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Molecular Switching in the Near Infrared (NIR) with a Functionalized Boron–Dipyrromethene Dye**

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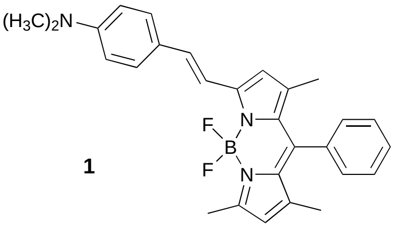
Recent developments in supramolecular chemistry and nanotechnology have stimulated interest in the design and the construction of molecular signaling systems capable of performing photo- and substrate-induced logic functions or redox-based switching actions.[1] At the molecular level, photons, that is their absorption or emission, often are the vehicle of choice for transduction of an electrochemically[2] or photochemically[3] generated signal. Examples range from photonic switches[4] to photo- or electrochromic devices[5] and to advanced micro- or nanomachines.[6] In particular, multifunctional dyes that are sensitive toward both external physical and chemical triggers provide a versatile basis for the construction of sophisticated switches that communicate, for instance, through changes in electrochromic and/or fluorescence properties. Over the past few years, the boron–dipyrromethene (BDP) chromophore has gained in importance in the design of such systems[2c, 3b, 7–9] since the BDP core is comparatively readily oxidized and reduced,[2c] a prerequisite for fluorescent switches relying on electron or charge transfer (CT),[3b, 7, 8] as well as for the generation of stable radical ions that show electrogenerated chemiluminescence upon charge recombination.[2c] In these systems, the *meso*-substituted BDP chromophore acts as in donor(D)–acceptor(A)-substituted biaryls so that the switching process hardly influences the absorption and emission wavelengths. However, for the design of more advanced molecular ensembles it would be highly desirable to generate signal changes by substrate interaction at a site conjugated to the BDP core. Since experience has shown that creation of an extensively delocalized amino radical cation would result in strong electrochromism, introduction of a proton-sensitive amino donor group seemed most suitable for the construction of such a multifunctional electro- and photochemical molecular switch. Here, we report the synthesis and spectroscopic and electrochemical properties of the 3-dimethylaminostyryl-substituted dye **1**, which, to the best of our knowledge, is the first example of an unsymmetrically substituted BDP dye carrying an analyte-sensitive (donor) group conjugated to the core.



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Compound **1** was synthesized by condensation of the tetramethyl derivative[7b] with *p*-dimethylaminobenzaldehyde using piperidinium acetate as catalyst.

Owing to the introduction of a donor-styryl-spacer group at the 3-position the spectrosocpic behavior of **1** is more reminiscent of D–A stilbenes[10a,b] or styryl bases,[10c] in contrast to *meso*-donor-substituted BDP dyes, where no direct electronic conjugation exists between both aryl subunits.[3b, 7b] As follows from Table 1 and Figure 1, the absorp-

Table 1. Spectroscopic data of **1** and **1**-H$^+$ in different solvents at 298 K.[a]

	Solvent	λ_{abs} [nm]	ε_{max} [$\text{M}^{-1}\text{cm}^{-1}$]	λ_f [nm]	Φ_f	τ_f [ns]	k_f[b] [10^8s^{-1}]	k_{nr}[b] [10^8s^{-1}]
1	MeCN	597	75000	731	0.13	0.94	1.4	9.2
1	THF	603	89000	672	0.58	3.21	1.8	1.3
1	Et_2O	594	98000	638	0.83	3.88	2.1	0.4
1	Bu_2O	598	101000	630	0.87	3.73	2.3	0.3
1	hexane	596	n.d.[c]	611	0.97	3.84	2.5	0.1
1-H$^+$	MeCN	553	100000	563	0.97	4.38	2.2	0.1
1-H$^+$	THF	558	100000	566	0.85	4.02	2.1	0.3
1-H$^+$	Et_2O	556	101000	563	0.90	4.24	2.1	0.2

[a] Experimental conditions: $c(\mathbf{1}) = 1 \times 10^{-6}\,\text{M}$, $\lambda_{exc} = 545$ and 595 nm for steady-state, 500 and 578 nm for time-resolved fluorescence measurements, proton source $HClO_4$. [b] $k_f = \Phi_f/\tau_f$, $k_{nr} = (1-\Phi_f)/\tau_f$. [c] Not determined due to low solubility.

