 1b; for synthetic details see the Supporting Information). The DHA/ VHF system shows UV/Vis photochromism that is particularly suitable for our present purposes and has been employed successfully in various molecular switches.^[5] The photochromic conversion of the alternant π system DHA into the non-alternant VHF occurs by means of a 10-electron rearrangement of the carbon framework, which strongly influences the electronic properties of the substituents attached to the photochromic system.^[6] The BDP chromophore provides favorable signaling features, as BDPs show green emission of high brightness and are also fluorophores that display photogenerated as well as electrochemically generated luminescence.^[7] Furthermore, the spectral and redox properties of both subunits complement each other well for the intended performance.

UV/Vis-spectrophotometric measurements of **1a** in chloroform clearly reveal the independence of both subchromophores, with main bands centered at 376 nm for the DHA and 527 nm for the BDP moiety (Table 1, Figure 1). The substantial difference between the lowest energy absorptions of DHA and BDP guarantees exclusive excitation of the



Scheme 1. The photochromic system dihydroazulene/vinylheptafulvene DHA/VHF (a) is combined with the fluorophore boron dipyrromethene (BDP) to give dyads 1a and 1b (b). The nonswitchable derivative 2 and the model fluorophore 3 (c) were used in control experiments.

Table 1: Absorption (in CHCl₃) and redox data (in MeCN) of 1a and 1b (E in mV vs. Fc⁺/Fc).

	$\lambda_{abs} [nm]$	E ^{red}	E ^{cred}	E ^{ox} _{1/2}	E ^{aox}
	([lg(ϵ)]/[lg(M^{-1} cm ⁻¹)])	[mV]	[mV]	[mV]	[mV]
1a	527 (4.86), 376 (4.60)	—1615	—1920	615	1025
1b	527 (4.90), 495 (4.69)	—1610	—1325	630	760

readout module, the BDP fluorophore, without initiating the "write-in process", the photoreaction of DHA. Cyclic voltammetry supports these findings. The reversible reduction $(E_{1/2} = -1615 \text{ mV vs. Fc}^+/\text{Fc})$ and oxidation $(E_{1/2} = +615 \text{ mV vs. Fc}^+/\text{Fc})$ of BDP and the irreversible reduction $(E_p = -1920 \text{ mV vs. Fc}^+/\text{Fc})$ and oxidation of DHA $(E_p = -1920 \text{ mV vs. Fc}^+/\text{Fc})$



Figure 1. Absorption and emission spectra of 1a and absorption spectrum of 1b in CH_2CI_2 ($c=5 \times 10^{-6} \text{ M}$).

+ 1025 mV vs. Fc⁺/Fc) are centered in the expected potential regions thus indicating electronically decoupled ground states.^[5d,7b] After excitation of **1a** in dichloromethane at $\lambda >$ 500 nm, the typical BDP emission with a maximum at 540 nm, a fluorescence quantum yield of 0.67, and a single exponential decay time of 4.06 ns is observed (Figure 2). Changing the



Figure 2. Emission spectrum of **1a** ($c = 1 \times 10^{-6}$ M) in CH₂Cl₂. Discrete signals: ECL spectrum of **1a** ($c = 1 \times 10^{-3}$ M) in acetonitrile/0.2 M Bu₄NPF₆. Applied potentials are marked in the cyclic voltammogram in the inset.^[8]

polarity of the solvent does not alter the spectroscopic properties significantly (Table 2). Furthermore, as the potential separation of BDP reduction and oxidation ($\Delta E_{\text{ox-red}} \approx 2.30 \text{ mV}$) is also sufficient to populate the excited state of the BDP in **1a** electrochemically, the dyad shows electro-

Table 2: Fluorescence properties of 1a, 1b, and 2.

