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Photoinduced electron transfer in isolated bichromophoric and solvated trichromophoric systems

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Abstract

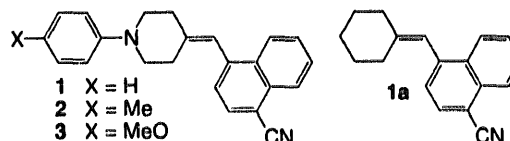
After local photoexcitation of the acceptor chromophore, fast and virtually barrierless charge separation over approximately 5 Å is observed under supersonic jet isolated conditions in three rigid donor–bridge–acceptor (D–br–A) systems in which D and A are separated by three σ bonds. It is suggested that low frequency intramolecular vibrational modes, discernible in the well-resolved excitation spectra, play a role in enabling efficient internal conversion between the locally excited and charge transfer states.

Insertion of an extra piperidine unit in the bridge elongates its overall length to seven σ bonds, while at the same time a tertiary nitrogen is added as an intermediate donor site. In the resulting trichromophoric systems (D₂–br–D₁–br–A), stepwise charge separation occurs in solution with a strong solvent dependence.

Keywords: Photoinduced electron transfer; Isolated bichromophoric systems; Solvated trichromophoric systems

1. Introduction

The recent experimental observation of photoinduced long-range charge separation [1–4] and charge shift [5] reactions in jet-cooled donor–bridge–acceptor (D–br–A) systems has revealed that excited state electron transfer (ET) across several saturated C–C bonds can take place in the absence of a solvent medium. As pointed out by Jortner et al. [6], this seems to be at variance with current semiclassical ET theory [7], where the reorganization of the solvent appears to be an essential requirement for the occurrence of ET. Alternatively, the relaxation process from the locally excited S₁ state (D^{*}–br–A or D–br–A^{*}) to the charge transfer (CT) state D⁺–br–A[−] may be regarded as a radiationless transition analogous to intersystem crossing and internal conversion, involving solely intramolecular vibrational modes. In this case, ET is favoured by a large density of accepting modes in the CT state, which are effectively coupled to the initially locally excited S₁ vibronic state. This implies that low frequency modes may play an important role in the ET process (currently, the relevance of low frequency internal



Scheme 1. Structures of the bichromophoric D–br–A systems 1–3 and the acceptor model 1a.

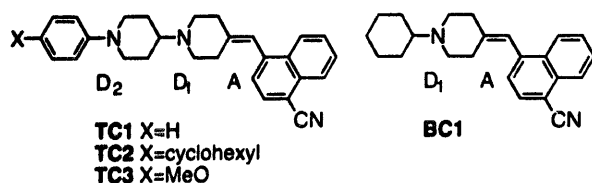
vibrations is also being considered for ET in solution [8]), especially if the energy gap between the S₁ and CT states is small [9].

We have found [10,11] that, in solution, excitation of either D or A in the rigidly bridged D–br–A molecules 1–3 (see Scheme 1) is followed by fast charge separation, resulting in the observation of a broad CT emission band. Compounds 1–3 incorporate a 1-vinyl-4-cyanonaphthalene (VCN) group as an electron acceptor and an anilino derivative as a donor, separated by a rigid hydrocarbon bridge which ensures a donor–acceptor distance (R_{DA}) of approximately 5 Å. Introduction of a methyl (2) or methoxy (3) group at the para position of the donor moiety has a direct influence on the ionization potential of the donor (in solution, the electrochemical oxidation potential of the donor moiety in 2 and 3 is expected to be lowered by 0.06 and 0.22 V respectively with respect to that of 1 [12]), leaving other relevant properties of the molecule, such as the S₀–S₁ transition energy, the acceptor electron affinity and R_{DA} , unaltered.

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Scheme 2. Structures of the trichromophoric D_2 - D_1 -A systems TC1-TC3 and the bichromophoric D_1 -A model BC1.

From the shift of the CT fluorescence maxima as a function of solvent polarity (as analysed by Lippert-Mataga plots), it has been concluded that: (i) the extended conformation with $R_{DA} \approx 5$ Å is retained in the CT state in all solvents for all three compounds; (ii) the energies of the CT state of **2** and **3** are lower than that of **1** by approximately 0.06 and 0.21 eV respectively; (iii) extrapolation to "zero polarity" suggests that the CT state is the lowest emissive state even in the gas phase for **1**, **2** and **3**.

