Long-Lived Triplet State Charge Separation in Novel Piperidine-Bridged Donor−Acceptor Systems

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Abstract: Two bichromophoric systems are presented that contain an *N*-alkylnaphthalimide electron acceptor and a 4-methoxyaniline (**3a**) or an aniline (**3b**) electron donor, respectively. Upon photoexcitation of **3a** in cyclohexane electron transfer occurs in the singlet manifold to afford the short-lived ($\tau_f = 0.75$ ns) $^1(D^+{-}A^-)$ state in *ca.* 70% yield. An important decay pathway of this $D^+{-}A^-$ state consists of intersystem crossing (ISC) to yield a triplet state localized on the naphthalimide moiety ($D{-}^3A$). In a slightly more polar solvent like di-*n*-butyl ether, an equilibrium between $D{-}^3A$ and $^3(D^+{-}A^-)$ is observed by means of transient absorption spectroscopy. Both species decay with an overall decay time of *ca.* 1 μs. Thus, upon changing the spin multiplicity of the $D^+{-}A^-$ state from singlet to triplet, an increase of its lifetime by three orders of magnitude is observed. In more polar solvents like dioxane, THF, and acetonitrile the $^3(D^+{-}A^-)$ state is the only species observed in the transient absorption spectrum, with decay times of *ca.* 1, 0.5, and 0.1 μs, respectively. The $D{-}^3A$ state is the precursor state for the $^3(D^+{-}A^-)$ state in these solvents. It is proposed that, upon increasing solvent polarity, the singlet charge-separation process is retarded as a result of the large driving force ($-\Delta G_S^\circ > 1$ eV), which allows the triplet pathway ($D{-}^1A \rightarrow D{-}^3A \rightarrow {}^3(D^+{-}A^-)$) to compete effectively. Compound **3b** possesses a somewhat weaker donor chromophore than **3a** resulting in a smaller driving force. The decay of the locally excited singlet state of **3b** occurs mainly *via* charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$). Only in the very polar solvent acetonitrile does the triplet pathway become competitive, and evidence is found for the formation of $^3(D^+{-}A^-)$.

Introduction

Photoinduced electron transfer processes in artificial bridged electron-donor (D)−electron-acceptor (A) systems are widely studied in order to understand factors that affect charge transfer (CT) rates and efficiencies.[1−5] One of the central goals in such research has been to mimic natural photosynthetic systems where the photoexcitation process is followed by multiple electron transfer steps, which lead to a long-lived trans-membrane charge-separated state in high yield.[6,7] Indeed, quite a number of multichromophoric systems, triads,[8−12] tetrads,[13,14] and even pentads[15] have recently been realized in which multistep charge transfer leads to a charge separation between the terminal chromophores. This, however, did not always[8] lead to a very significant increase in the lifetime of the charge separation, probably because the energy gap between the fully charge-separated state and the ground state in such systems tends to be small, which implies that charge recombination occurs under close-to-“optimal” conditions.

In principle the rate of charge recombination should also be retarded if the ground and charge-separated states of a donor−bridge−acceptor system have a different spin multiplicity. An illustration of this phenomenon was given as early as 1988 by Smit and Warman[16] in their investigation of the polymethylene-bridged compounds **1a**−**d**, synthesized in our laboratory, that contain a carbazole donor and a tetrachlorophthalimide acceptor (see Figure 1). While earlier investigations[17] had shown that the singlet charge-separated state ($^1(D^+{-}A^-)$) of these compounds is short lived (*ca.* 20 ns), Smit and Warman found that a triplet charge-separated state ($^3(D^+{-}A^-)$) is populated which has a lifetime in the microsecond range. Whether this triplet

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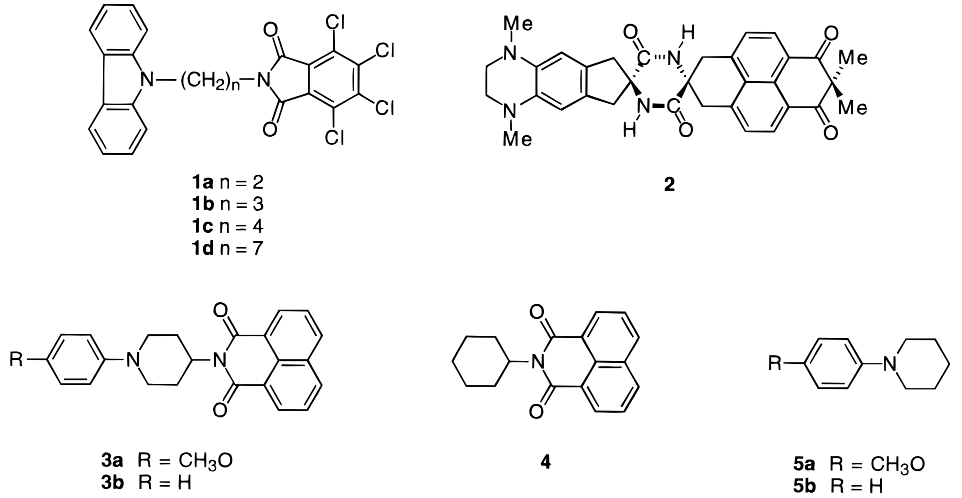

Figure 1. Compounds studied by Smit and Warman (**1a**−**d**), by Anglos *et al.* (**2**), and in this work: bichromophoric (D−A) systems **3a** and **3b** and single chromophore compounds **4** (A), **5a** (D), and **5b** (D).

CT state has the singlet CT state or a local triplet state (^{3}LE) as its precursor could not be decided unequivocally. Moreover, the flexible nature of the bridge does not allow decisive information about the conformation of the CT state to be obtained.

Earlier studies on *intra*molecular charge separation in the triplet manifold are scarce. Studies on *inter*molecular triplet charge-separation processes are, however, quite ubiquitous.[18−23] In this case the time required for ISC in the locally excited singlet state (^{1}LE → ^{3}LE) is provided by the time it takes for the primarily excited species to diffuse toward its partner to a distance small enough for electron transfer to occur. Charge separation in the triplet manifold ($^3\text{LE} \rightarrow {}^3(\text{D}^+{-}\text{A}^-)$) thereby becomes an efficient process. A similar order of events can be envisaged in *intra*molecular systems where D and A are linked by long flexible bridges as in **1d** or the systems studied by Shafirovich *et al.*[24]

A potential problem in generating the $^3(\text{D}^+{-}\text{A}^-)$ state, along this route, in more rigidly linked *intra*molecular systems, is the competition between the local ISC (^{1}LE → ^{3}LE) and singlet charge transfer ($^1\text{LE} \rightarrow {}^1(\text{D}^+{-}\text{A}^-)$). Obviously the energy of $^3(\text{D}^+{-}\text{A}^-)$ must be lower than that of ^{3}LE ($E_\text{T}{}^{00}$), which in turn is lower (often considerably) than that of ^{1}LE ($E_\text{S}{}^{00}$). Thus, there is a large driving force for charge separation from the ^{1}LE state, which, across short spacers, can allow extremely rapid electron transfer with rates of up to 10^{11}−10^{12} s^{-1}.[3,25−27] Only in rare cases can ISC (^{1}LE → ^{3}LE) compete with such rates. Although intramolecular charge separation in a ^{3}LE state has been reported in a number of papers,[28−31] the efficiency of the triplet pathway was limited in these cases due to substantial charge separation occurring in the singlet manifold.

