DOI: 10.1002/cphc.201200510

## Effect on Charge Transfer and Charge Recombination by Insertion of a Naphthalene-Based Bridge in Molecular Dyads Based on Borondipyrromethene (Bodipy)

Andrew C. Benniston,<sup>\*[a]</sup> Sophie Clift,<sup>[a]</sup> Jerry Hagon,<sup>[a]</sup> Helge Lemmetyinen,<sup>[b]</sup> Nikolai V. Tkachenko,<sup>\*[b]</sup> William Clegg,<sup>[c]</sup> and Ross W. Harrington<sup>[c]</sup>

The photophysical properties of two related dyads based on a *N*,*N*-dimethylaniline donor coupled to a fully-alkylated boron dipyrromethene (Bodipy) acceptor are described. In one dyad, **BD1**, the donor unit is attached directly to the Bodipy group, whereas in the second dyad, **BD2**, a naphthalene spacer separates the two units. Cyclic voltammograms recorded for the two dyads in deoxygenated MeCN containing a background electrolyte are consistent with the reversible one-electron oxidation of the *N*,*N*-dimethylaniline group and the reversible one-electron reduction of the Bodipy nucleus. There is a reasonable driving force ( $\Delta G_{CT}$ ) for photoinduced charge transfer from the *N*,*N*-dimethylaniline to the Bodipy segment in MeCN. The charge-transfer state is formed for **BD1** extremely fast (1.5 ps), but decays over 140 ps to partially restore the ground state. On the other hand, the charge-transfer state for **BD2** is formed more slowly, but it decays extremely rapidly. Charge recombination for both dyads leads to a partial triplet formation on the Bodipy group. The naphthalene spacer group is extremely efficient at promoting back electron transfer.

## 1. Introduction

The ultimate aim of bio-inspired artificial photosynthesis is to create a fully operational system, capable of efficient capture of natural sunlight and its storage in the form of chemical energy.<sup>[1]</sup> As with any scientific jigsaw puzzle, there are many pieces that need to fall into place before any real working prototype is to emerge. The primary reaction in natural photosynthesis is the light-induced separation of charge across a membrane involving embedded pigments and transferable quinone (Q) electron acceptors.<sup>[2]</sup> Mimicking this primary charge-separation process in custom-built molecular systems has been intensely studied over many years.<sup>[3]</sup> In many cases the molecular architectures were designed to promote a cascade of electrontransfer events, so as to separate charge both spatially and temporally.<sup>[4]</sup> Successful systems are especially notable from the groups of Gust,<sup>[5]</sup> Osuka,<sup>[6]</sup> Sauvage<sup>[7]</sup>, and many others.<sup>[8]</sup> With the complexity in design comes the need to perform multiple synthetic procedures and purifications, generally yielding a small amount of material at the end. At the other extreme; very basic systems, though far easier to manufacture, do not generally offer long-lived charge-transfer (CT) character.<sup>[9]</sup> In discussing a long-lived photo-generated species we should identify its spin character. Triplet CT states are likely to live for long times but store less energy,<sup>[10]</sup> whereas singlet CT states generally show the opposite behavior.<sup>[11]</sup>

In an attempt to identify basic molecular dyads for the efficient capture of sunlight, and with a capacity to form singlet CT states, our attention was drawn to the boron dipyrromethene [Bodipy (BD)] chromophore.<sup>[12]</sup> The basic unit has a number of positive traits. 1) It is highly colored, absorbing

well into the visible region. 2) Triplet formation is unfavoured from the first-excited singlet state by inter-system-crossing. 3) The redox chemistry of the unit is reversible and the radical anion/cations are robust. 4) The synthetic procedures are well established to produce workable quantities of material in good yields.<sup>[13]</sup>

In our earlier employed dyads the quinone unit was used as electron acceptor, and positioned with or without a phenylene spacer in two positions on the Bodipy core.<sup>[14]</sup> The photoin-duced CT state produced comprised  $BD^{+}-Q^{-}$ , but lifetimes were too short for practical considerations. The alternative methodology is to use the Bodipy unit as an electron acceptor and to provide a suitable electron donor (D) in proximity. In

 [a] Prof. A. C. Benniston, S. Clift, Dr. J. Hagon Molecular Photonics Laboratory, School of Chemistry Newcastle University Newcastle upon Tyne, NE1 7RU (UK) Fax: (+44) 191 222 6929 E-mail: a.c.benniston@ncl.ac.uk
[b] Prof. H. Lemmetyinen, Dr. N. V. Tkachenko

- [0] Prof. H. Lemmergineri, Dr. N. V. Tkachenko Department of Chemistry and Bioengineering Tampere University of Technology PO Box 541, 33101 (Finland) E-mail: nikolai.tkachenko@tut.fi
- [c] Prof. W. Clegg, Dr. R. W. Harrington Crystallography Laboratory, School of Chemistry Newcastle University Newcastle upon Tyne, NE1 7RU (UK)
- $\car{l}$  Supporting information for this article is available on the WWW under
- http://dx.doi.org/10.1002/cphc.201200510.

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

🛞 WILEY 师

1

# CHEMPHYSCHEM

this case the photoinduced CT state produced comprises  $BD^{-}-D^{+}$ . There are several examples in the literature where this basic strategy is used, especially in the field of sensors using a dialkylamino substituent as donor.<sup>[15]</sup> Detailed studies of the photophysical properties of the compounds are less common.<sup>[16]</sup> The most basic system is **BD1** (Scheme 1) comprising a *N*,*N*-dimethylaniline group linked directly to the Bodipy



**Scheme 1.** Reagents and Conditions: a) DCM, TFA, RT; b) DDQ, *N,N*-diisopropylethylamine, BF<sub>3</sub>·Et<sub>2</sub>O; c) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> (2.0 m), THF, reflux.

core. In a similar derivative, deactivation of the Bodipy excited state was shown to be efficient.<sup>[17]</sup> Based on this observation we speculated (wrongly) that any formed CT state would be extremely short-lived. In order to separate the donor and acceptor groups a naphthalene unit was incorporated in a new dyad, **BD2** (Scheme 1). Synthetically, such a procedure represented no challenge, but the excited-state dynamics for **BD2** proved to be more interesting. The slower CT-state formation seen for the dyad **BD2** compared to **BD1** by naphthalene insertion is counteracted by ultrafast charge recombination. The naphthalene spacer appears to be an efficient conduit for back electron transfer.

