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Ultrafast Photoinduced Electron Transfer in Viologen-Linked BODIPY Dyes

Denis Frath,[a] James E. Yarnell,[b] Gilles Ulrich,[a] Felix N. Castellano,*[b] and Raymond Ziessel*[a]

New boron-dipyrromethene (BODIPY) dyes linked to viologen are prepared and their photophysical and electrochemical properties are investigated. Both synthesized molecules have similar electronic absorption spectra with the absorption maximum localized at 517 and 501 nm for dye **1** and dye **2**, respectively. They exhibit well-defined redox behavior, highlighting the presence of BODIPY and viologen subunits, with little perturbation of the redox potential of both subunits with respect to the parent compounds. Both dyes are heavily quenched by photoinduced electron transfer from the BODIPY to the viologen subunit. The transient absorption technique demonstrates that dye **2** forms the viologen radical within a timeframe of 7.1 ps, and that the charge-separated species has a lifetime of 59 ps. Sustained irradiation of dye **2** in the presence of a tertiary amine allows for the accumulation of BODIPY–methyl-4,4′-bipyridinium (BODIPY–MV^+), as observed by its characteristic absorption at 396 and 603 nm. However, dye **2** does not generate catalytic amounts of hydrogen under standard conditions.

1. Introduction

Photosynthesis is an elegant way to use solar energy, and it has recently had a renewed interest from the scientific community.[1,2] Photoinduced electron transfer (PET) is responsible for charge separation in natural photosynthesis. Methylpyridinium cations (viologen templates) have been extensively used as electron acceptors during the last fifty years[3–7] and have become a common tool in many sophisticated assemblages.[8–12] A large variety of photosensitizers have been linked to viologen subunits to facilitate intramolecular PET. Porphyrins,[13–15] $[Ru(bpy)_3]$,[16,17] pyrene,[18] 1,8-naphtilimide,[19] and many others[20–22] have been studied. In addition, photoinduced charge separation can also be obtained by using self-assembled systems.[23–28]

Interestingly, in many of these artificial systems, a long-lived charge-separated state is often observed.[29–31] This remarkable property has been exploited in various scientific fields, including analytical methods,[32] photocurrent generation,[33–35] energy migration,[36,37] catalysis,[38] and photoinduced production of hydrogen.[39–42]

Boron-dipyrromethene (BODIPY) dyes are convenient fluorescent dyes that have been used for biochemical labeling,[43] as part of photonic molecular systems such as laser dyes, in mesomorphic materials, organogelators, and as dopants in light emitting devices.[44,45] Our interest in planar frameworks stems from the fact that their optical properties (absorption, emission, quantum yield) can be tuned by modifying the pyrrole substituents,[46–48] the central *meso*-position,[49] and/or the boron substituent.[50] Their extraordinary spectroscopic and redox properties[51–58] prompt us to link, for the first time, viologen modules to the dye to promote PET.

Jones et al. have previously described intermolecular electron transfer between commercially available BODIPY dyes and viologen in a bimolecular system.[59] Diffusion-controlled fluorescence quenching is observed when the energetics of the donor and acceptor are properly adjusted.[59] Herein, we report the synthesis, as well as electrochemical and spectroscopic properties, of two new viologen-linked BODIPY dyes. Transient absorption experiments highlight a very fast PET from the BODIPY core to the viologen acceptor.

2. Results and Discussion

2.1 Synthesis

Preparation of BODIPY **A** and **B**, as well as that of 1-methyl-4,4′-bipyridinium (MV^+) and 1-(ammonioethyl)-1′-methyl-4,4′-bipyridinium ($MAEV^{3+}$), was conducted following previously described methods.[60–62] Dye **1** was synthesized from Krypto-BODIPY (Krypto represents ethyldimethyl pyrrole) and the pro-

[a] Dr. D. Frath, Dr. G. Ulrich, Dr. R. Ziessel
Laboratoire de Chimie Organique et Spectroscopies Avancées
ICPEES, UMR 7515 au CNRS, Ecole Européene de Chimie
Polymère, et Matériaux, 25 rue Becquerel
67087 Strasbourg Cedex (France)
Fax: (+33) 3-68-85-26-89
E-mail: ziessel@unistra.fr
Homepage: http://icpees.unistra.fr/lcosa/

[b] Dr. J. E. Yarnell, Prof. F. N. Castellano
Department of Chemistry and Center for Photochemical Sciences
Bowling Green State University, Bowling Green
Ohio, 43403 (USA)
E-mail: castell@bgsu.edu