In a recent study, however, Anglos *et al.*[32] described the very interesting rigidly bridged system **2** (Figure 1), which shows a different behavior. It was found that in **2** photoexcitation of the acceptor chromophore is followed by extremely rapid ISC (^{1}LE → ^{3}LE) and consecutive electron abstraction from the powerful diaminobenzene donor across the cyclic dipeptide bridge. Population of a triplet CT state of **2** occurred with nearly unit quantum yield, and a lifetime of 3.35 μs (in THF) was reported for this species, where "hole" and "electron" are separated by seven σ bonds.

In this paper we report that a long-lived triplet CT state can also be formed in high yield with a much smaller separation between D and A than in **2**. This has been achieved *via* the piperidine bridging scheme in the bichromophoric system **3**, where an aniline-type donor and a naphthalimide acceptor are separated by only four σ bonds (Figure 1). The piperidine bridge provides a conformationally well-defined system.[33−35] As models for the isolated chromophores, *N*-cyclohexyl-1,8-naphthalimide (**4**), *N*-(4-methoxyphenyl)piperidine (**5a**), and *N*-phenylpiperidine (**5b**) were also studied.

Experimental Section

Materials. Spectrograde solvents were used for all fluorescence and transient absorption measurements. Dry THF was distilled from sodium/benzophenone prior to use. Acetonitrile was dried and stored on neutral alumina prior to the cyclic voltammetry measurement. Butyronitrile (Fluka) was distilled (under N_2 atmosphere) from CaH_2 prior to use. 1,8-Naphthalimide was obtained from Aldrich and used as received.

Instrumentation and Procedures. All measurements were made at room temperature. Infrared (IR) spectra were obtained from $CHCl_3$ solutions, using a Perkin-Elmer 298 spectrometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in $CDCl_3$ using

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a Bruker AC 200 (200 MHz), Bruker WM 250 (250 MHz), or a Bruker ARX 400 (400 MHz) spectrometer. The latter was also used for ^{13}C NMR (APT) and COSY spectra in $CDCl_3$. Chemical shifts are given in ppm downfield from tetramethylsilane. Melting points are not corrected. Column chromatography was performed with the indicated solvent using Janssen Chimica silicagel (0.030−0.075 mm grain). R_f values were obtained by using thin-layer chromatography (TLC) on silicagel-coated plastic sheets (Merck silicagel 60 F_{254}) with the same solvent as for column chromatography. High-resolution electron impact mass measurements (MS) were carried out using a Jeol JMS-SX/SX102A tandem mass spectrometer.

The electronic absorption spectra were recorded on a Hewlett Packard 8451A diode array spectrophotometer. Fluorescence spectra were measured using a Spex Fluorolog 2 with correction for the wavelength dependence of the detection system containing a RCA C31034 photomultiplier. Fluorescence decay curves of **3a** and **4** were measured by means of time-correlated single photon counting (SPC) ($\lambda_{ex} = 317$ nm, fwhm = *ca.* 22 ps). The setup has been described earlier.[9] A total of 2048 channels of the Multi Channel Buffer (EG&G Ortec 918 ADCAM) working in a pulse-height analysis mode were used. The channel widths used were 2.5, 5, and 10 ps/channel. Fluorescence decay curves of **3b** were measured with a nanosecond time scale setup, described earlier,[36] using a Lumonics Pulse Master EX748 XeCl Excimer laser ($\lambda_{ex} = 308$ nm, fwhm *ca.* 7 ns) as an excitation source. This laser was also used for recording the flash photolysis transient absorption spectra, along with a 450-W high-pressure Xe arc as the probe light, pulsed with a Müller Elektronik MSP05 pulser. The overall time resolution of this setup is *ca.* 10 ns.[9] Concentrations of the studied compounds were *ca.* 10^{-5} M for the fluorescence measurements and *ca.* 10^{-4} M for transient absorption measurements ($A = 0.1$ at λ_{ex} in a 1-cm cell). The samples were carefully deoxygenated by purging with argon (*ca.* 15 min) or by repetitive freeze−pump−thaw cycles.

Spectroelectrochemistry. The UV−vis spectroelectrochemical experiment with **4** was performed on a Perkin-Elmer Lambda 5 UV−vis spectrophotometer connected to a 3600 data station. An OTTLE cell[37] equipped with a Pt-minigrid working electrode (32 wires/cm) and quartz/CaF_2 windows was used at room temperature. The working electrode surroundings were masked carefully to avoid spectral interference with the non-electrolyzed solution. Controlled-potential electrolysis within the OTTLE cell was carried out by a PA4 (EKOM, Czech Republic) potentiostat. The sample solution in butyronitrile was prepared and handled under an N_2 atmosphere. The concentrations of the electrolyzed compound **4** and the $(nBu)_4NPF_6$ supporting electrolyte were 5×10^{-3} and 3×10^{-1} M, respectively.

The reduction potential of **4** was determined by cyclic voltammetry using a gas-tight three-electrode cell and a Bank Electronic POS 73 Wenking Potentioscan potentiostat coupled to a HP 7090A measurement plotting system. The measurements were carried out in deoxygenated acetonitrile containing tetraethylammonium tetrafluoroborate (TEAFB) (*ca.* 0.1 M) as supporting electrolyte and at sweep rates of 100−400 mV/s. A platinum disk (2 mm) working electrode with a Pt gauze auxiliary electrode was used in combination with a saturated calomel reference electrode (SCE) connected to the cell *via* a 3M KCl salt bridge.

Synthesis. The method used for the synthesis of the imide systems was reported earlier by Demmig and Langhals.[38] Reaction of 1-(4-methoxyphenyl)piperidin-4-ylamine or 1-phenylpiperidin-4-ylamine with 1,8-naphthalic anhydride affords the bichromophoric systems **3a** and **3b**, respectively. The acceptor-model system **4** is obtained from reaction of cyclohexylamine with 1,8-naphthalic anhydride. 1-Phenylpiperidin-4-ylamine was synthesized *via* a known[39] route from 1-phenylpiperidone (*via* the oxim derivative). 1-(4-Methoxyphenyl)-piperidin-4-ylamine was obtained analogously from 1-(4-methoxyphenyl)piperidone. The synthesis of the donor-reference systems **5a** and **5b** has been described elsewhere.[40] Numbering for assignment of NMR resonances is shown in Figure 2. Wherever appropriate, this system of numbering is maintained throughout the experimental section. Assignment of the ^1H and ^{13}C NMR signals was done on the basis of $^1H-^1H$ shift-correlated 2D NMR (COSY), $^{13}C-^1H$ COSY, and long-range $^{13}C-^1H$ COSY.