The latter feature, in particular, made it worthwhile to study the fluorescence behaviour of **1-3** in a supersonic jet.

Furthermore, we have extended the coupling pattern employed in the bichromophoric D-br-A systems **1-3** to produce the homologous trichromophoric D_2 -br- D_1 -br-A systems TC1-TC3 (see Scheme 2) which contain a tertiary nitrogen as the intermediate electron donor site (D_1).

2. Results and discussion

2.1. Supersonic jet spectroscopy of bichromophores **1-3**

Fig. 1 shows the onset of the excitation spectrum of jet-cooled **2**, which is similar to that obtained for the analogues **1** and **3**. Comparison with the acceptor reference compound **1a** (which lacks the anilino donor moiety) shows that the spectrum can be attributed to the VCN chromophore. By analogy with the related compounds benzyliidenecyclopentane and benzyliidenecyclohexane [13], the spectrum is dominated by long and constant progressions in a vibrational mode of very low frequency (13.5 cm^{-1} for **2**). These are probably attributable to the torsional vibration around the single bond that connects the vinyl and naphthalene groups, with the progression resulting from the significantly increased planarity of the S_1 state of VCN compared with S_0 .

Importantly, the lowest observed transitions in the excitation spectra of **1**, **2** and **3** are at exactly the same energy (325.14 nm), indicating that our assumption that the modification of the donor group should have very little effect on the S_0 - S_1 excitation energy is fully justified. In contrast, the emission spectra obtained for jet-cooled **1**, **2** and **3** are very different from each other (see Fig. 2), with maxima at 372, 377 and 395 nm respectively. Furthermore, they are strongly red shifted with respect to the VCN fluorescence maximum of compound **1a**, which is located at approximately 338 nm (not shown). Apparently, although the initially excited species is clearly the same for **1a** and **1-3** (as judged by the

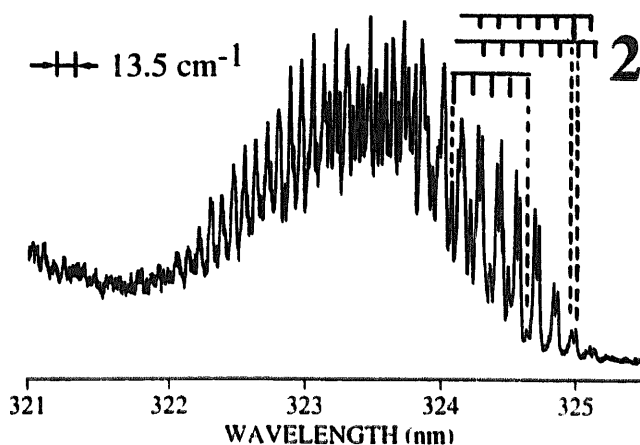


Fig. 1. Fluorescence excitation spectrum of **2**. Three progressions are identified with a regular vibrational spacing of 13.5 cm^{-1} .

similarity of the excitation spectra), the emitting species is not, indicating that for **1-3** efficient relaxation occurs to a state that is lower in energy than the D-br- A^* state. (Although it has been shown [14] that energy transfer from A^* to D is a possible relaxation process for jet-cooled D-br-A compounds comparable with **1-3**, the D^* -br-A state in our series is too high in energy to account for the red-shifted emission band.) Since our solution phase CT emission data [10,11] lead to predicted gas phase maxima in the range 360–385 nm, i.e. within approximately 15 nm from those found in the jet, we attribute the observed emission to CT fluorescence. Moreover, the red shifts of approximately 360 cm^{-1} (0.045 eV) for **2** and 1570 cm^{-1} (0.195 eV) for **3** relative to **1** are close to the differences between the oxidation potentials of the donors [12], which provides convincing evidence for the assignment of these bands to CT emission.