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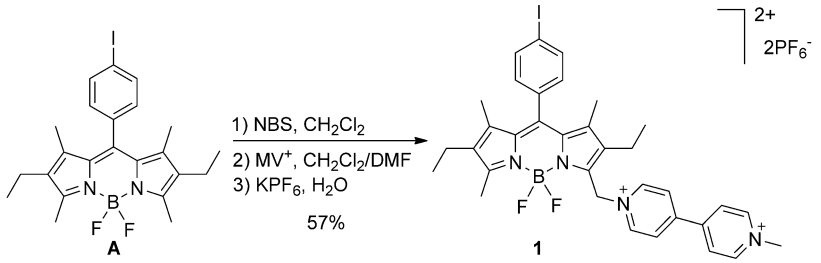
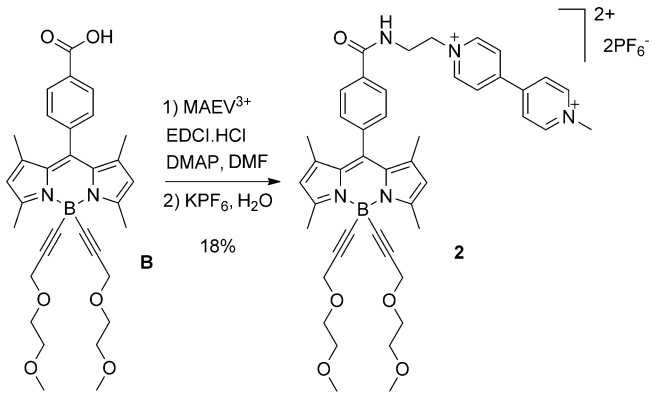


Scheme 1. Synthesis of BODIPY–viologen dye **1**.

cedure consisted of a three-step protocol (Scheme 1). In the first step, the α-methyl group of BODIPY **A** was brominated by using *N*-bromosuccinimide (NBS). The intermediate was not isolated because of its high reactivity towards nucleophiles, and it reacted with methylviologen in the polar solvent to yield the desired product.[63] Counter-ions were exchanged in a solution of potassium hexafluorophosphate in water. Dye **1** precipitated out of the medium during anion metathesis, with a 57% yield over three steps and no additional purification of the final compound was needed (see the Experimental Section).

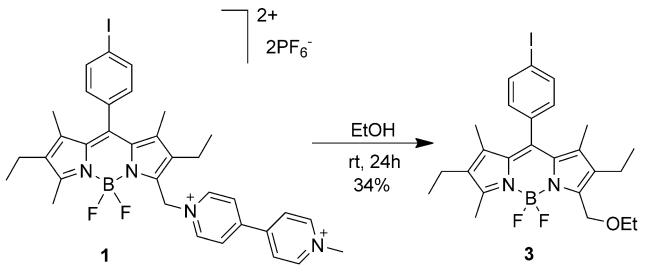
Dye **2** was constructed from Knorr-BODIPY (Knorr represents dimethylpyrrole) and was prepared by using a two-step protocol (Scheme 2). The reaction consisted of a peptidic coupling between the carboxylic acid of BODIPY **B** and the amine of viologen, followed by counter-ion exchange. The low global yield (18%) of the reaction can be explained by the poor solubility of viologen during the first step. However, it is important to stress that no purification was needed to produce dye **2** in a clean manner (see the Experimental Section).



Scheme 2. Synthesis of BODIPY–viologen dye **2**.

2.2 Absorption and Photoluminescence Spectroscopy

The photophysical properties of dye **1** were recorded in distilled dichloromethane. The absorption spectra exhibit a maximum at 510 nm with an extinction coefficient reaching 29000 $M^{-1}cm^{-1}$. No fluorescence is observed for dye **1** under these conditions. This observation supports the hypothesis that PET from the BODIPY to the viologen moiety is responsible for the fluorescence quenching (vide infra). The situation is different in ethanol, in which a progressive recovery of the fluorescence at 541 nm is observed. This was thought to be caused by chemical evolution of the dye, in which the viologen module would act as a leaving group in a nucleophilic substitution with the solvent used during the measurement. An experiment performed in ethanol (Scheme 3) at room temperature confirmed this hypothesis. A solution of dye **1** in ethanol was stirred for 24 h, and dye **3** was isolated in a 34% yield. This



Scheme 3. Chemical reaction highlighting how labile viologen is in dye **1**.

compound has the same spectroscopic characteristics as dye **3** prepared under different preparative conditions.[63] An ethoxy group replaces the viologen fragment and the optical properties of the BODIPY dye are restored (emission wavelength, $\lambda_{em} = 541$ nm, quantum yield, $\Phi_{fluo} = 0.65$, and fluorescence lifetime, $\tau = 5.55$ ns).[63] This substitution reaction is relatively fast (shown in Figure 1) with trace amounts of ethanol (0.1%) present as a stabilizer in dichloromethane.