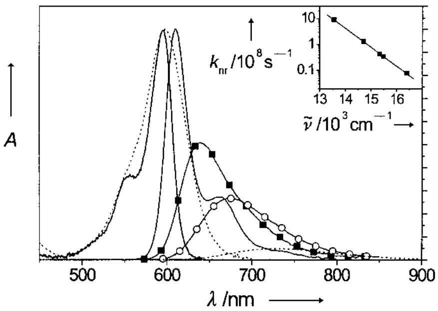

Figure 1. Absorption (normalized; absorption *A*) and emission spectra (fluorescence intensity *F*) of **1** at 298 K (——: in hexane, ■: in Bu_2O, ○: in THF, - - - -: in MeCN; absorption spectra in THF and Bu_2O omitted for better clarity, experimental conditions, see Table 1). In the inset, a plot of lnk_{nr} versus the emission maximum is shown (—— fit; $r = 0.999$).

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tion band is centered at 598 ± 5 nm and shows no solvent-dependent shifts which suggests that the ground-state dipole moment is rather small.[11] The BDP-like shape for **1** (narrow and structured, with high ε, Table 1, Figure 1),[7, 9a] is only seen in hexane and the band slightly broadens (while maintaining high ε) as the solvent polarity increases. On the other hand, the fluorescence of **1** is strongly dependent on the polarity of the solvent; the band broadens (full width at half maximum (fwhm) increases from 890 cm^{-1} (main band only) in hexane to 2390 cm^{-1} in MeCN) and the maximum λ_f shifts to the near infrared (NIR; from 611 nm in hexane to 731 nm in MeCN, Figure 1, Table 1), indicative of an intramolecular CT process. Only the emission spectrum in hexane displays the typical BDP features, that is a slightly Stokes-shifted, mirror-symmetrical band (Figure 1).[7, 9a] In more polar solvents, the band steadily shifts to the red and no well-separated dual emission is found here as, for example, in the case of some 8-dimethylanilino-substituted BDP dyes.[3b, 7b] Very remarkable behavior is revealed in the inset of Figure 1; the semi-logarithmic plot of the rate constant of nonradiative deactivation k_{nr} versus the emission maximum yields a linear correlation of $r = 0.999$. According to the energy gap rule,[12] this decrease in fluorescence quantum yield (Φ_f) and lifetime (τ_f, see Table 1) with increasing emission wavelength is attributed to the acceleration of internal conversion (ic) as the energy gap between the excited and the ground state decreases. Thus, the positive solvatokinetic effect observed does not arise from the population of differently emitting species during the lifetime of the excited state,[10a,c] but the quenching of the only emitting, highly polar ^{1}CT state[13] is caused by an increase of k_{ic}.[14] Nonetheless, because of the high intrinsic fluorescence yield of ^{1}CT, Φ_f of **1** is still comparatively high in acetonitrile (Table 1).[15]