The most remarkable aspect of the emission spectra is that the local VCN fluorescence (found at 338 nm for **1a**) is completely quenched at all excitation energies studied for **2** and **3**. For compound **1**, which has the weakest donor of the

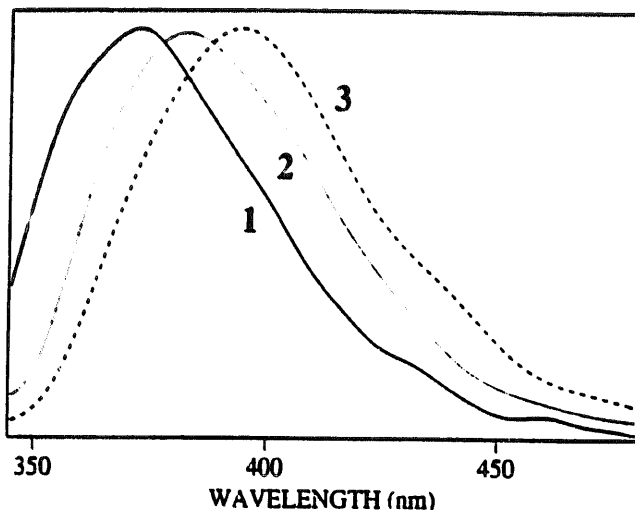


Fig. 2. Smoothed fluorescence spectra of **1**, **2** and **3** on excitation at 321 nm.

three molecules, the local 338 nm emission is observed on excitation near the origin, while excitation with an excess energy larger than approximately 60 cm^{-1} leads to a broadening of this band, and excitation with an excess energy of more than 170 cm^{-1} results in the CT band centred at 372 nm. From these observations, we conclude that a very low barrier for charge separation exists in **1**, whereas the lowering of the CT state in **2** and **3** makes full charge separation possible without any excess energy being required. The absence of local emission implies that the ET rate is on the picosecond timescale, which is remarkably fast under these solvent-free conditions. In this connection, it is interesting to note that the low frequency vibration which is active in the excitation spectrum is expected to contribute substantially to a large density of states even at relatively low energy gaps. In addition, this mode is presumably effectively coupled to the CT state, since it involves a rotational motion towards planarity within the acceptor chromophore, which enhances the electron acceptor strength by increasing the π conjugation.

Interestingly, although the electronic coupling between D and A must be appreciable to account for the fast ET, the sharp and well-resolved excitation spectra indicate that no direct CT excitation takes place and that the locally excited state must have a definite lifetime (greater than 10 ps) before conversion to the CT state occurs. This is in contrast with the situation recently found in a study of two rigid D–br–A compounds with more powerful D–A pairs [4], where the strong mixing between the S_1 and CT states resulted in extremely broad excitation bands.

In conclusion, our results show that not only in solution [10,11], but even under fully isolated conditions, the D–br–A molecules **1–3** are capable of long-range charge separation after photoexcitation of the acceptor chromophore, without the need for strong internal reorganization [15].

2.2. Trichromophoric systems TC1–TC3 in solution

As discussed above, the D–A pairs incorporated in **1–3** can undergo virtually complete photoinduced charge separation at a distance $R_{DA} \approx 5\text{ Å}$ irrespective of the dielectric properties of the surrounding medium. While this interesting finding will be discussed in more detail elsewhere [16], we now compare it with the behaviour of the homologous compounds TC1–TC3 (see Scheme 2) in solution.

In the D_2 –br– D_1 –br–A compounds TC1–TC3 similar D_2 –A pairs are incorporated, but at a larger distance, and furthermore an intermediate donor site (D_1) is introduced in the form of a tertiary nitrogen centre. In these systems, two charge separated states are accessible in principle: $CS1 = D_2^+ \text{--} \text{br--} D_1^+ \text{--} A^-$ and $CS2 = D_2^+ \text{--} \text{br--} D_1 \text{--} \text{br--} A^-$. Obviously the energy of the fully charge separated state CS2 should be lowered relative to that of CS1 by lowering the oxidation potential of D_2 (such as occurs in the series TC1 \rightarrow TC2 \rightarrow TC3) as well as by increasing the dielectric constant of the medium.