In order to prepare a mixed dye with increased stability under nucleophilic conditions, we prepared hybrid dye **2**, in which the viologen fragment is connected in the eight-position and is less prone to nucleophilic attack. The photophysical properties of dye **2** were recorded in dichloromethane, which confirmed the chemical and photochemical stability of the dye. The absorption maximum is observed at 501 nm with an extinction coefficient of 44000 $M^{-1}cm^{-1}$ (Figure 2). As previously found for dye **1**, the steady-state fluorescence is heavily quenched, whereas dye **2** exhibits an emission at 517 nm with a quantum yield below 1%.

2.3 Cyclic Voltammetry

To ensure that the linked viologen subunit functioned as an electron acceptor, cyclic voltammograms were recorded for dyes **1** and **2** in dichloromethane containing background electrolyte and referenced to ferrocene [half-wave potential, $E_{1/2} = 0.38$ V vs a saturated calomel electrode (SCE)] as an internal

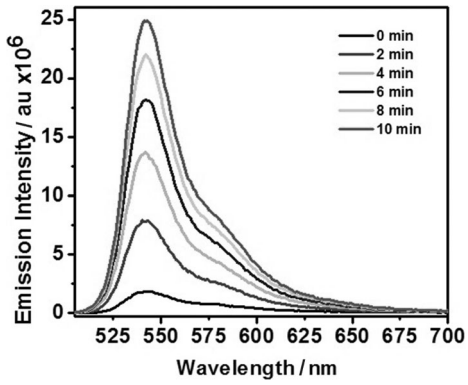


Figure 1. Evolution of the emission spectra of dye **1** in dichloromethane stabilized with ethanol.

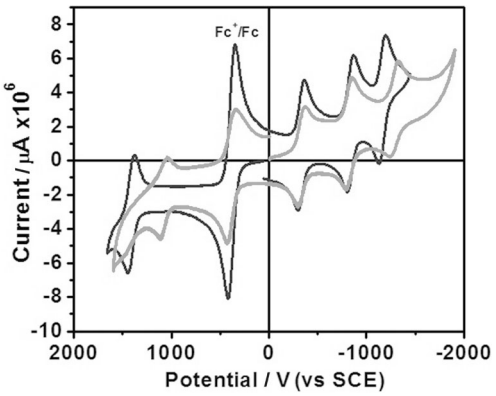


Figure 3. Cyclic voltammogram of dye **1** (black line) and dye **2** (grey line) in dichloromethane with $TBAPF_6$ as the supporting electrolyte at RT.

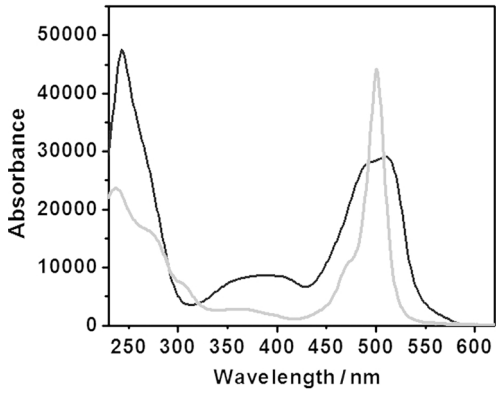


Figure 2. Electronic spectra of dye **1** (black line) and dye **2** (grey line) in dichloromethane.

Table 1. Electrochemical data for the hybrid BODIPY–viologen dyes **1** and **2**, and the appropriate reference compounds.[a]

Compound	E_{ox} [V] (ΔE [V])	E_{red} [V] (ΔE [V])
BODIPY **A**	+1.02 (0.06)	−1.24 (0.07)
BODIPY **B**	+1.08 (0.06)	−1.44 (0.07)
$MAEV^{3+}$	–	−0.44 (0.06)
		−0.95 (0.06)
dye **1**	+1.41 (0.07)	−0.33 (0.07)
		−0.84 (0.06)
		−1.16 (0.07)
dye **2**	+1.08 (0.07)	−0.34 (0.07)
		−0.83 (0.06)
		−1.29 (0.07)