	Solvent	$arPhi_{f}^{[a]}$	$ au_{ m f}[m ns]^{[m b]}$
1a	MeCN ^[c]	0.62	3.96
	CH ₂ Cl ₂ ^[d]	0.67	4.06
	Et ₂ O ^[e]	0.66	3.87
1 b	MeCN ^[c]	0.01	0.03
	CH ₂ Cl ₂ ^[d]	0.01	0.02
	Et ₂ O ^[e]	0.01	0.03
2	MeCN ^[c]	0.16	0.88
	CH ₂ Cl ₂ ^[d]	0.27	1.72
	Et ₂ O ^[e]	0.67	4.13

[a] Relative to fluorescein 27 in 0.1 N NaOH (0.90 ± 0.03),^[14] ± 5% (**1 a**, **2**) ±15% (**1 b**). [b] At 298 K, ±0.003 ns. [c] $\lambda_{abs}/\lambda_{em}$ =523/536 nm. [d] $\lambda_{abs}/\lambda_{em}$ =526/540 nm. [e] $\lambda_{abs}/\lambda_{em}$ =524/536 nm. chemiluminescence (ECL) (Figure 2, discrete signals).^[8] The strong fluorescence emission and electrochemically generated luminescence let us thus define 1a as the ON state of the system.

Irradiation of **1a** at 366 nm induces the uniform photoconversion to 1b, which is apparent from the isosbestic points, the decrease of the band at 376 nm, and the appearance of a new band at 476 nm in the absorption spectrum (Figure 1). The BDP absorption remains virtually unaffected, stressing the fact that both modules of dyad 1b are also decoupled in the ground state. Again, cyclic voltammetry provides support: the BDP reduction ($E_{1/2} = -1610 \text{ mV vs. Fc}^+/\text{Fc}$) and oxidation $(E_{1/2} = +630 \text{ mV} \text{ vs. } \text{Fc}^+/\text{Fc})$ are negligibly shifted relative to values for 1a. Moreover, the typical irreversible reduction ($E_p = -1325 \text{ mV}$ vs. Fc⁺/Fc) and oxidation ($E_p =$ $+760 \text{ mV vs. } \text{Fc}^{+}/\text{Fc})$ of the VHF unit of **1b** are found at far lower potentials than those of DHA in **1a**.^[3c,5d] Photoconversion of 1a to 1b occurs with a quantum yield of ca. 0.01. This is quite low in comparison to other DHA/VHF systems and can be attributed to an overlap of the oscillator-weak $S_2 \leftarrow S_0$ transition localized on BDP^[7e] and the intense $S_1 \leftarrow S_0$ transition of DHA. Furthermore, analysis of the fluorescence excitation spectra revealed that despite the very weak fluorescence of DHA at room temperature ($\Phi_{\rm f} \approx 10^{-4}$),^[6a] energy transfer from DHA to BDP might play an additional, competitive role here. The OFF state 1b is thermally reconverted to **1a** with $t_{1/2} = 350$ min at room temperature.

In contrast to **1a**, **1b** shows a strongly reduced, typical green BDP emission upon excitation at $\lambda > 500 \text{ nm.}^{[9]} \Phi_{\text{f}}$ drops remarkably from 0.67 to 0.013 (Figure 3) and the fluorescence



Figure 3. Change of the emission intensity during the photoreaction of 1 a ($c=1 \times 10^{-6}$ m in CH₂Cl₂) to 1 b with excitation of the BDP at 505 nm. Inset: Reversibility of the switch as shown by several cycles of irradiation and back-reaction.

lifetime is shorter (Table 2). The quenching mechanism can be rationalized in terms of intramolecular fluorescence resonance energy transfer (FRET). The broad absorption spectrum of the VHF fragment, which stretches well beyond 550 nm,^[6] and the narrow emission band of the BDP unit, centered between 530 and 540 nm, show considerable overlap. Analysis of the FRET process and its features yields a spectral overlap integral $J = 2.6 \times 10^{14} \text{ m}^{-1} \text{ cm}^{-1}$ and an effective interaction radius $R_0 = 39 \text{ Å}$.^[10] Assuming that no other processes contribute significantly to the deactivation of the excited state of the BDP, we calculate the donor–acceptor distance of the FRET partners to be 15.1 Å,^[11] which

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corresponds within ± 0.2 Å to the distance between the BDP core and the center of the VHF unit as obtained for the ground-state geometry optimized by semiempirical AM1 calculations. Moreover, the absence of solvatokinetic behavior of 1b, that is, that the quenching process is not significantly accelerated upon increasing the polarity of the solvent, led us to assume that photoinduced electron transfer (PET) plays a negligible role here. Control experiments with 2, where the DHA/VHF moiety has been replaced with a nonswitchable dihydro-VHF group that isolates the *p*-dicyanovinylbiphenyl from the cycloheptatrienyl fragment (Scheme 1c), support these findings. The spectral characteristics of the BDP fluorophore in 2 are very similar to those of 1a/1b (Table 2). Furthermore, the fluorescence of 2 in nonpolar solvents is as bright as that of 1a. Upon increasing solvent polarity, a slight quenching of the BDP emission in 2 is observed. The latter is apparently connected to the moderate PET activity of the para-cyanovinylbiphenyl group,^[12] emphasizing the fact that the entire VHF unit is mandatory for the performance of 1b. As expected, after the photoreaction to 1b, the latter remains ECL-silent, and 1b thus represents the OFF state of the system.

