

## UvA-DARE (Digital Academic Repository)

### Two-step photoinduced charge separation and unexpectedly fast one-step charge recombination in a linked Donor2-Donor1-Acceptor system

van Dijk, S.I.; Wiering, P.G.; van Staveren, R.; van Ramesdonk, H.J.; Brouwer, A.M.; Verhoeven, J.W.

**DOI**

[10.1016/0009-2614\(93\)85673-C](https://doi.org/10.1016/0009-2614(93)85673-C)

**Publication date**

1993

**Published in**

Chemical Physics Letters

[Link to publication](#)

**Citation for published version (APA):**

van Dijk, S. I., Wiering, P. G., van Staveren, R., van Ramesdonk, H. J., Brouwer, A. M., & Verhoeven, J. W. (1993). Two-step photoinduced charge separation and unexpectedly fast one-step charge recombination in a linked Donor2-Donor1-Acceptor system. *Chemical Physics Letters*, 214(5), 502-506. [https://doi.org/10.1016/0009-2614\(93\)85673-C](https://doi.org/10.1016/0009-2614(93)85673-C)

**General rights**

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

**Disclaimer/Complaints regulations**

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

*UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)*

# Two-step photoinduced charge separation and unexpectedly fast one-step charge recombination in a linked donor<sub>2</sub>-donor<sub>1</sub>-acceptor system

Saskia I. van Dijk, Piet G. Wiering, Richard van Staveren, Hendrik J. van Ramesdonk, Albert M. Brouwer and Jan W. Verhoeven

Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

Received 30 July 1993; in final form 9 September 1993

Photoinduced sequential two-step electron transfer occurs upon excitation of the 1,3-diphenylpropanedioato boron oxalate electron acceptor in a novel trichromophoric donor<sub>2</sub>-donor<sub>1</sub>-acceptor (D<sub>2</sub>-D<sub>1</sub>-A) system. The D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> state is fluorescent, while the D<sub>2</sub><sup>+</sup>-D<sub>1</sub><sup>-</sup>-A<sup>-</sup> state is observed by transient absorption. The final giant dipole state, which is formed in ≈90% yield, is remarkably short-lived.

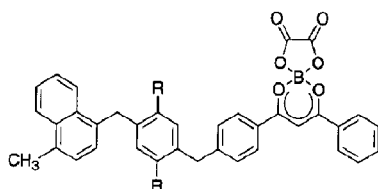
## 1. Introduction

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<sub>2</sub>-D<sub>1</sub>-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<sub>2</sub><sup>+</sup>-D<sub>1</sub><sup>-</sup>-A<sup>-</sup>. The decay of this state is easily monitored because charge recombination is

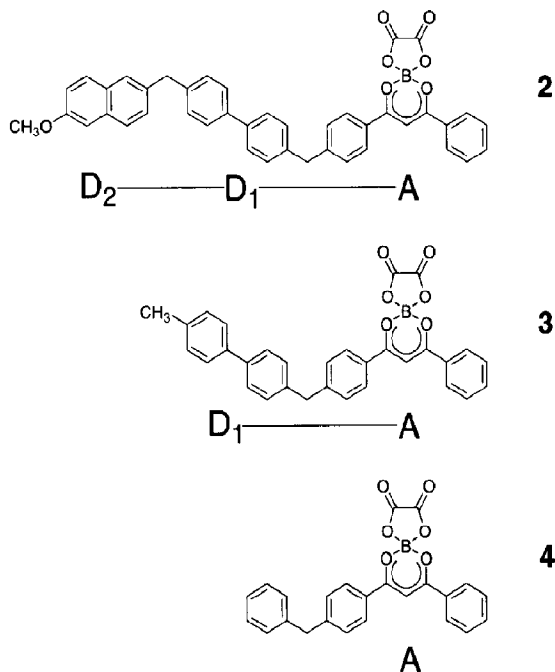
accompanied by a characteristic charge transfer fluorescence D<sub>2</sub><sup>+</sup>-D<sub>1</sub><sup>-</sup>-A<sup>-</sup> → D<sub>2</sub>-D<sub>1</sub>-A + hν<sub>CT</sub> (τ<sub>CR</sub> = 42 ns, φ<sub>f</sub> = 0.015 in benzene, λ<sub>max</sub> = 635 nm). The relatively fast charge recombination between D<sub>2</sub> and A and the partly radiative nature of this process indicate that there is substantial electronic coupling between the two units. Although the D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> state is thermodynamically accessible in **1a**, as shown by the behaviour of the corresponding D<sub>1</sub>-A compound [6] it is not observed as an intermediate state. In order to establish the involvement of the D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> state in the charge separation between D<sub>2</sub> and A, D<sub>1</sub> was replaced by a much weaker donor, i.e. in **1b**. In this compound the D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> state is of higher energy than the A\* state (except in very polar solvents [7]) thereby rendering the D<sub>2</sub>-D<sub>1</sub>-A\* → D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> charge separation process endothermic. Nevertheless the long range charge separation and charge recombination processes in **1b** (τ<sub>CR</sub> = 27 ns in benzene) occur with rates similar to those in **1a**. This indicates that the intermediate D<sub>2</sub>-D<sub>1</sub><sup>+</sup>-A<sup>-</sup> state probably plays no role in the charge separation between D<sub>2</sub> and A, and single step long range electron transfer prevails.