[a] Potentials determined by using cyclic voltammetry in deoxygenated dichloromethane solution containing 0.1 M $TBAPF_6$ at a solute concentration of ca. 1.5 mM and at RT. Potentials were standardized to ferrocene (Fc) as an internal reference and converted to the SCE scale assuming that $E_{1/2}(Fc/Fc^{+}) = +0.38$ V ($\Delta Ep = 60$ mV) vs SCE. Error in $E_{1/2}$ is ±15 mV.

standard (Figure 3). Peak assignment was performed by adding an equimolar amount of the genuine dye without the viologen acceptor and/or methylviologen. The reversible oxidation peak corresponds to $E_{1/2} = 1.41$ V (vs SCE) for dye **1**, and $E_{1/2} = 1.08$ V (vs SCE) for dye **2** is safely ascribed to formation of the BODIPY radical cation. Non-substituted BODIPY dyes are reversibly oxidized around 1.02 V.[64–66] The fact that dye **1** is more difficult to oxidize, by 390 mV, reflects the presence of a positive charge in the 3-position, which resists the oxidation. This observation is in line with previous results obtained with styryl-substituted BODIPY dyes.[67]

The first two reversible, one-electron reduction steps are safely assigned to the viologen fragment, with the potentials being similar to genuine methylviologen when analyzed under the same conditions (see Table 1). The third reversible reduction wave is assigned to the reduction of the BODIPY core to the radical anion. This reduction wave for dye **2** is facilitated by 150 mV, despite the presence of the doubly reduced viologen fragment and the effective conjugation in this substitution position of the BODIPY dye. It was previously observed that the formation of the BODIPY radical anion shifts anodically with respect to non-substituted BODIPY dyes. Based on these various electrochemical results, it is possible to confirm the likelihood of light-induced electron transfer occurring in polar media (vide infra).

To calculate the driving force for PET, the value of the redox potential in the excited state must be determined. This value is obtained by subtracting the energy needed to obtain the excited state from the redox potential in the ground state. The excited-state energy (E_{00}) can be estimated (±5%) from the tangent of the high-energy part of the emission peaks of BODIPY **A** and **B**, and is shown to be 2.33 eV for BODIPY **A** and 2.43 eV for BODIPY **B** (ΔE in eV ≈ 1240/λ in nm). This provides the the following redox potentials of the excited states: $BODIPY^*/BODIPY^{\bullet+}$ $E_0 = -0.92$ V for dye **1** and $E_0 = -1.35$ V for dye **2**. After applying the Rehm–Weller equation[68,69] to our system, and neglecting Coulombic factors, we obtained the simplified equation for the change in Gibbs-free energy, $\Delta G = E_0(BODIPY^*/BODIPY^{\bullet+}) - E_0(viologen/viologen^{\bullet-})$. From this, we are able to obtain ΔG values of approximately −590 and −1010 meV for PET from the BODIPY to the viologen fragment in dyes **1** and **2**, respectively. The thermodynamic driving force is in favor of a PET-based mechanism and explains the quenching of luminescence in dyes **1** and **2**.

2.4 Continuous Photolysis

Irradiation of a solution of dye **2** in dimethylformamide (DMF) and water in the presence of triethanolamine (TEOA) under anaerobic conditions results in the appearance of two new bands at 396 and 603 nm, characteristic of the viologen radical.[70] Notice that the main absorption at 497 nm decreases weakly after 1 h irradiation (Figure 4). When molecular oxygen is reintroduced into the cell, the bands at 396 and 603 nm disappear and the main absorption band at 517 nm remains similar. This shows the photochemical stability of the dye, and it also provides indirect evidence for PET from the BODIPY* to the linked viologen residue, as anticipated by the Rehm–Weller-calculated driving force. We previously noticed that the boron-substituted BODIPY dye displayed an improved photochemical stability owing to the B–F substitution by B–ethynyl.[57] Unfortunately, sustained photolysis of dye **2** by using a solar lamp (300 W, 1.5 AM filter) in the presence of colloidal platinum and ethylenediaminetetraacetic acid (0.04 M) at pH 4.8 in a mixture of water and DMF did not produce catalytic amounts of molecular hydrogen, and it is not competitive compared to previously developed systems.[71,72]

