Two-step photoinduced charge separation and unexpectedly fast one-step charge recombination in a linked donor$_2$–donor$_1$–acceptor system

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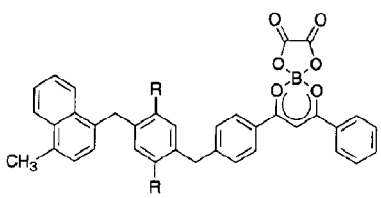
Photoinduced sequential two-step electron transfer occurs upon excitation of the 1,3-diphenylpropanedioato boron oxalate electron acceptor in a novel trichromophoric donor$_2$–donor$_1$–acceptor (D_2–D_1–A) system. The D_2–D_1^+–A^- state is fluorescent, while the D_2^+–D_1–A^- state is observed by transient absorption. The final giant dipole state, which is formed in ≈90% yield, is remarkably short-lived.

1. Introduction

Light-induced stepwise charge separation processes are currently a topic of intensive investigations, both in order to enhance the understanding of the reactions that play a central role in natural photosynthetic reaction centres [1–4] as well as part of efforts to develop new materials with useful electro-optical properties. In an earlier study [5] we presented system **1a** (scheme 1) that consists of a photoexcitable 1,3-diphenylpropanedioato boron oxalate electron acceptor (A) and two electron donors that are connected in a linear array: D_2–D_1–A.

After excitation of the acceptor chromophore of compound **1a** charge separation with a quantum yield near unity occurs, resulting in a charge separated state best depicted as D_2^+–D_1–A^-. The decay of this state is easily monitored because charge recombination is accompanied by a characteristic charge transfer fluorescence D_2^+–D_1–$A^- \rightarrow D_2$–D_1–$A + h\nu_{CT}$ ($\tau_{CR}=42$ ns, $\phi_f=0.015$ in benzene, $\lambda_{max}=635$ nm). The relatively fast charge recombination between D_2 and A and the partly radiative nature of this process indicate that there is substantial electronic coupling between the two units. Although the D_2–D_1^+–A^- state is thermodynamically accessible in **1a**, as shown by the behaviour of the corresponding D_1–A compound [6] it is not observed as an intermediate state. In order to establish the involvement of the D_2–D_1^+–A^- state in the charge separation between D_2 and A, D_1 was replaced by a much weaker donor, i.e. in **1b**. In this compound the D_2–D_1^+–A^- state is of higher energy than the A* state (except in very polar solvents [7]) thereby rendering the D_2–D_1–$A^* \rightarrow D_2$–D_1^+–A^- charge separation process endothermic. Nevertheless the long range charge separation and charge recombination processes in **1b** ($\tau_{CR}=27$ ns in benzene) occur with rates similar to those in **1a**. This indicates that the intermediate D_2–D_1^+–A^- state probably plays no role in the charge separation between D_2 and A, and single step long range electron transfer prevails.



1a : R=Me
1b : R=H

Scheme 1.

In order to reduce the direct electronic coupling between D_2 and A system **2** was now synthesised, in which the D_2/A distance is increased as compared

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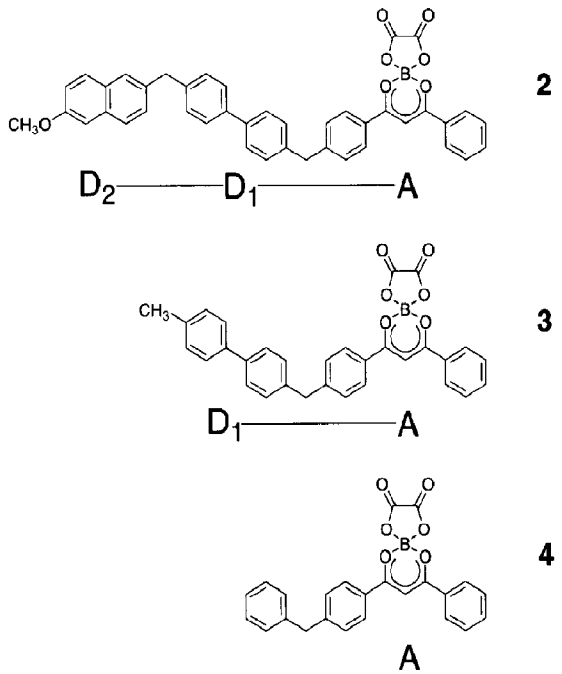