## 2. Results and Discussion

## 2.2.1. Synthesis

Despite the plethora of Bodipy derivatives in the literature,<sup>[18]</sup> very little has been reported on the synthesis and characterization of **BD1**. The non-alkylated version is known as well as the diethyl and carboxylic acid derivatives.<sup>[19]</sup> We were especially interested in the fully-alkylated version, since this imparts good electrochemical stability to the final Bodipy dye, and affords some protection from sacrificial breakdown reactions with free radicals.<sup>[20]</sup> Following standard conditions the coupling of *p*-dimethylaminobenzaldehyde with 2,4-dimethyl-3-ethylpyrrole followed by oxidation and chelation to the BF<sub>2</sub> unit afforded **BD1** in 22% yield as a red solid. To construct **BD2**, the basic strategy was to introduce the naphthalene unit at the beginning and link the donor group at the end by stan-

dard cross-coupling conditions. Hence, compound 1 was produced in a manner similar to that for **BD1**, bearing a reactive aryl bromide for Suzuki coupling.<sup>[21]</sup> The desired compound **BD2** was produced in overall 68% yield as a red solid. All compounds were fully characterised by standard analytical techniques (e.g. NMR spectroscopy, mass spectrometry, melting point).

Single crystals were obtained for **BD1** and **BD2** and subjected to X-ray structure determinations. The molecular structures of the two compounds are displayed in Figure 1. The basic fea-



Figure 1. X-ray crystallographically-determined molecular structures for BD2 (top) and BD1 (bottom). Hydrogen atoms are omitted for clarity.

tures of the Bodipy segment are in agreement with other structures in the literature.<sup>[22]</sup> From the structure determinations it was possible to obtain the accurate distance between the donor (dimethylamine) and acceptor (dipyrrin) groups for the two dyads. The center-to-center distances (as shown in Figure 1) are calculated from the nitrogen atom to the centroid of the middle ring in the dipyrrin core. The insertion of the naphthalene group roughly results in a 60% increase in distance between the donor and acceptor units. The steric constraints imposed by the two 1,7-dimethyl groups mean that the N,N-dimethylaniline group is almost orthogonal to the plane of the dipyrrin (79.2°) for BD1. In structure BD2 it is the naphthalene group that is nearly orthogonal (82.4°), and as a consequence the N,N-dimethylaniline subunit is less constrained. The group is now, at least in the solid state, more in plane with the dipyrrin group. In solution, the N,N-dimethylaniline could rotate freely, however, evidence from <sup>19</sup>F NMR spectroscopy (see the Supporting Information) show that the naphthalene subunit is simply rocking on its axis and not spinning freely.

### 2.2.2. Molecular Orbital Calculations

The spatial localisation of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for both dyads were calculated using the B3LYP/6-311G density functional theory (DFT) method and Gaussian 03.<sup>[23]</sup> The orbitals are represented in Figure 2. For both moHOMOs for the two dyads is likely due to the insertion of the naphthalene group. The HOMO–LUMO gap of 2.81 eV for **BD2** represents the energy associated with a one-electron transfer from the Me<sub>2</sub>N (electron donor) to the Bodipy (electron accept-or). The corresponding energy gap for **BD1** is 3.10 eV (i.e. HOMO–1 to LUMO). The calculated energy gaps are rather large since there is no solvation contributing to the stabilization. However, the general trend of a larger energy gap for **BD1** compared to **BD2** is consistent with our electrochemistry experiments (Section 2.2.3). It is also worth noting that the energies of the HOMO–1 (**BD1**) and the HOMO (**BD2**) differ by a modulus of 240 mV.

#### 2.2.3. Electrochemistry

Cyclic-voltammetry experiments were carried out for the two derivatives in dry MeCN containing tetra-n-butylammonium 0.2 м tetrafluoroborate (TBATFB) as background electrolyte. The oxidative scan segment for the voltammogram of BD2 contained a one-electron guasi-reversible wave at  $E_{1/2} = +0.84 \text{ V}$  (90 mV) versus Ag/AgCl associated with the oxidation of the amine. On further scanning a quasi-reversible wave corresponding to the oxidation of the Bodipy site was observed at

 $E_{1/2}$  = + 1.09 V (140 mV) versus Ag/AgCl. In the reductive potential window a one-electron quasi-reversible wave was seen at  $E_{1/2}$  = -1.13 V versus Ag/AgCl, and is associated with the reduction of the Bodipy group (see the Supporting Information). The energy difference ( $\Delta E$ ) between the potentials for oxidation of the amine and reduction of the Bodipy was 1.97 V. The solubility of **BD1** in MeCN is rather poor and hampered the collection of

lecular dyads the LUMO is exclusively localised on the dipyrromethene segment. The nature of the appended aromatic in the *meso* position does not affect the energy of the orbital significantly. The HOMO for **BD1** is localised on the dipyrromethene segment, whereas the HOMO–1 is located on the *N*,*N*dimethylaniline group. The difference in energy between the orbitals is rather modest (160 mV). In comparison, the DFT-calculated HOMO for **BD2** is localised on the *N*,*N*-dimethylaniline group, with very little electron density residing on the intervening naphthalene unit. The HOMO–1 resides on the dipyrromethene, and again the difference in energy between the two orbitals is small (136 mV). The variance in ordering of the

6-311G basis set. Energies are in eV.

a good-quality cyclic voltammogram. The oxidative scan for **BD1** was dominated by two one-electron quasi-reversible waves located at +1.13 V (90 mV) and +1.31 V (190 mV) versus Ag/AgCl. The first wave was the oxidation of the amine and the second was the oxidation of the Bodipy group. The single wave observed at  $E_{1/2} = -1.03$  V (80 mV) on reductive scanning was again the reduction at the Bodipy site. The corresponding value for  $\Delta E$  was 2.16 V. It is noted that  $\Delta E_{BD1} > \Delta E_{BD2}$ . The difference in potentials for the oxidation of the amine ( $E_{BD1}-E_{BD2}$ ) is 290 mV, which is in good agreement with the corresponding computer-calculated value.