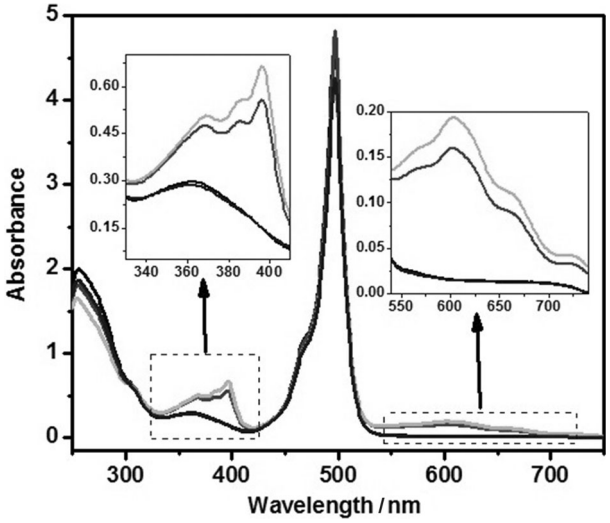


Figure 4. Electronic spectra of 1.10×10^{-4} M dye **2** in degassed water/DMF (9:1) solution with addition of 0.04 M TEOA (black line), after 15 min irradiation (dark grey line), after 1 hour irradiation (light grey line), and after air was bubbled through solution (black line). The solution had a pH value of 7 and was irradiated by using a 300 W lamp.

2.5 Transient Absorption

Figure 5 A displays the excited-state absorption difference spectra for dye **1** measured on an ultrafast time scale. The excited state of the BODIPY is characterized by the broad excited-state absorption band from 350 to 450 nm and ground-state bleach centered at 530 nm. The formation of the methylviologen radical can be seen by the absorbance at 396 nm and the weak, broad absorbance at 603 nm. Charge recombination happens almost immediately, so there is little methylviologen radical to be seen in the transient data. The growth of the methylviologen radical absorbance reaches its maximum approximately 2 ps after the laser pulse, and then decays immediately. Figure 5 B shows the transient at 400 nm, revealing the formation and decay of the methylviologen radical. The time constant for the electron transfer that forms the charge-separated species is approximately $\tau = 0.8 \pm 0.1$ ps, with charge recombination occurring at $\tau = 6.3 \pm 0.4$ ps, as calculated from the transient absorption spectra at 615 nm.

The excited-state absorption difference spectra for dye **2** were also measured on an ultrafast time scale, as shown in Figure 6 A. Dye **2** displays a slightly different excited-state absorbance than dye **1** with a broad peak centered at 360 nm. The formation of the methylviologen radical can be seen by the sharp absorbance at 396 nm and the weak, broad absorbance at 603 nm. Figure 6 B shows an enlarged view of the growth of the methylviologen radical absorbance at 396 nm. The growth of the methylviologen radical absorbance reaches its maximum approximately 15 ps after the laser pulse. Figure 6 C shows the transient at 400 nm, revealing the formation and decay of the methylviologen radical. The time constant for the electron transfer that forms the charge-separated species is approximately $\tau = 7.1 \pm 0.6$ ps, with charge recombination occurring at $\tau = 58.9 \pm 0.9$ ps, as calculated from the transient absorption spectra at 615 nm (Figure S1).

The main reason for fast back-electron-transfer in dye **1** with respect to dye **2** is that, in tetrahydofuran (THF), the viologen fragment in dye **1** is folded above the flat BODIPY core, which makes the back-electron-transfer process faster in dye **1** compared to dye **2**. In the latter case, it is likely that the viologen fragment cannot approach the BODIPY core because of the presence of the phenyl ring, which tilts the viologen moiety out of the plane. The possibility of decay of the charge-transfer state to the BODIPY triplet state is excluded in the absence of

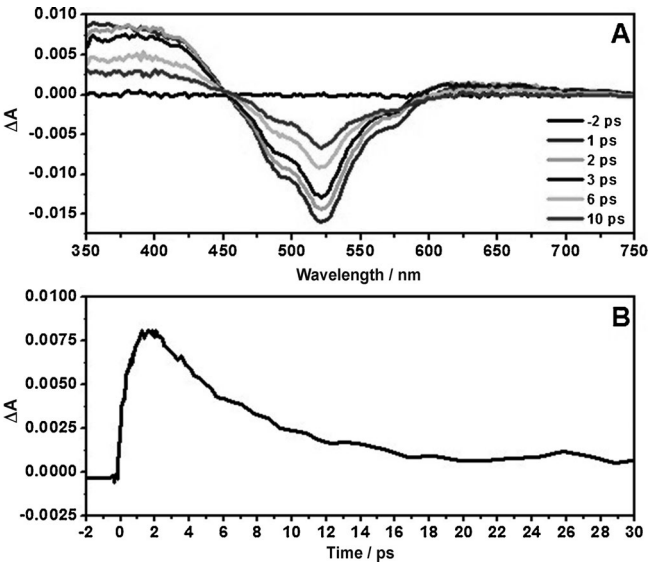


Figure 5. A) Excited-state absorption spectra of dye **1** in THF following 520 nm pulsed excitation (110 fs FWHM) with experimental delay times indicated. B) Excited-state transient of 400 nm of dye **1** in THF following 520 nm pulsed excitation (110 fs FWHM).

