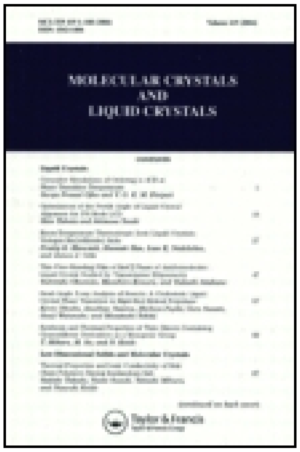

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Multistep Photoinduced Electron Transfer in a Photoacceptor Terminated Molecular Triode

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Version of record first published: 04 Oct 2006.

To cite this article: N. A. C. Bakker , P. G. Wiering , A. M. Brouwer , J. M. Warman & J. W. Verhoeven (1990): Multistep Photoinduced Electron Transfer in a Photoacceptor Terminated Molecular Triode, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 31-40

To link to this article: http://dx.doi.org/10.1080/15421409008047438

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 31–40
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Printed in the United States of America

MULTISTEP PHOTOINDUCED ELECTRON TRANSFER IN A PHOTOACCEPTOR TERMINATED MOLECULAR TRIODE

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Abstract A molecular "triode" (3) is described containing a nonconjugatively interconnected array (D_2–D_1-P_a) of two potential one-electron donor (D) moieties and a powerful photoacceptor (P_a). In a related "diode" (2) consisting of the array D_1-P_a excitation of the photoacceptor, P_a, induces charge-separation as detected by time resolved microwave conductivity (TRMC) measurements and as evidenced from the observation of charge transfer emission resulting from radiative recombination. The latter emission is quenched in the triode **3** indicating occurrence of virtually complete consecutive electron transfer from D_2 to D_1. Instead **3** displays a much weaker charge transfer emission at longer wavelength attributed to direct radiative recombination from D_2 to P_a. Fluorescence lifetime measurements and TRMC data show that the recombination in **3** is significantly slowed down as compared to the shorter range recombination in **2**.

INTRODUCTION

Long-range and potentially long-lived photoinduced charge separation could be obtained via a series of thermodynamically down-hill, short-range electron transfer steps along an extended array of redox centres. In the wake of the recent progress[1] on the structure and function of the natural photosynthetic apparatus, this concept has received considerable renewed interest. If we limit our attention to systems comprising three redox centres ("triodes") already four modes of operation may be envisaged differing

$$D\text{–}P_d\text{–}A \xrightarrow{h\nu} \;\longrightarrow\; D\text{–}P_d^{+}\text{–}A^{-} \;\longrightarrow\; D^{+}\text{–}P_d\text{–}A^{-} \qquad (1)$$

$$D\text{–}P_a\text{–}A \xrightarrow{h\nu} \;\longrightarrow\; D^{+}\text{–}P_a^{-}\text{–}A \;\longrightarrow\; D^{+}\text{–}P_a\text{–}A^{-} \qquad (2)$$

$$P_d\text{–}A_1\text{–}A_2 \xrightarrow{h\nu} \;\longrightarrow\; P_d^{+}\text{–}A_1^{-}\text{–}A_2 \;\longrightarrow\; P_d^{+}\text{–}A_1\text{–}A_2^{-} \qquad (3)$$

$$D_2\text{–}D_1\text{-}P_a \xrightarrow{h\nu} \;\longrightarrow\; D_2\text{–}D_1^{+}\text{-}P_a^{-} \;\longrightarrow\; D_2^{+}\text{–}D_1\text{-}P_a^{-} \qquad (4)$$

SCHEME 1

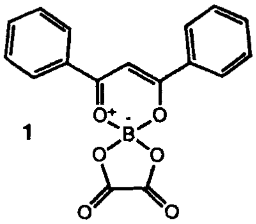
with respect to the position and function of the photoactivated centre. These are schematized in Scheme 1, where D and A indicate centres whose *primary* role is electron donation and –acceptation respectively, while P is the photoactive centre, that may either act as a primary acceptor (P_a) or donor (P_d).