In order to reduce the direct electronic coupling between D<sub>2</sub> and A system **2** was now synthesised, in which the D<sub>2</sub>/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  $\beta$  values in the range of  $0.8$  to  $1.4 \text{ \AA}^{-1}$  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  $420 \text{ nm}$ . 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-

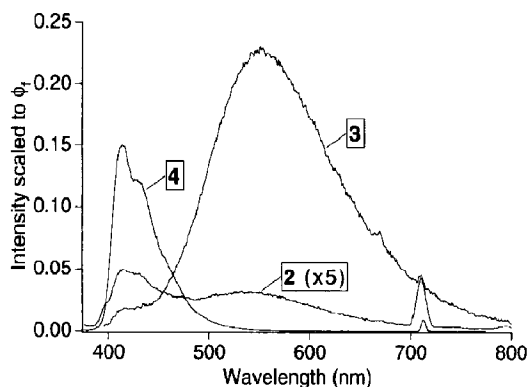


Fig. 1. Fluorescence spectra of **2**, **3** and **4** in dioxane ( $\lambda^{ex} = 355 \text{ nm}$ ). The maximum intensities of the emission bands correspond with the fluorescence quantum yield.

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

Compound	L(ocal) E(mission) ( $A^* \rightarrow A$ )		CT emission ( $D_1^+ - A^- \rightarrow D_1 - A$ )	
	$\lambda_{max}$ (nm)	$\tau$ (ps)	$\lambda_{max}$ (nm)	$\tau$ (ps)
<b>2</b>	423	<10	546	450
<b>3</b>	425 (sh)	<10	555	14000
<b>4</b>	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  $\approx 700$  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  $\approx 420$  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

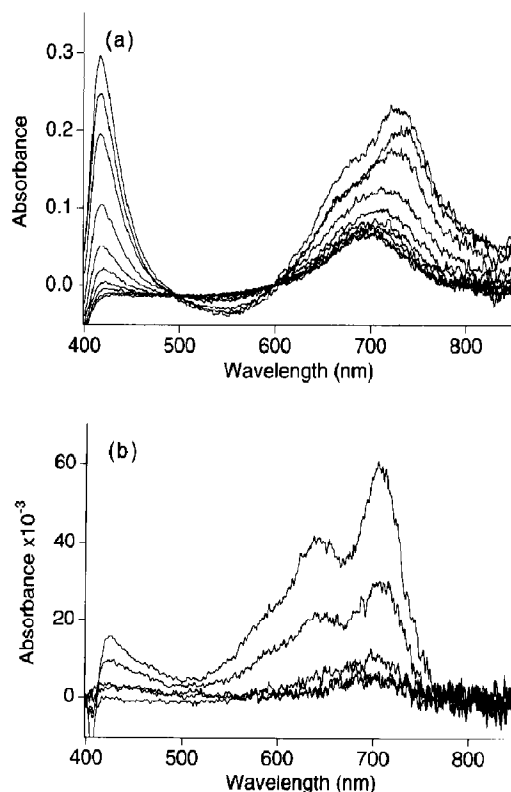


Fig. 2. Transient absorption spectra of (a) **3** and (b) **2** in dioxane ( $\lambda^{ex} = 355$  nm). In both figures the spectrum with the greatest absorbance is taken at the maximum of the laser pulse (fwhm  $\approx 8$  ns), while the successive spectra are recorded with 5 ns increment delay.

