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Solvent-dependent Switching between Two Dipolar Excited States in a Rigidly Extended Trichromophoric System

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We present a novel, rigidly extended trichromophoric system (**1**) that consists of a central naphthalene (N) chromophore interposed between an *N,N*,4-trimethylaniline electron donor (D) and a 4-cyanobenzamide electron acceptor (A). Upon photoexcitation, quantitative charge transfer occurs to yield the fluorescent D^+-N^--A state. In non-polar solvents such as cyclohexane and benzene this is the predominantly formed charge-transfer (CT) state. In a slightly more polar solvent, such as dioxane, a second electron transfer step occurs, resulting in the formation of the non-fluorescent 'giant dipolar' $D^+-N^--A^-$ state with > 95% efficiency. Nanosecond transient absorption spectroscopy of **1** in cyclohexane and benzene shows rapid formation ($k_{isc} \approx 0.7 \times 10^9 \text{ s}^{-1}$) of a triplet state localised on the naphthalene chromophore ($\lambda_{max} = 440 \text{ nm}$). In dioxane and more polar solvents absorptions are observed that correspond to the donor radical cation (D^+) and the acceptor radical anion (A^-) ($\lambda_{max} = 370$ and 500 nm). The lifetime of the $D^+-N^--A^-$ state is 6 ns in dioxane. As the absorption characteristics of both excited states differ profoundly, this implies that a subtle change of the polarity of the surrounding medium induces a dramatic change of the transient absorption spectra. Time-resolved microwave conductivity (TRMC) measurements confirm the increase of the excited state dipole moment of **1** from 19 D for D^+-N^--A in cyclohexane to 42 D for $D^+-N^--A^-$ in dioxane.

In bichromophoric electron donor–acceptor systems the number of CT states energetically accessible *via* photoexcitation is in general limited to one (D^+-A^-). When extra chromophores ($N_1, N_2, N_3, \dots$) with graded weaker donor or acceptor properties are interposed between D and A in a linear array, the number of such states rises steeply to *e.g.* three in a triad (D^+-N^--A , $D-N^+-A^-$ and $D^+-N^--A^-$) and six in a tetrad. The availability of additional CT states with smaller charge separation provides the possibility to design systems in which a very large charge separation distance between the terminal D and A groups can be realised *via* a number of smaller (and therefore in general faster) electron-transfer steps, analogous to the scheme used by nature in photosynthesis. Various synthetic tri-, tetra- and even penta-chromophoric systems have been described recently^{1–9} in which such a scheme is employed. It has proven not to be a trivial task to tune the relative rates of all possible decay pathways following photoexcitation such that an overall large charge separation is indeed realised with high quantum efficiency. In this paper we present data on the novel trichromophoric system **1** of the type D–N–A (see Scheme 1), which shows a very pronounced solvent dependence of its CT kinetics and can actually be switched quantitatively between different charge-separated states by a subtle variation of solvent polarity. The chromophores incorporated in **1** have well defined photophysical and redox properties and they are linked by saturated hydrocarbon spacers in such a way that their distances are rigidly defined. Compounds **2** and **3** serve as models for the bichromophoric subunits D–N and N–A of **1**, while **4–8** are models for the isolated chromophores.

which the energy of the charge-separated state $E_{D^+-A^-}$ (in eV) is calculated by considering it as a solvent-separated ion pair with centre to centre distance R (in Å) and effective ionic radii r (in Å), equal for D and A, submerged in a continuous dielectric with relative permittivity ϵ_s .

Results and Discussion

Energetic Considerations

An estimate of the relative energies of the various charge separated states in **1** can be obtained by applying eqn. (1)¹⁰ in

Scheme 1 Trichromophoric system (**1**), the bichromophoric (**2** and **3**) and the single chromophore (**4**, **5**, **6**, **7** and **8**) models used in this study

$$E_{D+A-} = E_{ox}(D) - E_{red}(A) + (14.4/r)(1/\epsilon_s - 1/37.5) - 14.4/\epsilon_s R \quad (1)$$

For our D and A species the one-electron oxidation and reduction potentials [$E_{ox}(D)$ and $E_{red}(A)$ in V] in acetonitrile ($\epsilon_s = 37.5$) are known (see Table 1). Even though the bridges in linked systems occupy part of the space available to the solvent in non-bridged ion pairs, it has been found^{5,11-15} that eqn. (1) can be applied successfully, at least if the bridges are arranged in an extended fashion as in 1-3. On the other hand it has been reported¹⁶ that for systems where electron transfer occurs along the minor axis of the molecule, as in bichromophoric cyclophanes, eqn. (1) strongly overestimates the solvent dependence of E_{D+A-} .

