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Photoinduced Charge Separation in Rigid Bichromophoric Compounds and Charge Transfer State Electron Transfer Reactivity

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Bichromophoric compounds giving, after photoexcitation, a locally excited state (LE) rapidly followed by an intramolecular charge transfer (CT) state were designed using a Paddon-Row type synthesis. The electron-accepting end of the CT state is chosen in order to play the role of an electron relay versus external acceptors. In this way, electron transfer photosensitization is made available by using the CT state of bichromophores. The photophysics of the synthesized bichromophores is discussed, and the reductive dechlorination of polychlorinated benzenes is used as a test reaction. The bichromophoric sensitizer is unexpectedly found to be totally regenerated: the reaction is shown to be initiated by an electron transfer from the CT state to the chlorinated quencher. A rapidly breaking radical anion leads to the dechlorination, while the recombination of the sensitizer radical cation with the released chloride anion opens the way to the sensitizer recovery.

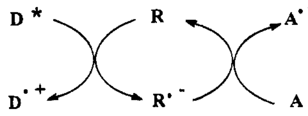
Introduction

In a photoreaction initiated by a photoinduced electron transfer (PET), it may be of interest to avoid reactions between the oxidized form of the donor ($D^{\bullet+}$) and the reduced form of the acceptor ($A^{\bullet-}$) in order to favor other processes. For this goal, the two species need to be formed at remote distances from each other. One way to realize this aim is to use an electron relay (R), as shown in Scheme 1. Reactions using this scheme have already been presented in the litterature. Bipyridinium derivatives were used as relays in the photoreduction of water[1,2] or carbon dioxide.[3] In other examples, biphenyl acts as a positive charge carrier between dicyanoanthracene and stilbene,[4] tetraphenylcyclopropanes[5] or benzotriazole.[6] Systems were made with viologen carriers shuttling between donor and acceptor trapped in matrices like sol−gel glasses.[7] Very efficient relaying was obtained when viologen derivatives were aligned in assemblies like in polymers[8] or at a micellar surface.[9]

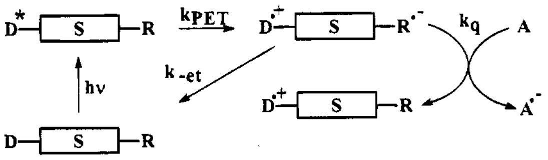
In the absence of a particular organization of the medium, drawbacks of this scheme may be important: it may be difficult to play with the relative concentrations of R and A in order to get a major relayed electron transfer. On the other hand, secondary reactions between $R^{\bullet-}$ and $D^{\bullet+}$ may replace the preceding undesirable side reactions. Another way to reach the goal is to try using bichromophores in which the relay is already attached to the electron donor through a rigid spacer (S). According to the Marcus theory, if the free enthalpy of the forward reaction (k_{PET}) is not too exergonic, this step must be faster than the back electron transfer (k_{-et}) so that the lifetime of the CT state is long enough to react (k_q) in the expected way (Scheme 2).

This type of system, but without the rigid spacer, has already been tested by us, starting with a TICT compound, the N (α-naphthyl) carbazole. A dual electron transfer reactivity of the CT state of this molecule was shown in two ways. On one hand, electron transfer rate constants, using acceptors or donors as quenchers, were correlated in acccordance with the Marcus theory. On the other hand, photochemical dechlorination was used in order to enlighten the anionic reactivity of the naphthalene end of the TICT. The cationic reactivity of the carbazolyl part of the TICT state was demonstrated by the sensitized quadricyclane photoisomerization.[10] The use of such a system as a photocatalyst has been recently suggested.[11]

SCHEME 1



SCHEME 2



The study of photoinduced electron transfer (PET) in bi- or multichromophoric compounds is a very active research field related to methods for harvesting and storing solar energy.[12] A lot of work has been done on multicomponent systems designed to mimic the photosynthesis. The creation of a charge separation state able to survive during a delay sufficient for its use in subsequent reactions is one of the goals of this type of work and several groups have developed elegant routes along this biomimetic strategy.[13−18]

A hydrocarbon chain bridging a donor and an acceptor is commonly considered an insulator. A PET in compounds of the $D-(CH_2)_n-A$ type is however possible and the effect of conformational changes linked to the methylene chain flexibility has been studied.[19−22] It became rapidly evident that the methylene chain folding is not a prerequisite for the PET and that an exciplex does not have a strong conformational preference.[23,24]

Verhoeven and colleagues used cyclohexane or a steroidal skeleton as a spacer between donors and acceptors, and their work indicates that rapid electron transfer rates are possible over appreciable distances, much greater than the sum of their van der Waals radii.[25−28] The effect of the distance has been studied on an elegant series of molecules with a spacer made of norbornane units,[29,30] and convincing proofs were given concerning the importance of the through bond interaction in those

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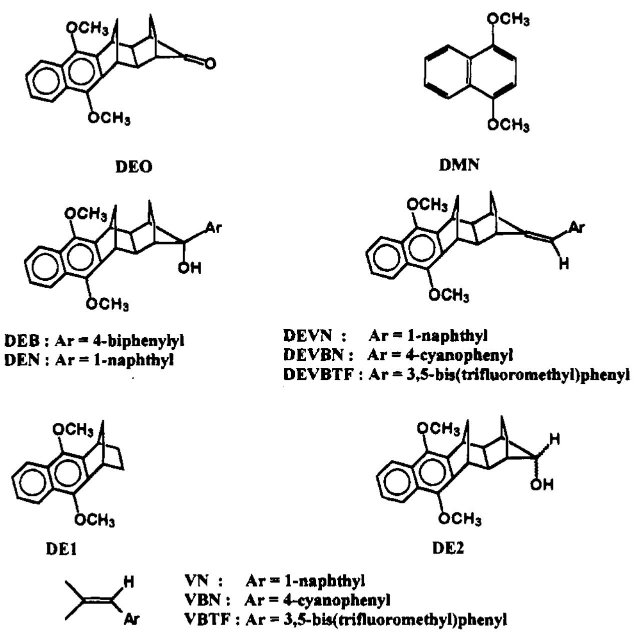
CHART 1



DEO

DMN

DEB : Ar = 4-biphenylyl
DEN : Ar = 1-naphthyl

DEVN : Ar = 1-naphthyl
DEVBN : Ar = 4-cyanophenyl
DEVBTF : Ar = 3,5-bis(trifluoromethyl)phenyl

DE1

DE2

VN : Ar = 1-naphthyl
VBN : Ar = 4-cyanophenyl
VBTF : Ar = 3,5-bis(trifluoromethyl)phenyl

intramolecular PET.[31-33] The subject is largely studied and reviewed and the effect of the parameters controlling long range electron transfer is very seriously examined: the redox driving force, the solvent and vibrational reorganization energies and the distance or relative orientation of the donor and acceptor.[34-35]

Although the photophysics of intramolecular photoinduced electron transfer have been extensively studied, the reactivity of charge transfer (CT) excited states in this type of supermolecule remains almost unexplored. Our first attempts about the use of a "Paddon-Row" type bichromophore in a photoreaction are discussed in this contribution.

