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Charge separation in the excited state of electron donor-acceptor compounds containing the piperazine moiety

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Three bridged electron donor-acceptor systems are investigated containing a 4-cyano-1-ethylnaphthalene electron-acceptor and piperidine (compound **1**), phenylpiperazine (**2**) and 4-methoxyphenylpiperazine (**3**) electron-donating groups. In the intramolecular charge-transfer states of **1** and **2**, the extent of charge separation is similar, but in compound **3** the positive charge is shifted towards the more powerful arylamine donor site, which results in a significantly greater dipole moment. Optical absorption spectra of model radical cations demonstrate that the predominant charge localization on the trialkyl nitrogen in **2** and on the aryl nitrogen in **3** are a consequence of the bistable nature of the piperazine donors.

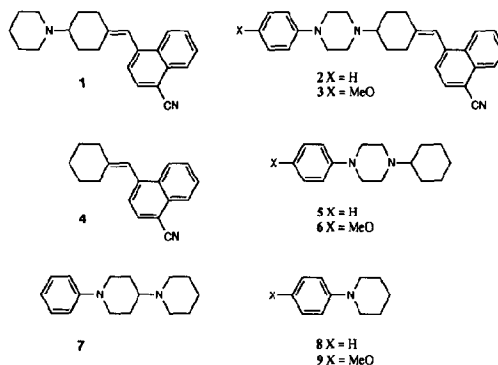
1. Introduction

Light-induced charge separation in donor-spacer-acceptor molecular systems has been shown to occur rapidly over distances up to at least 15 Å, giving rise to excited species with dipole moments as large as 77 D and lifetimes up to 0.7 μs [1]. Electron transfer over greater distances, or through less efficient connecting bridges, can be achieved by a sequence of steps in multichromophoric systems, a process which mimics photosynthesis. Impressive results in this field have been achieved by Gust, Moore and co-workers [2] and recently by Wasielewski et al. [3]. Other examples of multichromophoric electron-transfer molecules have been reported in the literature [4]. Regrettably, the complexity of most of the systems prepared to date limits the insight that can be obtained about the individual events that make up the overall process.

In this paper, we describe some results obtained with compounds of the type acceptor-bridge-donor₁-bridge-donor₂, designed in such a way that the acceptor chromophore carries the initial excitation energy. This implies that the subsequent charge-

separation steps, if they occur, will take place sequentially and unidirectionally.

The general concept is expressed in compounds **2** and **3**, which contain an ethenylcyanonaphthalene electron-acceptor chromophore and have the potential donor sites linked together in a piperazine ring. For reference, the acceptor-bridge-donor₁ compound **1** and the acceptor model system **4** are included in the study (scheme 1).



Scheme 1. Compounds investigated.

The interaction between the two nitrogen atoms in piperazine and its derivatives constitutes a problem of general interest. Photoelectron spectra of symmetrical derivatives fail to reveal a significant splitting of the lowest ionization potentials, related to the ejection of a lone-pair electron [5]. From the ESR spectrum of the radical cation of *N,N*-dimethylpiperazine, a weak interaction between the nitrogen atoms was inferred [6]. Recently, the optical absorption spectrum of this species was also reported [7], and it was attributed to a structure with charge delocalization. On the other hand, the peak oxidation potential (in a linear sweep voltammogram) of dimethylpiperazine (0.89 V versus SCE) has been reported to be slightly higher than that of *N*-methylpiperidine (0.80 V) [8], indicating the absence of a strong stabilizing interaction between the nitrogen atoms in the radical cation. The values of the oxidation potentials reported, however, should be used with care in view of the irreversible nature of the one-electron oxidation [9]. In the case of dimethylpiperazine, a considerable *N-N* interaction in the excited singlet state was invoked to explain the shift of the emission maximum compared to *N*-methylpiperidine [10], but for *N*-alkyl-*N'*-aryl piperazines the fluorescence spectra were similar to those of the aniline analogues, indicating that the excitation is essentially localized on the aromatic moiety [11].