To obtain from eqn. (1) a semiquantitative estimate of the CT-state energies we used the electrochemically determined redox potentials (Table 1) of the chromophores and set all ionic radii at 3.3 Å, which experience has shown to be a reasonable value for small aromatic systems.¹⁰ The only additional parameter then needed is the centre to centre distance, R , of the ionic species in 1. For the naphthalene radical anion and cation the centre of charge should clearly coincide with the geometric centre of the chromophore. Also for the acceptor A, in which the benzene ring is 1,4-substituted by two substituents of approximately equal electron-withdrawing power, the centre of the aromatic ring is probably close to the centre of charge in its radical anion. For the aniline donor however, the centre of charge in its radical cation is likely to be rather close to the nitrogen. Taking these factors into account, R values for D^+-N^--A , $D-N^+-A^-$ and D^+-N-A^- are 3.5, 6.1 and 9.6 Å, respectively, (obtained from Dreiding models, see also Scheme 1). These R values were used to calculate the energies plotted in Fig. 1 as a function of the solvent relative permittivity (ϵ_s), together with the virtually solvent-independent energies of the lowest singlet and triplet states of the naphthalene chromophore, which are the lowest locally excited states.

Note that the latter values, as well as the redox properties of the naphthalene chromophore, are, in principle, influenced by the alkyl substituents present in D-N-A, D-N and N-A. This is evident upon comparison of the data given in Table 1 for naphthalene (N:6) with those of 1,2,3,6,7,8-hexahydropyrene (HHP:7). Since these effects are relatively small in comparison with other uncertainties inherent in the application of eqn. (1), we have nevertheless consistently used the well documented properties of naphthalene itself to construct Fig. 1. Although caution has to be taken with the quantitative aspects of the energies plotted in Fig. 1, at least useful information on the relative energies of different excited states can be obtained.

Inspection of Fig. 1 reveals that all three CT states of 1 should, in principle, be accessible from the singlet excited state of the central naphthalene chromophore even in rather

Fig. 1 Estimated energies of locally excited and CT states in 1 as a function of the solvent relative permittivity. $E_{ox}(D) = 0.76$, $E_{ox}(N) = 1.54$, $E_{red}(N) = -2.56$, $E_{red}(A) = -1.88$, $R(D^+-N^--A) = 3.5$, $R(D^+-N-A^-) = 9.6$, $R(D-N^+-A^-) = 6.1$, $r_{ion} = 3.3$, $^1N^* = 3.94$, $^3N^* = 2.64$.

non-polar solvents. Furthermore it appears that whereas the D^+-N^--A state is most stable in non-polar media, the larger stabilisation of the giant dipole D^+-N-A^- in more polar solvents should allow it to become the most stable one in media with $\epsilon_s > 3$. Interestingly the $D-N^+-A^-$ state is predicted to be less stable than the other CT-states irrespective of solvent polarity.

Photophysical Behaviour of the Bichromophoric Models 2 (D-N) and 3 (N-A)

In Fig. 2 the electronic absorption spectra of 2 and 3 are given, together with that of naphthalene (6) and the donor model (4) or the acceptor model (8). Fig. 3 gives spectra of models for the separate chromophores together with that of 1 (D-N-A).

For all three multichromophoric systems (1, 2, 3) the absorptions of the separate chromophores can be recognised. The red edge of the spectra is clearly dominated by the structured absorption of the (substituted) naphthalene chromophore which, as state above, harbours the lowest locally excited singlet state in our molecules with $E_{00}^S = 3.94$ eV (6) and $E_{00}^S = 3.79$ eV (7) (Table 1).

While naphthalene and its alkylated derivatives are known to display a strong and structured fluorescence in the 320-370 nm region, such emission is virtually absent for both 2 and 3 in all solvents investigated. It is reasonable to attribute this quenching to the occurrence of fast intramolecular electron transfer where the naphthalene acts as the acceptor or the donor in 2 and 3, respectively. As discussed above (Fig. 1) such electron transfer should indeed be energetically feasible in both 2 and 3. From the fact that we are unable to detect any residual naphthalene fluorescence, it must be concluded

Table 1 Oxidation (E_{ox}) and reduction (E_{red}) potentials of separate chromophore models (see Scheme 1) (in acetonitrile vs. SCE) with some photophysical parameters (in cyclohexane)

chromophore	τ_s/ns	E_{00}/eV		redox potentials/V	
		E_{00}^S	E_{00}^T	E_{ox}	E_{red}
<i>N,N</i> -dimethylaniline (5)	2.4 ^a	3.93 ^b	2.99 ^c	0.76 ^d	
naphthalene (6)	96 ^a	3.94 ^e	2.64 ^a	1.54 ^a	-2.56 ^f
1,2,3,6,7,8-hexahydropyrene (7)	18 ^g	3.79 ^h		1.29 ⁱ	
4-(piperidine-1-carbonyl)-benzonitrile (8)	—	4.30 ^k	3.05 ^k		-1.88

^a Ref. 23; ^b Ref. 36; ^c Ref. 37; ^d data for *N,N*-diethylaniline taken from Ref. 38; ^e Ref. 39; ^f Ref. 38; ^g in *n*-hexane; ^h obtained from the intersection of absorption and fluorescence spectra; ⁱ irreversible wave, we note that for 1,4,5,8-tetramethylnaphthalene 1.16 V vs. SCE has been reported³⁸; ^k data for 1,4-dicyanobenzene²³ as no fluorescence was observed for 8.