Results and Discussion

Bichromophore Synthesis. Bichromophoric compounds with a dimethoxynaphthalene (DMN) donor moiety and an electron-accepting relay were synthesized. Firstly, the intermediate DEO was prepared according to the well-detailed Paddon-Row route[29] and the bichromophores were obtained from DEO using Grignard or Wittig–Horner reactions. DMN, DE1, DE2, and the vinylic reference compounds were also prepared (Chart 1).

Electronic Absorption Spectra. UV spectra of the bichromophoric compounds were recorded, and no noticeable difference was found when these spectra were compared with the sum spectra of the constituting DE1 or DE2 and vinyl reference chromophores. This was found in all tested solvents. The spectrum of DEVN in acetonitrile is compared with DE1 and VN as an example (Figure 1).

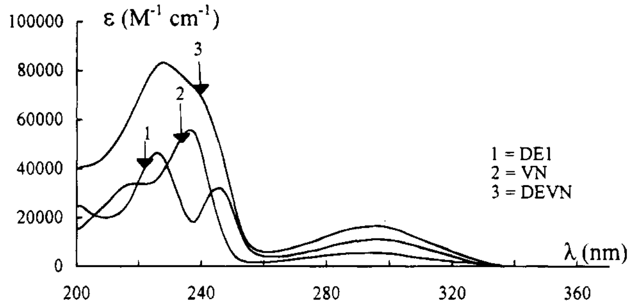


Figure 1. Absorption spectra of DEVN and corresponding model compounds in acetonitrile.

In compounds similar to DEVN but with two cyano substituents instead of Ar and H, the electronic interaction is significant as evidenced by Oevering et al.[29] A detectable interaction, attributed to charge transfer, was still present if a supplementary norbornyl unit is incorporated in the hydrocarbon spacer. In our case, no significant interaction was detected, probably due to the expected weakness of the charge transfer between ground state dimethoxynaphthalene and the weak acceptors used in our chromophores.

Fluorescence Spectra. Fluorescence data for the reference compounds DMN, DE1, and DE2 are given in Table 1. The solvent effect on the emission wavelength is found to be significant and very similar for the three molecules.

TABLE 1: Solvent Effect (λ_{max} in nm) on the Fluorescence of Reference Molecules

solvent	DMN	DE1	DE2
cyclohexane	356	350	350
benzene	374	372	372
diethyl ether	368	362	362
ethyl acetate	376	374	374
tetrahydrofuran	376	372	372
dichloromethane	385	385	385
ethanol	386	382	382
acetonitrile	390	388	388

TABLE 2: Fluorescence Quantum Yields Φ_f and Lifetimes (τ in ns)[a]

solvent	DMN	DE1	DE2	DEB	DEN
cyclohexane	0.46	0.36 (5.4)	0.36 (5.4)	0.36	0.36
benzene	0.43	0.31 (4.5)	0.31	0.31	0.30
diethyl ether	0.38	0.30	0.30	0.30	0.29
ethyl acetate	0.40	0.38 (4.8)	0.37	0.38	0.38
tetrahydrofuran	0.30	0.25	0.25	0.25	0.20
dichloromethane	0.22	0.17 (2.8)	0.18	0.17	0.14
ethanol	0.29	0.34	0.34	0.34	0.27
acetonitrile	0.29 (5.5)	0.33 (4.6)	0.33 (4.6)	0.33 (4.6)	0.26 (3.4)

[a] Excitation at 320 nm, degassed by argon bubbling for 10 min.

This solvent effect can be used to estimate the excited state dipole moment (μ_e) with the help of the following equation in which wavenumbers are plotted against the Δf parameter of the solvent:[29]

$$\bar{\nu}_e = \bar{\nu}_{e(0)} - \frac{2\mu_e^2}{hca^3}\Delta f \tag{1}$$

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \tag{2}$$

The obtained dipole moments (eliminating the benzene measurements) are in the range 6–7 D, depending on the value taken for the molecule radius (a = 3.5–4 Å). This value is surprisingly high for a simple naphthalene derivative. However it is in the range of the dipole moment observed by Desvergne et al. in a study of excited 1,4-dialkoxyanthracene.[36]

Fluorescence quantum yields and lifetimes were measured in several solvents. Anthracene in ethanol (Φ_F = 0.27) was used as the standard.[37] The data obtained for all molecules showing a single fluorescence are given in Table 2. DEB and DEN, even in polar solvents, were found to behave exactly as DE1 or DE2: a single fluorescence with the same shape and comparable efficiency. This still corresponds to the local excited state (LE) of the dimethoxynaphthalene and is shown in Figure 2. In the case of DEN, a drop in the quantum yield is observed in weakly and strongly polar solvents.

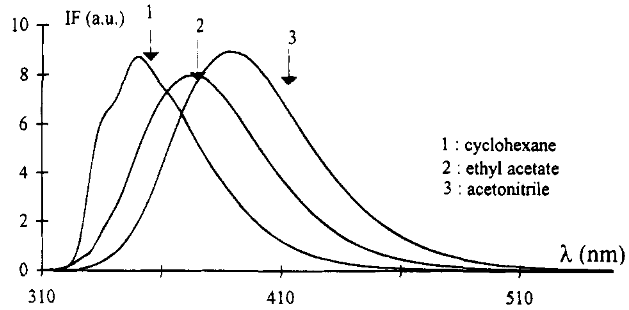


Figure 2. Emission spectra of DE1 (excitation at 300 nm).

