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Photoinduced charge separation in a donor–acceptor functionalized 2,3-diphenylbutadiene: charge transport over a doubly bifurcated π-spacer

Bas C. van der Wiel,[a] René M. Williams[b] and Cornelis A. van Walree*[a]

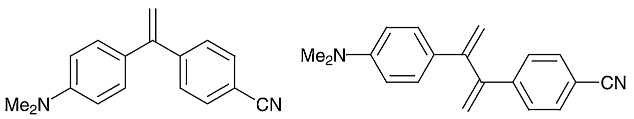
[a] *Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, 3584, CH Utrecht, The Netherlands. E-mail: c.a.vanwalree@chem.uu.nl; Fax: +3130-2534533; Tel: +3130-2531036*

[b] *Molecular Photonic Materials, van't Hoff Institute for Molecular Science, Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018, WV Amsterdam, The Netherlands*

Received 23rd September 2004, Accepted 29th September 2004
First published as an Advance Article on the web 15th October 2004

By studying photoinduced charge transfer processes in 2-(4-cyanophenyl)-3-(4-*N*,*N*-dimethylaminophenyl)-1,3-butadiene it is shown that insertion of branching points in a π-conjugated pathway has a relatively small effect on the donor–acceptor interaction.

The occurrence of charge transport in organic compounds and materials is determined by the electronic coupling between the active components and depends strongly on the pathway connecting them. This path is mostly composed of π-bonds arranged in a linear fashion, but conjugation paths of different topology receive increasing attention.[1–4] Among these are branched π-systems, which are of large interest since they represent topological two-dimensional conducting systems and can give rise to quantum interference effects.[5,6] An important question in this context is to what extent bifurcation points, *i.e.* the atoms where different linear π-conjugation paths meet, can mediate charge transport. Although there are reports on photoinduced charge separation in donor–acceptor functionalized branched π-systems (which can also be referred to as cross-conjugated systems)[7–9] the possibility to transport charges over two or more branching sites has to our knowledge not yet been explored. In this communication we report this phenomenon by showing that photoinduced charge separation occurs in the donor–acceptor functionalized 2,3-diphenylbutadiene **DA2** (Scheme 1).† In this compound three linearly conjugated moieties can be distinguished: a 4-*N*,*N*-dimethylaminostyrene system, a 4-cyanostyrene system and a 1,3-butadiene system. The dimethylaminophenyl donor and the cyanophenyl acceptor are separated by two branching points. To obtain more insight into the charge transporting ability of the conjugation path in **DA2**, the photophysics of this compound are compared with that of donor–acceptor 1,1-diphenylethene **DA1**, of which the conjugation path incorporates only a single branching point. The synthesis and some properties of **DA1** have been reported previously.[9]



DA1 **DA2**

Scheme 1

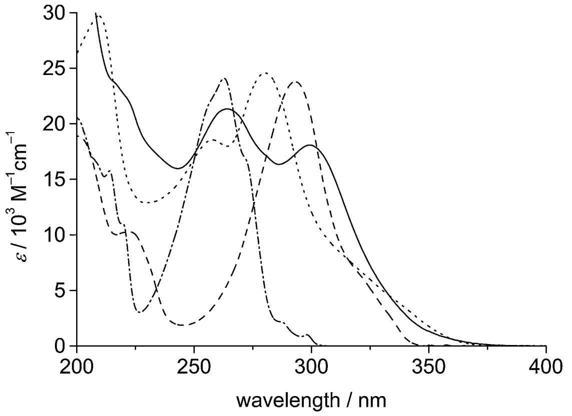


Fig. 1 UV spectra in cyclohexane of **DA2** (solid line) and **DA1** (dotted line) along with spectra of the reference chromophores 4-*N*,*N*-dimethylaminostyrene (dashed line) and 4-cyanostyrene (dash-dotted line).