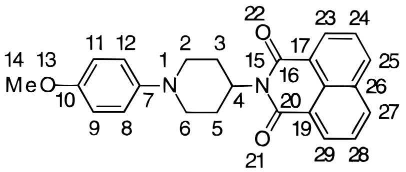

Figure 2. Numbering scheme of **3a**; H and C atoms in **3b** and **4** are labeled correspondingly.

***N*-(1-(4-Methoxyphenyl)-4-piperidinyl)-1,8-naphthalimide (2-[1-(4-methoxyphenyl)piperidin-4-yl]benz[*de*]isoquinoline-1,3-dione) (3a).** The reaction was carried out under a dry-N_2 atmosphere. 1,8-Naphthalic anhydride (1.64 g, 8.24 mmol) was dissolved in 200 mL of DMF and heated to 120 °C. A solution of 1-(4-methoxyphenyl)piperidin-4-ylamine in 50 mL of DMF was added dropwise and the mixture was stirred over night at 120 °C, whereupon the solvent was evaporated. The solid was dissolved in CH_2Cl_2 and 1,8-naphthalic anhydride was filtered off. The filtrate was evaporated to dryness and the residue was submitted to repeated crystallization from CH_2Cl_2. Crude product was obtained in a 1.58 g yield. Column chromatography of 148 mg of this solid using CH_2Cl_2 as eluent afforded **3a** as a yellow solid (90.8 mg, 0.25 mmol, 32%). R_f 0.20. Mp 212.7−214.1 °C. IR (cm^{-1}) 2980, 2940, 2920, 2800, 1690 (C=O), 1650 (C=O), 1615, 1580 (C=C). ^1H NMR (400 MHz) δ 8.58 (d, 2H; H23, H29), 8.19 (d, 2H; H25, H27), 7.74 (t, 2H; H24, H28), 6.98−6.94 (m, 2H; H8, H12), 6.86−6.82 (m, 2H; H9, H11), 5.14 (m, 1H; H4), 3.77 (s, 3H, OCH_3), 3.66 (d, 2H; $H2_{eq}$, $H6_{eq}$), 3.01 (qd, 2H; $H3_{eq}$, $H5_{eq}$), 2.84 (t, 2H; $H2_{ax}$, $H6_{ax}$), 1.78 (d, 2H; $H3_{ax}$, $H5_{ax}$). ^{13}C NMR (100 MHz) 164.60 (C16, C20), 153.66 (C10), 146.14 (C7), 133.63 (C25, C27), 131.47 (C26), 131.19 (C23, C29), 128.20 (C18), 126.95 (C24, C28), 123.13 (C17, C19), 118.96 (C8, C12), 114.37 (C9, C11), 55.58 (C14), 51.95 (C4), 51.77 (C2, C6), 28.44 (C3, C5). High-resolution MS: found *m/z* 386.1630; calcd for $C_{24}H_{22}N_2O_3$ *m/z* 386.1630.

***N*-Cyclohexyl-1,8-naphthalimide (2-cyclohexylbenz[*de*]isoquinoline-1,3-dione) (4).** A solution of cyclohexylamine (1.5 g, 15 mmol) and acetic acid (3 mL) in 45 mL of DMF was added dropwise to 1,8-naphthalic anhydride (2.0 g, 10 mmol) in 30 mL of DMF at 40 °C. The mixture was stirred at 40 °C for 30 min and at 150 °C for 4 h. After the mixture was cooled to room temperature the solvent was evaporated and the residue was washed with water and dissolved in CH_2Cl_2. The CH_2Cl_2 layer was washed with water and saturated sodium bicarbonate solution and dried with Na_2SO_4, and the solvent was evaporated. The residue was dissolved in DMF/acetic acid, a saturated sodium bicarbonate solution was added, and the mixture was heated for 30 min at *ca.* 100 °C. The solid was filtered off and dissolved in CH_2Cl_2. This solution was washed with water and saturated $NaHCO_3$, dried with Na_2SO_4, and evaporated to dryness. Crystallization of the residue from ethanol yielded **4** as light yellow needles (1.22 g, 4.37 mmol, 44%). Mp 231−233 °C. IR 3080−3000, 2930, 2850, 1695, 1655, 1630, 1590. ^1H NMR (250 MHz) δ 8.52 (d, 2H; H23, H29), 8.14 (d, 2H; H25, H27), 7.70 (t, 2H; H24, H28), 5.01 ("t", 1H; H4), 2.54 (q, 2H; $H3_{ax}$, $H5_{ax}$), 1.89 ("d", 2H; $H3_{eq}$, $H5_{eq}$), 1.73 ("d", 3H; $H1_{eq}$, $H2_{eq}$, $H6_{eq}$), 1.55−1.22 (m, 3H; $H1_{ax}$, $H2_{ax}$, $H6_{ax}$). High-resolution MS: found *m/z* 279.1254; calcd for $C_{18}H_{17}NO_2$ *m/z* 279.1259. UV (acetonitrile), $\lambda(\epsilon)$: 332 (12300 M^{-1} cm^{-1}), 346 (11300 M^{-1} cm^{-1}).

***N*-(1-Phenyl-4-piperidinyl)-1,8-naphthalimide (2-(1-phenylpiperidin-4-yl)benz[de]isoquinoline-1,3-dione) (3b).** The same method was employed as described for **4** using 1-phenylpiperidin-4-ylamine (2.05 g, 12 mmol), acetic acid (2 mL), and 1,8-naphthalic anhydride (1.34 g, 7 mmol). Crystallization from CH_2Cl_2/*n*-hexane afforded **3b** as yellow needles (250 mg, 0.70 mmol, 10%). Mp 249−250 °C. IR 3100−2860, 2810, 1695, 1655, 1625, 1590. ^1H NMR (200 MHz) δ 8.57 (d, 2H; H23, H29), 8.18 (d, 2H; H25, H27), 7.74 (t, 2H; H24, H28), 7.37−7.18 (m, 2H; H9, H11), 6.99 (d, 2H; H8, H12), 6.83 (t, 1H; H10), 5.23 ("t", 1H; H4), 3.84 ("d", 2H; $H2_{eq}$, $H6_{eq}$), 3.20−2.80