# CHEM**PHYS**CHEM

### 2.2.4. Absorption and Fluorescence

The electronic absorption spectra for BD1 and BD2 in dilute MeCN are shown in Figure 3. The typical sharp strong absorption band associated with the Bodipy-centered S<sub>0</sub>-S<sub>1</sub> electronic transition is observed at 520 and 525 nm for BD1 and BD2, respectively. The small red shift of 5 nm in  $\lambda_{ABS}$  for **BD2** is likely



Figure 3. Room-temperature absorption spectra recorded for BD1 (grav) and BD2 (black) in dilute MeCN.

the result of a partial conjugation with the naphthalene unit. The much weaker Bodipy-based S<sub>0</sub>-S<sub>2</sub> absorption profile for **BD2** is obscured by the  $\pi$ - $\pi$ \* electronic transitions of the naphthalene group. Extremely weak room-temperature fluorescence was observed from dilute MeCN solutions of highly purified samples of BD1 or BD2. The emission profiles were reasonably good mirror images of the absorption bands. The Stokes shifts were again typical for Bodipy-like chromophores.<sup>[24]</sup> Upper limits of fluorescence quantum yields ( $\phi_{\rm FLU}$ ) for BD1 and BD2 were 0.0003 and 0.002, respectively. Fluorescence lifetimes ( $\tau_s$ ) were too short to be measured by the conventional time-correlated single-photon-counting technique. As discussed later, femtosecond up-conversion spectroscopy provided reliable values for  $\tau_s$ . Selected data for the two dyads are collected in the Supporting Information.

#### 2.2.5. Time-Resolved Studies

The steady-state measurements performed on both dyads were consistent with efficient excited-state deactivation. To obtain a more comprehensive temporal picture of events, femtosecond time-resolved transient-absorption experiments were carried out. The samples were excited with a 70 fs laser pulse delivered at 385 nm and 50-70 time-resolved spectra were recorded in a 200-1000 ps time frame depending on the relaxation time of the sample. The data were fitted globally to obtain relaxation-time constants and the decay-component spectra associated with them. Results of the measurements for BD1 in MeCN are presented in Figure 4. At a very early time delay there is a clear bleach effect centered at 521 nm. In addition, there is a negative transient absorption in the range of 540-600 nm, where virtually no ground-state absorption of the sample is observed. This negative absorption arises from



Figure 4. Top: Transient-absorption decay components obtained from threeexponential fit of pump-probe data of BD1 in MeCN. Corresponding time constants are 1.5 ps ( $\bullet$ ), 140 ps ( $\blacksquare$ ), and roughly 1 ns ( $\blacktriangle$ ). Bottom: Time-resolved transient-absorption spectra at a number of delay times obtained after group-velocity dispersion compensation.

stimulated emission. With a time constant of 1.5 ps, the negative absorption evolves into a transient-absorption band with maximum at around 580 nm. By comparison to previous results this new feature was assigned to the Bodipy-based radical anion.<sup>[25]</sup> The band relaxes with a time constant of 140 ps. However, after relaxation of the band, some bleaching of the ground-state absorption band remains, indicating that roughly one quarter of initially excited molecules are still in an excited state.

The time profile of the transient-absorption evolution at 580 nm and fluorescence decay of the sample measured using up-conversion techniques are presented in Figure 5. The strong almost instant negative absorption at 580 nm is transformed into a positive absorption with the same time constant as the fluorescence decay of the sample. This supports that the negative absorption originates from stimulated emission, as well as the fact that the charge-separated state is formed from a singlet excited state.

A similar transient absorption experiment was performed with BD2 in MeCN but the results turned out to be difficult to analyse and the measurements were repeated in a number of solvents including DMF, THF, and toluene. The results of pumpprobe measurements of BD2 in DMF and comparison of the transient absorption time profile at 580 nm with the fluorescence decay are presented in Figures 6 and 7.

The transient absorption signal for BD2 decays much faster than that for **BD1**, but the emission decay relaxes more slowly for BD2 than for BD1. At the same time the number of intermediate states in relaxation for the excited state of BD2 is similar to that for BD1. A few reactions take place in the same timescale of a few picoseconds, which makes quantitative anal-



Figure 5. Transient-absorption time profiles at 580 nm (top) and fluorescence decay at 550 nm (bottom) of BD1 recorded in MeCN.



**Figure 6.** Top: Transient-absorption decay components obtained from threeexponential fit of pump-probe data of **BD2** in DMF. Bottom: Time-resolved transient-absorption spectra at a number of delay times obtained after group-velocity dispersion compensation.

ysis a difficult task. However, the shape of the 12 ps component for **BD2** resembles that of the 140 ps component for **BD1**, showing an absorption band around 580 nm. This band could be attributed to the charge-separated state. The electron transfer takes place at the singlet excited state with a time constant close to 7 ps. This time constant could be seen in the



Figure 7. Transient-absorption time profiles at 580 nm (top) and fluorescence decay at 550 nm (bottom) of **BD2** recorded in DMF.

fluorescence decay and the disappearance of negative absorption in the 540–600 nm part of the spectrum. The lifetime of the charge-transfer state (CTS) is only 12 ps, and the small difference in formation- and decay-time constants makes the band at 580 nm almost invisible. Still, close inspection of the transient-absorption kinetics at 580 nm shows that after simultaneous relaxation of stimulated (negative) absorption and fluorescence a positive absorption is formed (Figure 7).

Two other differences between the transient absorption responses of **BD1** and **BD2** were that for the latter there was a short-lived component, 0.1 ps, but practically no long-lived component. The short-lived component could be attributed to internal conversion from the second-excited singlet state to the first. This is a fast and almost unresolved process, since the time resolution of the instrument used was 0.2 ps. The internal conversion is probably even faster in the case of **BD1**, which precluded its detection for this compound. The virtually missing long-lived component in the case of **BD2** was explained by fast charge recombination and is discussed in Section 2.2.6.

In THF the differences between charge-separation and -recombination time constants were larger for **BD2** and the characteristic Bodipy-based radical anion band in the 550–620 nm region could be seen better (see the Supporting Information and comments therein). Additionally, all features of the timeresolved spectra of **BD2** in MeCN, DMSO and THF were similar and generally the same conclusions could be drawn for the transient states formed in all three solvents. Unfortunately, careful comparison of photoinduced reactions in **BD1** and **BD2** in THF and other tested solvents of moderate polarity was precluded by the poor solubility of **BD1**, therefore the following discussion is mainly limited to polar solvents.

# **CHEMPHYS**CHEM

## 2.2.6. Interpretation

Based on molecular-modeling calculations and electrochemistry results a basic model for singlet excited-state deactivation for the two dyads was proposed (Figure 8). In the polar solvent



Figure 8. Simplified energy diagram showing possible contributions to excited state deactivation of the Bodipy and the formed CTS.