Fig. 2 Electronic absorption spectra of (a) 2 in acetonitrile, 4 in *n*-hexane and 6 in acetonitrile; (b) 3, 6 and 8 in acetonitrile. Data for 4 were obtained from Krijnen.⁴⁰

Fig. 3 Electronic absorption spectra of 1, 7 and 8 in acetonitrile and 4 in *n*-hexane. The absorbance of 1 was scaled to the sum of the spectra of 4, 7 and 8 at 254 nm.

that the rate of electron transfer in 2 and 3 exceeds, by at least two orders of magnitude, the decay rate of the isolated naphthalene chromophore. The latter amounts to $1/\tau$ ($1/96$ ns) $\approx 1 \times 10^7$ s⁻¹, implying that photoinduced charge separation in 2 and 3 occurs with $k_{es} \geq 10^9$ s⁻¹.

Interestingly, and as already reported by Rettig *et al.*¹⁷ for a very closely related system, 2 not only shows quenching of local fluorescence by intramolecular charge separation, but also displays CT fluorescence from the charge-separated state thus populated. In Fig. 4 this strongly solvatochromic and structureless emission is shown (see also Table 2), while for comparison the structured and virtually solvent-independent fluorescence of HHP (7) is also displayed.

The occurrence of CT fluorescence not only testifies that photoinduced charge separation has indeed occurred, but also allows us to determine important properties of the CT state, *viz.* its lifetime and the magnitude of its dipole moment.

From the fluorescence decay data compiled in Table 2, the lifetime of the CT state in 2 is found to be relatively short and rather solvent independent, varying from 1.82 ns in *n*-hexane to 1.17 ns in acetonitrile. The small solvent dependence of the lifetime is remarkable because, as evident from the strong red shift of the CT fluorescence, the energy gap separating the CT state and the ground state decreases considerably in more polar solvents. In general, this has been found to enhance strongly the rate of charge recombination to the ground state, which is typical Marcus inverted-region behaviour.¹⁸ Therefore the relative insensitivity of the lifetime to solvent polarity found for 2 may indicate that the main decay path of its CT

Fig. 4 Fluorescence spectra of 2 (—) ($\lambda_{ex} = 320$ nm) and 7 (---) ($\lambda_{ex} = 300$ nm); much smaller slits were used for 7 than for 2 [ϕ_f (7 in cyclohexane) = 0.84]

Table 2 CT-fluorescence characteristics of D-N (2) and D-N-A (1): emission maxima, λ_{max}/nm ; fluorescence quantum yields, ϕ_f (%) and fluorescence lifetimes, τ_f/ns

solvent	Δf	2 $D^+-N^- \rightarrow D-N + h\nu$			1 $D^+-N^--A \rightarrow D-N-A + h\nu$		
		λ_{max}	ϕ_f	τ_f	λ_{max}	ϕ_f	τ_f
<i>n</i> -hexane	0.092	382	1.4	1.82	401	1.2	
cyclohexane	0.100	385	1.4	1.90	403	1.2	1.80
benzene (BZ)	(0.119)	421	0.4	1.50	442	0.3	1.50
dioxane (DX)	(0.122)	440	0.4	1.45	456	0.2	0.12; ca. 5 ^a
di- <i>n</i> -butyl ether	0.194	409	0.8	1.70	425	0.4	
di-isopropyl ether	0.237	414	0.6	1.62	431	0.2	
diethyl ether	0.251	426	0.4	1.53	428	0.1	0.051
ethyl acetate	0.292	445	0.3	1.31	— ^b	<0.01	
THF	0.308	444	0.4	1.46	459	<0.01	0.014
acetonitrile	0.393	492	0.2	1.17	487	<0.01	

^a Biexponential; ^b no CT emission maximum could be determined.

state is not directly to the ground state. This point will be discussed further below.

The solvatochromicity of CT fluorescence maxima (ν_{ct} in cm^{-1}) can in general be adequately quantified¹⁹ via the Lippert–Mataga equation:

$$\nu_{ct} = \nu_{ct}(0) - (2\mu^2/hc\rho^3)\Delta f = \nu_{ct}(0) - (10070\mu^2/\rho^3)\Delta f \quad (2)$$

$$\Delta f = [(\epsilon_s - 1)/(2\epsilon_s + 1)] - [(n^2 - 1)/(4n^2 + 2)] \quad (2a)$$

In eqn. (2) the gas-phase position is given by $\nu_{ct}(0)$, while μ is the (increase in) dipole moment in the CT state (in Debye)[†] and ρ the effective radius (in Å) of a spherical cavity in which the molecular dipole fits. For ρ we took²⁰ 40% of the long axis of the molecule, this yielded $\rho = 4.85$ Å for **2** (determined from X-ray structure²¹).