One possible explanation for the fluorescence drop in DEN could be an intramolecular singlet energy transfer: this is possible (about 3 kcal endergonicity if the singlet energies of DMN and naphthalene are considered). However, this explanation does not hold if the solvent effect, as shown on the emission wavelengths (Table 1) is considered. The excited states of these molecules are stabilized in more polar solvents by about 3 kcal if the difference between solvents like ethyl acetate and acetonitrile is considered: this stabilization would render the energy transfer more difficult in the most polar solvents, in contradiction with the observed trend of the fluorescence efficiency.

Another explanation is the occurrence of a charge transfer from the LE to the naphthalene electron-accepting chromophore, which is a slightly better acceptor than biphenyl.[38-40] This small difference (less than 200 mV in reduction potential), associated with the fact that electron transfer to biphenyl is slowed down when compared to naphthalene, due to some extra "inner" reorganization barrier,[41] seems sufficient to explain the change in the fluorescence behavior when going from DEB to DEN.

The feasibility of a PET in the bichromophores is rather easily estimated on thermodynamic grounds using eq 3.[30,42]

$$\Delta G^\circ = 23.06\,(E_{\mathrm{ox}}^{\mathrm{D}} - E_{\mathrm{red}}^{\mathrm{A}} - E_{00}) - \frac{e^2}{\epsilon R_{\mathrm{c}}} - \frac{e^2}{r}\left(\frac{1}{37.5} - \frac{1}{\epsilon}\right) \tag{3}$$

In this equation, E_{ox} and E_{red} are the redox potentials (in volts) of the donor and acceptor. E_{oo} is the energy (in volts) stored in the excited chromophore. The next term is an estimation of the Coulombic stabilization energy of the charge transfer state with R_{c} being the center to center distance between the two chromophores. The redox potentials are as measured in acetonitrile ($\epsilon = 37.5$), and their values are corrected by the last term of the equation for their use in other solvents of dielectric constant ϵ. The r value is the mean radius of the chromophores (in angstroms).

This equation is used with the following values: $E_{\mathrm{ox}} = 1.10$ V,[29] $E_{\mathrm{red}} = -2.59$ V (reduction potential of naphthalene[39] taken in the absence of a known value for 1-naphthylcarbinol), $E_{\mathrm{oo}} = 3.75$ V,[29] $R_{\mathrm{c}} = 10.5$ Å, $r = 4.5$ Å. The estimated free enthalpy of the intramolecular charge transfer in DEN is exergonic in acetonitrile (−2.2 kcal) and ethanol (−1.6 kcal), and slightly endergonic in dichloromethane and in THF (1.3 and 2.2 kcal). It reaches strongly endergonic values in the nonpolar solvents (17 kcal in cyclohexane) and this is in line with the trends observed on the relative fluorescence intensities of DEN compared to the DE1 or DE2 model molecules. The ratio starts to drop when the electron transfer becomes significantly favored by the solvent polarity.

The intramolecular electron transfer rate constants may be calculated according to eq 4 using the quantum yields of the bichromophores and of the reference compounds measured in the same solvents together with the reference compound lifetime:

$$k_{\mathrm{PET}} = \frac{\Phi_{\mathrm{ref}} - \Phi_{\mathrm{bic}}}{\tau_{\mathrm{ref}}\Phi_{\mathrm{bic}}} \tag{4}$$

With lifetimes only, the eq 5 may be used:

$$k_{\mathrm{PET}} = \frac{1}{\tau_{\mathrm{bic}}} - \frac{1}{\tau_{\mathrm{ref}}} \tag{5}$$

Equation 4 used with values measured in dichloromethane and acetonitrile or eq 5 (in acetonitrile only) gives k_{PET} values between 5×10^{7} and 8×10^{7} s^{-1}.

In DEVN, DEVBN, or DEVBTF, the fluorescence in nonpolar solvents remains very similar to the one observed for DE1. When the solvent polarity increases, a drastic decrease of the LE fluorescence is observed and a new bathochromic, unstructured, and broad fluorescence emerges which may be attributed to a CT state. The dual fluorescence is observed for DEVBTF and DEVBN in weakly and strongly polar solvents while strongly polar solvents are needed in the case of DEVN.

Emission spectra of DEVBTF in different solvents are presented in Figure 3 while the fluorescence data for the three bichromophores are summarized in Table 3. That the bathochromic emission is related to a charge transfer state is confirmed by the strong dependence of its wavelength on the solvent polarity. This solvatochromism has been used in order to estimate the dipolar moment of the CT state, using again eqs 1 and 2. The CT states dipole moments are estimated around 50 D, a value which corresponds to a charge separation over a distance of 10.5 Å. The used cavity radius (a in eq 1) was 7.5 Å, as estimated from molecular models.

A very clear effect of solvent polarity on fluorescence quantum yields is shown in Table 3, in spite of a rather low accuracy of the individual reported values. This poor accuracy is due to the weak fluorescences of the LE and CT states as well as to the partial overlapping of the two bands. The order of magnitude of the k_{PET} values in those bichromophoric compounds may be calculated by starting again from the experimental fluorescence quantum yields and lifetimes. For DEVBTF and DEVBN, values are located between 1×10^{10} and 7×10^{10} s^{-1} and the same is true for DEVN in acetonitrile. These values are higher than in DEN and this was to be expected, according to the Marcus model, since the reduction potentials of the accepting moiety are more favorable to the PET than in DEN. These values, as measured in acetonitrile and versus SCE, are

$$E^{1/2}_{(\mathrm{VN/VN}^{\bullet-})} = -2.33 \pm 0.10\ \mathrm{V}$$

$$E^{1/2}_{(\mathrm{VBTF/VBTF}^{\bullet-})} = -2.10 \pm 0.10\ \mathrm{V}$$

$$E^{1/2}_{(\mathrm{VBN/VBN}^{\bullet-})} = -2.03 \pm 0.10\ \mathrm{V}$$

In the case of DEVN, the CT state fluorescence is only weakly detectable in acetonitrile and DMF in spite of the fact that a significant drop of the LE fluorescence is registered in these solvents. This means that the CT state is formed but that its decay is much faster than for the other bichromophoric systems. One viable explanation may be that in the case of DEVN, a back electron transfer from the CT state leads, more efficiently as in the other cases, to a local triplet state. A triplet state located on the dimethoxynaphthalene chromophore is expected around 61 kcal,[43] and 60 kcal if located on naphthalene. We may consider that the singlet and triplet CT state are degenerated, as accepted in the case of TICT states.[44,45] Looking to the thermodynamics of PET in DEVN, DEVBTF, or DEBN