MeCN the fully-formed singlet charge-transfer states (<sup>1</sup>CTS) are situated at about 220 mV (**BD1**) and 390 mV (**BD2**) below the respective Bodipy S<sub>1</sub> states. The Gibbs free-energy changes ( $\Delta G_{CT}$ ) for the formation of the <sup>1</sup>CTS, calculated using Equation (1), are -234 meV (**BD1**) and -374 meV (**BD2**).

$$\Delta G_{\rm CT} = F(E_{\rm D} - E_{\rm A}) - E_{\rm 00} + W \tag{1}$$

Here,  $E_D$  and  $E_A$  are the oxidation and reduction potentials for the donor and acceptor respectively.  $E_{00}$  is the mid-point in the crossing of the absorption and fluorescence spectra for the donor (**BD1** = 2.34 eV, **BD2** = 2.31 eV), and *W* is the Coulombic work term. In MeCN these terms are only -54 meV (**BD1**) and -34 meV (**BD2**) for the two dyads.

On spin considerations a lower-lying <sup>3</sup>CTS must also be considered. If the <sup>1</sup>CTS–<sup>3</sup>CTS energy gap is small, given by 2*J*, where *J* is the spin–spin exchange integral, then the intersystem-crossing rate ( $k_2$ ) may be extremely fast.<sup>[26]</sup> This scenario opens up an efficient pathway to populate the triplet state on the Bodipy segment (rate =  $k_3$ ). Direct population of the Bodipy triplet state from the <sup>1</sup>CTS is another feasible option (rate =  $k_1$ ), as well as direct restoration of the ground state (rate =  $k_{DREC}$ ). The value for  $k_1$  depends very much on the orientation between the orbitals on the dimethylaniline and the Bodipy. In an orthogonal arrangement the charge-transfer process is accompanied by a change in the orbital angular momentum which facilitates the necessary spin flip to form a triplet. Direct recombination from <sup>3</sup>CTS to the ground state is

a spin-forbidden process and therefore presumably slow. Intersystem crossing from the Bodipy S<sub>1</sub> to T<sub>1</sub> state is known to be in the order of  $10^6 \text{ s}^{-1}$ .<sup>[27]</sup> The energy of the triplet state is about 1.6 eV above the ground state.

Transient-spectroscopic evidence for BD1 supported that the <sup>1</sup>CTS is formed extremely fast ( $k_{CTS} = 7 \times 10^{11} \text{ s}^{-1}$ ). The rate for decay of the <sup>1</sup>CTS (second decay component) is considerably slower ( $6.4 \times 10^9 \text{ s}^{-1}$ ). Discrimination between rates for charge separation and charge recombination is good (~100), especially considering the close proximity of the donor to the acceptor. It is worth noting that a similar effect was witnessed for a closely-spaced pyridinium-based Bodipy dyad.<sup>[28]</sup> The value for  $k_{\text{DREC}}$  is around 5.4×10<sup>9</sup> s<sup>-1</sup> for a driving force ( $\Delta G_{\text{DREC}}$ ) of -2.11 eV, putting the electron-transfer process well into the Marcus-inverted region. The long-lived component in the transient records is assigned to the triplet localised on the Bodipy segment. Similar observations have been reported previously.<sup>[29]</sup> Thus, part of the process in charge recombination leads to triplet formation, which is known to occur readily in orthogonally arranged geometries.<sup>[30]</sup> Given the yield of the Bodipy triplet the value for  $k_1$  (or  $k_3$ ) is about  $1 \times 10^9$  s<sup>-1</sup>. The driving force ( $\Delta G_{\text{TF}}$ ) for this process is in the order of about -0.5 eV, and electron transfer is likely to occur in the so-called Marcusnormal region.

The scenario for **BD2** is rather different. The <sup>1</sup>CTS is formed much more slowly, about  $1.4 \times 10^{11}$  s<sup>-1</sup>, and relaxes much faster, about  $0.8 \times 10^{11}$  s<sup>-1</sup>. The slower charge transfer can be expected, considering the longer distance between the donor and acceptor parts, but the faster charge recombination requires a deeper analysis to be understood. In the frame of the semiclassical Marcus electron-transfer theory [Eq. (2)] the reaction-rate constant is:

$$k_{\rm et} = \frac{2\,\pi^{3/2}}{h} \frac{V^2}{\sqrt{\lambda k_{\rm B}T}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\,\lambda k_{\rm B}T}\right] \tag{2}$$

where h is the Planck constant,  $k_{\rm B}$  is the Boltzmann constant,  $\Delta G$  is the reaction free energy,  $\lambda$  is the reorganization energy, and V is the electronic coupling matrix element. For the forward- and back-electron transfers the reorganization energy and electronic coupling can be assumed to be the same, therefore the ratio of the charge-separation and -recombination rate constants depends only on the reorganization energy,  $\lambda$ . Therefore, the reorganisation energy can be evaluated from known charge-transfer and -recombination rate constants, and free energies of the states.<sup>[31]</sup> The calculations provided 1.06 eV and 1.14 eV as the reorganisation energies for BD1 and BD2, respectively. These estimations agree with the expectation of a higher reorganisation energy for BD2 relative to that of BD1 since the charge-transfer distance is greater for BD2. Also the values of the energies are reasonable for this type of dyads. The energies can be used to draw Franck-Condon energy diagrams for the two compounds in polar solvent, as presented in Figure 9 (see the Supporting Information for calculation details). The essential difference in position of the CTS energy profiles is that for BD2 the profile is shifted down (lower free

6 www.chemphyschem.org © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

## *KK* These are not the final page numbers!



Figure 9. Franck-Condon energy diagram for BD1 (-----) and BD2 (-----) in polar solvent. GS = ground state.

energy of the CTS) and away from the excited state (higher reorganisation energy), relative to that of **BD1**.

The potential barrier for the charge separation is somewhat smaller for **BD2**, which could accelerate the electron transfer as compared to **BD1**. The distance between the donor and acceptor is essentially larger for **BD2**, resulting in a weaker electronic coupling and a slowing down of the electron-transfer rate. The net result is roughly a four times slower electron-transfer rate for **BD2**. For the charge recombination the key factor is a much lower potential barrier in the case of **BD2**. The barrier for charge recombination is virtually equal to that of charge separation, according to the small difference in the reaction-rate constants. In comparison to **BD1**, a hypothetical slowing down for charge recombination, due to smaller electronic coupling (longer CT distance), is over-compensated by the much lower charge-recombination potential energy barrier, making the reaction much faster for **BD2**.