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Table 1. Half-Wave Potentials of the Oxidation (E_{ox}) and Reduction (E_{red}) of Separate Chromophore Models (see Figure 1) (Cyclic Voltammetry at the Pt Disk Electrode in Acetonitrile *vs* SCE), along with Some Photophysical Parameters (in Cyclohexane)

	E^{00} (eV)		redox potentials (V)	
chromophore	E_S^{00}	E_T^{00}	E_{ox}	E_{red}
N-cyclohexyl-1,8-naphthalimide (**4**)	3.63[a]	2.29[a]		-1.34[g]
N-(4-methoxyphenyl)piperidine (**5a**)	3.69[b]	2.99[c]	0.61[d]	
N-phenylpiperidine (**5b**)	3.91[e]	2.95[f]	0.81[d]	

[a] Data for *N*-methyl-1,8-naphthalimide, ref 41; E_T^{00} from phosphorescence at 77 K. [b] Data for *N*,*N*-dimethyl-4-methoxyaniline, ref 52. [c] Data for *N*,*N*-dimethyl-4-methoxyaniline, ref 64. [d] Reference 52. [e] Reference 65. [f] Data for *N*,*N*-diethylaniline, ref 66. [g] This work.

(m, 4H; $H2_{ax}$, $H6_{ax}$, $H3_{eq}$, $H5_{eq}$), 1.80 ("d", 2H; $H3_{ax}$, $H5_{ax}$). High-resolution MS: found *m/z* 356.1523; calcd for $C_{23}H_{20}N_2O_2$ *m/z* 356.1525. UV (acetonitrile), $\lambda(\epsilon)$: 256 (14800 M^{-1} cm^{-1}), 332 (13500 M^{-1} cm^{-1}), 346 (12300 M^{-1} cm^{-1}).

Results

Separate Chromophores. Compound **4** was used as a reference system for the acceptor chromophore whereas **5a** and **5b** served as donor references. Relevant photophysical and redox data are compiled in Table 1. Clearly, the lowest locally excited singlet state of **3** is located on the imide acceptor moiety (E_S^{00}(A) = 3.63 eV, Table 1). Upon excitation at 308 nm this chromophore also absorbs most of the light (ϵ_{308}(**3a**) = 8500 L mol^{-1} cm^{-1}, ϵ_{308}(**3b**) = 7000 L mol^{-1} cm^{-1}, ϵ_{308}(**4**) = 6000 L mol^{-1} cm^{-1}), and very rapid energy transfer ^{1}D−A → D−^{1}A is likely to occur anyway in the smaller fraction of molecules which are initially excited in the donor unit. It is known that naphthalimides undergo efficient intersystem crossing causing a short singlet-state lifetime and low fluorescence quantum yields.[17,41,42] Indeed, compound **4** displays only very weak emission ($\phi_f = 2 \times 10^{-4}$ (τ_f = 1.0 ns) in cyclohexane, increasing to $\phi_f = 1 \times 10^{-3}$ in acetonitrile), with maxima at 376 and 380 nm. The intersystem-crossing yield of *N*-methyl-1,8-naphthalimide has been reported to decrease slightly from 1.0 in hexane to 0.94 in acetonitrile.[42] It seems reasonable to assume that the intersystem-crossing yields of **4** are also close to unity.

In nanosecond flash photolysis, the excited state absorption spectrum of **4** in cyclohexane (Figure 4a) shows a structured absorption band with maxima at 352, 412 (sh), 436, and 465 nm that can be attributed to the triplet state of the acceptor chromophore[42] with an apparent decay time of τ = 14.4 μs.[43]

To allow accurate assignment of the transient absorption spectra of the bichromophoric systems, the UV−vis spectra of the radical ions of isolated chromophores were obtained. The UV−Vis spectra of the radical cations of *N*-phenylpiperidine (λ_{max} 485 nm (ϵ = 4600 M^{-1} cm^{-1})) and of *N*-(4-methoxyphenyl)piperidine (λ_{max} 505 nm (ϵ = 6000 M^{-1} cm^{-1})) are known from the literature.[44] The spectra of the radical cation of *N*-(4-methoxyphenyl)piperidine and of the radical anion of **4**, the latter recorded by application of UV−vis spectroelectrochemistry, are shown in Figure 3. The absorption maxima of the radical anion of **4** in butyronitrile are observed at 229 (ϵ = 21200 M^{-1} cm^{-1}), 269 (ϵ = 16600 M^{-1} cm^{-1}), 347 (ϵ = 3800 M^{-1} cm^{-1}), 416 (ϵ = 23550 M^{-1} cm^{-1}), 489 (ϵ = 3550 M^{-1} cm^{-1}), 736 (ϵ = 3000 M^{-1} cm^{-1}), and 818 nm (ϵ = 5100 M^{-1} cm^{-1}). (The extinction coefficients given have been corrected for the 95% conversion of **4** into its radical anion, which could maximally be achieved in the spectroelectrochemical reduction under retention of isosbestic points.)

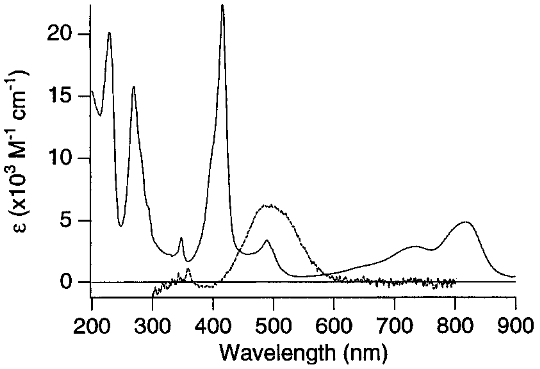

Figure 3. UV−vis spectra of the radical cation of 1-(4-methoxyphenyl)-4-piperidine in acetonitrile (dashed line), scaled to ϵ = 6000 at 505 nm,[44] and the radical anion of **4** in butyronitrile (solid line).

Bichromophoric System 3a. Compound **3a** displays in cyclohexane a weak local emission in the 370-nm region (τ = 0.3 ns). In the 600-nm region, a very weak, broad CT emission was observed (λ_{max} = *ca.* 610 nm, $\phi_f < 4 \times 10^{-4}$), which grew with a time constant of 0.25 ns and decayed with τ_f = 0.75 ns. From the decrease of the fluorescence decay time of the locally excited state emission relative to compound **4**, we can estimate that the charge-separation process for **3a** in cyclohexane, which affords the singlet CT state (D−^{1}A → ^{1}(D$^+$−A$^-$)), occurs with *ca.* 70% yield and a rate of *ca.* 4×10^9 s^{-1}.