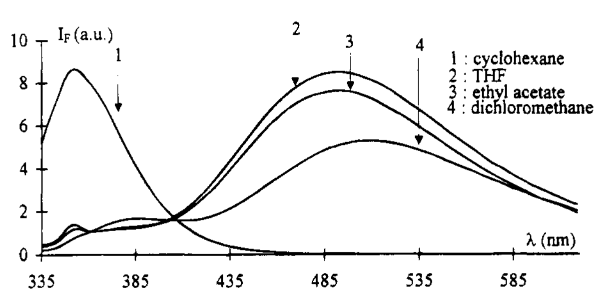


Figure 3. Solvent effect on the DEVBTF fluorescence spectra.

in a solvent like THF, we find that the CT state must be located at 82, 77, or 75 kcal. This means that the free enthalpy of a back electron transfer from the CT to a local T_1 is about −22 kcal for DEVN. Using the conventional formula for the calculation of the intrinsic barrier for the solvent reorganization in such an electron transfer, values are found, in this same solvent, to lie between 20 and 25 kcal. Thus, it would not be surprising that in the DEVN bichromophore the free enthalpy of this back electron transfer corresponds to the reorganization barrier, and this means that it would be at the maximum of the Marcus curve.

In ethanol solvent, the CT state fluorescence was never observed, and this is probably due to the quenching of this state by this protic solvent. A reasonable explanation might be a proton transfer between the solvent and the radical anionic moiety of the CT state. One example of a similar quenching has already been shown in the litterature.[46] On the same line, the absence of a CT state emission in DEN may tentatively be related to the presence in the molecule of a hydroxyl group on the radical anionic side of the CT state. Furthermore, quenching experiments by methanol have been done on the CT states of the three bichromophoric systems in acetonitrile. Linear Stern−Volmer relations were observed with the following constants (in M^{-1}): 0.1 (DEVN), 1.4 (DEVBTF), 1.0 (DEVBN).

As far as the goal of this work is concerned, the most important point to stress is the almost total LE quenching due to the PET: whenever the fluorescence quantum yields or lifetimes are considered, the LE state only survives to an extent of between 2 and 5% in solvents like acetonitrile or DMF. This is the first condition to be met in order to look at the CT state reactivity.

Quenching of the CT States. Having in mind the use of bichromophoric CT states as electron transfer reagents, the best way to test this reactivity is to measure the CT emission quenching by appropriate acceptors or donors. This redox behavior has been tested with polychlorobenzene acceptors (hexachlorobenzene = $PhCl_6$, pentachlorobenzene = $PhCl_5$) and with DABCO as a donor. The LE state is localized on the donor side of our bichromophores and competing PET pathways (k_q and k'_q) may be expected (Scheme 3), leading to the following Stern−Volmer equations for the CT and LE states:

$$\frac{I^0_{CT}}{I_{CT}} = 1 + k_q\tau_{CT}[A] \qquad (6)$$

$$\frac{I^0_{LE}}{I_{LE}} = 1 + k'_q\tau_{LE}[A] + k_q\tau_{CT}[A] + k_qk'_q\tau_{LE}\tau_{CT}[A]^2 \qquad (7)$$

Values of the Stern−Volmer and quenching constants are shown in Table 4 together with reference values obtained for the DE1 molecule. Two fluorescence quenching experiments are shown in Figures 4 and 5.

The quenching measurements gave linear Stern−Volmer graphs for the LE as well as for the CT fluorescence bands. For the CT state, the quadratic equation is reduced to an observed straight line which confirms that the LE state only survives to a negligible extent (between 2 and 5% according to Table 3).

The Stern−Volmer graphs gave K_{SV} values leading to an overestimate of the corresponding k'_q when measurements are made at the emission wavelength of the LE state (360 nm). Values higher than diffusion rate constants are even obtained in this way. This is due to the partial overlapping of the two emission bands: the LE fluorescence decrease is the result of the sum of both LE and CT fluorescence quenchings. This has been confirmed in the following way: the decreasing intensities of the fluorescence observed at 360 and 377 nm in the case of DEVN quenched by $PhCl_6$ in DMF (Figure 4) were simulated and correctly fitted to the results using this summation hypothesis. The used k'_q value was the one measured on the DE1 reference molecule (given in Table 4). The contribution of the CT emission to the LE band was found to be 27% at 360 nm and 35% at 377 nm.

All the observed results are coherent with the model proposed in Scheme 3: the CT and LE states of the bichromophoric compounds are intercepted by the quenchers. The quenching of the LE state, even if effective, only influences the CT state quenching in a negligible amount. What is clearly shown by these results is that even with a diffusional quenching of the LE state, it remains possible to mainly induce a reaction starting from the CT state.

Photoreductive Dechlorination. In order to confirm the reactivity of the radical anionic part of the CT state of DEVN, dechlorination experiments were performed on hexa- and pentachlorobenzenes in DMF as solvent. This type of reaction has already been used in the similar context of the TICT state reactivity of naphthylcarbazole (NC): the TICT state was found to initiate dechlorination, and the NC sensitizer was consumed at a rate that almost corresponds to the dechlorinated product formation.[10] The CT state of DEVN was found to be active in those dechlorinations as well, and the results are presented in Table 5. A striking difference with the TICT system is that, in the DEVN case, the sensitizer is only slowly consumed with respect to the dechlorination progress. In the two experiments presented here, a sensitizer turnover (obtained from the ratio between the dechlorinated products and the consumed sensitizer) of about 8 is observed with normal degassing of the mixture. In the case of prolonged argon bubbling, higher turnovers were observed. DEVBTF was also used as a dechlorination sensitizer: the same behavior was observed but the dechlorination rate was slowed down by a factor of about 3.

It is known that the dechlorination of polychlorobenzenes may be sensitized by triplet energy donors,[47] and it was therefore necessary to verify that a conventional triplet-triplet energy transfer is not involved. In order to check for this mechanism, *cis*-piperylene and TMDD (tetramethyldiazetine dioxide[48]), two very efficient triplet quenchers have been added to the photolysis mixture (in concentration ranges of 5 × 10^{-2} M). This method already allowed us to make the distinction between electron or energy transfer mechanism in the case of the naphthylcarbazole TICT compound.[10] The reactions photosensitized by DEVN or by DEVBTF were not affected by the presence of TMDD or *cis*-piperylene. Furthermore, *cis*-piperylene was found to be weakly isomerized during the photolysis. These experiments exclude an energy transfer from a CT or LE T1 state to the polychlorinated aromatic triplet state.