The electronic coupling discussed above can also be estimated from Equation (2) for a known reaction-rate constant and the free and reorganisation energies.<sup>[32]</sup> The calculations yielded 690 and 25 cm<sup>-1</sup> for **BD1** and **BD2**, respectively. These values are reasonable, and accounting for the difference in donor-acceptor distance between the dyads, which is 4.3 Å. The expected decrement factor in the exponential dependence of the electron-transfer rate constant on the distance is 0.8  $Å^{-1}$ , which is again a reasonable value for a phenylene-like linker between the donor and the acceptor. The semi-classical ET theory is known to overestimate the rate constants in the inverted Marcus regime. In this particular case, not only a quantitative picture predicted by the theory explains the observed differences between BD1 and BD2 fairly well, but also the qualitative estimations are self-consistent and agree with similar estimations made for analogous systems.

There is an indication in Section 2.2.5 that charge recombination results in triplet localisation on the Bodipy group. The long-lived component in the transient-absorption measurements of **BD1** (>1 ns, Figure 4) is attributed to the triplet state. The relative bleaching of the ground-state absorption associated with this component is roughly 25%, which gives a conversion rate from the CTS to the Bodipy triplet state of about  $2 \times 10^9$  s<sup>-1</sup>. The mechanism of conversion can be relatively complex, that is through changing multiplicity of the CTS first, followed by relaxation to the lower-lying locally-excited triplet state of the Bodipy chromophore. The triplet state is virtually non-existent in the excitation relaxation of BD2, as can be seen from the weak intensity of the long-lived component in the transient-absorption measurements (Figure 6). There are at least two reasons for this. First of all, the conversion to the triplet state competes with the charge recombination which returns the system directly to the ground state. Since the charge recombination is much faster for BD2, the relative amount of molecules relaxing through the triplet state is smaller, even if the rate constants for this reaction pathway are the same as for BD1. Secondly, the reaction rates for the relaxation through the triplet are expected to be slower for BD2 than those for BD1, since the potential barrier is higher and the electronic coupling is smaller.

## 3. Conclusions

The naphthalene unit as a spacer appears to be a good conduit for supporting CTS formation, at least in cases where the donor is N,N-dimethylaniline and the acceptor is Bodipy. Unfortunately, the orbitals and their energies for the bridge appear to be ideally suited to promote rapid charge recombination.<sup>[33]</sup> Clearly, this situation is not conducive for the creation of a long-lived <sup>1</sup>CTS in a simple molecular dyad. The question to ask is: what is the effect of adding additional units between the donor and acceptor? The next in the series is the binaphthalene group, which is itself interesting since it is chiral by restricted rotation. The separation distance will increase by around 40% and  $k_{\rm CTS}$  should decrease to about  $1 \times 10^{10} \, {\rm s}^{-1}$  assuming a simple exponential decay model. Of course, a secondary consideration is the twist angle ( $\theta$ ) in the binaphthalene, since electron-transfer rates are known to be highly dependent on  $\theta$ .<sup>[34]</sup> We expect to explore the role of the binaphthalene in promoting electron transfer in a new dyad currently in preparation in the group.

## **Experimental Section**

## Materials

Bulk chemicals were purchased at the highest purity possible from Aldrich Chemical Co. and used as received unless otherwise stated. Tetra-*n*-butylammonium tetrafluoroborate (TBATFB) purchased from Fluka was recrystallized several times from methanol and dried thoroughly under vacuum before being stored in a desiccator. Standard solvents were dried by literature methods before being distilled and stored under nitrogen over 4 Å molecular sieves. Spectroscopic-grade solvents were used in all fast-kinetic experiments and fluorescence/absorption-spectroscopy measurements.

#### Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with either Bruker AVANCE 300 MHz, JEOL 400 MHz, or JEOL Lambda 500 MHz spectrometers. <sup>11</sup>B and <sup>19</sup>F NMR spectra were recorded using the 400 MHz spectrometer. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra are referenced relative to the residual deuterated solvent. The <sup>11</sup>B NMR chemical shift is referenced relative to  $BF_3$ ·Et<sub>2</sub>O ( $\delta$  = 0), and the <sup>19</sup>F NMR chemical shift is given relative to  $CFCI_3$  ( $\delta = 0$ ). Routine mass spectra and elemental analyses were obtained using in-house facilities. MALDI mass spectra were recorded at the EPSRC-sponsored Mass Spectrometry Service at Swansea. Absorption spectra were recorded using a Hitachi U3310 spectrophotometer and corrected fluorescence spectra were recorded using a Lambda Advanced F 4500 spectrometer. Uncorrected melting points were measured using a Stuart SMP11 apparatus and typically carried out twice to check for consistency in the readings. Crystallographic data for BD1 were collected at Beamline 19 of Diamond Light Source with synchrotron radiation, whereas data for BD2 were collected on an Agilent Techologies Gemini A Ultra diffractometer. CCDC 886352 and 886353 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre through www.ccdc.cam.ac.uk/ data request/cif.

Cyclic voltammetry experiments were performed using a fully automated HCH Instruments Electrochemical Analyzer and a three electrode set-up consisting of a platinum working electrode, a platinum wire-counter electrode and a Ag/AgCl reference electrode. Ferrocene was used an internal standard. All studies were performed in deoxygenated CH<sub>3</sub>CN containing TBATFB (0.2 M) as background electrolyte. The solute concentrations were typically 0.1 mm. Redox potentials were reproducible to within  $\pm$  15 mV.

## **Time-Resolved Absorption Measurements**

Femto- to pico-second time-resolved absorption spectra were collected using a pump-probe technique described previously.<sup>[35]</sup> The femtosecond pulses of a Ti-sapphire generator were amplified by using a multipass amplifier (CDP-Avesta, Moscow, Russia) pumped by a second harmonic of the Nd:YAG Q-switched laser (model LF114, Solar TII, Minsk, Belorussia). The amplified pulses were used to generate second harmonic (420 nm) for sample excitation (pump beam) and the white light continuum for a time-resolved spectrum detection (probe beam). The samples were placed in 1 mm rotating cuvettes, and averaging of 100 pulses at a 10 Hz repetition rate was used to improve the signal-to-noise ratio. The typical response time of the instrument was 150 fs (fwhm). Absorption spectra were recorded prior to and after all experiments to check for compound degradation.