In a polar medium like acetonitrile, no CT emission was found for **3a**. The local emission (λ_{max} = 372 nm, $\phi_f = 1 \times 10^{-3}$) in this solvent is stronger than that in cyclohexane. In fact, the intensity is equal, within the limits of accuracy (±10%), to that of **4** in acetonitrile, indicating that for the decay of the locally excited singlet state of **3a** in acetonitrile charge transfer is a minor route.

The transient absorption spectra of **3a** in cyclohexane reveal clearly the local triplet state of the acceptor with absorption maxima at 355, 412 (sh), 437, and 464 nm, which decay on a microsecond time scale (Figure 4A). At *t* = 0 ns (maximum of the laser pulse) a short-lived (<2 ns) band at 414 nm is, however, present which can reasonably be ascribed to the radical anion absorption of the imide acceptor (see Figure 3). Thus, the short-lived ^{1}(D$^+$−A$^-$) state that was observed by its long-wavelength emission could also be identified in the transient absorption spectrum. We note that spectra were recorded at intermediate points in time which are not shown in Figures 4 and 5.

In the transient absorption spectra of **3a** in di-*n*-butyl ether (Figure 4B) the acceptor triplet is visible (352, 466 nm) (compare with Figure 4A), as well as bands corresponding with the D$^+$ and A$^-$ radical ion absorptions (see Figure 3). All main absorptions (414 nm (A$^-$) and 466 nm (D$^+$, A$^-$, and ^{3}A)) decay with the same time constant of *ca.* 1 μs. In the long-wavelength region of the absorption spectrum, a weak absorption band can be discriminated at *ca.* 800 nm. The noise on this band, which is a result of the low probe light intensity and low sensitivity of the detector in that wavelength region, makes assignment dubious. We note, however, that the radical anion of the acceptor reference system **4** displays an absorption in this long-wavelength region (see Figure 3).

In benzene (not shown), the absorption spectra are dominated by long-lived (τ = *ca.* 0.9 μs) absorptions of ^{3}(D$^+$−A$^-$), with

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(42) Wintgens, V.; Valat, P.; Kossanyi, J.; Biczók, L.; Demeter, A.; Bérces, T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 411.

(43) A single exponential function was used to describe the decay, although it is known[42] that the triplet decay in naphthalimides involves mixed first- and second-order kinetics.

(44) Brouwer, A. M.; Mout, R. D.; Maassen van den Brink, P. H.; Warman, J. M.; Jonker, S. A. *Chem. Phys. Lett.* **1991**, *180*, 556.

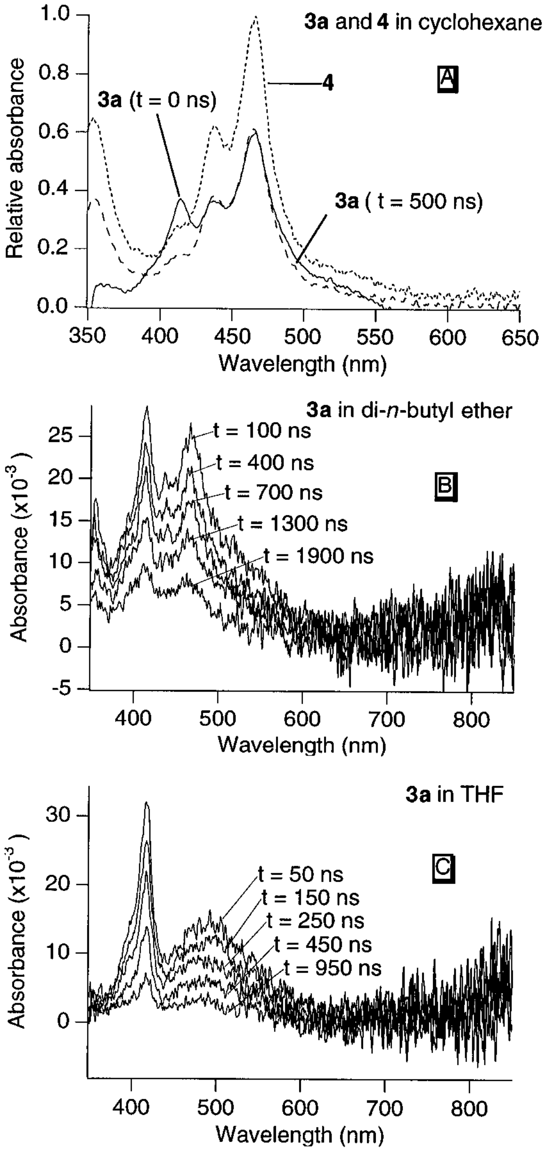

Figure 4. Transient absorption spectra of (A) **4** (dotted line) and **3a** in cyclohexane ($t = 0$ ns (solid line); $t = 500$ ns (dashed line)), (B) **3a** in di-*n*-butyl ether, and (C) **3a** in THF. The intensity of the spectrum of **4** corresponds to $\phi_{\rm ISC} = 1$ (see text). The intensity of the spectrum of **3a** in cyclohexane at $t = 0$ ns corresponds to $\phi_{\rm ISC} = 0.6$ (see text).

maxima at 416 and 500 nm, that correspond with the absorption spectra of the A^- and D^+ radical ions. At $t = 0$ ns (maximum of the laser pulse) and at $t = 5$ ns, a minor absorption due to $D{-}^3A$ is observed at 466 nm.

In dioxane and the more polar solvents THF and acetonitrile only two long-lived absorption bands are observed at *ca.* 415 nm and *ca.* 491 nm, which correspond with the acceptor and donor radical ions, respectively. This is illustrated for the THF case in Figure 4C. Note that, again, weak absorption is present in the >750-nm region that can be attributed to the radical anion. The decay time of the radical ion absorptions in dioxane is *ca.* 1 μs (*i.e.* the same as in di-*n*-butyl ether). In THF and acetonitrile the energy gap between the $^3(D^+{-}A^-)$ state and the ground state is reduced, which results in a decrease of the lifetime to 0.5 and 0.1 μs, respectively (see Discussion).

Bichromophoric System 3b. To obtain further information on the relation between the energy of the CT state and the formation of a triplet CT state, we studied the system with a somewhat weaker donor (**3b**) (Table 1). In cyclohexane, di-*n*-butyl ether, and diethyl ether weak, short-lived CT emission bands are observed with maxima at *ca.* 570 (τ < 1 ns), *ca.* 630 (τ < 1 ns) and >660 nm, respectively. This CT emission demonstrates the occurrence of a singlet state charge-separation process in **3b** in these solvents.