Protonation drastically alters the electron-donating properties of the dimethylamino group and consequently "switches off" any charge transfer interaction. This results in typical BDP-like narrow, structured and solvent-polarity-independent absorption and emission bands (Figure 2), the latter of high fluorescence yield in all the acidified solvents employed (Table 1). The absorption bands of **1**-H$^+$ are blue-shifted by about 40 nm compared to those of **1**, and the width of the band is further reduced (fwhm ca. 700 cm^{-1} for **1**-H$^+$ and 950 cm^{-1} for **1** in hexane), stressing the influence of the conjugated (unprotonated) dimethylamino substituent on the spectroscopic properties of **1** in solvents of any polarity. This proton-induced spectral switching along with the high fluorescence yields observed in all the experiments qualifies **1** as a very suitable sensor molecule for communicating local environmental properties in solution. By employing pulsed or modulated laser diodes as excitation sources (the fluorescence lifetimes of ≥ 1 ns do not require highly sophisticated equipment), the temporal and spectral information on solvent polarity can be read out in the region between 590 and 750 nm, while the presence of protons can be monitored between 550 and 620 nm. Thus, with a simple single excitation/dual emission wavelength measurement of the fluorescence decay kinetics, solvent polarity and acidity can be probed independently at, for example, 670 and 560 nm, respectively.

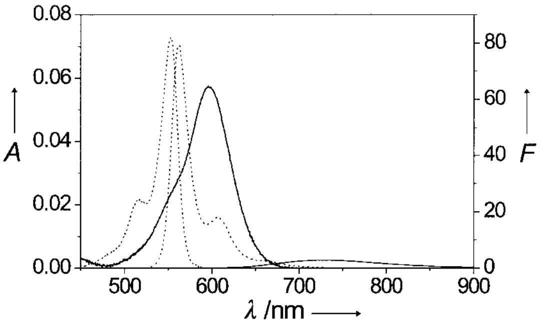

Figure 2. Steady-state spectra of **1** (——) and **1**-H$^+$ (····) in acetonitrile at 298 K (the emission spectra are normalized at the same optical density at the excitation wavelength 545 nm, experimental conditions, see Table 1).[19]

Besides chemical switching, **1** can be reversibly reduced to give the radical anion (−1635 mV vs. ferrocene/ferrocenium (Fc/Fc$^+$)) and be reversibly oxidized to give a radical cation and a dication at 105 and 430 mV, respectively. The oxidations occur at much lower potentials than in other donor-substituted BDP systems[2c, 9b] which indicates extensive delocalization in the radical cation. Whereas the radical anion shows a strong absorption at 562 nm ($\varepsilon = 58000$) but only very weak absorption bands in the NIR ($\varepsilon < 1000$ at 788 and 890 nm), the radical cation shows a sharp and very intense ($\varepsilon = 130000$) band at 754 nm (Figure 3).

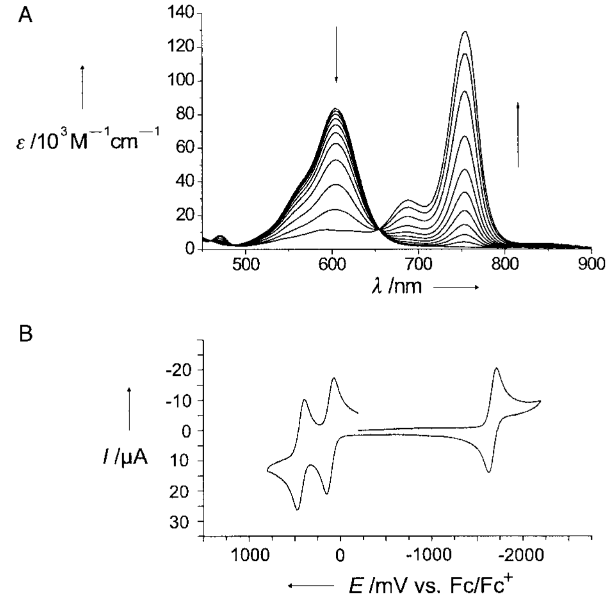

Figure 3. A) Spectra taken during the oxidation of **1** to the radical cation (CH_2Cl_2/0.1 M TBAHFP); B) cyclic voltammogram of **1**.

In summary, the first unsymetrically substituted BDP dye with an analyte-responsive receptor in the polymethinic part of the chromophore presented herein is a multifunctional molecular system that can either be utilized for highly sensitive probing of solvent polarity and acidity through measuring fluorescence or can be employed as an efficient dual-mode chemical (protons)/electrochromic switch in the red/NIR, operating already at very low voltages.