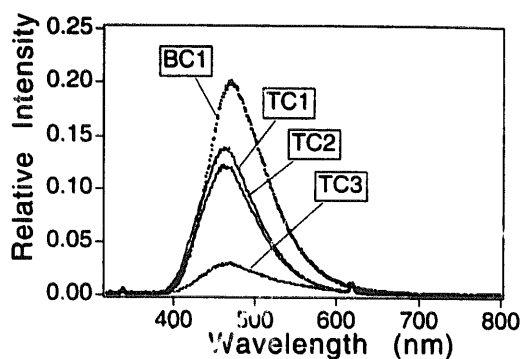


Fig. 3. Fluorescence spectra of BC1 and TC1–TC3 in di-*n*-propylether. Note the strongly reduced fluorescence intensity of TC3.

While a complete analysis of the temperature-dependent photophysical behaviour of TC1–TC3 will be published separately [17,18], we wish to report that the inversion of the relative energies of the CS1 and CS2 states indeed occurs in the trichromophores.

As shown in Fig. 3, all trichromophores display broad CT fluorescence in solvents of low polarity at a position identical to that of the bichromophoric D_1 –A model BC1. This emission thus results from radiative deactivation of the CS1 state.

Interestingly, the emission intensity of the trichromophores becomes progressively smaller on lowering the D_2 oxidation potential and in TC3 it is strongly quenched. This behaviour can be explained (see Fig. 4) by the transformation of the CS1 into the CS2 state, which provides the additional radiationless decay channel (k_{12}) for the CS1 state in TC1–TC3 which is not available in BC1.

The energy gap between CS1 and CS2 for TC2 in ether solvents appears to be sufficiently small and the rate of the back reaction (k_{21}) sufficiently fast to make delayed CS1 fluorescence, by repopulation of CS1 from CS2, possible. Thus the decay of the CS1 fluorescence of TC2 in ether solvents is clearly biexponential (see Fig. 5), with a very pronounced change in the contribution of the fast (direct) and slow (delayed) components with a change in solvent. In principle, this allows us to analyse in great detail the relative energies of the CS1 and CS2 states [17,18], thereby enabling quantification of the difference in solvation energy brought about by the well-defined change in charge separation distance between these states.

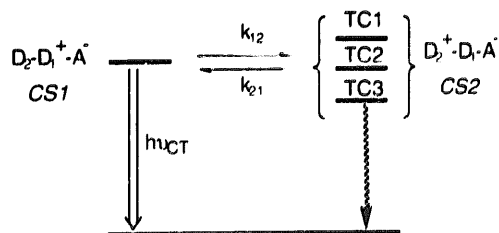


Fig. 4. Qualitative energy diagram showing the relative energies of the (fluorescent) CS1 and (non-fluorescent) CS2 states for TC1–TC3 in ether solvents.

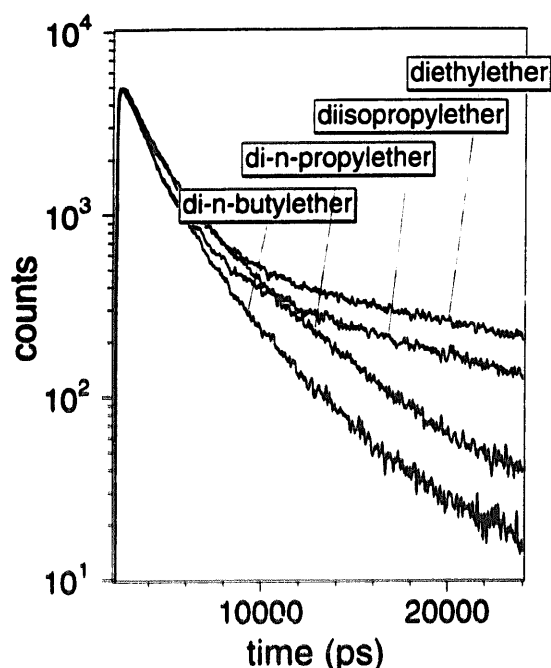


Fig. 5. Fluorescence decay observed for the CT emission of TC2 in four different ethers at 20 °C.

In conclusion, the extension of the bichromophores 1–3 to the trichromophores TC1–TC3 has shown that the anilino-vinylcyanonaphthalene D–A pair provides a useful combination for the realization of multistep long-range charge separation via the multipiperidine bridging scheme introduced in the trichromophores. Extension of this scheme to longer bridges involving more than one intermediate redox centre is under active investigation.

Acknowledgements

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