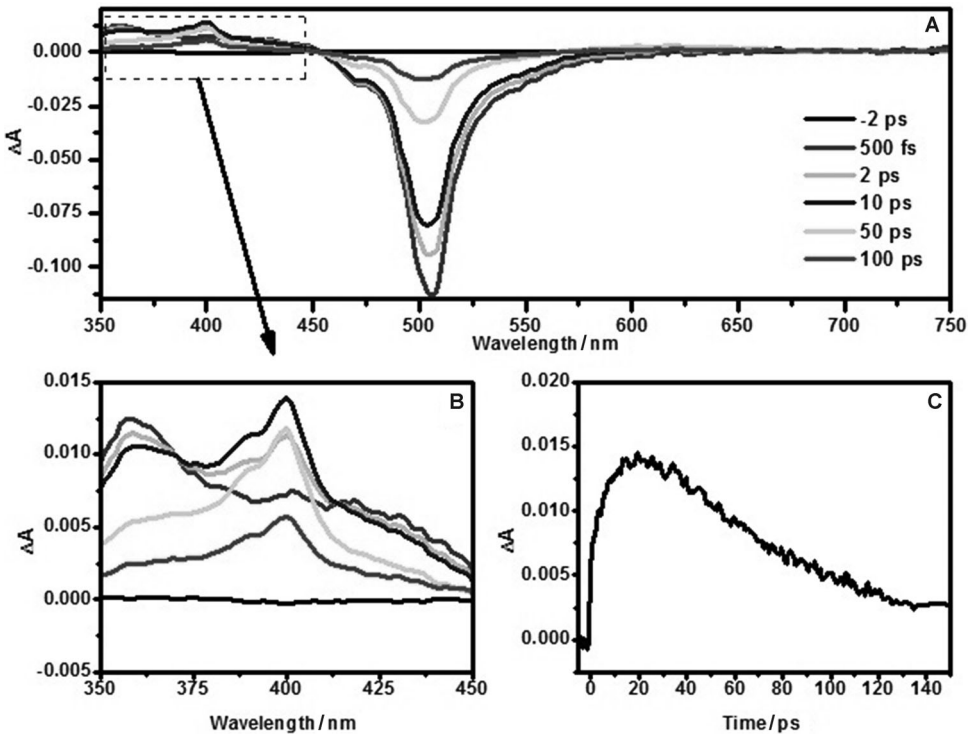


Figure 6. A) Excited-state absorption spectra of dye **2** in ethanol following 505 nm pulsed excitation (110 fs FWHM) with experimental delay times indicated. B) Expanded view of the excited-state absorption spectra for dye **2** using the same data presented in panel A. C) Excited-state transient of 400 nm of dye **2** in ethanol following 505 nm pulsed excitation (110 fs FWHM).

a heavy atom (i.e. there is no iodo group or transition metal).[44] BODIPY dyes are usually resistant to triplet formation, and no emission of the triplet at low temperature has been observed under standard conditions. In a similar system, but involving a appended iridium complex, the triplet state lies at 1.69 eV.[73]

3. Conclusions

Two new hybrid BODIPY–viologen dyes were prepared by using a convergent protocol. Two different substitution positions were selected in order to study the stability and spectroscopic properties of the two hybrid materials. In one case, the fluoride substituents were replaced by short polyethyleneglycol chains to promote solubility in polar solvents. Both molecules had similar electronic absorption spectra, with maxima at 517 and 501 nm for dye **1** and dye **2**, respectively, and the emission was heavily quenched when compared to the model BODIPY dye. Dye **1** suffered from chemical instability in the presence of nucleophilic solvents such as ethanol. The product of this reaction was isolated and assigned as an ethoxy-substituted molecule, the fluorescence of which was characteristic of BODIPY dyes. The electrochemical data of dyes **1** and **2** show little influence of the BODIPY residue on the redox activity of the viologen fragment, which remained similar to standard viologen derivatives. The interplay of redox and spectroscopic data estimated a strong driving force (above 1000 mV) for PET from the BODIPY* to the viologen acceptor. An ultrafast transient-absorption technique showed the formation of the viologen radical cation with absorbances at 396 and 603 nm, that is, in agreement with literature data. Charge separation occurred within 7.1 ps for dye **2**, with a charge recombination time of 59 ps. This process was faster for dye **1**, for which the charge separation occurred within 0.8 ps and charge recombination occurred within 6.3 ps. Continuous photolysis of the dyes in the presence of palladium colloids did not produce catalytic amounts of hydrogen. Further engineering of BODIPY-linked catalysts is currently in progress to effectively use BODIPY dyes as antennae to promote photocatalytic reactions.