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 ( $\approx 8$  ns fwhm) used in the nanosecond exper-

iments (see fig. 2b). Preliminary picosecond transient absorption measurements show a decay time of  $\approx 1$  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  $H_{\text{DA}}$  the electronic coupling. In a commonly applied semi-classical model [9] the Franck-Condon factor depends on internal reorganisation energy  $\lambda_{\text{i}}$ , along a high-frequency vibrational mode, the low-frequency (solvent) reorganisation energy  $\lambda_{\text{s}}$  and the driving force  $\Delta G^{\circ}$ . 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  $\Delta G^{\circ}$ . In order to maintain sufficient driving force in the charge separation steps, the  $\text{D}_2$  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  $\approx 0.16$  eV smaller in **2** than in **1**.

Marcus has described a dielectric continuum model for  $\lambda_{\text{s}}$  [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  $\Delta e$  is the transferred electronic charge,  $\epsilon_0$  is the permittivity of free space,  $n$  and  $\epsilon$  are the solvent refractive index and dielectric constant,  $d_{\text{D}^+}$  and  $d_{\text{A}^-}$  are the diameters of donor and acceptor and  $R_{\text{D}^+\text{A}^-}$  is their centre-to-centre separation. As the charges are  $\approx 4$  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  $\lambda_{\text{s}}$  of 0.15 eV, together can lead to a rate increase by a factor of  $\approx 15$ . 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  $k_{\text{r}}$  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.

### Acknowledgement

The authors wish to thank Dr. R. Pansu and J.F. Delouis from the Laboratoire de Physico-Chimie des Rayonnements, Université Paris-Sud, Orsay, France for performing picosecond transient absorption experiments.

## References

- [1] M.R. Wasielewski, *Chem. Rev.* 92 (1992) 435.
- [2] A.M. Brouwer, C. Eijkelhoff, R.J. Willemse, J.W. Verhoeven, W. Schuddeboom and J.M. Warman, *J. Am. Chem. Soc.* 115 (1993) 2988.
- [3] A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.* 115 (1993) 4577.
- [4] R.M. Hermant, P.A. Liddell, S. Lin, R.G. Alden, H.K. Kang, A.L. Moore, T.A. Moore and D. Gust, *J. Am. Chem. Soc.* 115 (1993) 2080.
- [5] N.A.C. Bakker, P.G. Wiering, A.M. Brouwer, J.M. Warman and J.W. Verhoeven, *Mol. Cryst. Liquid Cryst.* 183 (1990) 31.
- [6] A.M. Brouwer, N.A.C. Bakker, P.G. Wiering and J.W. Verhoeven, *J. Chem. Soc. Chem. Commun.* (1991) 1094.
- [7] S.I. van Dijk, to be published.
- [8] M.N. Paddon-Row, A.M. Oliver, J.M. Warman, K.J. Smith, M.P. de Haas, H. Oevering and J.W. Verhoeven, *J. Phys. Chem.* 92 (1988) 6958.
- [9] G.L. Closs and J.R. Miller, *Science* 240 (1988) 440.
- [10] C.C. Moser, J.M. Keske, K. Warncke, R.S. Farid and P.L. Dutton, *Nature* 355 (1992) 796.
- [11] B.A. Leland, A.R. Joran, P.M. Felker, J.J. Hopfield, A.H. Zewail and P.B. Dervan, *J. Phys. Chem.* 89 (1985) 5571.
- [12] H. Heitele and M.E. Michel-Beyerle, *J. Am. Chem. Soc.* 107 (1985) 8286.
- [13] T. Shida, *Electronic absorption spectra of radical ions* (Elsevier, Amsterdam, 1988).
- [14] M.A. Fox, C.-C. Chen and J.N.N. Younathan, *J. Org. Chem.* 49 (1984) 1971.
- [15] J.O. Howell, J.M. Goncalves, C. Amatore, L. Klasinc, R.M. Wightman and J.K. Kochi, *J. Am. Chem. Soc.* 106 (1984) 3968.
- [16] I.R. Gould, D. Ege, J.E. Moser and S. Farid, *J. Am. Chem. Soc.* 112 (1990) 4290.
- [17] R.A. Marcus, *J. Chem. Phys.* 24 (1956) 966.
- [18] I.R. Gould, D. Noukakis, L. Gomez-Jahn, J.L. Goodman and S. Farid, *J. Am. Chem. Soc.* 115 (1993) 4405.
- [19] D.G. Johnson, M.P. Niemczyk, D.W. Minsek, G.P. Wiederrecht, W.A. Svec, G.L. Gaines III and M.R. Wasielewski, *J. Am. Chem. Soc.* 115 (1993) 5692.
- [20] M.R. Wasielewski, M.P. Niemczyk, D.G. Johnson, W.A. Svec and D.W. Minsek, *Tetrahedron* 45 (1989) 4785.