We show in the present work that considerable differences in the charge distribution in the piperazine fragment occur in the charge-transfer excited states of compounds **2** and **3** formed after excitation of the acceptor group in solvents of moderate polarity. The interaction between the *N* atoms in the radical cations of the donor₁-donor₂ fragment is further investigated by comparing the optical absorption spectra of the radical cations of the model systems **5**, **6** and **7** (scheme 1) with the spectra of the radical cations of 1-phenylpiperidine **8** and 1-(4-methoxyphenyl)piperidine **9**.

2. Results

2.1. Fluorescence measurements

The fluorescence spectra of compounds **1**, **2** and **3** in solvents of medium polarity are typical for the oc-

currence of light-induced intramolecular electron transfer. In addition to a fluorescence band around 370 nm, ascribed to radiative decay of the initially formed acceptor excited state, a broad emission at longer wavelengths is observed. On the basis of its large solvatochromicity, this can be attributed to radiative charge recombination (charge-transfer (CT) fluorescence). In more polar solvents the CT emission is further red-shifted and reduced in intensity. Fluorescence spectra of **1**, **2**, **3** and **4** in di-*n*-butyl ether are shown in fig. 1.

In table 1, the wavenumbers of the CT emission

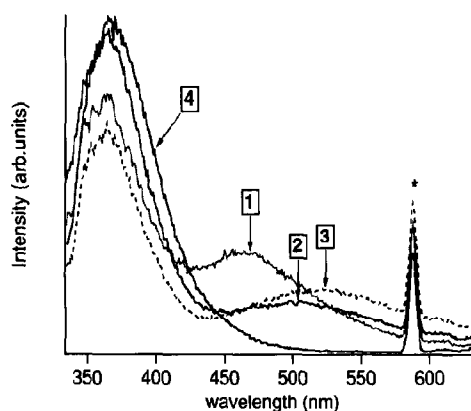


Fig. 1. Fluorescence spectra of **1-4** in di-*n*-butyl ether. The band at 588 nm labeled with an asterisk is due to second-order excitation light.

Table 1

Maxima of CT-emission bands (σ , 10^3 cm^{-1}) and corresponding fluorescence lifetimes τ (ns; in parentheses) of compounds **1**, **2** and **3**; solvatochromic shift $2\mu^2/hcp^3$ and estimated dipole moments μ (D)

Solvent	Δf ^{a)}	1	2	3
trans-decalin	0.110	b)	b)	23.3
<i>n</i> -butyl ether	0.194	21.4(11)	19.8	19.1(19)
<i>n</i> -propyl ether	0.213	20.7	19.2	18.5
isopropyl ether	0.237	20.1(3)	18.7	17.6
ethyl ether	0.251	19.6	18.0	17.0
benzene		20.7(4)	19.2(11)	18.6(14)
dioxane		18.8(4)	18.2(6)	16.7(9)
$2\mu^2/hcp^3$		30.6	29.8	44.7
μ		22.3	24.4	31.0

^{a)} From eq. (1a) in text.

^{b)} No CT fluorescence observed.

maxima and fluorescence decay times are reported. The quantum yields are of the order of, or lower than 1% in all cases.

From the plot of the wavenumber of maximum emission σ_{CT} versus the solvent polarity parameter Δf (eq. (1a) according to eq. (1b), see below), the slope $2\mu^2/hcp^3$ was obtained [12], which was used to estimate the excited-state dipole moment μ . Benzene and dioxane, which are known to behave anomalously in this analysis [13], were not included in the fit

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}, \quad (1a)$$

$$\sigma_{CT} = \sigma_{CT}(0) - \frac{2\mu^2}{hcp^3} \Delta f. \quad (1b)$$

The cavity radius ρ was estimated from the molecular volume as calculated from the molecular weight and the estimated density of 0.8 g cm^{-3} , which is typical of low molecular weight organic materials. The dipole moments derived in this way are given in table 1. Although based upon a small set of experimental data and subject to the uncertainties inherent to the simple model employed, they are seen to agree well with the TRMC results reported below.