In Fig. 1 UV spectra of **DA1** and **DA2** are shown, along with spectra of the reference chromophores 4-*N*,*N*-dimethylaminostyrene and 4-cyanostyrene.[9] For both **DA1** and **DA2** a charge transfer (CT) absorption is discernible as a shoulder near 340 nm, at the red edge of the strong 4-*N*,*N*-dimethylaminostyrene ^1L_a transition situated at 280–299 nm. From difference spectra (not shown) molar CT absorption coefficients of 2800 (**DA1**) and 2140 (**DA2**) M^{-1} cm^{-1} were obtained. Although, as expected, the intensity of the CT band in **DA2** is weaker than in **DA1**, it is in fact still quite substantial. Hence, in the compound with two branching points a significant ground state donor–acceptor interaction is still present.

Fluorescence maxima ν_{fl}, quantum yields Φ_{fl} and lifetimes τ_{fl} of **DA1** and **DA2** in various solvents are collected in Table 1. It is evident that the fluorescence of both compounds is strongly solvatochromic, indicative of the formation of a highly dipolar, charge separated state. In Fig. 2 the fluorescence maxima are plotted against the solvent polarity according to the relationship[10]

$$\nu_{fl} = \nu_{fl}(0) - \frac{2\mu_e^2}{hc\rho^3} \times \Delta f \quad \text{with} \quad \Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \qquad (1)$$

in which $\nu_{fl}(0)$ represents the gas phase fluorescence wavenumber, μ_e the excited state dipole moment, h the Planck constant, c

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† The synthesis of **DA2** will be published elsewhere. Analytical data: Found: C, 83.04; H, 6.57; N, 10.06. Calc. for $C_{19}H_{18}N_2$: C, 83.18; H, 6.61, N 10.21%; δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.55–7.45 (2 × 2 H, 2 × d, Ar-H), 7.21 (2 H, d, $J_{1,3}$ 9.06 Hz, Ar-H), 6.59 (2 H, d, $J_{1,3}$ 9.06 Hz, Ar-H), 5.64 (1 H, d, $J_{1,2}$ 1.65 Hz, C=CH$_2$), 5.49 (2 × 1 H, 2 × d, C=CH$_2$), 5.15 (1 H, d, $J_{1,2}$ 1.65 Hz, C=CH$_2$), 2.92 (6 H, s, NMe$_2$); δ_C(75 MHz; $CDCl_3$; Me_4Si) 150.3 (*C*-NMe$_2$), 149.1 (*C*=CH$_2$), 148.5 (*C*=CH$_2$), 145.1, 132.2, 128.2, 128.0, 127.1, 119.1 (CN), 118.2 (C=*C*H$_2$), 113.5 (C=*C*H$_2$), 112.1, 111.0, 40.5 (NMe$_2$); ν_{max}(ATR)/cm^{-1} 2888, 2812, 2231, 1610, 1524, 1505, 1362, 1199, 925, 888, 843, 814.

DOI: 10.1039/b414791j

Table 1 Fluorescence properties of **DA1** and **DA2**[a]

		DA1				**DA2**			
Solvent	Δf	$\nu_{fl}/10^3$ cm^{-1}	Φ_{fl}	τ_{fl}/ns	$k_{rad}/10^6$ s^{-1}	$\nu_{fl}/10^3$ cm^{-1}	Φ_{fl}	τ_{fl}/ns	$k_{rad}/10^6$ s^{-1}
Cyclohexane	0.100	25.71	0.087	2.2	39.5	24.36	0.084	4.4	19.1
Di-*n*-butyl ether	0.193	22.86	0.20	[b]		21.55	[b]	[b]	
Diethyl ether	0.251	21.48	0.19	18.5	10.2	20.28	0.044	6.7	6.6
Ethyl acetate	0.292	19.03	0.082	[b]		17.99	0.044	[b]	
THF	0.308	19.03	0.13	16.9	7.6	17.92	0.062	9.0	6.8
Acetonitrile	0.392	16.53	0.0018			[c]			
$-2\mu_e^2/hc\rho^3/10^3$ cm^{-1}		32.2 ± 1.8				31.5 ± 2.5			
$\nu_{fl}(0)/10^3$ cm^{-1}		29.0 ± 0.5				27.6 ± 0.6			
R^d		−0.994				−0.994			

[a] Fluorescence maxima ν_{fl} and quantum yields Φ_{fl} of **DA1** were taken from ref. 9. [b] Not determined. [c] No fluorescence observed. [d] Correlation coefficient.