Recently much attention has been focussed[2] on the synthesis of triodes (and higher order systems[3]) containing porphyrin derivatives as a P_d unit inspired by the role of this type of chromophore in natural photosynthesis. A limited number[2b] of active type (1) triodes was thus realized as well as at least one type (3) system[4]. Interestingly these successful studies were preceded by a few efforts[5,6] - including ours - to realize systems with a P_a photoreceptor in a type (4) configuration. Since photoactivated electron acceptors have found applications in intermolecular electron transport schemes effecting electron transfer induced photochemistry[7a], and photopolymerization[7b], we felt it to be of great importance to pursue further the incorporation of such P_a units in multicentre photoactivated electron transport chains. In the present paper we provide the first evidence for the feasibility of such a type (4) scheme to achieve long-range charge separation with a very high (>90%) quantum efficiency.

RESULTS AND DISCUSSION

Choice of the Photoacceptor

A type (4) triode, operating in an overall singlet mode, evidently requires P_a to be a chromophore that can be excited selectively at longer wavelength than either D_1 or D_2. Furthermore D_1 should be a relatively weak electron donor. This not only serves to avoid excessive energy wastage in the first charge separation step, but also to allow sufficient freedom in choosing D_2 groups that have an oxidation potential low enough to make the second step fast and irreversible. These conditions imply that P_a should combine a relatively long-wavelength absorption with strong excited state acceptor properties. Chromophores which nicely fulfil these requirements are constituted by the synthetically flexible acceptors that result from reaction of β-diketonate anions and various Lewis acids. Compound **1** epitomizes the plethora of such acceptors. The one electron reduction potential of **1** was determined by cyclic voltammetry to be as low as –0.6 V (vs. SCE in acetonitrile).This characterizes it as a powerful electron acceptor already in the ground state, that may be compared[8] to e.g. p-benzoquinone (- 0.51V) and 1,4-naphthoquinone (- 0.71V).



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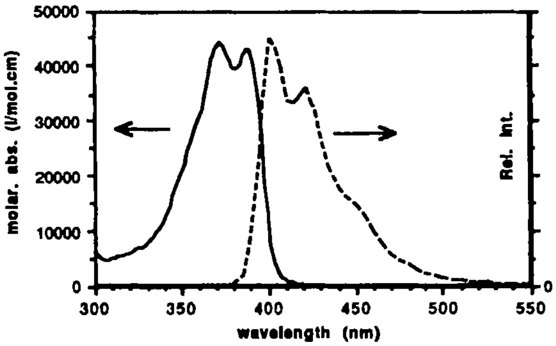


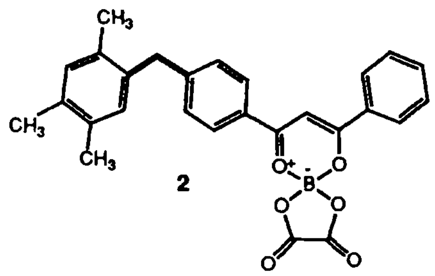
FIGURE 1 Absorption (——) and fluorescence (- - -) spectrum of 1 in ethylacetate.

TABLE I Electronic emission data for 1
Fluorescence maximum in nm, quantum yield in %, lifetime in ps.

solvent	λ	Φ	τ
di-n-butylether	400	34	778
diisopropylether	399	20	503
diethylether	401	34	985
ethylacetate	403	60	1731

As shown in Fig. 1, compound 1 displays strong absorption in the near UV (ε_{max} 43000 at 372 nm in ethylacetate) with minor solvent dependence, as well as rather efficient fluorescence in the visible (see also Table I).