2.2. Time-resolved microwave-conductivity measurements

Time-resolved microwave-conductivity (TRMC) experiments [14] reveal the presence of highly polar transient species upon flash photolysis of **1**, **2** and **3** in benzene and dioxane. The relevant experimental data are presented in table 2. In addition to the short-lived transient TRMC signal reported, an additional long-lived species producing a weak signal was observed in some cases. The dipole moments reported in table 2 have been derived as described previously

[14] from kinetic fits to the TRMC transients assuming a quantum yield of unity for the formation of the short-lived transient species.

In saturated hydrocarbon solvents, compounds **1** and **2** show no CT emission, while TRMC reveals no or only weak transient signals. Compound **3** displays two CT-fluorescence bands and a TRMC transient with double-exponential decay kinetics. This we ascribe to two different conformers in the charge-transfer excited state, one extended and one folded. The former is characterized by a strong, short-lived contribution to the TRMC signal and a short-lived CT emission at $\approx 23300 \text{ cm}^{-1}$ (in trans-decalin), while the latter gives rise to a weaker, longer-lived TRMC component and a corresponding CT emission at $\approx 18700 \text{ cm}^{-1}$. The rate of the electrostatically driven conformational change depends very strongly on the dielectric properties of the solvent: in trans-decalin ($\epsilon = 2.17$), it is markedly slower than in *n*-hexane ($\epsilon = 1.88$), and in di-*n*-butyl ether (and more polar solvents, $\epsilon \geq 3.09$), it is too slow to compete effectively with the decay of the excited singlet species. A study of the interesting behavior of compound **3** in different saturated hydrocarbon solvents will be reported separately [15].

2.3. Electronic absorption spectra of donor radical cations

The distribution of charge in the $(D_1-D_2)^{+\cdot}$ fragment would be expected to influence its optical absorption spectrum. The spectra of the radical cations of model compounds **5**, **6**, **7**, **8** and **9**, generated by pulse radiolysis of oxygen-saturated solutions of the parent amines in cyclohexane [16,17], are shown in fig. 2.

Surprisingly, the spectrum of the radical cation of 1-cyclohexyl-4-phenylpiperazine **5** resembles that of a trialkylamine [18], with the characteristic aniline

Table 2
Lifetime τ (ns) and dipole moments μ (D) of CT states derived from the TRMC signals

	1		2		3	
	benzene	dioxane	benzene	dioxane	benzene	dioxane
τ	6	6	10	8	15	10
μ	23.3	21.4	25.2	24.1	33.4	37.8

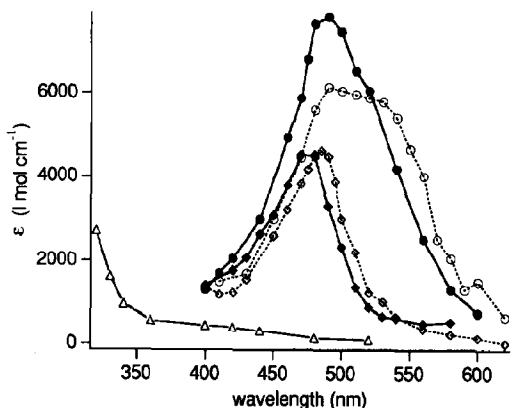


Fig. 2. Optical absorption spectra of radical cations. (Δ), 5; (\bullet), 6; (\blacklozenge), 7; (\diamond), 8; (\circ), 9.

band in the 450 to 500 nm region being completely absent. The spectrum of the isomeric 1-phenyl-4-(1-piperidine)piperidine 7 is, in contrast, quite similar to that of 1-phenylpiperidine 8. 1-cyclohexyl-4-(4-methoxyphenyl)piperazine 6 gives rise to a radical-cation spectrum which resembles that of 1-(4-methoxyphenyl)piperidine 9, although it is less broadened towards long wavelengths. The spectra of the 1-arylpiperidines 8 and 9 are almost identical to those of the corresponding dimethylanilines [16,18,19].

2.4. Model calculations of structural features

In their ground state, the molecules investigated exist in fully extended conformations in which the nitrogen-containing ring is equatorially attached to the methylenecyclohexane ring. This is confirmed by the characteristic splitting pattern in the ^1H NMR spectra of the axial hydrogen at the junction. Both rings are known to exist almost exclusively in chair-type conformations in neutral ground-state species.