Scheme 2.

to **1a**, **b**. Although rotations around the aryl–methylene bonds may give rise to different ground state rotamers the rigidity of the biphenyl unit guarantees a distinct increase of the average D_2/A distance by ≈4 Å. Because of the exponential distance dependence [8–10] of the electronic coupling this may be expected to slow down $D_2 \leftrightarrow A$ electron transfer by one to two orders of magnitude, all other factors being equal. The exponential distance (R_{DA}) dependence of electron transfer rates $k_{ET} \propto \exp(-\beta R_{DA})$ varies with the medium interposed, but β values in the range of 0.8 to 1.4 $Å^{-1}$ have been found in condensed media [8–11]. In fact experimental evidence exists [3,12] for a rate reduction by a factor of 10 to 20 upon elongation of the donor/acceptor distance in donor–bridge–acceptor systems when a 1,4-phenylene bridge component is replaced by a 4,4′-biphenylene unit.

We will now discuss the behaviour of the new D_2–D_1–A system **2** in relation to the corresponding D_1–A system **3** and the isolated acceptor model system **4** (scheme 2).

2. Results and discussion

In all cases the locally excited state (LE) of the acceptor possesses the lowest excitation energy. In the isolated acceptor, represented by **4**, this LE state is highly emissive and in most solvents displays a structured emission (see fig. 1 and table 1) around 420 nm. In both **2** and **3** this local emission is almost fully quenched. For bichromophoric donor–acceptor compound **3** a strong, broad and structureless emission instead occurs at longer wavelength. Because of its shape, position and solvatochromism (see ref. [6]) the new emission can be attributed to radiative charge recombination (CT emission) of the D_1^+–A^- state. This CT state is formed in nearly quantitative yield from the precursor D_1–A^* LE state and decays with a lifetime of ≈14 ns in dioxane (see table 1). In the trichromophoric system **2** the LE emission of A^* is again almost fully quenched. Interestingly, a weak long wavelength emission can be detected (see fig. 1) in the same region where **3** dis-

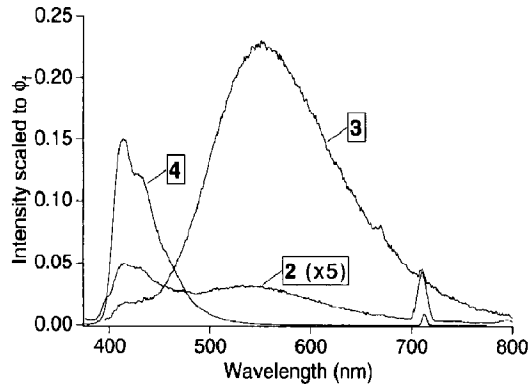

Fig. 1. Fluorescence spectra of **2**, **3** and **4** in dioxane (λ^{ex}=355 nm). The maximum intensities of the emission bands correspond with the fluorescence quantum yield.

Table 1
Emission characteristics of **2**, **3** and **4** in dioxane (see fig. 1)

Compound	L(ocal) E(mission) ($A^* \rightarrow A$)		CT emission (D_1^+–$A^- \rightarrow D_1$–A)	
	λ_{max} (nm)	τ (ps)	λ_{max} (nm)	τ (ps)
2	423	<10	546	450
3	425 (sh)	<10	555	14000
4	411, 428	410	–	–

plays its charge transfer emission. Therefore this is attributed to radiative recombination from a state with D_2–D_1^+–A^- character. The short lifetime of this emission in **2** as compared to **3** indicates that its weakness is not caused by inefficient formation of the D_2–D_1^+–A^- state but rather by an additional radiationless decay path not available in **3**. From this we infer that in **2** the D_2–D_1^+–A^- state is efficiently (>95%) converted to the fully charge separated state D_2^+–D_1–A^-. The latter apparently is not fluorescent – in contrast to that in **1a**, **b** – and can therefore not be detected by emission spectroscopy.