The reactivities of the NC TICT state and of the DEVN CT states may be compared on the basis of their quenching rate constants by $PhCl_5$ in acetonitrile. The k_q rate constants were

TABLE 3: Fluorescence Data of Bichromophores 4[a–c]

	DEVN		DEVBTF			DEVBN		
	Φ_f^{LE}	Φ_f^{CT}	Φ_f^{LE}	Φ_f^{CT}	λ_{max}^{CT}	Φ_f^{LE}	Φ_f^{CT}	λ_{max}^{CT}
cyclohexane	0.36		0.36			0.367		
diethyl ether	*d*		*d*	*d*	419	*d*	*d*	441
ethyl acetate	0.11		0.006	0.021	493	0.003	0.018	509
THF	0.08		0.001	0.025	493	0.001	0.029	510
dichloromethane	0.08		0.003	0.012	511	0.002	0.017	551
ethanol	0.12		0.006			0.005		
acetonitrile	0.005 (0.32)	0.001 (7)	0.002 (0.23)	0.001	*e*	0.001	0.001	*e*
DMF	*d* (0.20)	*d* (13.6)	*d* (0.11)	*d* (12.7)	600	*d*	*d*	712

[a] Fluorescence quantum yields measured versus anthracene for LE and quinine sulfate for CT. [b] Wavelength in nm. [c] Values in parentheses are lifetimes in ns. [d] Not measured. [e] Broad flattened peak with undefined maximum.

SCHEME 3

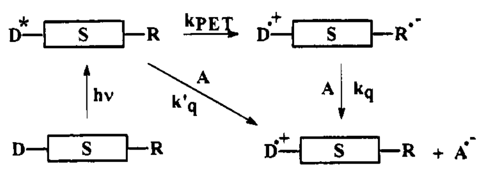


TABLE 4: Fluorescence Quenchings of DEVN, DEVBTF, and DE1

fluorophore	solvent	quencher	K_{SV}[a] (M^{-1})	k_q (M^{-1} s^{-1})	K'_{SV}[b] (M^{-1})	k'_q (M^{-1} s^{-1})
DEVN	DMF	$PhCl_6$	92	6.8	22	"109"[d]
DEVN	CH_3CN	$PhCl_5$	45	6.5	8	"26"[d]
DEVBTF	CH_2Cl_2	$PhCl_5$	24	1.9	2	"20"[d]
DEVN	CH_3CN	DABCO	23	3.3		
DEVN	DMF	DABCO	34	2.4		
DE1	DMF	$PhCl_6$			65[c]	14
DE1	dmf	$PhCl_5$			82[c]	18
DE1	CH_2Cl_2	$PhCl_5$			33[c]	7

[a] Measured at 560 nm. [b] Measured at 360 nm. [c] Measured at 390 nm. [d] Apparent rate constants due to spectral overlap with the CT emission band (see text).

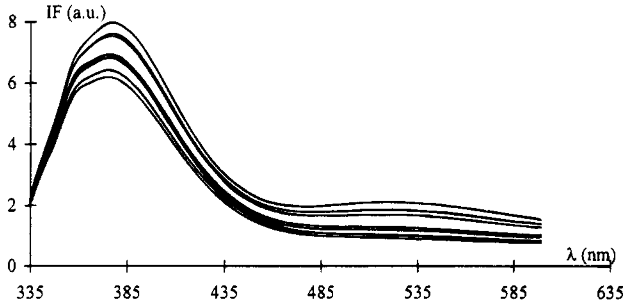


Figure 4. Fluorescence quenching of DEVN by hexachlorobenzene in DMF.

found respectively at 2.4 × 10^9 and 6.5 × 10^9 M^{-1} s^{-1}, and an electron transfer from the TICT to the $PhCl_5$ was shown to be responsible for the quenching.[10] The values are in the same order of magnitude, and this may be taken as an argument showing that electron transfer is again responsible for the quenching of the DEVN CT state. Furthermore, the electron-donating species, in the TICT as in the CT state, is a very similar radical anionic naphthalene moiety. The DEVN CT state may intuitively be expected to be somewhat more reactive since the distance between the negative and the positive charges is higher in the CT than in the TICT, leading to a lower Coulombic stabilization. A further argument favoring the electron transfer mechanism is the decrease of the dechlorination rate when going from the DEVN to the DEVBTF case: on thermodynamic grounds, the free enthalpies of the LE (D^*-S-R) states and of the ion pair states ($D^{\bullet+}-S-R$/ $PhCl_5^{\bullet-}$) are localized at the same energy levels. The difference arises from the intermediate CT state ($D^{\bullet+}-S-R^{\bullet-}$) energy level: this state is lower for DEVBTF (by 0.2 V), and the efficiency of the electron transfer to the polychlorinated aromatic quencher is thus expected to decrease.

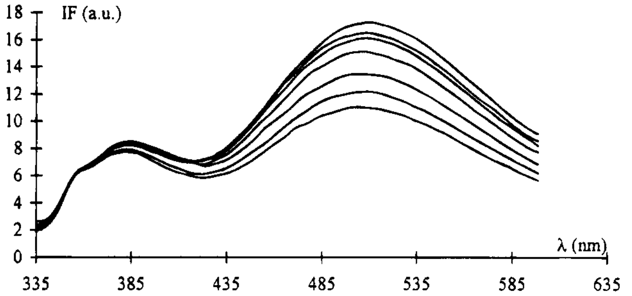


Figure 5. Fluorescence quenching of DEVBTF by pentachlorobenzene in CH_2Cl_2.