As shown in Fig. 5 the linear dependence of ν_{ct} on Δf required by eqn. (2) indeed applies. The data for benzene and 1,4-dioxane are not included in the fit, because it is well known that the latter solvents stabilise dipolar states more effectively than predicted from their bulk dielectric properties.²² The slope of the regression line in Fig. 2 is $18\,700\text{ cm}^{-1}$ from which $\mu = 14.6$ D (for $\rho = 4.85$ Å) is obtained. The slope corresponds very well with an earlier estimate made by Rettig *et al.*¹⁷ for a closely related system. We note that the dipole moment of **2** corresponds to an effective charge separation distance of two unit charges of *ca.* 3.1 Å, which is quite close to the $R = 3.5$ Å derived from models and used above to estimate the energy of the charge-separated state (Fig. 1).

Having established beyond doubt that photoexcitation of **2** leads quantitatively to intramolecular charge separation, we now turn to the pathways by which this CT state decays. The low quantum yield of CT fluorescence (Table 2) demonstrates that radiationless pathways are dominant in all solvents. From Fig. 1 it appears that such pathways may either populate the ground state directly or involve intersystem crossing to the local naphthalene triplet (³N). Nanosecond transient absorption measurements indicate that the latter pathway is dominant, accounting for more than 90% of the overall decay in non-polar as well as in polar solvents. In fact, the absorption of this long-lived species [$\tau \approx 14.4\text{ }\mu\text{s}$ in cyclohexane for **2** (inset Fig. 6)] fully dominates the transient spectra and ³N is the only species detected in such measurements (Fig. 6), because the absorption of the CT species is too small to be seen on the nanosecond timescale. The ³N spectrum of **2**

Fig. 5 CT emission frequency (ν_{ct}) of **2** as a function of solvent polarity Δf

[†] 1 Debye (D) $\approx 3.335\,64 \times 10^{-30}$ C m.

Fig. 6 Transient absorption spectra of **2** in cyclohexane and THF and **6** in cyclohexane. The spectra shown correspond to the spectra at the maximum of the laser pulse, all samples had the same absorption at the excitation wavelength (308 nm) and were excited with the same laser energy. The inset shows the decay of ³N of **2** in cyclohexane at 428 nm.

[$\lambda_{\text{max}} = 384(\text{sh})$, 405, 428 nm in cyclohexane] is somewhat red-shifted and broadened compared with that of naphthalene itself [$\lambda_{\text{max}} = 373$, 392, 414 nm in cyclohexane (Fig. 6)]. When we assume equal oscillator strengths and use a triplet yield of 75% for naphthalene itself²³ the ³N yield in **2** is calculated to be essentially 100% in cyclohexane, di-*n*-butyl ether, ethyl acetate and THF. The transient absorption spectra of the two extremes (**2** in cyclohexane and THF) are shown in Fig. 6, together with that of naphthalene in cyclohexane.

It thus appears that, in all solvents, the rate of intersystem crossing to ³N largely determines the lifetime of the CT state in **2**. We tentatively propose that this is the basis for the remarkably small effect of solvent polarity on the lifetime noted above (Table 2). Whereas direct decay to the ground state is expected to respond sharply to changes in the large energy gap brought about by different solvents, this is not necessarily so for intersystem crossing to ³N. The latter process not only involves an additional spin flip, but also the energy gap involved is much smaller (Fig. 1), which brings the process closer to the Marcus optimal region. Under such conditions the rate of electron transfer can become essentially solvent independent as a result of compensating effects between changes in driving force and solvent reorganisation energy.²⁴ We note, in passing, that the essentially quantitative triplet yield of **2** makes it a potentially useful triplet sensitizer in applications where a naphthalene triplet is known to be active.

While, as discussed above, charge recombination pathways in **2** can be positively identified from fluorescence and transient absorption measurements, this is not so for **3**. For this bichromophore full quenching of the local naphthalene fluorescence indicates that fast and complete charge separation occurs, as predicted to be energetically feasible (Fig. 1). However, **3** gave no CT fluorescence, nor could significant transients be detected in nanosecond absorption measurements. Apparently the CT state of **3** undergoes very rapid ($> 10^9\text{ s}^{-1}$) dark recombination to the ground state not allowing for a detectable concentration to build up on a nanosecond timescale.

Photophysical Behaviour of **1** (D–N–A)

In Fig. 7 the fluorescence of **1** in various solvents is shown (its essentially solvent independent absorption spectrum was

Fig. 7 Fluorescence spectra of **1** in various solvents ($\lambda_{\text{ex}} = 308$ nm)

shown in Fig. 3). As for **2** and **3**, the spectra are devoid of any significant local emission ($k_{\text{cs1}} > 10^9 \text{ s}^{-1}$, see Scheme 2), but show typical solvatochromic CT fluorescence in solvents of low polarity.

