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Two-step photoinduced charge separation and unexpectedly fast one-step charge recombination in a linked donor₂-donor₁-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 donor₂-donor₁-acceptor (D₂-D₁-A) system. The D₂-D₁⁺-A⁻ state is fluorescent, while the D₂⁺-D₁-A⁻ state is observed by transient absorption. The final giant dipole state, which is formed in ≈90% yield, is remarkably short-lived.

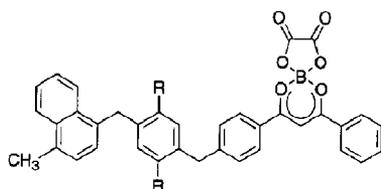
1. Introduction

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: D₂-D₁-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 D₂⁺-D₁-A⁻. The decay of this state is easily monitored because charge recombination is

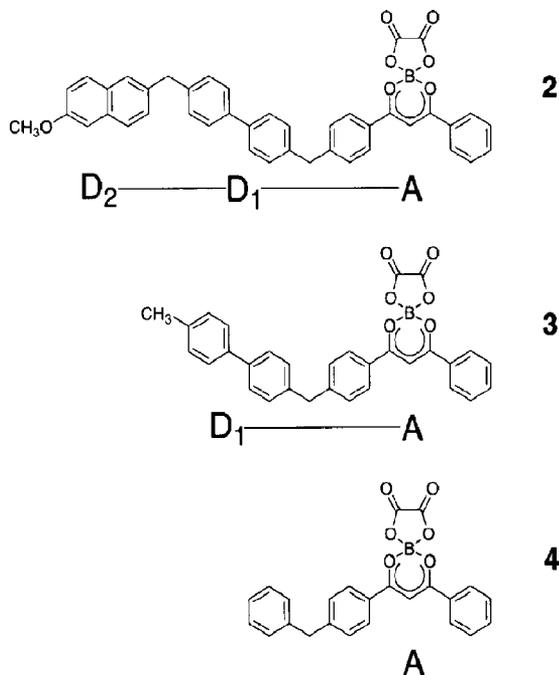
accompanied by a characteristic charge transfer fluorescence D₂⁺-D₁-A⁻ → D₂-D₁-A + hν_{CT} (τ_{CR} = 42 ns, φ_f = 0.015 in benzene, λ_{max} = 635 nm). The relatively fast charge recombination between D₂ and A and the partly radiative nature of this process indicate that there is substantial electronic coupling between the two units. Although the D₂-D₁⁺-A⁻ state is thermodynamically accessible in **1a**, as shown by the behaviour of the corresponding D₁-A compound [6] it is not observed as an intermediate state. In order to establish the involvement of the D₂-D₁⁺-A⁻ state in the charge separation between D₂ and A, D₁ was replaced by a much weaker donor, i.e. in **1b**. In this compound the D₂-D₁⁺-A⁻ state is of higher energy than the A* state (except in very polar solvents [7]) thereby rendering the D₂-D₁-A* → D₂-D₁⁺-A⁻ charge separation process endothermic. Nevertheless the long range charge separation and charge recombination processes in **1b** (τ_{CR} = 27 ns in benzene) occur with rates similar to those in **1a**. This indicates that the intermediate D₂-D₁⁺-A⁻ state probably plays no role in the charge separation between D₂ and A, and single step long range electron transfer prevails.

In order to reduce the direct electronic coupling between D₂ and A system **2** was now synthesised, in which the D₂/A distance is increased as compared



Scheme 1.