TABLE 5: DEVN-Sensitized Photodechlorination of Polychlorobenzenes in DMF

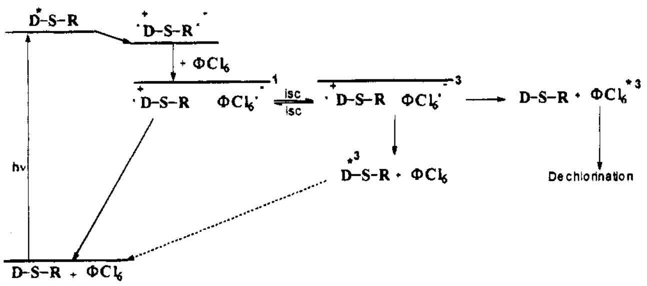
	$PhCl_6$ dechlorination[a] ($[PhCl_6]_o = 15 \times 10^{-3}$ M, $[DEVN]_o = 1.1 \times 10^{-3}$ M)		$PhCl_5$ dechlorination[a] ($[PhCl_5]_o = 41 \times 10^{-3}$ M, $[DEVN]_o = 1.3 \times 10^{-3}$ M)			
			10^3 [tetrachlorobenzenes] (M)			
time (min)	10^3 [$PhCl_5$] (M)	10^3 [DEVN] (M)	1,2,3,5	1,2,4,5	1,2,3,4	10^3 [DEVN] (M)
30	0.54	1.08	0.19	0.69	0.45	1.25
60	1.00	1.07	0.36	0.87	0.73	1.19
90	1.47	1.05	0.59	1.28	1.06	1.13
120	1.83	1.03	0.64	1.47	1.27	1.08
150	2.23	1.00	0.83	1.80	1.48	0.99
210	2.85	0.76	0.88	2.16	1.63	0.76
240[b]	2.91	1.24				

[a] 45 min of degassing with Ar before irradiation. Turnovers may be calculated around 8. [b] Separate experiment with 90 min of degassing with Ar before irradiation and $[PhCl_6]_o = 7.6 \times 10^{-3}$ M $[DEVN]_o = 1.28 \times 10^{-3}$ M. Turnovers may be estimated around 80.

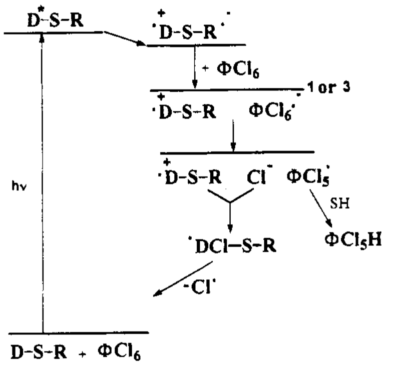
After the PET between the CT state of DEVN and the polychlorobenzene quencher, a radical cation centered on the dimethoxynaphthalene moiety of the bichromophore is formed. In order to explain the observed turnover, some regenerating pathway must be found leading from this radical cation to the starting sensitizer. In the absence of a sacrificial donor in the medium, a proton loss leading to a radical and a subsequent hydrogen abstraction from the solvent were suspected. However no deuterium incorporation was detected in the sensitizer after the photoreaction has been run in perdeuterated DMF: this shows that hydrogen abstraction from the solvent does not play a significant role in the sensitizer cycling.

An attractive hypothesis for reconciling the high sensitizer turnover with the electron transfer mechanism, described in Scheme 4, must be evaluated. This should lead to the $PhCl_6$ triplet which is said to be dechlorinated.[47] Globally, this reaction scheme may be viewed as a singlet–triplet energy transfer, as

SCHEME 4



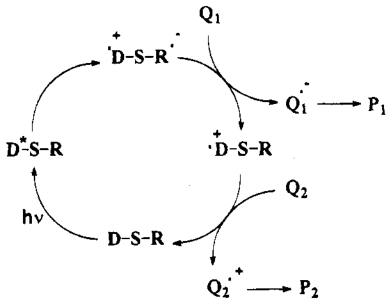
SCHEME 5



was already suggested in a few examples in the past,[49] or more recently.[50,51] The singlet−triplet energy transfer is presented here as a two-step Dexter type electron exchange. A forward electron transfer from the CT state to the polychloroaromatic quencher may be very rapidly followed by the intersystem crossing in the geminate ion pair. If back electron transfer occurs in the singlet ion pair, this will lead, by a photon wasting away, to the starting reactants. On the contrary, if the back electron transfer takes place in the triplet ion pair, the local triplet state of the starting bichromophore or of $PhCl_6$ may result. When considering the energetics of the concerned excited state levels, one can see that, starting from a LE at 86 kcal, the ion pair state may be localized at 64 kcal according to the redox potentials E_{ox} of 1.1 V [30] and E_{red} for $PhCl_6$ (−1.67 V).[51,52] The local triplet states of DE1 and $PhCl_6$ are located at 61 and 73 kcal, respectively. We thus may expect that the uphill back electron transfer leading to the chloroaromatic triplet will not be predominant. In a similar context Previtali et al. effectively showed that the T1 state of pyrene (48 kcal) is formed by the quenching of its singlet state by 1,2,4-trichlorobenzene (T1 = 79 kcal) and we think that their observations may be explained by a forward and a back electron transfer, as presented in Scheme 4.[49] For these reasons, we do not think that Scheme 4 is the best explanation of our results.

An alternative explanation allows us to get rid of the uphill back electron transfer: as shown in Scheme 5, a C−Cl bond mesolysis should occur in the ion pair leading to the $PhCl_5$ radical. If this radical escapes from the cage or abstracts a hydrogen from the solvent, a caged radical cation−chloride anion pair is left. Since radical cations are known to be trapped by nucleophiles,[53] a recombination between the donor radical cation and the chloride anion may lead to a cyclohexadienyl type radical. A chlorine atom may be released from this species, restoring the aromatic sensitizer. Besides avoiding the uphill reactions, explaining the absence of triplet state quenching and explaining the sensitizer turnover, Scheme 5 also avoids the uphill homolytic bond breaking in the T1 state of $PhCl_6$. The endergonic bond rupture of chlorinated aromatic triplet states has always been a problem in the interpretation of the results of direct or sensitized photolyses and was at the origin of the proposals of triplet exciplexes or excimers as plausible dechlorination pathways.[51,54,55]

SCHEME 6



Conclusion

An electron transfer has been shown to be initiated from an intramolecular CT state, and in this sense, the aim of the work has been reached: a CT state may be used as an intramolecular relaying precursor in electron transfer photochemistry. In this precursor the initially electron-accepting relay is converted ("umpolung") into the electron-donating initiator. However, our results are clear examples of photochemical systems in which the frontier between electron and energy transfer is not easy to define. As shown, a triplet state reactivity was a possible explanation for the sensitizer regeneration but this mechanism is questioned due to the energetics of the involved states.