In these solvents the CT fluorescence of **1** is not only similar in position but also in quantum yield and lifetime to that of **2** (Table 2). This clearly indicates that, in such non-polar media, excitation of **1** only populates the $\text{D}^+-\text{N}^--\text{A}$ state, which corroborates the prediction that this is the most stable CT state in such solvents (Fig. 1).

Transient absorption experiments in cyclohexane and benzene indicate that, as for **2**, charge recombination in these solvents mainly populates the local naphthalene triplet state [λ_{max} cyclohexane: 412(sh), 435 nm; benzene: 420(sh), 444 nm]. The ^3N absorption of **1**, in which the naphthalene chromophore is tetra-substituted, is even more red-shifted and broadened with respect to that of naphthalene (see Fig. 6) than for the di-substituted naphthalene in **2**. **7** is a better reference system for the naphthalene chromophore in **1** than naphthalene itself: the ^3N absorption of **7** shows its maximum at 453 nm and has a similar shape to that of **1** in cyclohexane [see Fig. 8(a)].

Interestingly, in solvents slightly more polar than benzene, the CT fluorescence of **1** decreases rather sharply both in quantum yield and in lifetime (Table 2) as compared with **2**, indicating the onset of a process depopulating the $\text{D}^+-\text{N}^--\text{A}$ state in **1**, which has no counterpart in **2**. The energetic consequence of enhancing solvent polarity, as depicted in Fig. 1, is that in more polar solvents an initial $\text{D}^+-\text{N}^--\text{A}$ state is transformed to the (non-fluorescent) giant dipolar $\text{D}^+-\text{N}-\text{A}^-$ state, thereby shortening the lifetime of the former. That such transformation indeed occurs is substantiated by the concomitant dramatic change of the transient absorption spectrum. As discussed above, in non-polar solvents this is very similar to that of **2**, as it is dominated by the absorption of

Scheme 2 Relative energies and interconversion pathways of locally excited and CT states in **1** (see text for specification of the indicated rate constants and the transient absorption maxima)

Fig. 8 Transient absorption spectra of (a) **1** and **7** in cyclohexane, (b) **1** in dioxane and (c) **1** in THF. The spectra shown in (a) are detected after the end of the laser pulse and decay on a μs timescale. In (b) and (c) the spectrum with the greatest absorbance is taken at the maximum of the laser pulse, then successive spectra are recorded at 2 ns intervals.

the local naphthalene triplet that quickly ($k_{\text{isc}} \approx 0.7 \times 10^9 \text{ s}^{-1}$) emerges from the initial $\text{D}^+-\text{N}^--\text{A}$ state. In slightly more polar solvents, however, where **2** still produces this local triplet with near-unit quantum efficiency, **1** displays a completely different transient absorption spectrum. In 1,4-dioxane [see Fig. 8(b)] only a minor long-lived feature around 440 nm attributable to ^3N is observed, while in addition stronger, but shorter-lived ($\tau \approx 6$ ns), bands occur with maxima at 370 and 500 nm.

Increasing solvent polarity further to *e.g.* THF suppresses the formation of the naphthalene triplet completely, and the transient absorption spectrum now decays with $\tau < 2$ ns over the whole wavelength region. The spectral shape [Fig. 8(c)] is very similar to a superposition of the spectra of the aniline donor radical cation [a relatively weak band centred around 470 nm ($\epsilon = 5000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)]²⁵ and especially the 4-(piperidine-1-carbonyl)-benzonitrile (**8**) acceptor radical anion. This radical anion displays²⁶ a strong sharp band at 368 nm ($\epsilon = 21490 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and a weaker broad maximum around 510 nm ($\epsilon = 9320 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). In THF the fluorescence of the $\text{D}^+-\text{N}^--\text{A}$ state in **1** is almost

fully quenched ($\tau_f \approx 14$ ps), as compared with **2** ($\tau_f = 1460$ ps), indicating a nearly quantitative transformation to the $D^+-N^--A^-$ state, with a rate $k_{cs2} \approx 1/14$ ps $\approx 7 \times 10^{10}$ s $^{-1}$.

The overall behaviour of **1** described above can be accounted for by the kinetic scheme given in Scheme 2. Essential in this scheme is the solvent-dependent branching that occurs from the initial CT state with a relatively small dipole moment (D^+-N^--A) to either the long-lived (μ s range) naphthalene triplet state (D^--N^--A) or to the relatively short-lived (ns range) giant dipole state $D^+-N^--A^-$. Since the latter states have very different absorption spectra and very different lifetimes, the behaviour of system **1** in transient absorption spectroscopy is both strongly solvatochromic and strongly solvatochronic.