The first absorption band and the fluorescence of 1 show a near mirror image relation typical for systems that undergo little conformational reorganization in the excited state. From the position of the mirror point (~395 nm) an effective E_{00} of 3.14 eV is estimated. Together with the electrochemical data this sets the effective oxidation potential of 1 in its S_1 excited state at + 2.54 V (rel. to SCE), which implies, that even moderate donor-type molecules should be able to quench the S_1 state of 1 via electron transfer.


2

A Diode System

The high electron accepting power of 1 in the excited state is substantiated nicely by the behaviour of the bichromophoric molecule 2, which contains an additional, non-conjugatively connected tetra-alkylbenzene unit as a potential electron donor.

For this molecule the typical structured fluorescence of the acceptor chromophore is strongly quenched and an additional broad, longwavelength emission appears, that shifts to longer wavelength and diminishes in intensity with increasing solvent polarity (see Fig. 2).

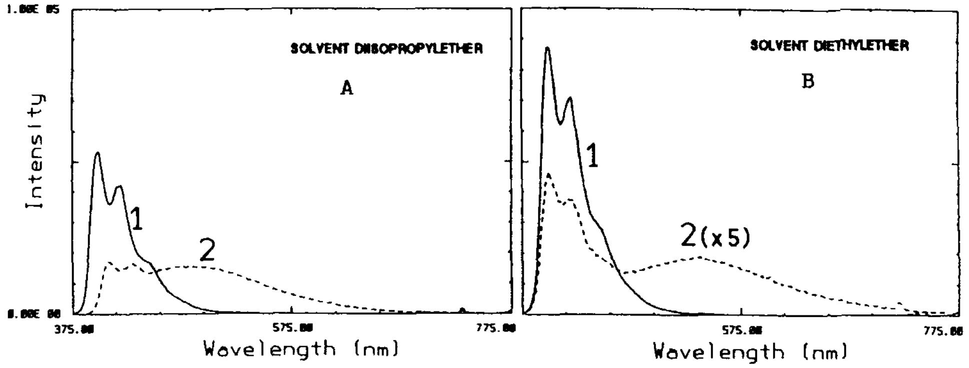
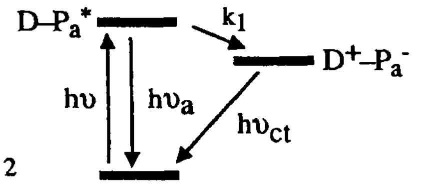


FIGURE 2 Comparison of the fluorescence spectra of **1** and **2** in diisopropylether (Fig. 2A) and in diethylether (Fig. 2B), note that in the latter the fluorescence intensity of **2** has been multiplied by a factor of five.

These phenomena are typical for occurrence of rapid photoinduced electron transfer populating a polar excited state that displays charge-transfer type emission ($h\nu_{ct}$) as schematized in Scheme 2, where $h\nu$ denotes excitation of the acceptor P_a, $h\nu_a$ its radiative decay, k_1 the intramolecular electron transfer rate from D to P_a, and $h\nu_{ct}$ the radiative decay of the polar excited state thus populated. The dual fluorescent properties of **2** provide direct access to the kinetics of these photophysical events. Thus for **2** the structured fluorescence of the acceptor is quenched to about 30% and about 10% of the intensity in **1** in the solvents diisopropylether and diethylether respectively (see Figs. 2A and 2B). This implies that charge separation in **2** occurs with 70% resp. 90% efficiency. From the known excited state lifetime of **1** (Table I), the charge separation rate constant k_1 in **2** may then be calculated to be $4.6x10^9$ and $9.1x10^9$ s^{-1} in diisopropylether and in diethylether respectively.