Our system has been shown to regenerate the sensitizer, an unexpected result if electron transfer is responsible for the reaction. This is probably related, as shown in Scheme 5, to the particular case of this photodechlorination. The possibility of using bichromophoric compounds as regenerated electron transfer sensitizers may however remain possible under other circumstances, for instance if sacrificial redox species are used in order to restore the photosensitzer. In our case, chloride anion, a product of the photoreduction, generated in the solvent cage, is assumed to play the role of the sacrificial donor: oxidation of the chloride anion passes through a recombination followed by the chlorine atom release. In more general cases, external sacrificial electron donors or acceptors may be used. A particular case of this design with a donor absorbing chromophore and an electron-accepting relay is presented in Scheme 6. Anyway, in order to design such systems, a delicate tuning of excitation energy, redox potentials, and triplet energy contents are needed.

Experimental Part

Materials. All the solvents used for spectroscopic measurements were commercial spectroscopic grade (Merck Uvasol) except acetonitrile and methanol which were HPLC grade (Rathburn and Roth, respectively) and used without further purification.

The studied compounds are presented in Chart 1. The bichromophores were synthesized from DEO, which was obtained according to published methods.[29]

DEB. A solution of 3.6 mmol of 4-bromobiphenyl in 12 mL of dry THF was added dropwise to a magnetically stirred refluxing suspension of 3.6 mmol of Mg turnings in 10 mL of dry THF containing a crystal of iodine. The mixture was then refluxed for a further 2 h. DEO (3 mmol) dissolved in 15 mL of dry THF was then slowly added and the reflux maintained over 6 h. After cooling, 30 mL of water were added and the solution neutralized with ammonium chloride. After extraction (ether), drying ($MgSO_4$), and solvent evaporation under reduced pressure, a white solid was obtained. The desired products were purified by column chromatography on silica gel (hexane–ethyl acetate: 30:70) and recrystallized (hexane with a few percent of ethyl acetate). Yield: 57%. Mp: 161 °C. Detailed NMR analysis was already published.[56] Mass (FAB, MNBA, +ions): *m/z* 489.4 (M + 1), 472.3, 251.2, 225.3, 211.2, 196.1, 181.1, 165.5, 151.9.

DEN was synthesized by the same method as DEB, starting from 1-bromonaphthalene. Yield: 58%. Mp: 134 °C. NMR: see ref 56. Mass (FAB, MNBA, +ions): *m/z* 463.3 (M + 1), 445.2, 227.0, 211.0, 196.0, 136.0, 127.0.

DEVN, DEVBN, and DEVBTF (bichromophores) and VN, VBN, and VBTF (model compounds) were synthesized from DEO and acetone, respectively, by the Wittig–Horner reaction. The phosphonates were derived from the appropriate bromomethyl aromatic compounds. A magnetically stirred solution of 45 mmol of $ArCH_2Br$ and 45 mmol of triethyl phosphite was heated at 110 °C under slightly reduced pressure during 1 h. The resulting yellow oil was then purified.

(1-Naphthyl)$CH_2PO(OEt)_2$ was purified by column chromatography on silica gel (ethyl acetate). Yield: 87%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.21 (t, $^3J_{H-H}$ = 7.10 Hz, 6H), 3.55–4.00 (m, 4H), 3.60 (d, $^2J_{H-P}$ = 21.98 Hz, 2H), 7.30–7.55 (m, 4H), 7.70–7.85 (m, 2H), 8.08 (d, 1H).

(3,5-Bis(trifluoromethyl)phenyl)$CH_2PO(OEt)_2$ was purified by column chromatography on silica gel (ethyl acetate–hexane: 75:25). Yield: 95%. ^{1}H NMR (200MHz, $CDCl_3$): δ 1.28 (t, $^3J_{H-H}$ = 7.05 Hz, 6H), 4.00–4.20 (m, 4H), 3.29 (d, $^2J_{H-P}$ = 21.97 Hz, 2H), 7.75–7.85 (m, 3H).

(4-Cyanophenyl)$CH_2PO(OEt)_2$ was purified by column chromatography on silica gel (ethyl acetate-methanol: 97:3). Yield: 94%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (t, $^3J_{H-H}$ = 7.00 Hz, 6H), 3.95–4.15 (m, 4H), 3.91 (d, $^3J_{H-P}$ = 22.35 Hz, 2H), 7.40–7.45 (m, 2H), 7.62 (d, $^3J_{H-H}$ = 8.23 Hz, 2H).

DEVN, DEVBN, and DEVBTF. The reaction was run at −78 °C under an Ar atmosphere. Dry diisopropylamine (5.5 mmol) and 2.5 mL of BuLi (2 M in hexane) were stirred for a few minutes, and 15 mL of dry THF was added. After the mixture was stirred for a further 10 min, 5.5 mmol of phosphonate dissolved in 10 mL of dry THF was slowly introduced and the stirring maintained for 45 min. DEO (5 mmol) dissolved in 20 mL of dry THF was slowly added. At the end of the addition, the reaction mixture was allowed to reach slowly room temperature. After 18 h of stirring and addition of 25 mL of water, the product was extracted (dichloromethane) and dried ($MgSO_4$), and solvent was evaporated under reduced pressure. White solids were obtained and purified.

DEVN was purified by column chromatogtaphy on silica gel (hexane–dichloromethane: 25:75) and recrystallization (hexane with a few percent of dichloromethane). Yield: 87%. Mp: 182 °C. NMR: see ref 56. Mass (EI, 70 eV): *m/z* 458.1 ($M^{\bullet +}$), 251.1, 229.1 (M^{2+}), 225.0, 223.0, 211.0, 193.0, 178.1, 165.1, 152.1.

DEVBTF was purified by column chromatography on silica gel (dichloromethane–hexane: 50:50) and recrystallization (methanol). Yield: 91%. Mp: 153 °C. NMR: see ref 56. Mass (EI, 70 eV): *m/z* 544.1 ($M^{\bullet +}$), 525.1, 251.1, 225.1, 211.0, 193.0, 181.1, 165.1, 152.0.

DEVBN was purified by column chromatography on silica gel (dichloromethane–hexane: 60:40) and recrystallization (hexane with few percent of ethyl acetate). Yield: 95%. Mp: 173 °C. NMR: see ref 56. Mass (EI, 70 eV): *m/z* 433.1 ($M^{\bullet +}$), 418.0, 251.0, 223.0, 211.0, 193.0, 180.0, 164.8, 152.0

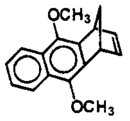
VN, VBN, and VBTF. The same procedure as the one used for the bichromophores has been used with the following amounts of starting materials: dry diisopropylamine, 22 mmol; BuLi, 11 mL (2 M in hexane); $ArCH_2PO(OEt)_2$, 21 mmol; dry acetone, 20 mmol. The resulting oil was further purified by column chromatography on silica gel.