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



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 $\approx 4 \text{ \AA}$. Because of the exponential distance dependence [8–10] of the electronic coupling this may be expected to slow down $D_2 \rightarrow A$ 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 \AA^{-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 $\approx 14 \text{ ns}$ 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-

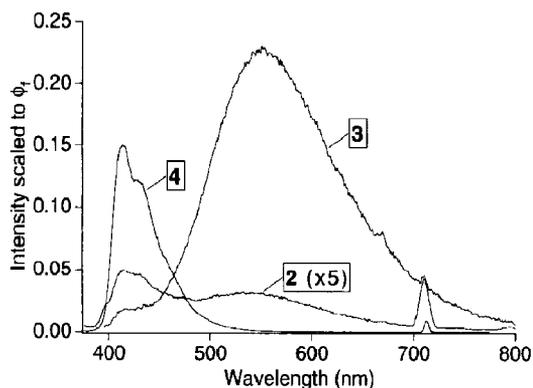


Fig. 1. Fluorescence spectra of **2, 3** and **4** in dioxane ($\lambda^{ex} = 355 \text{ nm}$). The maximum intensities of the emission bands correspond with the fluorescence quantum yield.

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 non-emissive – 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

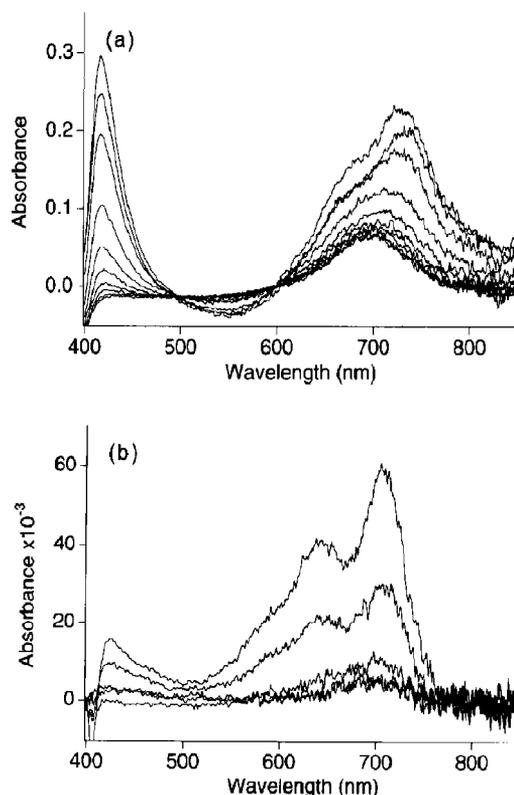


Fig. 2. Transient absorption spectra of (a) **3** and (b) **2** in dioxane ($\lambda^{ex} = 355$ nm). In both figures the spectrum with the greatest absorbance is taken at the maximum of the laser pulse (fwhm ≈ 8 ns), while the successive spectra are recorded with 5 ns increment delay.

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 ($\approx 90\%$ 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 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

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

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_{i} , along a high-frequency vibrational mode, the low-frequency (solvent) reorganisation energy λ_{s} and the driving force ΔG° . 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° . In order to maintain sufficient driving force in the charge separation steps, the D_2 moiety was changed from methylnaphthalene (oxidation potential $E(\text{D}_2)_{\text{ox}} = 1.51$ V in acetonitrile versus SCE [14]; ($E(\text{D}_1)_{\text{ox}} = 1.79$ V [15])) in **1a** to methoxynaphthalene ($E(\text{D}_2)_{\text{ox}} = 1.35$ V; $E(\text{D}_1)_{\text{ox}} = 1.66$ V [16]) in **2**. This implies that (neglecting Coulombic and solvation effects) the energy gap between $\text{D}_2^+ - \text{D}_1 - \text{A}^-$ 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],

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

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 $R_{\text{D}^+\text{A}^-}$ is their centre-to-centre separation. As the charges are ≈ 4 Å further apart in the $\text{D}_2^+ - \text{D}_1 - \text{A}^-$

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_{r} 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 $\text{D}^+ - \text{B}^+ - \text{A}^-$ 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 $H_{\text{D}_2\text{A}}$ in **2** is evidently reduced as compared to that in **1**, the expected increase of the lifetime of the $\text{D}_2^+ - \text{D}_1 - \text{A}^-$ 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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