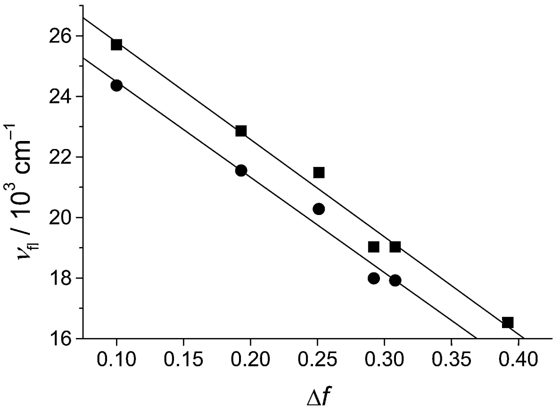

Fig. 2 Fluorescence solvatochromism plots of **DA1** (squares) and **DA2** (circles). The lines represent best linear fits of the data to eqn. (1).

the light velocity and ρ the solute cavity radius. The solvent polarity parameter Δf is a function of the dielectric constant ε and the refractive index n. The linear fit of the fluorescence data to eqn. (1) (see Table 1) shows that the solvatochromic sensitivity μ_e^2/ρ^3 is similar for the two compounds. Upon use of cavity radii ρ of 4.5 and 4.7 Å,‡ CT state dipole moments of 17.9 and 18.9 D are calculated for **DA1** and **DA2**, respectively. Not only are the excited state dipole moments of the same order of magnitude, but also the deviations of the data points from the best fits are very systematic. These observations suggest that the CT state structures of **DA1** and **DA2** are very alike and can be directly compared. This is of interest since Coulomb attraction between the oppositely charged donor and acceptor chromophores may lead to conformational changes in the CT excited state.[11,12] Although this is not possible for **DA1** (only rotation along the two phenylene–vinylidene formal single bonds can occur), **DA2** possesses the conformational freedom to adopt a sandwich-like structure. Based on the similar solvatochromic plots this does not appear to occur. This is confirmed by time-resolved fluorescence measurements, which did not disclose any conformational processes on the timescale between 30 ps and a few nanoseconds. It is noteworthy that despite the large similarity there is an offset between the solvatochromic plots. This originates either from different redox potentials or from different reorganization energies of **DA1** and **DA2**.

The radiative rate constant k_{rad} ($k_{rad} = \Phi_{fl}/\tau_{fl}$) scales with the square of the electronic coupling between the (relaxed) CT state and the ground state[13,14] and reflects the communication between the donor and acceptor groups. Unfortunately, the k_{rad} data in cyclohexane are not completely unambiguous for the evaluation of the donor–acceptor interaction, as in this solvent the decay kinetics are likely to be affected by mixing with locally excited states.[15,16] Nevertheless, the same qualitative trend is observed as in diethyl ether and THF: the radiative decay rate of **DA2** is smaller than that of **DA1**, but the difference is not very pronounced. In diethyl ether and THF the square root of k_{rad} of **DA2** amounts to 80 and 94% of that of **DA1**, respectively. Despite that some care must be taken as states involved in the fluorescence and absorption process may differ in character, this is in good agreement with the molar CT absorption coefficients. These are also a crude measure of the donor–acceptor coupling and the value for **DA2** is 76% of the coefficient of **DA1**.

In conclusion, both the absorption and fluorescence data show that there is a relatively limited decrease in donor–acceptor interaction upon introduction of a second branching site in the 1,1-diphenylethene conjugation path. Charge transport over the doubly bifurcated π-system of **DA2** proves to be possible and is even relatively facile. This implies that the type of branched π-systems considered here may be used in the development of materials with multiple conduction channels.

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‡ As documented elsewhere,[9] the cavity radius of **DA1** was estimated by comparison with related compounds. The radius of **DA2** is assumed to be 0.2 Å larger.