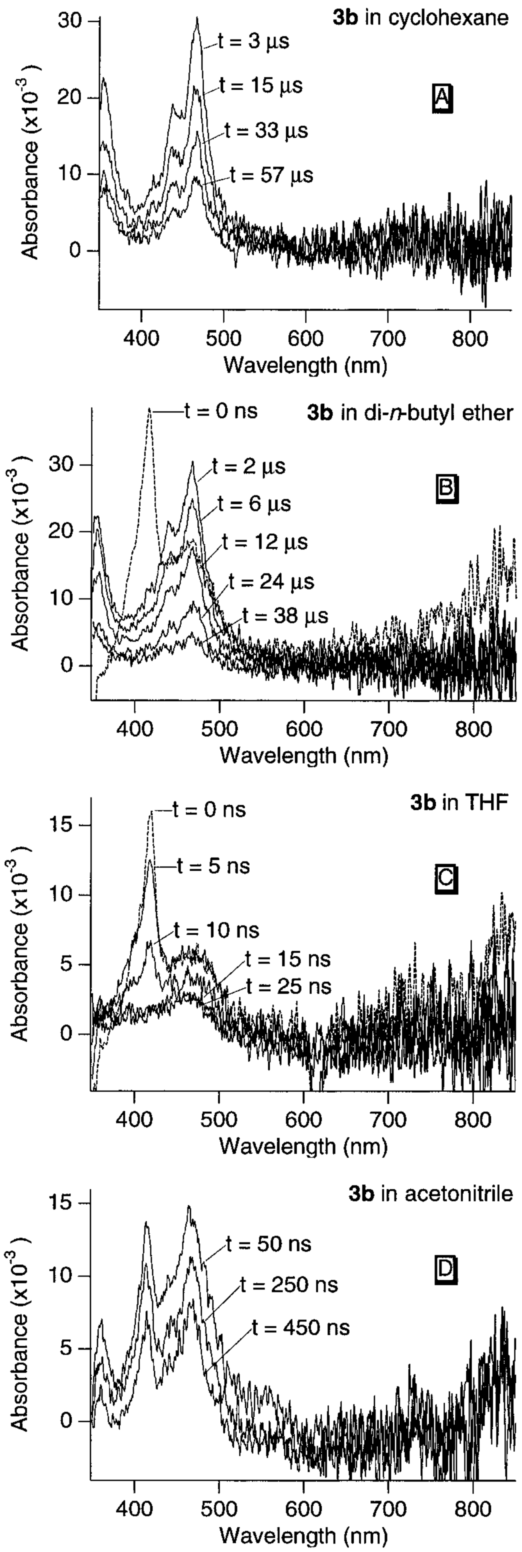

Figure 5. Transient absorption spectra of **3b** in (A) cyclohexane, (B) di-*n*-butyl ether, (C) THF, and (D) acetonitrile.

To obtain further information on the excited state decay pathways, transient absorption experiments were performed (Figure 5). In cyclohexane, the only state observed for **3b** is the imide triplet state with maxima at 354, 439 and 467 nm (Figure 5a) and an apparent decay time of 29.9 μs. The $^1(D^+{-}A^-)$ state, which was detected by its fluorescence, could not be observed with our nanosecond transient absorption apparatus nor was a long-lived $^3(D^+{-}A^-)$ state found.

Also in di-*n*-butyl ether the triplet absorptions, originating from the imide chromophore, dominate the transient spectra of **3b** (λ_{max} = 355, 440, 467 nm, Figure 5B). At 416 nm, however, a short-lived transient absorption band is observed, which corresponds with the main absorption of the radical anion of the acceptor. Thus, the $^1(D^+{-}A^-)$ state, detected by CT fluorescence, is now also detected by transient absorption. In THF, transient absorptions that correspond with the radical ions are observed at 418 nm (A^-) and 469 nm (D^+, A^-) (Figure 5C). These absorptions decay on a time scale of *ca.* 10 ns. Virtually no imide triplet state is observed in this solvent. This result implies that in THF the singlet charge-separated state is formed efficiently upon photoexcitation, but this does not lead to a $^3(D^+{-}A^-)$ state.

In acetonitrile, absorptions at 360, 414, and 468 nm are observed that can again be attributed to D^+, A^-, and ^3A (Figure 5D). The decay time of these species is in the microsecond range, indicating that they result from an equilibrium between $D{-}^3A$ and $^3(D^+{-}A^-)$.

Discussion

From the fluorescence and transient absorption data it was concluded that upon photoexcitation of **3a**/**3b** the decay pathways of the locally excited singlet state ($D{-}^1A$) consist of two competing processes *viz.* ISC ($D{-}^1A \rightarrow D{-}^3A$) and charge separation ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$). The transient absorption band at 415 nm, corresponding with A^-, and the band at 465 nm, which corresponds with $D{-}^3A$, are clear marker bands that provide a powerful tool for the assignment of the observed transient absorptions.

For **3a** in cyclohexane charge separation occurs in the singlet manifold with ca. 70% yield. The CT fluorescence grew with the same rate constant as the local emission decayed (0.3 ns) indicating that, as expected, the locally excited singlet acceptor state is the precursor state of the (singlet) charge-separated state. The short-lived singlet CT state is observed not only by its emission but also in the transient absorption spectra. The nanosecond transient absorption spectra of **3a** in cyclohexane (Figure 4A), detected at the maximum of the laser pulse, show a short-lived absorption that corresponds with A^-. The spectra are dominated, however, by an absorption band that can be assigned to a triplet state localized on the imide chromophore.[42]

By comparison with a measurement on 1,8-naphthalimide (ϕ_{ISC} = 0.95),[42] the yield of $D{-}^3A$ for **3a** in cyclohexane was estimated to be *ca.* 0.6. We therefore scaled the intensity of the absorption of **3a** in Figure 4A at t = 0 ns (maximum laser pulse) to ϕ_{ISC} = 0.6 at λ_{max} (465 nm). After 500 ns hardly any decay of the acceptor triplet state has occurred, while the 414-nm band has disappeared due to decay of the CT state. Fluorescence measurements showed that the yield of the charge separation from the locally excited singlet state of **3a** in cyclohexane is *ca.* 0.7. The contribution of direct ISC from $D{-}^1A$ ($D{-}^1A \rightarrow D{-}^3A$) is therefore *ca.* 0.3. We determined that the total ISC yield observed is *ca.* 0.6, hence about half of the $D{-}^3A$ state population is obtained by back electron transfer with ISC from the $^1(D^+{-}A^-)$ state ($^1(D^+{-}A^-) \rightarrow D{-}^3A$).

Upon increasing the solvent polarity, ISC ($D{-}^1A \rightarrow D{-}^3A$) can compete effectively with charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$). This leads to an equilibrium for **3a** in di-*n*-butyl ether between $D{-}^3A$ and $^3(D^+{-}A^-)$, both species decaying with an apparent decay time of *ca.* 1 μs (Figure 4B). Thus, upon changing the multiplicity of the charge-separated state from singlet to triplet, its decay time is increased by *ca.* three orders of magnitude. The radical ion absorption bands only indicate the presence of $D^+{-}A^-$, but do not give information about the spin state. The very long lifetime, however, can only be explained assuming that the $D^+{-}A^-$ state has triplet multiplicity.