In conclusion, we have presented a photochromic pair of BDP-DHA/VHF dyads as a versatile all-optically controllable switch, for which irradiation with near-UV light serves as the input and luminescence at 540 nm as the output. Furthermore, the readout signal of the ON state 1a can be generated by conventional photoexcitation as well as electrochemically; in other words, the system shows photogated electrochemiluminescence. Light-induced conversion of 1a to **1b** is accompanied by a 50-fold decrease of luminescence, defining the system as a true ON/OFF photoswitch. We have demonstrated here that the outstanding photo- and electrochemical properties of both modules, DHA/VHF and BDP, can be combined synergistically for highly interesting alloptical photochromic molecular switches. The ECL findings also indicate potential applications in gated organic lightemitting diodes (OLEDs).^[13]

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- a) M. A. van der Horst, K. J. Hellingwerf, Acc. Chem. Res. 2004, 37, 13-20; b) F. M. Raymo, Adv. Mater. 2002, 14, 401-414; c) J.-M. Lehn, Proc. Natl. Acad. Sci. USA 2002, 99, 4763-4768; d) A. P. de Silva, N. D. McClenaghan, Chem. Eur. J. 2004, 10, 574-586.
- [2] a) R. R. Rando, *Chem. Rev.* 2001, 101, 1881–1896; b) W. R. Briggs, E. Huala, *Annu. Rev. Cell Dev. Biol.* 1999, 15, 33–62; c) A. R. Cashmore, J. A. Jarillo, Y. L. Wu, D. M. Liu, *Science* 1999, 284, 760–765; d) Y. Han, S. Braatsch, L. Osterloh, G. Klug, *Proc. Natl. Acad. Sci. USA* 2004, 101, 12306–12311.
- [3] a) M. Irie, Chem. Rev. 2000, 100, 1683; b) J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995, pp. 124–138; c) J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely, K. M. Rapp, Angew. Chem. 1989, 101, 1541–1542; Angew. Chem. Int. Ed. Engl. 1989, 28, 1494–1496.