#### **Fluorescence Lifetime Measurements**

Ultrafast fluorescence decays were measured by an up-conversion method as described previously.<sup>[35]</sup> The instrument (FOG100, CDP, Moscow, Russia) utilizes the second harmonic (420 nm) of a 50 fs Ti:sapphire laser (TiF50, CDP, Moscow, Russia) pumped by an Ar ion laser (Innova 316P, Coherent). The samples were placed in a rotating disk-shaped 1 mm cuvette. A typical resolution for the instrument was 150 fs (fwhm).

## Data analysis

8

Time-resolved transient-absorption data were manipulated using a freely available software package. In a typical analysis the whole collection of differential absorption spectra were inspected over the full time scale, and decay kinetics obtained at two specifically chosen wavelengths using an appropriate number of exponentials and instrument response function. Lifetimes obtained by a leastsquares fit to the kinetic model were also checked by a global analysis at several different wavelengths. Up-conversion fluorescence lifetimes were obtained by fitting the single-photon-counting data to different kinetic models using a variable Gaussian instrument response function. Analysis was attempted using monoto tri-exponentials and the stretched exponential function. Best fits were judged by the usual methods of remaining residuals and sigma value.

### **Preparation of BD1**

TFA (2 drops) was added dropwise to a stirred solution of 2,4-dimethyl-3-ethylpyrrole (1.88 mL, 14 mmol, 2.1 equiv.) and 4-dimethylaminobenzaldehyde (1.0 g, 6.7 mmol, 1.0 equiv.) in DCM (250 mL). The reaction mixture was stirred at room temperature until consumption of the aldehyde was complete (checked by TLC). DDQ (1.60 g, 7.0 mmol, 1.05 equiv) was then added in a single portion, and the reaction was left with stirring overnight at room temperature. The following day N,N-diisopropylethylamine (14.00 mL, 80.4 mmol, 12.0 equiv.) and BF<sub>3</sub>·Et<sub>2</sub>O (14.26 mL, 113 mmol, 16.8 equiv.) were added, and the reaction was left with stirring for 6 h at room temperature. The reaction mixture was washed with water (3×100 mL) and brine (3×100 mL). The separated organic fractions were dried (MgSO<sub>4</sub>), filtered, and the solvent was removed in vacuo to yield a black/dark violet residue with a green tint. This was chromatographed on silica gel using toluene as eluent to afford a red solid (0.648 g, 22% yield). This solid was then frozen in ether and the solvent removed at the pump and finally washed with petrol. Mpt. > 250 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta =$  7.06 (d, J = 8.7 Hz, 2 H), 6.78 (d, J = 8.7 Hz, 2H), 3.02, (s, 6H, N-(CH<sub>3</sub>)<sub>2</sub>), 2.53 (s, 6H), 2.31 (q, J=7.4, 4H), 1.26 (s, 6 H), 0.99 ppm (t, J = 7.4 Hz, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta =$  $152.93, \ 150.56, \ 141.55, \ 138.58, \ 132.33, \ 131.48, \ 128.96, \ 123.06,$ 112.33, 40.38, 17.08, 14.64, 12.42, 11.93 ppm.  $^{11}\mathrm{B}\;\mathrm{NMR}\;\;\mathrm{(CDCI_3,}$ 160 MHz):  $\delta = -0.115$  ppm (t,  $J_{av} = 34.45$  Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 470 MHz):  $\delta = -145.66$  (q, J = 28.59 Hz,). IR (neat):  $\tilde{\nu} = 2958$ , 2923, 2854 (C–H), 1527, 1473 (C=C, C=N), 1183 cm<sup>-1</sup> (B–F). EI-MS : *m/z* calc. for  $C_{25}H_{32}BF_2N_3 = 423$  fnd. 424 [*MH*]<sup>+</sup>.

## Preparation of 1

TFA (2 drops) was added dropwise to a stirred solution of 2,4-dimethyl-3-ethylpyrrole (1.46 mL, 10.84 mmol, 2.1 equiv.) and p-bromonaphthaldehyde (1.21 g, 5.16 mmol, 1.0 equiv.) in DCM (200 mL). The reaction mixture was stirred at room temperature until the consumption of the aldehyde was complete (checked by TLC). DDQ (1.23 g, 5.4 mmol, 1.05 equiv) was then added in a single portion, and the reaction was left with stirring overnight at room temperature. The following day N,N-diisopropylethylamine (10.79 mL, 61.92 mmol, 12.0 equiv) and BF<sub>3</sub>·Et<sub>2</sub>O (10.99 mL, 86.69 mmol, 16.8 equiv.) were added, and the reaction was left with stirring for 6 h at room temperature. The reaction mixture was washed with water and brine. The separated organic fractions were dried (MgSO<sub>4</sub>), filtered, and the solvent removed in vacuo to yield a pink/purple residue with a greenish tint. The residue was chromatographed on silica gel using toluene as eluent to afford a purple/green solid (1.55 g, 59% yield). This solid was then frozen in ether and the solvent removed at the pump and washed with petrol. Mpt. = 197–198 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.34 (d, J = 8.2 Hz, 1 H, aromatic), 7.91 (d, J=7.3 Hz, 1 H, aromatic), 7.89 (d, J=8.2 Hz, 1 H, aromatic), 7.64 (t, J=7.1 Hz, 1 H, aromatic), 7.51 (t, J=7.1 Hz, 1 H, aromatic), 7.29 (d, J=7.3 Hz, 1 H, aromatic), 2.61 (s, 6 H, CH<sub>3</sub>), 2.27 (q, J = 7.5 Hz, 4H,  $CH_2CH_3$ ), 1.02 (s, 6H,  $CH_3$ ), 0.96 ppm (t, J =7.5 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 154.07$ , 137.81, 136.94, 133.24, 133.03, 132.76, 131.86, 130.97, 129.75, 127.89,

www.chemphyschem.org © 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

127.83, 127.23, 126.42, 125.57, 123.72, 16.85, 14.42, 12.41, 11.14 ppm. <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.00 (t,  $J_{av}$  = 32.0 Hz). <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  = -145.6 ppm (broadened multiplet). IR (neat):  $\tilde{\nu}$  = 2963, 2928, 2870 (C–H), 1534, 1474 (C=C, C=N), 1182 cm<sup>-1</sup> (B–F).