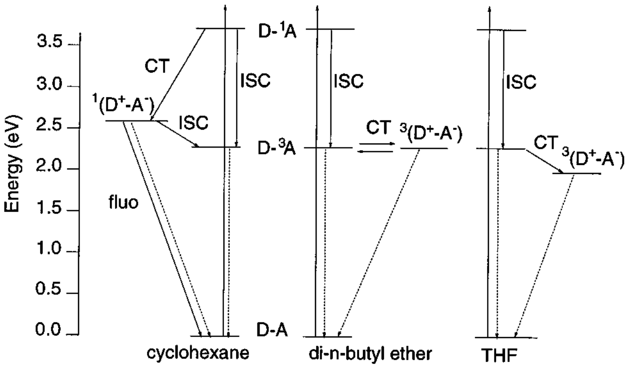

Figure 6. Energy scheme for the excited states of **3a** in cyclohexane, di-*n*-butyl ether, and THF (see text).

An estimate of the energies of the charge-separated states can be obtained by applying eq 1,[45] in 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 the center-to-center distance R (in Å) and effective ionic radii r (in Å) equal for D and A, submerged in a dielectric continuum with relative permittivity ϵ_s. Even though the bridges in linked systems occupy part of the space available to the solvent in nonbridged ion pairs, it has been found that eq 1 can be applied successfully, at least if the bridges are arranged in an extended fashion as in **3a** and **3b**.[3,9,46−50]

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

For the D and A species under study, the one-electron oxidation and reduction potentials ($E_{ox}(D)$ and $E_{red}(A)$) in acetonitrile are known (see Table 1). To obtain an estimate of the CT-state energies in different solvents, we set the ionic radii r at 4.1 Å, which experience has shown to be a reasonable value for small aromatic systems.[51,52] The distance between the centers of charge of the donor and acceptor is denoted in eq 1 by the symbol R. For *N*-(4-methoxyphenyl)piperidine the center of charge is likely to be close to the nitrogen. For the acceptor chromophore the center of charge should coincide with the center of the chromophore. We thus obtained R = 6.8 Å. These parameters have been used to construct Figure 6. For the locally excited states the data of Table 1 have been applied. The energy diagram obtained for **3a** in cyclohexane is in good agreement with the excited state behavior that was deduced from fluorescence and transient absorption spectra. In Figure 6 it can be seen that the degeneracy of $D{-}^3A$ and $D^+{-}A^-$ states in di-*n*-butyl ether, as revealed by the transient absorption spectra, is predicted by eq 1. An equilibrium between a locally excited

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(52) Scherer, T. Ph.D. Thesis, University of Amsterdam, 1994.

triplet state and a $D^+{-}A^-$ state was also reported by Anglos *et al.* for their bichromophoric system **2** in toluene.[32]

From the transient absorption data of **3a** in di-*n*-butyl ether (Figure 4B) it is concluded that the $^3(D^+{-}A^-)$ and $D{-}^3A$ states are similar in energy in this solvent, because D^+, A^-, and ^3A absorptions decay with the same time constant. In benzene, however, the transient absorption spectra of **3a** are dominated by long-lived absorptions that correspond with D^+ and A^-. Only during the laser pulse are D-^{3}A absorptions observed. We tentatively assume that for **3a** in benzene, formation of $D{-}^1A$ upon photoexcitation is followed by rapid ISC ($D{-}^1A \rightarrow D{-}^3A$) to yield the $D{-}^3A$ state, and from this state charge transfer occurs to afford the $^3(D^+{-}A^-)$ state. Thus in benzene, the $^3(D^+{-}A^-)$ state is lower in energy than the $D{-}^3A$ state, whereas in di-*n*-butyl ether these two states are degenerate. Hence benzene acts as a slightly more polar solvent than di-*n*-butyl ether for the charge-separated state of **3a**. It is, however, known[53] that benzene stabilizes dipolar states more effectively than expected from its bulk dielectric properties.

Upon photoexcitation of **3a** in more polar solvents like dioxane, THF, and acetonitrile, rapid ISC ($D{-}^1A \rightarrow D{-}^3A$) occurs, which is followed by charge separation in the triplet manifold ($D{-}^3A \rightarrow {}^3(D^+{-}A^-)$). The $^3(D^+{-}A^-)$ state is clearly indicated by absorption bands that correspond with D^+ and A^-. In fact, the transient absorption spectra are a superposition of these bands. The decay time of the $^3(D^+{-}A^-)$ state of **3a** decreases upon increasing solvent polarity, *i.e.* from 1 μs to 0.5 μs and 0.1 μs in dioxane, THF, and acetonitrile, respectively. This behavior corresponds with the "energy gap-law",[54,55] which strongly suggests that the decay pathway of the $^3(D^+{-}A^-)$ state is directly to the ground state, rather than by ISC within the $D^+{-}A^-$state ($^3(D^+{-}A^-) \rightarrow {}^1(D^+{-}A^-)$). For the latter spin-inversion process a large solvent effect is not expected.

Figure 6 documents, according to eq 1, that the charge-separated state is energetically accessible from the $D{-}^3A$ state in polar solvents like THF, which is in full agreement with the observed behavior. The rate of ISC ($D{-}^1A \rightarrow D{-}^3A$) in the isolated naphthalimide chromophore (**4**) is somewhat smaller in acetonitrile than in cyclohexane.[42] The lack of charge transfer in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$) of **3a** in acetonitrile can therefore not be the consequence of faster ISC ($D{-}^1A \rightarrow D{-}^3A$), but must be due to retardation of the singlet charge transfer itself (see below).

We will now discuss bichromophoric system **3b**. From the experimental data of **3b** it is concluded that the decay of its locally excited singlet state occurs *via* charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$). Only in the very polar solvent acetonitrile there is evidence for the formation of a triplet charge-separated state. For **3b**, the CT emission in cyclohexane is found at a shorter wavelength (*ca.* 570 nm) compared with that of **3a** in the same solvent (*ca.* 610 nm), as expected for a weaker donor−acceptor pair (see eq 1, Table 1).

The transient absorption spectra of **3b** in cyclohexane display a long-lived triplet absorption that is localized on the imide moiety. The short-lived $^1(D^+{-}A^-)$ state, which was detected by its emission, was not observed in the transient absorption spectrum. In the more polar solvent di-*n*-butyl ether, however, the A^- marker band at 416 nm is observed, which decays with a time constant in the nanosecond range. Thus for **3b** in di-*n*-butyl ether, the $^1(D^+{-}A^-)$ state is evidenced by both its emission and the absorption band that corresponds with A^-. The absorption corresponding with the radical cation is overshadowed by the strong $D{-}^3A$ absorption. The transient absorption spectra in both cyclohexane and di-*n*-butyl ether are dominated by the $D{-}^3A$ absorption. This situation is thus similar to that of **3a** in cyclohexane (Figure 6).