In Scheme 2 it is indicated that electron transfer within the initial CT state leading to the giant dipole state may become reversible at intermediate solvent polarities, where these two states should be almost degenerate. Under such conditions the CT fluorescence emerging from the D^+-N^--A state is expected to show biexponential decay²⁷ and this was indeed observed in dioxane (Table 2). In this solvent we find a fast component ($\tau_1 = 120$ ps) attributed to direct emission from the D^+-N^--A state of which the lifetime is shortened by the rapid forward step ($k_{cs2} \approx 8 \times 10^9$ s $^{-1}$) and a slower ($\tau_2 \approx 5$ ns) component attributed to delayed fluorescence by thermal repopulation of the emissive D^+-N^--A state from the non-emissive giant dipolar state. This interpretation is supported by the fact that the lifetime of the giant dipolar state, as found from transient absorption spectroscopy (see above), corresponds with that of the delayed fluorescence. This view is substantiated further by time-resolved microwave conductivity (TRMC), as described in the next section.

TRMC Experiments

A direct method to determine the magnitude of charge separation and the kinetic behaviour of transient dipolar species is provided by the TRMC technique capable at present^{28,29} of nanosecond time-resolution. The sensitivity and selectivity of this method is well demonstrated by the ability to detect the D^+-N^- dipolar transient formed upon excitation of **2** in both cyclohexane and dioxane [Fig. 9(a)]. This is not possible *via* transient absorption measurements with similar time-resolution because of the overwhelming absorption of the local naphthalene triplet, a species which does not give a TRMC signal.

From the TRMC traces recorded for **2** and using the lifetimes found from CT fluorescence (Table 2), dipole moments of 16 D are estimated for the CT state of **2** in both cyclohexane and dioxane. This value compares quite well with that estimated above from the fluorescence solvatochromism (14.6 D).

In Fig. 9(b) TRMC transients for compound **1** in cyclohexane and dioxane are shown. For the former solvent the height of the transient is, if anything, slightly less than that for compound **2**, whereas for dioxane it is very much larger. Compound **1** would be expected to have a longer rotational relaxation time because of its larger size which, for the same dipole moment, would result in a decrease in the TRMC signal. When this, and the lifetimes of the transients, are taken into account, the dipole moments are estimated to be 19 D in cyclohexane and 42 D in dioxane. The former value is only slightly larger than that found for compound **2** indicating that the degree of charge separation is similar and hence that a further electron-transfer step does not occur. For dioxane, however, the large increase by 26 D indicates a further separation of charges by slightly more than 5 Å to a total of *ca.* 9 Å which would correspond to the formation of

Fig. 9 TRMC signals in cyclohexane and dioxane of (a) **2** and (b) **1**

the $D^+-N^--A^-$ state. This substantiates the conclusions reached on the basis of the optical data.

Interestingly, in benzene as solvent, compound **1** is found to display a net dipole moment of 31 D, which lies between the values expected for D^+-N^--A and $D^+-N^--A^-$. This indicates that, for this solvent, the two states are very similar in energy and exist in dynamic equilibrium involving electron hopping between the N and A moieties.

Concluding Remarks

The results described above show that the novel coupling approach employed in **1** leads to trichomophores for which sufficient electronic interaction between each pair of adjacent chromophores exists to make electron transfer in such a pair very rapid if sufficient driving force is provided. The relative energies of the various CT states can be predicted with a high degree of reliability from the redox data of the constituting chromophores and their, thanks to the coupling scheme, well defined relative distances. In the present case of system **1** a subtle variation of solvent polarity allows one to switch between two of the three feasible CT states. These two are reached from a locally excited state *via* one- and two-electron-transfer steps between adjacent chromophores. Because the redox properties of all three chromophores in **1** can be readily modified by substitution, it is expected that it will be possible to design similar systems that can be switched between all three possible CT states. This and the expansion of the coupling approach employed in **1** to the development of multichromophoric systems with an even higher number of energetically accessible CT states are topics of ongoing research.

Experimental

1,2,3,6,7,8-hexahydronaphthalene was purchased from Aldrich and used without further purification. Naphthalene was obtained

from J. T. Baker Chemical Co. The synthesis of compounds 1, 2, 3 and 8 will be published elsewhere.³⁰ Spectrograde solvents (Merck or Aldrich) were used. The samples were carefully deoxygenated by bubbling with argon (ca. 15 min). The concentrations were ca. 10^{-5} mol dm⁻³ for the fluorescence measurements and ca. 10^{-4} mol dm⁻³ for transient absorption measurements. The electronic absorption spectra were recorded on a Cary 3 UV-VIS spectrophotometer (Varian).

Fluorescence spectra were measured using a Spex Fluorolog 2 apparatus with correction for the wavelength dependence of the detection system containing an RCA C31034 photomultiplier. The recorded emission spectra were all normalised to identical absorption at the excitation wavelength. The quantum yields of fluorescence of 1 and 2 were obtained by determining the integrated intensity relative to the integrated fluorescence of 2 in cyclohexane at the same excitation wavelength. The ϕ_f of 2 in cyclohexane and of HHP were determined relative to 9,10-diphenylanthracene ($\phi_f = 90\%$)³¹ determined at the same excitation wavelength in cyclohexane. The quantum yields were corrected for changes in the refractive index of the solvent compared with cyclohexane.