VN was eluted with pentane. Yield: 76% as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.86 (s, 3H), 1.93 (s, 3H), 6.49 (s, 1H), 7.20–8.01 (m, 7H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.17, 26.49, 124.75, 125.30, 125.53, 125.54, 125.72, 126.70, 128.17, 132.07, 135.61, 139.01, 139.37, 139.49. Mass (EI, 70 eV): *m/z* 182.0 ($M^{\bullet +}$), 167.0, 164.9, 152.0, 141.0, 115.0, 89.0.

VBTF was eluted with hexane–dichloromethane (50:50). Yield: 86% as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.86 (d, 2H), 1.94 (d, 3H), 6.29 (broad s, 1H), 7.64 (s, 2H), 7.69 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.06, 24.46, 119.49, 122.85, 123.63, 128.67, 131.68, 139.58, 140.84. Mass (EI, 70 eV): *m/z* 268.0 ($M^{\bullet +}$), 253.0, 249.0, 233.0, 213.0, 199.1, 177.0, 164.0, 115.0.

VBN was eluted with hexane–dichloromethane (60:40). Yield: 95% as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.86 (s, 1H), 1.93 (s, 1H), 6.25 (s, 1H), 7.28–7.30 (m, 2H), 7.55–7.77 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.21, 26.65, 109.14, 118.71, 123.78, 129.00, 131.53, 138.85, 143.19. Mass (EI, 70 eV): *m/z* 157.1 ($M^{\bullet +}$), 142.1, 129.1, 115.1, 102.1, 89.1.

DE1 has been obtained by hydrogenation of the following DMNBD which is an already described intermediate[29] in the synthesis of DEO. DMNBD (12 mmol) and 0.3 g of Pd/C (10%) were placed with 75 mL of ethyl acetate in a Parr pressure reactor. After 24 h, the hydrogenation was stopped and the mixture filtered over Celite. The solution was evaporated under reduced pressure to give a white solid which was recrystallized in ethanol. Yield: 91%. Mp: 73.5–74 °C. NMR : see ref 56. Mass (EI, 70 eV): *m/z* 254.1 ($M^{\bullet +}$), 239.1, 226.1, 211.0, 196.0, 193.0, 181.0, 165.1, 152.1, 139.1.



DMNBD

DE2 $NaBH_4$ (12 mmol), 2 mL of aqueous NaOH (10%), and 20 mL of ethanol were stirred in a round-bottom flask. DEO (3 mmol) dissolved in 10 mL of a THF/EtOH (1/1) mixture was slowly added. After 6 h, 15 mL of water was added and the solution was neutralized with HCl. After extraction (CH_2Cl_2), drying ($MgSO_4$), and solvent evaporation under reduced pressure, a white solid was obtained. The final product was purified by column chromatography on silica gel (dichloromethane) and recrystallized in ethanol. The yield was 100% as a mixture of α and β isomers in a ratio of ~30:70, as determined by NMR. Mp: 185–186 °C. ^{1}H NMR (200 MHz, $CDCl_3$): major isomer δ 1.39 (2H), 1.50 (2H), 1.53 (1H), 2.03 (1H), 2.04 (2H), 2.27 (2H), 3.55 (2H), 3.65 (1H), 3.88 (6H), 4.01 (1H), 7.32 (2H), 7.96 (2H); minor isomer δ 1.50 (1H), 1.56 (2H), 1.75 (2H), 1.83 (2H), 2.04 (1H), 2.13 (2H), 3.53 (2H), 3.65 (1H), 3.87 (6H), 7.33 (2H), 7.96 (2H), ^{13}C NMR (50 MHz, $CDCl_3$): major isomer δ 21.13, 40.03, 43.15, 43.55, 45.33, 61.17, 84.22, 121.60, 124.61, 127.32, 138.34, 143.08, minor isomer δ 21.09, 40.66, 42.84, 43.82, 44.24, 61.22, 80.17, 121.65, 124.71, 127.32, 137.70, 142.95. Mass (EI, 70 eV): *m/z* 336.1 ($M^{\bullet +}$), 321.0, 303.1, 287.1, 225.1, 193.0, 181.0, 165.0, 125.1.

DMN was prepared according to a known recipe.[57] The product was isolated by chromatography on a silica gel column (hexane−ethyl acetate: 75:25) and then twice recrystallized in ethanol. White crystals were obtained with a 46% yield. Mp: 87−87.5 °C (lit. 86−87 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.95 (s, 6H), 6.70 (broadened s, 2H), 7.42−7.68 (m, 2H), 8.12−8.25 (m, 2H).

Methods. Electronic absorption spectra were recorded on an SLM-AMINCO DW2000 spectrophotometer at room temperature. Corrected fluorescence spectra were taken on an SLM-AMINCO 48000s spectrofluorometer with correction factors supplied by the company. The absorbance of the solutions at the excitation wavelength was about 0.1. The fluorescence quantum yields were measured with solutions bubbled with Ar for 10 min. Anthracene in ethanol and quinine sulfate in 0.1 N H_2SO_4 were taken as standards. Fluorescence lifetime measurements were done by SPT in the laboratory of De Schryver[58] and by phase shift fluorescence on an SLM-AMINCO 48000s working from 1 to 250 MHz and equipped with a Xe lamp. For the bichromophoric compounds the phase fluorometer of Valeur[59] has been used with a He/Cd laser working at 325 nm as the excitation source.

The photolyses were performed in Pyrex tubes with solutions deaerated by 45 min of Ar bubbling. They were performed in a Rayonet reactor equipped with 10 black phosphor RPR 3500 Å lamps. During the reaction, samples were taken through a septum under argon to follow the progress of the photolysis by GC and/or HPLC.

The redox potentials were measured at room temperature in acetonitrile distilled over P_2O_5 and CaH_2 just before use. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.1 M) (Fluka puriss). A mercury drop electrode was used with a large platinum grid as the counter-electrode. The potentials were measured relative to the saturated calomel electrode and were found to be nonreversible.

NMR spectra were recorded on Varian Gemini 200 with TMS as the internal standard.

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