As the totally charge separated state of **2** is nonemissive – indicating that weak coupling between the outer chromophores has indeed been achieved – flash photolysis experiments were performed to observe the D_2^+–D_1–A^- state and determine its lifetime. For comparison the transient optical absorption of the D_1^+–A^- state of **3** was also investigated. After photoexcitation of the acceptor chromophore of **3** in dioxane, a band at 416 nm of the biphenyl radical cation [13] and a superposition of bands of the biphenyl radical cation (700 nm [13]) and the boron oxalate radical anion (641, 706 nm [7]) are readily observed (see fig. 2a). The sharp biphenyl radical cation band at 416 nm has a larger extinction coefficient than the combined absorptions of D_1^+ and A^- at ≈700 nm. These absorptions can be seen to decay on a time scale comparable with the lifetime (14 ns) of the CT emission attributed to the D_1^+–A^- state (see table 1). After the radical cation and radical anion absorptions have disappeared, as the CT state has decayed, a long-lived structureless absorption at 700 nm is present. This absorption originates from the triplet state of the boron oxalate electron acceptor as is known from transient absorption measurements of **4** [7]. The formation of the triplet state of the acceptor chromophore in **3** must take place from the CT state, because direct intersystem crossing of the $^1A^*$ excited state is prevented by the rapid charge separation process.

After photoexcitation of **2** the distinct structured absorption of the boron oxalate radical anion A^- (641, 706 nm) dominates the transient absorption spectrum (see fig. 2b). An additional weak absorption at ≈420 nm is present in fig. 2b. This absorption in contrast to the biphenyl radical cation absorption in the spectrum of **3** (fig. 2a) is weak

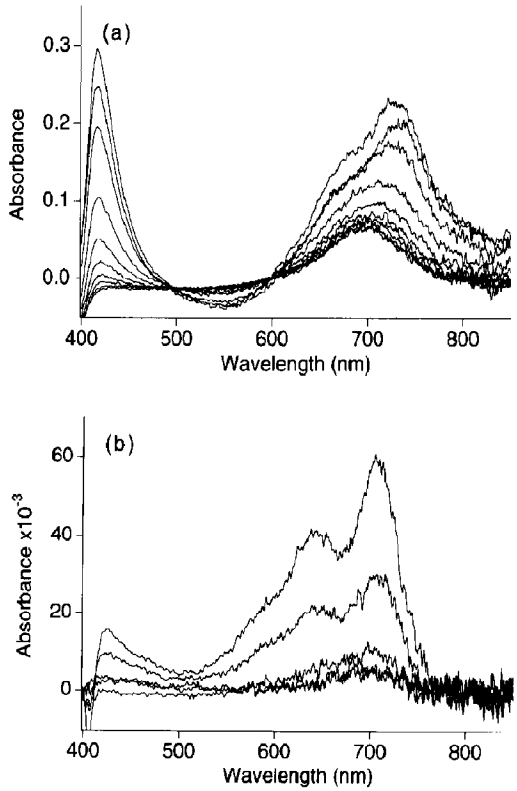

Fig. 2. Transient absorption spectra of (a) **3** and (b) **2** in dioxane (λ^{ex}=355 nm). In both figures the spectrum with the greatest absorbance is taken at the maximum of the laser pulse (fwhm≈8 ns), while the successive spectra are recorded with 5 ns increment delay.

compared to that of the A^- absorption in the long wavelength region of the spectrum. The 420 nm band might originate from the intermediate D_2–D_1^+–A^- state, which is short-lived and therefore present in low concentration only. Alternatively this band can be attributed to the D_2^+ species: preliminary studies [7] on methoxynaphthalene radical cations reveal an absorption band in this region which is much weaker than that of the biphenyl radical cation. Thus, although a small contribution of the D_2–D_1^+–A^- state to the absorption spectrum cannot be excluded, we are most likely observing the D_2^+–D_1–A^- state of which the spectrum is dominated by the structured band of A^-. This confirms that D_2^+–D_1–A^- is formed efficiently (≈90% after two steps).