Experimental Section

All reactions were performed in distilled solvent and under a dry argon atmosphere. All chemicals were used as received from commercial sources without further purification. Viologen derivatives and BODIPY starting materials were prepared according to literature.[1] Thin layer chromatography (TLC) was performed on silica gel or aluminum-oxide plates coated with fluorescent indicator.

The 200 (^{1}H), 300 (^{1}H), 400 (^{1}H), 50 (^{13}C), 75 (^{13}C), 100 (^{13}C) MHz nuclear magnetic resonance (NMR) spectra were recorded at room temperature with deuterated solvents, and residual protonated solvent signals were used as internal references. UV/Vis spectra were recorded by using a dual-beam grating spectrophotometer with a 1 cm quartz cell. All fluorescence spectra were corrected. The fluorescence quantum yield (Φ_{exp}) was calculated from Equation (1).

$$\Phi_{cmp} = \Phi_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{\eta^2}{\eta_{ref}^2} \quad (1)$$

in which I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength, and η is the refractive index of the medium. Rhodamine 6G was used as the reference ($\Phi = 0.88$ in ethanol, $\lambda_{ex} = 488$ nm). Luminescence lifetimes were measured on a spectrofluorimeter, which utilized software with a time-correlated single photon mode coupled to a Stroboscopic system. The excitation source was a laser diode ($\lambda =$ 310 nm). No filter was used for the excitation. The instrument response function was determined by using a light-scattering solution (LUDOX).

Electrochemistry

Electrochemical measurements were obtained by using cyclic voltammetry with a conventional three-electrode arrangement. The

measurements were performed on a BAS CV-50W voltammetric analyzer equipped with a platinum microdisk (2 mm^2) working electrode and a silver wire counter electrode. Ferrocene was used as an internal standard and was calibrated against a SCE reference electrode, separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electroactive substrate in deoxygenated and anhydrous dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The quoted $E_{1/2}$ potentials were reproducible within 10 mV.

Transient Absorption

The laser system for the ultrafast transient-absorption measurement has been described previously.[74] The 800 nm laser pulses were produced at a 1 kHz repetition rate by using a mode-locked Ti:sapphire laser (Hurricane, Spectra-Physics). The pulse width was determined to be 110 fs at full-width half-maximum (FWHM) by using an autocorrelator (Positive Light). The output from a Hurricane instrument was then split into pump (85%) and probe (8%) beams. The pump beam (800 nm) was sent into an optical parametric amplifier and the output was tuned to 505 and 520 nm for dye **1** and dye **2**, respectively. The energy of the pump beam was 3 $\mu J\,pulse^{-1}$. The probe beam (800 nm) was delayed by a delay stage (MM 4000, Newport) and then focused into a CaF_2 crystal for white-light continuum generation between 330 and 800 nm. An optical chopper was used to modulate the excitation beam at a frequency of 100 Hz and to obtain the value of the transient-absorption signal. The relative polarization between the pump and the probe beams was set at the magic angle (54.7°). The pump and probe beams were overlapped in the sample. The flow cell (Spectrocell Inc., 0.7 mL volume with 2 mm path length), pumped by a variable flow peristaltic lab pump (VWR), was used to prevent photodegradation of the sample. After passing through the flow cell, the continuum was coupled to an optical fiber and put into a CCD spectrograph (Ocean Optics, S2000). Data acquisition was achieved by using an in-house LabVIEW (National Instruments) software routine.

Preparation of Dye 1

NBS (35.7 mg, 0.3 mmol) was added a solution of BODIPY **A** (101.0 mg, 0.2 mmol) in dichloromethane (4 mL). The resulting solution was protected from light and stirred at room temperature for 30 min. DMF (4 mL) and MV^+ (59.5 g, 0.2 mmol) were added and stirred for 30 min at room temperature. The resulting product was precipitated by addition of ether, centrifuged and washed with further ether. The product was then dissolved in the minimum amount of DMF and added drop-wise to a solution of KPF_6. The dark red precipitate was filtered and washed with ether.