The geometry of the model system 1-(4-methylenecyclohexyl)-4-methylpiperazine was optimized by means of a molecular-mechanics calculation (MMX, PCModel [20]) and the interatomic distances between the nitrogen atoms and the endocyclic carbon atom of the methylene group were found to be 4.3 and 7.2 Å, respectively.

The structures of several amine radical cations were optimized by means of AM1 calculations [21,22] using the unrestricted Hartree-Fock formalism. The

results show that in all cases two distinct species can be obtained, with the positive charge essentially localized on one or the other of the nitrogen centers. Thus, semi-empirical AM1 calculations support the idea that piperazines can be regarded as bifunctional electron-donor systems.

3. Discussion

The TRMC and fluorescence measurements presented above clearly demonstrate the occurrence of fast light-induced intramolecular electron transfer in the bi- and tri-chromophoric compounds investigated. An important conclusion which can be drawn from the combined results is that the quantum yield for formation of the dipolar state must approach 100% for the donor-acceptor compounds 1-3, given the fact that the dipole moments from fluorescence solvatochromicity and TRMC (based on unit quantum yields) agree and are compatible with the dipole moment expected on the basis of the structure (except for 2).

Surprisingly, the acceptor emission at 370 nm is only partially quenched (comparing to 4) even in polar solvents (at most 50% in acetonitrile). Since the observed fluorescence quantum yield of the reference compound 4 is only low ($\leq 1\%$), we have to consider the possibility that this emission originates from an impurity, or from a small fraction of the molecules which is in an "inactive" conformation. The fluorescence can be related to the low-energy UV absorption band ($\lambda_{\text{max}}=316$ nm, $\epsilon=10000$ [11]; $f \approx 0.2$), which corresponds to a radiative lifetime of about 5 ns. The observed quantum yield and lifetime ($\ll 1$ ns) [23] are consistent with this. Thus, if the fluorescence is caused by a minor species, this species should be responsible for the major part of the optical absorption, which is clearly unlikely. Moreover, analyses by HPLC and ^1H NMR spectroscopy reveal no impurities. An alternative explanation of the observations is that an efficient non-radiative process takes about 99% of the excited molecules to a non-fluorescent intermediate state, from which electron transfer occurs in the donor-substituted compounds. These remarkable properties of the acceptor chromophore used here (and in previous work

in our laboratory) [24] clearly deserve further detailed investigation.

For compounds **1** and **2**, similar dipole moments are found in their charge-transfer excited states. This suggests that the positive charge is mainly localized on the first donor unit in **2**, the aliphatic amino nitrogen atom. The presence of the second aniline donor does, however, appear to stabilize the $D_2-D_1^+-A^-$ state, as deduced from the bathochromic shift of the CT fluorescence of **2** compared with that of **1**. Our initial thought was that the Coulomb force between the charged sites might have prevented the additional charge migration to give the $D_2^+-D_1-A^-$ species. The UV/VIS absorption spectrum of the radical cation of 1-cyclohexyl-4-phenylpiperazine **5** convinced us that, in contrast to expectation, there is an intrinsic preference for the charge to be predominantly located on the trialkyl nitrogen rather than on the aniline nitrogen atom! In complete contrast, the isomeric 1-phenyl-4-(1-piperidine)piperidine **7** gives rise to a radical cation with an absorption spectrum similar to that of *N,N*-dimethylaniline (and *N*-phenylpiperidine **8**). Our tentative explanation is that the aniline moiety is intrinsically the better electron donor, but also more suited to stabilize, by through-bond interaction, a positive charge on the 4-position in the six-membered ring. In the piperazine system, this interaction is strong enough to invert the stability of the two radical ions, while in **7**, where one additional bond is present between the nitrogens, this stabilization is less important. The small blue-shift of the radical-cation spectrum of **7** relative to that of **8** (and that of **6** relative to **9**) may be due to the stabilization of the ground state of the radical ion. The reason for the more effective stabilization by the aniline nitrogen in comparison with an aliphatic amino group is probably that it has a flattened conformation, which allows a more effective through-bond coupling [25].