Furthermore the emissive nature of the charge separated state allows us to determine the



SCHEME 2

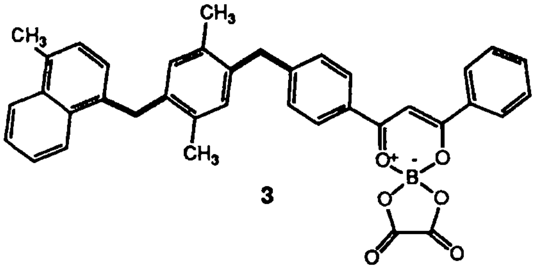
rate of charge recombination. Thus, using a the detection wavelength at a position beyond the region in which $h\nu_a$ occurs, allowed determination of the lifetime of the charge transfer fluorescence ($h\nu_{ct}$), which gave τ_{ct} = 7.5 ns and 3 ns in diisopropylether and in diethylether. This implies that the charge recombination in **2** occurs considerably slower than the charge separation, which is in line with the larger energy gap involved in the former process. This evidently is an important advantage in view of the planned extension with an additional redox centre, since it provides a considerable latitude for the time window in which further charge separation steps could occur.

In conclusion system **2** constitutes a bichromophoric unit that fulfils the requirements for extension into a type(4) triode and at the same time displays emissive properties extremely helpful in kinetic analysis of charge separation and charge recombination dynamics.

A Triode System

System **3** is the first type(4) triode now realized on the basis of **1** and **2**. It extends **2** with a slightly more powerful electron donor (D_2) unit constituted by a 1,4-dialkylnaphthalene moiety. It is of interest to discuss here the driving force for electron transfer from D_2 to the radical cation of D_1 (= D_1^{+}) as this forms the basis for the second part of the two-step charge separation intended to occur in type(4) triodes.

Taking 1,2,4,5-tetramethylbenzene (durene) and 1,4-dimethylnaphthalene as models for the D_1 and D_2 units we estimate from the reported electrochemical oxidation potentials of +1.79 V[9] and +1.51 V[10] (rel. to SCE in acetonitrile) a value of 0.28 eV for the driving force of the reaction $D_2 + D_1^{+} \rightarrow D_2^{+} + D_1$. A closely similar value (0.27 eV) is obtained if we use gas-phase ionization potentials[11] (durene I_p=8.05 eV; 1,4-dimethylnaphthalene I_p=7.78 eV). Thus the driving force for the electron transfer from D_2 to D_1^{+} is sufficiently large[12] to allow for a virtually barrierless transfer. It should be realized, however, that the actual situation in the triode is more complex because the hole created on D_1 during the first photoinduced electron transfer will still be within the Coulomb field of the negative charge created on P_a. Especially in solvents of low dielectric constant this might reduce considerably the driving force of a second electron transfer step which increases the charge separation.



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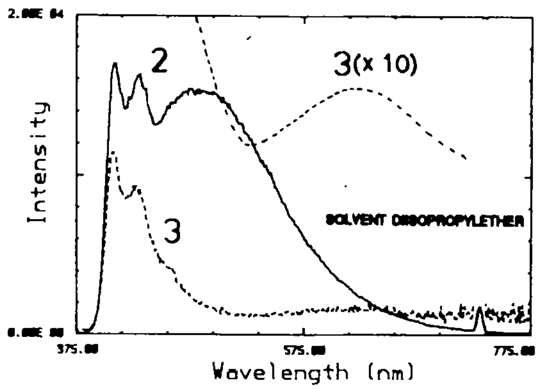
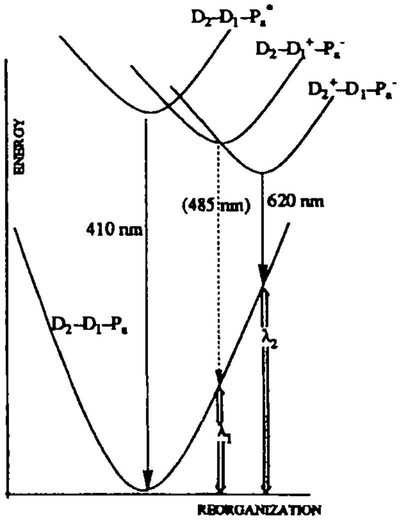


FIGURE 3 Comparison of the fluorescence spectra of diode 2 and triode 3 in diisopropylether. Smoothing was applied to the enhanced spectrum of 3.