To our surprise the decay time of D_2^+–D_1–A^- is very short: it decays within the width of the laser pulse (≈8 ns fwhm) used in the nanosecond exper-

iments (see fig. 2b). Preliminary picosecond transient absorption measurements show a decay time of ≈ 1 ns (monitored at 640 nm). Thus although efficient stepwise charge separation has now been achieved by elongation of the distance between the outer chromophores in **2** as compared to **1**, the charge recombination rate has at the same time increased! We tentatively attribute this remarkable phenomenon to a a pronounced increase of the Franck–Condon factor for the charge recombination process.

The rate of electron transfer can be expressed (see e.g. ref. [9]) by

$$k_{ET} = \frac{4\pi^2}{h} H_{DA}^2 \, \mathrm{FCWD} \, , \qquad (1)$$

in which FCWD represents the Franck–Condon factor and H_{DA} the electronic coupling. In a commonly applied semi-classical model [9] the Franck–Condon factor depends on internal reorganisation energy λ_ν along a high-frequency vibrational mode, the low-frequency (solvent) reorganisation energy λ_s and the driving force ΔG^0. For the charge recombination process, which occurs in the "inverted region", a decrease of the energy gap and an increase of the reorganisation energies lead to a larger Franck–Condon factor.

In going from **1** to **2** we have reduced the absolute value of ΔG^0. In order to maintain sufficient driving force in the charge separation steps, the D_2 moiety was changed from methylnaphthalene (oxidation potential $E(D_2)_{ox} = 1.51$ V in acetonitrile versus SCE [14]; ($E(D_1)_{ox} = 1.79$ V [15])) in **1a** to methoxynaphthalene ($E(D_2)_{ox} = 1.35$ V; $E(D_1)_{ox} = 1.66$ V [16]) in **2**. This implies that (neglecting Coulombic and solvation effects) the energy gap between D_2^+–D_1–A^- and the ground state is ≈ 0.16 eV smaller in **2** than in **1**.

Marcus has described a dielectric continuum model for λ_s [17],

$$\lambda_s = \frac{(\Delta e)^2}{4\pi\epsilon_0}\left(\frac{1}{d_{D+}} + \frac{1}{d_{A-}} - \frac{1}{R_{D+A-}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right), \qquad (2)$$

in which Δe is the transferred electronic charge, ϵ_0 is the permittivity of free space, n and ϵ are the solvent refractive index and dielectric constant, d_{D+} and d_{A-} are the diameters of donor and acceptor and R_{D+A-} is their centre-to-centre separation. As the charges are ≈ 4 Å further apart in the D_2^+–D_1–A^- state in **2** compared to **1**, the solvent reorganisation energy in **2** is larger than in **1a**, **b**. Numerical evaluations of the Franck–Condon factor [7] reveal that a decrease of the energy gap by 0.16 eV and an increase of λ_s of 0.15 eV, together can lead to a rate increase by a factor of ≈ 15. The effect of changing oxidation potentials and solvent reorganisation energies on the charge recombination process in aromatic radical ion pairs was recently demonstrated by Gould et al. [18]. In their case however, the two charges have opposite effects on the rate, leading to a relatively small increase of k_d with decreasing energy gap.

Finally we note that Wasielewski et al. have reported D–bridge–A systems [19,20] where lowering the oxidation potential of the bridging unit significantly enhances the charge recombination rate, although the charge separation rate is not affected. This effect was attributed to superexchange involving D–B^+–A^- virtual states. The operation of such a mechanism in compounds **1** and **2** could be another factor contributing to the unexpected fate of long-range charge separated state in **2**.

In conclusion, efficient photoinduced two-step electron transfer occurs in the novel trichromophoric system **2**. While the electronic coupling H_{D_2A} in **2** is evidently reduced as compared to that in **1**, the expected increase of the lifetime of the D_2^+–D_1–A^- state is not realised, probably mainly as a result of the concomitant increase of the FCWD due to changes in oxidation potentials and solvent reorganisation energy. These findings are of obvious importance for the design of multi-centre redox systems directed at achievement of large and long-lived charge separation and will be discussed in more detail in future publications.

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