In compound **3**, a substantially larger charge-transfer distance ($\approx 7 \text{ \AA}$) is achieved. The introduction of a methoxy substituent into the phenyl group (which reduces the ionization potential by $\approx 0.1 \text{ eV}$ [26]) is apparently sufficient to shift the charge mainly to the aromatic amino nitrogen. Still, there is readily observable charge-recombination fluorescence. Interestingly, the progressively weaker

coupling of the donor and acceptor sites in **1**, **2** and **3** is reflected in an increasing lifetime.

In an earlier paper from our laboratory on piperazine-based trichromophoric systems, Mes et al. [27] reported that 1-phenyl-4-(2-naphthylmethyl)-piperazine and its 4-methoxyphenyl analog give CT species differing in their emission energy by 0.1 eV, which is just the difference in ionization potential of *N,N*-dimethylaniline and 4-methoxy-*N,N*-dimethylaniline [26]. From this, and from the almost identical fluorescence solvachromicity of the two compounds, it was concluded that the positive charge in both of these systems is mainly located on the aniline nitrogen. A possible explanation for the apparent discrepancy with the results presented here is that Mes' compounds can adopt a conformation in which Coulomb stabilization favors a charge shift to the aromatic donor site. In our compounds **1** and **2**, there is little opportunity for such a conformational change, while in **3**, with a $D_2^+-D_1-A^-$ charge distribution, we do indeed observe a dynamic conformational process, but only in saturated hydrocarbon solvents [15].

4. Conclusions

In trichromophoric compound **2**, a charge-transfer excited state of the $D_2-D_1^+-A^-$ is formed upon UV excitation of the acceptor chromophore. A further electron transfer to give $D_2^+-D_1-A^-$ is apparently unfavorable. This is in line with the intrinsic preference of charge localization on the aliphatic amino nitrogen atom found for the radical cation of 1-cyclohexyl-4-phenylpiperazine **5**. A slightly better electron donor replacing D_2 is sufficient to result in the formation of the $D_2^+-D_1-A^-$ species, as demonstrated for compound **3**.

5. Experimental

The syntheses of the compounds will be described in a separate paper. Fluorescence spectra were recorded on a Spex Fluorolog II emission spectrometer. The excitation wavelength was chosen to be 294 nm, an absorption maximum of the reference-compound phenanthrene (fluorescence quantum yield

0.125) [28], allowing the use of a cut-off filter centered at 305 nm, which does not affect significantly the acceptor emission band. All samples for fluorescence measurements were degassed by purging with argon for at least 20 min and had an absorbance of $0.10 \pm 0.02 \text{ cm}^{-1}$. Time-resolved fluorescence spectra were obtained using a Lambda Physik excimer laser at 308 nm and an EG&G OMA system. Decays at single wavelengths were recorded using a transient digitizing system as described in detail elsewhere [29].

The TRMC measurements were carried out and analyzed as fully described elsewhere [14]. Briefly: the solutes, absorbance $\approx 1 \text{ cm}^{-1}$, were photo-excited using the 308 nm, XeCl line of a Lumonics excimer laser with a fwhm pulse width of 5 ns and an integrated intensity of approximately 10 mJ/cm^2 per pulse. The change in microwave power reflected by the cell containing the solution of interest was monitored using a Tektronix 7912 transient digitizer. The pulse shape was monitored using a subnanosecond time-response photodiode. The time response of the microwave cavity, which was the limiting factor in the overall rise time and equal to approximately 5 ns, was determined from the reflection characteristics of the cavity. Data analysis involved numerically solving the appropriate rate equations for formation and decay of intermediates using the Runge-Kutta method including the known pulse shape and time response, and correcting for the variation of light intensity with penetration as described previously [14].

Amine radical cations were generated by pulse radiolysis (3 MeV electrons, 50 ns pulse width) of oxygen-saturated solutions of the amines ($10^{-3} \text{ mol l}^{-1}$) in cyclohexane [16].

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