As can be seen from Fig.3, system 3 retains the weak local $P_a{}^* \rightarrow P_a$ fluorescence found in 2 indicating that - not unexpectedly - the primary charge separation is little modified. The strong charge transfer fluorescence displayed by 2 in various low polarity solvents (see Fig. 2), however, is fully absent for 3 evidencing that a new and very efficient relaxation pathway has become available for in the latter, which may be identified as a virtually quantitative secondary electron transfer from D_2 to D_1 (see Scheme 1). Interestingly, in a number of solvents a weak structureless emission is observed for 3 at longer wavelength than the CT emission of 2. Thus, while in diisopropylether 2 displays CT emission at 485 nm (2.55 eV), 3 displays a much weaker broad emission at 620 nm (2.0 eV) in this solvent (see Fig. 3). We attribute this 'new' emission to radiative relaxation of the fully charge separated state involving direct recombination of charge be-



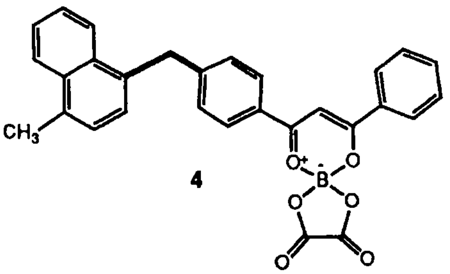
SCHEME 3

Schematic energy diagram for triode system 3 in diisopropylether, rationalizing the dual fluorescence and visualizing the effect of reorganization energies.

Note that a small barrier has been implemented for the first charge separation step, while the second charge separation is assumed to occur virtually barrierless in accordance with the complete absence of the eventual "diode" emission at 485 nm.

tween the terminal chromophores. The electronic coupling for this recombination is obviously small, explaining the weakness of the emission, but we note that the observation of radiative charge recombination across distances similar to that involved here is not without precedent[13,14].

Scheme 3 gives a qualitative representation of the energetics involved in the various photophysical processes following excitation of 3 and furthermore extends Scheme 2 by also visualizing the effect of nuclear reorganization (both internal and solvent) accompanying the charge migration. In Scheme 3 it has been assumed that the overall reorganization energy of in the fully charge separated state (λ_2) is larger than that of the intermediate state (λ_1). This is in line with the fact that the bathochromic shift of the charge transfer fluorescence of 3 relative to 2 of 0.55 eV (in diisopropylether) surpasses the difference in oxidation potential of D_1 and D_2, that was estimated to be 0.28 V (see above).



4

Additional support for this assumption comes from the emissive behaviour of the bichromophoric diode system 4, that incorporates P_a and D_2 in a configuration identical to that of P_a and D_1 in 2. As shown in Fig. 4 this molecule displays a behaviour qualitatively similar to 2 but modified according to the stronger donor properties of D_2. Thus the local emission of P_a is now quenched almost completely, indicating an enhanced rate of charge separation k_1, and the charge transfer emission appears at longer wavelength than that of 2, e.g. in diisopropylether at 576 nm a bathochromic shift of 0.39 eV with respect to 2, comparable to the difference in oxidation potential of D_1 and D_2, indicating that for 2 and 4 the reorganization energies are similar.

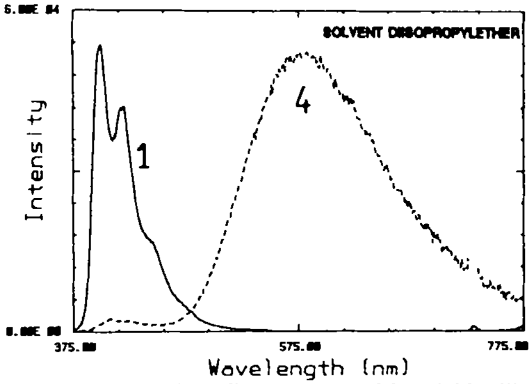


FIGURE 4 Comparison of the fluorescence of 1 and 4 in diisopropylether.