## **Preparation of BD2**

A solution in THF (20 mL) of 1 (0.15 g, 0.295 mmol, 1.0 eg), 4-dimethylaminophenyl boronic acid (0.10g, 0.620 mmol, 2.1 eqiv.) and sodium carbonate (0.093 g, 0.885 mmol, 3 eqiv.) in water was degassed for an hour prior to addition of the catalyst, tetrakis(triphenylphosphine) palladium(0) (0.02 g, 0.024 mmol, 0.08 eqiv.). The reaction was then heated with continuous stirring overnight at 60°C. The following morning the crude reaction mixture was left to cool before being filtered through a glass pipette plugged with cotton wool to remove the unreacted catalyst. The residual solvent was then removed under vacuum and the crude material taken up in DCM, washed with sodium carbonate solution (0.6 M) and dried over sodium sulfate. It was then filtered and the DCM removed in vacuo to yield a black/dark violet residue with a green tint. The residue was chromatographed on silica gel using toluene as eluent to afford a red solid (0.11 g, 68% yield). This solid was then frozen in ether and the solvent removed at the pump and washed with petrol. Mpt. > 250 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 8.11$  (d, J =7.5 Hz, 2H), 7.87 (d, J=7.5 Hz, 2H), 7.46, (m, 4H), 6.91 (d, J=9 Hz, 2H), 3.07 (s, 6H, N-(CH<sub>3</sub>)<sub>2</sub>), 2.59 (s, 6H), 2.28 (q, J=7.3, 4H), 1.07 (s, 6H), 0.97 ppm (t, J=7.3 Hz, 6H).  $^{13}$ C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta =$ 11.25, 12.56, 14.61, 17.05, 40.56, 112.21, 125.49, 125.76, 125.95, 126.14, 126.27, 126.53, 126.65, 130.94, 131.43, 131.74, 131.93, 132.43, 132.61, 138.34, 138.99, 141.80, 149.95, 153.68 ppm. <sup>11</sup>B NMR (CDCl\_3, 160 MHz):  $\delta\!=\!0.0192$  ppm (t,  $J_{\rm av}\!=\!33.22$  Hz).  $^{19}{\rm F}$  NMR (CDCl\_3, 470 MHz):  $\delta = -145.39$  ppm (broadened multiplet). EI-MS: *m/z* calc. for  $C_{35}H_{38}BF_2N_3 = 549$  fnd. 550 [*MH*]<sup>+</sup>.

## Acknowledgements

We thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support (EP/G04094X/1 and EP/F03637X/1) and Diamond Light Source for synchrotron diffraction facilities. The EPSRC-sponsored Mass Spectrometry Service at Swansea is also thanked for collecting mass spectra.

**Keywords:** charge transfer · charge separation photophysics · spectroscopy · triplet formation

- M. Wasielewski, Chem. Rev. **1992**, *92*, 435–461; T. Meyer, Acc. Chem. Res. **1989**, *22*, 163–170; D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. **2001**, *34*, 40–48; A. C. Benniston, A. Harriman, Mater. Today **2008**, *11*, 26–34; L. C. Sun, L. Hammarstrom, B. Akermark, B. Styring, Chem. Soc. Rev. **2001**, *30*, 36–49.
- [2] Concepts in Photobiology: Photosynthesis and Photomorphogenesis (Eds.: G. S. Singhal, G. Renger, S. K. Sopory, K. D. Irrgang, Govindjee), Springer, Dordrecht, 1999.
- [3] T. Nakamura, M. Fujitsuka, Y. Araki, O. Ito, J. Ikemoto, K. Takimiya, Y. Aso, T. Otsubo, J. Phys. Chem. B 2004, 108, 10700–10710; S. A. Vail, P. J. Krawczuk, D. M. Guldi, A. Palkar, L. Echegoyen, J. P. C. Tomé, M. A. Fazio, D. I. Schuster, Chem. Eur. J. 2005, 11, 3375–3388; M. T. Colvin, A. Butler Ricks, A. M. Scott, D. T. Co, M. R. Wasielewski, J. Phys. Chem. B 2012, 116, 1923–1930.
- [4] R. E. Palacios, G. Kodis, S. L. Gould, L. de La Garza, A. Brune, D. Gust, T. A. Moore, A. L. Moore, *ChemPhysChem* 2005, 6, 2359–2370.
- [5] D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 1993, 26, 198-205.