Fluorescence decay curves were measured by means of picosecond time-correlated single-photon counting (SPC) ($\lambda_{ex} = 317$ nm, FWHM = ca. 22 ps). A mode-locked Argon-ion laser (Coherent 468 AS Mode locker and Coherent Innova 200 laser) was used to pump synchronously a DCM dye-laser (Coherent model 700). An acousto-optic cavity dumper with driver (Coherent 7220 Cavity dumper and 7200 Cavity dumper driver) was used to produce pulses at a repetition rate of 3.8 MHz. The pulse width was ca. 8 ps as measured with an autocorrelator. Frequency doubling was achieved with a BBO crystal (Inrad, 6 mm, cutting angle 37.1°). Since the frequency doubled light is horizontally polarised, two Newport 10D20 RM2 45° mirrors were used to rotate the polarisation direction and thus obtain vertically polarised light. To avoid depolarisation effects in the decay curves, an analyser was placed before the Carl Zeiss M 20 monochromator to collect light only at the 'magic angle'. The fluorescence light was monitored at right angles to the incident light beam. A 6 μ m micro-channel plate photomultiplier (Hamamatsu R3809U) was used; the obtained signal was amplified by a Hewlett Packard 8347A 3 GHz amplifier. The stop-signal for the time-to-amplitude converter (Tennelec TC864 TAC/biased amp) was taken from an Antel FS 1010 (bias voltage, -70 V) photodiode monitoring a fraction of the fundamental laser beam. The stop-signal was electronically delayed with a Tennelec TC 412A delay. Quad constant fraction discriminators (CFD) provided the correct voltage signals for the TAC. To avoid crosstalk two modified CFDs³² were used (Tennelec TC455 and TC454 for start and stop, respectively). The TAC was operated in the reversed configuration. Pile-up distortion was avoided by working at an average detection rate of less than 1% of the excitation frequency. The output pulses of the TAC were fed into 1024 channels of the multi-channel buffer (EG&G Ortec 918 ADCAM) working in pulse height analysis mode. The channel widths used were 5, 10 and 25 ps per channel. Data thus obtained were fed into a microcomputer. All fluorescence data were measured at room temperature. The response function (FWHM ca. 22 ps) was obtained by monitoring at the Raman band of a cell filled with demineralised water. The cells were painted black with camera-varnish on two adjacent sides to avoid reflection at the quartz/air boundary. The decay traces were deconvoluted with a home-written program;³³ an algorithm developed by Maquardt³⁴ was used for the non-linear iterative least-square fitting.

Flash photolysis transient absorption spectra were obtained using a Lumonics Pulse Master EX748 XeCl

Excimer laser ($\lambda_{ex} = 308$ nm, FWHM ca. 7 ns) as excitation source and a 450 W high-pressure Xe arc as the probe light, pulsed with a Müller Elektronik MSP05 pulser. The probe light, after passing through the sample cell, was dispersed via a spectrograph (EG&G model 1234) equipped with a 150 lines mm⁻¹ grating and a 250 μ m slit resulting in a 6 nm spectral resolution. This was coupled to a gated, intensified diode array detector (EG&G model 1421), forming part of an EG&G OMA III data handling system. A gate of 5 ns was used for detection. For triggering purposes a digital delay generator (DDG) EG&G model 9650 was used.

The transient absorption single-wavelength-decay experiments were triggered by use of the above described DDG. The samples were excited using the described XeCl Excimer laser. An EG&G low-pressure metal-can Xe lamp FX504 with an FYD-506 Lite PAC and PS-302 power supply was used as the probe light. A 5 μ F capacitor giving a pulse width of 5 μ s (measured 1/3 from the top) was used. The decay trace was monitored using an RCA 1P-28 photomultiplier via a Zeiss MQII monochromator. The signal of the detector was fed into a Tektronix 11302 oscilloscope, triggered by the DDG. The scope traces are digitised with a Tektronix DCS01 digitising video camera and data thus obtained fed into a microcomputer. The response function was obtained by monitoring at 308 nm and firing the laser at the sample. The absorbance was obtained from the decay trace using a home-written Igor Pro³⁵ macro. Thereupon deconvolution was performed using a home-written deconvolution program.³³

The TRMC technique ($\lambda_{ex} = 308$ nm, FWHM ca. 7 ns) and the methods of data reduction have been fully described elsewhere.^{28,29} Dilute solutions (ca. 10^{-4} mol dm⁻³) of the compounds studied, were prepared with UV spectroscopic grade solvents. These solutions were deoxygenated by bubbling with CO₂ (ca. 15 min).