Lifetime of Charge Separation

The CT type fluorescence shown by the bichromophoric systems **2** and **4** as well as by the trichromophoric system **3** provides a unique opportunity to measure the lifetime of the charge separation in these systems from the CT fluorescence lifetimes.

Table II compiles relevant data as obtained by this technique in a number of solvents.

TABLE II Lifetime of charge separation (in ns) as determined from CT-fluorescence [and TRMC]

solvent	2	3	4
benzene	9 [9]	42 [46]	21 [22]
di-n-butylether	7	38	16
diisopropylether	7.5	20	13
diethylether	3	a)	9

a) CT fluorescence too weak to measure lifetime.

While the relatively strong CT fluorescence displayed by **2** allows lifetime measurements in a variety of solvents, this is more limited for **3**.

In order to obtain an independent check of the viability of the lifetimes thus obtained, we have also performed some preliminary measurements with the time resolved microwave conductivity (TRMC) technique[15], which allows direct observation of the formation and decay of (di)polar species in nondipolar solvents. As can be seen from the data compiled in Table II the lifetimes determined from the CT fluorescence and from the TRMC measurements show excellent agreement. Furthermore it is evident that extension of diode **2** into triode **3** leads to a significant increase of the lifetime of the charge separated state. Interestingly the lifetime of charge separation in **4** tends to be larger than that in **2**. Since the efficiency of the charge separation in **4** also exceeds that in **2** (compare Fig. 2A and Fig. 4) diode **4** appears an attractive system for extension into a triode by addition of a more powerful donor as D_2. Since the charge separation lifetime of **4** extends over many nanoseconds, it appears possible to link this donor by means of a much more extended bridge than the simple methylene group employed in **3** without loss of the high quantum efficiency of overall charge separation, but with reduction of the rate of recombination from D_2 to P_a, implying a further significant increase of the charge separation lifetime. Synthesis of such systems is now in progress and will be reported in forthcoming publications.

EXPERIMENTAL

Syntheses of **1-4** will be described in a separate publication, for all compounds the structure was ascertained by NMR spectroscopy and high-resolution mass spectrometric determination of the elemental composition.

Electronic absorption measurements were made on a Hewlett-Packard 8451A diode array spectrometer. Corrected emission spectra were obtained using a SPEX Fluorolog-2 spectrometer. Fluorescence quantum yields were determined by electronic integration of the emission spectra for carefully deoxygenated solutions with an absorption ≤ 0.2 at the excitation wavelength (365 nm) using 9,10-diphenylanthracene as a reference (Φ = 0.9 in cyclohexane[16]).

Fluorescence lifetimes in the picosecond range were obtained by time correlated single photon counting using the equipment described extensively before[17] (excitation wavelength 364 nm).

For fluorescence lifetimes ≥ 3ns a set-up was used which employs single-shot decay measurements[18]. The sample solution is excited by the 308 nm pulse (~7 ns fwhm) of a Lambda Physik EMG-101 XeCl-excimer laser. The emerging fluorescence is detected by an RCA 1P28 photomultiplier, wired for fast response, via a Zeiss MQII monochromator. The signal of the photomultiplier is fed into a Tektronix 11302 500 MHz oscilloscope triggered by the laser light via a photodiode. A Tektronix DCS01 camera system is used to digitize the oscilloscope trace, which is then analyzed using a homewritten program based on iterative reconvolution.

Cyclic voltammetry was performed using a glassy carbon working electrode and an Ag/AgCl/KCl (sat.) reference electrode (-40 mV relative to the saturated calomel electrode (sce)) in acetonitrile containing 0.1 M tetraethylammonium tetrafluoroborate as a supporting electrolyte.

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