- [6] A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno, K. Nozakild, J. Am. Chem. Soc. 1993, 115, 4577– 4589.
- [7] E. Baranoff, J. P. Collin, L. Flamigni, J.-P. Sauvage, Chem. Soc. Rev. 2004, 33, 147–155.
- [8] Y. Wu, Y. Li, H. Li, Q. Shi, H. Fu, J. Yao, Chem. Commun. 2009, 6955– 6957.
- [9] J. W. Verhoeven, H. J. van Ramesdonk, M. M. Groeneveld, A. C. Benniston, A. Harriman, *ChemPhysChem* 2005, *6*, 2251–2260.
- [10] J. Hu, B. Xia, D. Bao, A. Ferreira, J. Wan, G. Jones II, V. I. Vullev, J. Phys. Chem. A 2009, 113, 3096–3107; K. P. Ghiggino, J. A. Hutchison, S. J. Langford, M. J. Latter, M. A.-P. Lee, M. Takezaki, Aust. J. Chem. 2006, 59, 179–185; S. I. van Dijk, C. P. Groen, F. Hartl, A. M. Brouwer, J. W. Verhoeven, J. Am. Chem. Soc. 1996, 118, 8425–8432.
- [11] D. Gust, T. A. Moore, A. L. Moore, F. Cao, D. Luttrul, J. M. DeGraziano, X. C. Ma, L. R. Makings, S.-J. Lee, T. T. Trier, E. Bittersmann, G. R. Seely, S. Woodward, R. V. Bensasson, M. Roug, F. C. De Schryver, M. Van der Auweraer, J. Am. Chem. Soc. **1991**, 113, 3638–3649; T. Honda, T. Nakanishi, K. Ohkubo, T. Kojima, S. Fukuzumi, J. Phys. Chem. C **2010**, 114, 14290– 14299.
- [12] R. Ziessel, G. Ulrich, A. Harriman, New J. Chem. 2007, 31, 496-501.
- [13] L. Wu, K. Burgess, Chem. Commun. 2008, 4933; M. Shah, K. Thangraj, M. L. Soong, L. Wolford, J. H. Boyer, I. R. Politzer, T. G. Pavlopoulos, Heteroat. Chem. 1990, 1, 389–399; A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, F. Bergstrom, L. B. A. Johansson, J. Org. Chem. 1999, 64, 7813–7819.
- [14] A. C. Benniston, G. Copley, H. Lemmetyinen, N. V. Tkachenko, Eur. J. Org. Chem. 2010, 2867–2877.
- [15] M. Baruah, W. Qin, R. A. L. Vallée, D. Beljonne, T. Rohand, W. Dehaen, N. Boens, Org. Lett. 2005, 7, 4377–4380; K. Rurack, M. Kollmannsberger, J. Daub, Angew. Chem. 2001, 113, 396–399; Angew. Chem. Int. Ed. 2001, 40, 385–387; R. Hu, E. Lager, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. Sing Wong, E. Peña-Cabrera, B. Zhong Tang, J. Phys. Chem. C 2009, 113, 15845–15853.
- [16] Q. Qin, M. Baruah, M. Van der Auweraer, F. C. De Schryver, N. Boens, J. Phys. Chem. A 2005, 109, 7371–7384.
- [17] M. Kollmannsberger, K. Rurack, U. Resch-Genger, J. Daub, J. Phys. Chem. A 1998, 102, 10211 – 10220.
- [18] A. Loudet, K. Burgess, Chem. Rev. 2007, 107, 4891–4932; T. E. Wood, A. Thompson, Chem. Rev. 2007, 107, 1831–1861.
- [19] E. Lager, J. Liu, A. Aguilar-Aguilar, B. Zhong Tang, E, Peña-Cabrera, J. Org. Chem. 2009, 74, 2053–2058; E. Y.-H. Yu, Z. Shen, H.-Y. Xu, Y.-W. Wang, T. Okujima, N. Ono, Y.-Z. Li, X.-Z. You, J. Mol. Struct. 2007, 827, 130–136; T. Kowada, J. Kikuta, A. Kubo, M. Ishii, H. Maeda, S. Mizukami, K. Kikuchi, J. Am. Chem. Soc. 2011, 133, 17772–17776.
- [20] R. Y. Lai, A. J. Bard, J. Phys. Chem. B 2003, 107, 5036-5042.
- [21] N. Miyura, T. Yanagi, A. Suzuki, Synth. Commun. 1981, 11, 513-519.
- [22] R. Ziessel, L. Bonardi, P. Retailleau, G. Ulrich, J. Org. Chem. 2006, 71, 3093-3102.
- [23] Gaussian 03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Yayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, **2004**.
- [24] A. C. Benniston, G. Copley, Phys. Chem. Chem. Phys. 2009, 11, 4124– 4131.
- [25] S. Hattori, K. Ohkubo, Y. Urano, H. Sunhara, T. Nagano, Y. Wada, N. V. Tkachenko, H. Lemmetyinen, S. Fukuzumi, J. Phys. Chem. B 2005, 109, 15368–15375.
- [26] J. W. Verhoeven, J. Photochem. Photobiol. C 2006, 7, 40-60.

ChemPhysChem 0000, 00, 1 – 11

 $\ensuremath{\mathbb{C}}$  2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! 77

www.chemphyschem.org

9

- [27] G. Ulrich, R. Ziessel, A. Harriman, Angew. Chem. 2008, 120, 1202-1219; Angew. Chem. Int. Ed. 2008, 47, 1184-1201.
- [28] A. Harriman, L. J. Mallon, G. Ullrich, R. Ziessel, ChemPhysChem 2007, 8, 1207-1214.
- [29] R. Ziessel, B. D. Allen, D. B. Rewinska, A. Harriman, *Chem. Eur. J.* 2009, 15, 7382–7393; A. C. Benniston, G. Copley, H. Lemmetyinen, N. V. Tkachenko, *ChemPhysChem* 2010, *11*, 1685–1692; J. Y. Lui, M. E. El-Kouly, S. Fukuzumi, D. P. K. Ng, *Chem. Asian J.* 2011, *6*, 174–179.
- [30] Z. E. X. Dance, S. M. Mickley, T. M. Wilson, A. Butler Ricks, A. M. Scott, M. A. Ratner, M. R. Wasielewski, *J. Phys. Chem. A* **2008**, *112*, 4194–4201.
- [31] A. C. Benniston, J. Hagon, X. He, H. Lemmetyinen, N. V. Tkachenko, W. Clegg, R. W. Harrington, Phys. Chem. Chem. Phys. 2012, 14, 3194–3199.
- [32] M. Isosomppi, N. V. Tkachenko, A. Efimov, H. Vahasalo, J. Jukola, P. Vainiotalo, H. Lemmetyinen, *Chem. Phys. Lett.* **2006**, 430, 36–40.
- [33] W. D. Oosterbaan, C. Koper, T. W. Braam, F. J. Hoogesteger, J. J. Piet, B. A. J. Jansen, C. A. van Walree, H. J. van Ramesdonk, M. Goes, J. W. Ver-

hoeven, W. Schuddeboom, J. M. Warman, L. W. Jenneskens, J. Phys. Chem. A 2003, 107, 3612–3624; M. T. Indelli, M. Orlandi, C. Chiorboli, M. Ravaglia, F. Scandola, F. Lafolet, S. Welter, L. De Cola, J. Phys. Chem. A 2012, 116, 119–131; T. Miura, A. M. Scott, M. R. Wasielewski, J. Phys. Chem. C 2010, 114, 20370–20379; A. Butler Ricks, G. C. Solomon, M. T. Colvin, A. M. Scott, K. Chen, M. A. Ratner, M. R. Wasielewski, J. Am. Chem. Soc. 2010, 132, 15427–15434; M. U. Winters, K. Pettersson, J. Mårtensson, B. Albinsson, Chem. Eur. J. 2005, 11, 562–573.

- [34] A. C. Benniston, A. Harriman, Chem. Soc. Rev. 2006, 35, 169-179.
- [35] N. V. Tkachenko, L. Rantala, A. Y. Tuaber, J. Helaja, P. H. Hynninen, H. Lemmetyinen, J. Am. Chem. Soc. 1999, 121, 9378–9387.

Received: June 23, 2012 Revised: July 24, 2012 Published online on ■■ ■, 2012

## ARTICLES



A bridge too far: Despite the fact that insertion of the naphthalene group into the Bodipy dyad (see picture, right opposite) increases the distance between the donor and acceptor, charge recombination is much faster when compared to the simple dyad (see picture, left opposite). A. C. Benniston,\* S. Clift, J. Hagon, H. Lemmetyinen, N. V. Tkachenko,\* W. Clegg, R. W. Harrington



Effect on Charge Transfer and Charge Recombination by Insertion of a Naphthalene-Based Bridge in Molecular Dyads Based on Borondipyrromethene (Bodipy)