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References

- 1 M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
- 2 D. Gust, T. A. Moore and A. L. Moore, *Acc. Chem. Res.*, 1993, **26**, 198.
- 3 S. I. van Dijk, P. G. Wiering, R. van Staveren, H. J. van Ramesdonk, A. M. Brouwer and J. W. Verhoeven, *Chem. Phys. Lett.*, 1993, **214**, 502.
- 4 A. M. Brouwer, C. Eijkelhoff, R. J. Willems, J. W. Verhoeven, W. Schuddeboom and J. M. Warman, *J. Am. Chem. Soc.*, 1993, **115**, 2988.
- 5 H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven and H. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258.
- 6 A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, T. Asahi, I. Yamazaki, Y. Nishimura, T. Ohno and K. Nozaki, *J. Am. Chem. Soc.*, 1993, **115**, 4577.
- 7 N. A. C. Bakker, P. G. Wiering, A. M. Brouwer, J. M. Warman and J. W. Verhoeven, *Mol. Cryst. Liq. Cryst.*, 1990, **183**, 31.
- 8 G. Mes, B. de Jong, H. J. van Ramesdonk, J. W. Verhoeven, J. M. Warman, M. P. de Haas and L. E. W. Horsman-van den Dool, *J. Am. Chem. Soc.*, 1984, **106**, 6524.
- 9 J. P. Sauvage, J. P. Collin, J. C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelli, L. Decola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993.
- 10 A. Weller, *Z. Phys. Chem. Neue Folge*, 1982, **133**, 93.
- 11 G. L. Gaines, M. P. O'Neil, W. A. Svec, M. P. Niemczyk and M. R. Wasielewski, *J. Am. Chem. Soc.*, 1991, **113**, 719.

- 12 J. M. Warman, K. J. Smith, M. P. de Haas, S. A. Jonker, M. N. Paddon-Row, A. M. Oliver, J. Kroon, H. Oevering and J. W. Verhoeven, *J. Phys. Chem.*, 1991 **95**, 1979.
- 13 P. M. Irvine, R. J. Harrison, G. S. Beddard, P. Leighton, J. K. M. Sanders, *Chem. Phys.*, 1986, **104**, 315.
- 14 A. D. Joran, B. A. Leland, P. M. Felker, A. H. Zewail, J. J. Hopfield and P. B. Dervan, *Nature (London)*, 1987, 508.
- 15 J. A. Schmidt, J.-Y. Liu, J. R. Bolton, M. D. Archer and V. P. Y. Gadzekpo, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1027.
- 16 H. Heitele, F. Pöllinger, K. Kremer, M. E. Michel-Beyerle, M. Futscher, G. Voit, J. Weiser and H. A. Staab, *Chem. Phys. Lett.*, 1992, **188**, 270.
- 17 W. Rettig, R. Haag and J. Wirtz, *Chem. Phys. Lett.*, 1991, **180**, 216.
- 18 R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966.
- 19 H. Beens, H. Knibbe and A. Weller, *J. Phys. Chem.*, 1967, **47**, 1183.
- 20 E. Lippert, *Z. Naturforsch. A.*, 1955, **10**, 541.
- 21 K. Goubitz, J. Fraanje, S. I. van Dijk and C. P. Groen, unpublished work.
- 22 P. Suppan, *Photochem. Photobiol.*, 1990, **50**, 293.
- 23 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 2nd edn., 1993.
- 24 J. Kroon, J. W. Verhoeven, M. N. Paddon-Row and A. M. Oliver, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1358.
- 25 T. Shida, *Electronic Absorption Spectra of Radical Ions*, Elsevier, Amsterdam, 1988.
- 26 F. Hartl and S. I. van Dijk, unpublished work, data in butyronitrile at -55°C .
- 27 R. J. Willemse, J. W. Verhoeven and A. M. Brouwer, *J. Phys. Chem.*, 1995, **99**, 5753.
- 28 M. P. de Haas and J. M. Warman, *Chem. Phys.*, 1982, **73**, 35.
- 29 W. Schuddeboom, Ph.D. Thesis, Delft University of Technology, 1994.
- 30 S. I. van Dijk and P. G. Wiering, in preparation.
- 31 D. F. Eaton, *Pure Appl. Chem.*, 1988, **7**, 1107.
- 32 D. Bebelaar, personal communication.
- 33 A. G. M. Kunst, SPECTRUM ANALYSER, Amsterdam, 1992.
- 34 D. W. Maquart, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.
- 35 WaveMetrics, IGOR PRO, version 2.01, Oregon, 1988–1994.
- 36 I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 2nd edn., 1971.
- 37 G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1980, **86**, 401.
- 38 H. Knibbe, Ph.D. Thesis, Free University, Amsterdam, 1969.
- 39 J. C. Scaiano, *Handbook of Organic Photochemistry*, CRC Press, Florida, 1989, vol. 1.
- 40 L. B. Krijnen, Ph.D. Thesis, University of Amsterdam, 1990.

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