- [4] a) G. M. Tsivgoulis, J.-M. Lehn, Angew. Chem. 1995, 107, 1188–1191; Angew. Chem. Int. Ed. Engl. 1995, 34, 1119–1122;
 b) N. P. M. Huck, B. L. Feringa, J. Chem. Soc. Chem. Commun. 1995, 1095–1096; c) H. Spreitzer, J. Daub, Liebigs Ann. 1995, 1637–1641; d) J. Daub, M. Beck, A. Knorr, H. Spreitzer, Pure Appl. Chem. 1996, 68, 1399–1404; e) T. Inada, S. Uchida, Y. Yokoyama, Chem. Lett. 1997, 321–322; f) A. Fernandez-Acebes, J.-M. Lehn, Adv. Mater. 1998, 10, 1519–1522; g) S. Tsuchiya, J. Am. Chem. Soc. 1999, 121, 48–53; h) J. M. Endtner, F. Effenberger, A. Hartschuh, H. Port, J. Am. Chem. Soc. 2000, 122, 3037–3046; i) T. B. Norsten, N. R. Branda, J. Am. Chem. Soc. 2001, 123, 1784–1785; j) V. W.-W. Yam, C.-C. Ko, N. Zhu, J. Am. Chem. Soc. 2004, 126, 12734–12735.
- [5] a) H. Spreitzer, J. Daub, *Chem. Eur. J.* 1996, 2, 1150-1158; b) J. Achatz, C. Fischer, J. Salbeck, J. Daub, *J. Chem. Soc. Chem. Commun.* 1991, 504-507; c) L. Gobbi, P. Seiler, F. Diederich, V. Gramlich, *Helv. Chim. Acta* 2000, 83, 1711-1723; d) T. Mrozek, J. Daub, A. Ajayaghosh in *Molecular Switches* (Ed.: B. L. Feringa), Wiley-VCH, Weinheim, 2001, pp. 63-106; e) J. Daub, C. Trieflinger, O. Kushnir, R. Prochazka, *Mol. Cryst. Liq. Cryst.* 2005, 430, 115-122.
- [6] a) H. Görner, C. Fischer, S. Gierisch, J. Daub, J. Phys. Chem.
 1993, 97, 4110-4117; b) J. Ern, M. Petermann, T. Mrozek, J. Daub, K. Kuldová, C. Kryschi, Chem. Phys. 2000, 259, 331-337; c) V. De Waele, U. Schmidhammer, T. Mrozek, J. Daub, E. Riedle, J. Am. Chem. Soc. 2002, 124, 2438-2439.
- [7] a) J. Karolin, L. B.-A. Johansson, L. Strandberg, T. Ny, J. Am. Chem. Soc. 1994, 116, 7801–7806; b) M. Kollmannsberger, T. Gareis, S. Heinl, J. Breu, J. Daub, Angew. Chem. 1997, 109, 1391–1393; Angew. Chem. Int. Ed. Engl. 1997, 36, 1333–1335; c) J. Daub, K. Kelnhofer, T. Gareis, A. Knorr, M. Kollmannsberger, Y.-H. Tak, H. Bässler, Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem. 1997, 38, 339–340; d) R. Y. Lai, A. J. Bard, J. Phys. Chem. B 2003, 107, 5036–5042; e) P. Toele, H. Zhang, C. Trieflinger, J. Daub, M. Glasbeek, Chem. Phys. Lett. 2003, 368, 66–75.
- [8] The ECL measurements were carried out with an unstirred solution ($c = 1 \times 10^{-3}$ M; supporting electrolyte: 0.1 M Bu₄NPF₆) in an electrochemical cell: Stefan Hien, PhD Thesis, University of Regensburg, **1995**. The potential was switched with alternation between the oxidation and reduction potentials (see inset of Figure 2, electrochemical switching frequency 1 s⁻¹, scan rate of the spectrometer: 240 nm min⁻¹). The spectrum consisting of discrete signals is the result of the relatively slow switching frequency. The bathochromic shift of ca. 20 nm between the fluorescence and the ECL spectrum is well known and can be attributed to reabsorption effects as a result of the higher dye concentration used in the ECL experiment and the different dielectric properties of the supporting electrolyte.
- [9] VHF was reported to be entirely nonfluorescent, see ref. [6a].
- [10] For a description of the analysis of FRET processes, see P. Wu, L. Brand, *Anal. Biochem.* **1994**, *218*, 1–13. The following equations apply: $k_{\text{FRET}} = (1/\tau_D)(R_0/r)^6$ with *r* being the distance between the FRET partners and τ_D the lifetime of the unperturbed donor **3** (5.15 ns in CH₂Cl₂). $R_0^6 = 8.875 \times 10^{-5} (\kappa^2 \Phi_D J/n^4)$ mit $J = JF_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$, where J is the overlap integral between the fluorescence of the donor (i.e. **3** in CH₂Cl₂) and the absorption of the acceptor, obtained after deconvolution of the absorption spectrum of **1b**, $\kappa^2 = 2/3$ is a geometry factor for random orientation of the two subunits, Φ_D is the fluorescence quantum yield of the unperturbed donor (here, for model **3**: $\Phi_D = 0.95$ in CH₂Cl₂), and *n* is the refractive index of the solvent.
- [11] If no other deactivation processes are present, k_{FRET} can be also expressed as $k_{\text{FRET}} = (1/\tau_{\text{DA}}) - (1/\tau_{\text{D}})$ with τ_{DA} being the fluorescence lifetime of the FRET ensemble. By combining the equations in refs.[10] and [11] one may calculate a value for *r*.

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- [12] J. Aihara, K. Araya, K. Chiba, Y. Matsunaga, Adv. Mol. Relax. Interact. Processes 1980, 18, 199–210.
- [13] K. Kelnhofer, A. Knorr, Y.-H. Tak, H. Bässler, J. Daub, Acta Polym. 1997, 48, 188-192.
- [14] J. Olmsted III, J. Phys. Chem. 1979, 83, 2581-2584.