Experimental Section

Steady-state absorption and fluorescence spectroscopy: Bruins Instruments Omega 10 spectrophotometer, Spectronics Instruments 8100 spectrofluorometer; details on the determination of the relative fluorescence quantum yields (Φ_f) and the correction of the fluorescence spectra are given in ref. [7b]; fluorescence standards: cresyl violet in methanol ($\Phi_f = 0.54 \pm 0.03$),[17a] rhodamine 101 in ethanol ($\Phi_f = 1.00 \pm 0.02$).[17b]

Time-resolved fluorescence spectroscopy: Unique laser impulse fluorometer with ps time resolution as described in ref. [17c] including a synchronously pumped dye (rhodamine 6G) laser (Spectra Physics); details on detection and temporal calibration are given in ref. [7b, 17c]; fitting procedure: reference convolution of cresyl violet decays (Globals Unlimited V2.2, Laboratory for Fluorescence Dynamics, University of Illinois).

Cyclic voltammetry: Solvent dichloromethane; reversible half-wave potentials $E_{1/2}$ [mV] versus ferrocene/ferrocenium as internal standard; conditions: scan rate 250 mV s^{-1}, supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP).

Spectroelectrochemistry: Solvent dichloromethane, OTTLE transmission cell with a minigrid-gold working electrode.[18]

Synthesis: 1,3,5,7-Tetramethyl-8-phenyl-difluorobordiazaindacene (65 mg, 0.2 mmol) [7b] and 4-dimethylaminobenzaldehyde (35 mg, 0.23 mmol) were refluxed for 26 h in a mixture of toluene (5 mL), glacial acetic acid (0.15 mL) and piperidine (0.18 mL) together with a small amount of molecular sieves (3 Å). After cooling to room temperature the mixture was placed on top of a silica column and eluted with CH_2Cl_2/hexane (1/1). The blue fraction was collected and recrystallized from $CHCl_3$/hexane to give **1** as purple needles (22 mg, 0.048 mmol, 24 %). M.p.: 288–291 °C; IR (KBr, $\tilde{\nu}$ in cm^{-1}): $\tilde{\nu} = 1178$ (B–F); ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3 H), 1.42 (s, 3 H), 1.54 (s, 3 H), 3.03 (s, 6 H), 5.96 (s, 1 H), 6.59 (s, 1 H), 6.70 (m, 2 H), 7.20 (d, 2 H, $J = 16.3$ Hz), 7.28–7.33 (m, 2 H), 7.45–7.55 (m, 6 H); HR-MS (EI, 70 eV): calcd for $C_{28}H_{28}N_3BF_2$ 455.2344, found 455.2352.

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[14] Note that during our studies no *trans–cis* isomerization was observed.

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An Efficient Cobalt(I) Catalyst System for the Selective 1,4-Hydrovinylation of 1,3-Dienes[**]

Gerhard Hilt,* François-Xavier du Mesnil, and Steffen Lüers

The selective 1,4-hydrovinylation of 1,3-dienes with alkenes under mild reaction conditions for the formation of new C–C bonds is of high synthetic interest.[1] For instance, ethylene and 1,3-butadiene are codimerised under rhodium catalysis on an industrial scale (DuPont synthesis). The resulting 1,4-hexadiene is then transformed into synthetic rubber and other unsaturated polymers.[2]

Recently we described a catalyst system ($[CoBr_2(dppe)]/ZnI_2/Bu_4NBH_4$ dppe = ethane-1,2-diylbis(diphenylphosphane)) for the efficient Diels–Alder reaction of acyclic 1,3-dienes with acetylenes.[3] When we attempted to use this catalyst system for the Diels–Alder reaction of acyclic 1,3-dienes, with substituted alkenes as the dienophile, none of the desired Diels–Alder product could be isolated. Instead the linear 1,4-hydrovinylation product **2** was isolated from the

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