Yield: 56%; ^{1}H NMR (300 MHz, [D_6]acetone) $\delta = 9.35$ (2H, d, $J =$ 6.6 Hz, Ar-CH), 9.30 (2H, d, $J = 6.9$ Hz, Ar-CH), 8.83 (2H, d, $J =$ 6.9 Hz, Ar-CH), 8.82 (2H, d, $J = 6.6$ Hz, Ar-CH), 8.06 (2H, d, $J =$ 8.1 Hz, Ar-CH), 7.31 (2H, d, $J = 8.1$ Hz, Ar-CH), 6.33 (2H, s, CH_2 viologen), 4.73 (3H, s, CH_3 viologen), 2.56 (2H, q, $J = 7.8$ Hz, CH_2 Et BODIPY), 2.54 (3H, s, CH_3 BODIPY), 2.42 (2H, q, $J = 7.5$ Hz, CH_2 Et BODIPY), 1.48 (3H, s, CH_3 BODIPY), 1.46 (3H, s, CH_3 BODIPY), 1.01 (3H, t, $J = 7.8$ Hz, CH_3 Et BODIPY), 0.95 ppm (3H, t, $J = 7.5$ Hz, CH_3 Et BODIPY); ^{13}C NMR (75 MHz, [D_6]acetone) $\delta = 165.5$, 151.6, 150.6, 147.9, 146.6, 144.7, 142.2, 139.8, 138.4, 136.9, 136.4, 135.5, 135.1, 132.0, 127.9, 96.0, 56.3, 49.5, 17.5, 15.5, 14.4, 13.6, 12.8, 12.0 ppm; MS (ESI): *m/z* (%): 783.1 (100) $[M-PF_6]^+$, 319.1 (15) $[M-2PF_6]^{2+}$; elemental analysis calcd (%) for $C_{34}H_{36}BF_{14}IN_4P_2$ (966.32): C 42.26, H 3.76, N 5.80; found: C 41.99, H 3.42, N 5.52.

Preparation of Dye 2

To a solution of BODIPY **B** (77.5 mg, 0.14 mmol), 4-dimethylaminopyridine (44.4 mg, 0.36 mmol) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (68.4 mg, 0.35 mmol) in DMF (1 mL), MV^+ (85.0 g, 0.17 mmol) was added. The resulting mixture was stirred for 20 h at room temperature. It was then added dropwise to a solution of KPF_6. The dark red precipitate was filtered and washed with ether.

Yield: 18%; ^{1}H NMR (300 MHz, [D_6]acetone) $\delta = 9.51$ (2H, d, $J =$ 6.3 Hz, Ar-CH), 9.35 (2H, d, $J = 6.3$ Hz, Ar-CH), 8.85 (2H, d, $J =$ 6.3 Hz, Ar-CH), 8.85 (2H, d, $J = 6.3$ Hz, Ar-CH), 8.32 (1H, t, $J = 5.1$ Hz, NH amide), 8.00 (2H, d, $J = 8.1$ Hz, Ar-CH), 7.48 (2H, d, $J = 8.1$ Hz, Ar-CH), 6.14 (2H, s, CH_2 BODIPY), 5.21 (2H, m, CH_2 viologen), 4.73 (3H, s, CH_3 viologen), 4.23 (2H, m, CH_2 viologen), 4.12 (4H, s, CH_2 PEG), 3.60 (4H, m, CH_2 PEG), 3.47 (4H, m, CH_2 PEG), 3.27 (6H, s, CH_3 PEG), 2.74 (6H, s, CH_3 BODIPY), 1.35 ppm (6H, CH_3 BODIPY); ^{13}C NMR (75 MHz, [D_6]acetone) $\delta = 168.1$, 156.7, 156.4, 151.2, 150.5, 147.9, 147.6, 147.5, 144.4, 142.1, 141.7, 139.5, 135.3, 129.9, 129.5, 128.9, 127.9, 127.8, 127.7, 122.6, 72.4, 69.4, 62.9, 59.7, 58.7, 49.4, 41.6, 36.2, 23.3, 16.3, 14.8 ppm; MS (ESI): *m/z* (%): 898.2 (100) $[M-PF_6]^+$, 376.5 (30) $[M-2PF_6]^{2+}$; elemental analysis calcd (%) for $C_{45}H_{52}O_5BF_{12}N_5P_2$ (1043.66): C 51.79, H 5.02, N 6.71; found: C 51.50, H 4.76, N 6.54.

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