Upon photoexcitation of **3b** in THF, the $^1(D^+{-}A^-)$ state is, again, readily formed as is observed by short-lived transient absorption bands that correspond with D^+ and A^-. Thus in THF charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$) can still prevail over ISC ($D{-}^1A \rightarrow D{-}^3A$). In this case virtually no $D{-}^3A$ absorption is observed, indicating that, for **3b** in THF, the $^1(D^+{-}A^-)$ state decays directly to the ground state. By applying eq 1 and the parameters denoted above, it was estimated that, for **3a** in THF, the $D^+{-}A^-$ and $D{-}^3A$ states are virtually degenerate ($E(D^+{-}A^-) - E_T{}^{00} = 2.24 - 2.29 = -0.05$ eV), which implies that there will be a small barrier, of the order of one fourth of the Marcus reorganisation energy, for the $^1(D^+{-}A^-) \rightarrow D{-}^3A$ process.

Importantly, the population of $^1(D^+{-}A^-)$ does not lead to formation of $^3(D^+{-}A^-)$. The short distance between the radical ions in our systems apparently allows for sufficient exchange interaction to give pure singlet and triplet character to the $^1(D^+{-}A^-)$ and $^3(D^+{-}A^-)$ states, respectively.[56−58] The "pure" $^3(D^+{-}A^-)$ state is apparently populated most effectively *via* the $D{-}^3A$ state.

In acetonitrile, the transient absorption spectra of **3b** display long-lived absorptions that can be attributed to D^+, A^-, and ^3A. This proves that compound **3b** can afford a long-lived charge-separated $^3(D^+{-}A^-)$ state, albeit only in a very polar medium.

From Figure 6 it is clear that for the $^3(D^+{-}A^-)$ state to become energetically accessible from $D{-}^3A$, a more polar solvent is necessary for **3b** than for **3a**. Apart from this trivial prerequisite, formation of $^3(D^+{-}A^-)$ requires that ISC ($D{-}^1A \rightarrow D{-}^3A$) is fast relative to the charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$, which in turn implies that the latter process has to be slowed down. The relative rate of ISC ($D{-}^1A \rightarrow D{-}^3A$) versus the rate of charge separation in the singlet manifold ($D{-}^1A \rightarrow {}^1(D^+{-}A^-)$) from the locally excited singlet state is discussed in the next paragraphs.

The driving force for charge separation in the singlet manifold ($\Delta G_S{}^\circ$) can be obtained from eq 2[45]

$$\Delta G_S{}^\circ = {}^1E_{D^+A^-} - E_S{}^{00} \tag{2}$$

where $E_S{}^{00}$ denotes the energy of the locally excited acceptor state (3.63 eV, Table 1). From eq 1 and using the thermodynamic parameters given above, an estimate of the energy of the singlet charge-separated state ($^1E_{D^+A^-}$) can be obtained. Using eq 2, $\Delta G_S{}^\circ$ was estimated to be −1.03 and −1.74 eV for **3a**, and −0.83 and −1.54 eV for **3b**, in cyclohexane and acetonitrile, respectively. Compound **3a** possesses a very strong donor−acceptor pair, which results in a very large driving force already in cyclohexane, which increases substantially in more polar solvents. It has been reported by Wasielewski *et al.*[59] that for such large energy gaps ($-\Delta G_S{}^\circ > 1$ eV) the rate of the charge separation decreases, irrespective of the solvent used, as the energy gap increases (the well-known "inverted region

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effect"[60−63]). Thus for **3a**, due to the large energy gap for charge separation in the singlet manifold, the $D-{}^1A \rightarrow {}^1(D^+-A^-)$ process is apparently slowed down upon increasing solvent polarity. As a result, ISC ($D-{}^1A \rightarrow D-{}^3A$) can compete effectively, and the $D-{}^3A$ state is formed in a high yield as an efficient precursor for the ${}^3(D^+-A^-)$ state (Figure 4B,C).

For system **3b** in cyclohexane, $-\Delta G_S°$ is estimated to be significantly smaller than 1 eV; therefore, the rate for charge separation in the singlet manifold is initially expected to increase upon increasing the solvent polarity.[60−63] Indeed, for **3b** in nonpolar solvents and solvents of intermediate polarity, emission from the ${}^1(D^+-A^-)$ state is observed, indicating that in these solvents the $D-{}^1A \rightarrow {}^1(D^+-A^-)$ process is fast compared with ISC ($D-{}^1A \rightarrow D-{}^3A$). This very rapid charge separation results in formation of ${}^1(D^+-A^-)$ and thus prevents the triplet pathway ($D-{}^1A \rightarrow D-{}^3A \rightarrow {}^3(D^+-A^-)$) to compete. In the very polar solvent acetonitrile, the energy gap for charge separation in the singlet manifold in **3b** is significantly larger than 1 eV ($-\Delta G_S° = 1.54$ eV), which in turn again slows down the $D-{}^1A \rightarrow {}^1(D^+-A^-)$ process and allows ISC ($D-{}^1A \rightarrow D-{}^3A$) to compete effectively. As a result, the long-lived ${}^3(D^+-A^-)$ state is populated (Figure 5D).

Conclusions

The data presented above demonstrate that we were successful in an attempt to design bichromophoric systems that afford a ${}^3(D^+-A^-)$ state with a lifetime in the microsecond range and a charge separation by four σ bonds. The *intra*molecular combination of a 4-methoxyaniline electron donor and a 1,8-naphthalimide electron acceptor (**3a**) is the most successful of the two systems studied. Compound **3a** contains a very strong donor−acceptor pair ($-\Delta G_S° > 1$ eV). As a result, the singlet charge separation ($D-{}^1A \rightarrow {}^1(D^+-A^-)$) is retarded upon increasing solvent polarity, and ISC ($D-{}^1A \rightarrow D-{}^3A$) competes effectively in benzene, di-*n*-butyl ether, and more polar solvents. From the thus obtained $D-{}^3A$ state, electron transfer occurs in the triplet manifold, to afford a long-lived triplet charge-separated state ($D-{}^3A \rightarrow {}^3(D^+-A^-)$). Bichromophoric system **3b** contains a somewhat weaker donor than **3a**, resulting in a smaller driving force compared with **3a** in the same solvent. Photoexcitation of **3b** leads to population of the singlet charge-separated state ($D-{}^1A \rightarrow {}^1(D^+-A^-)$). Only in the very polar solvent acetonitrile was evidence found for formation of a long-lived triplet charge-separated state.

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