Long-Lived Charge Separation in Novel Axial Donor–Porphyrin–Acceptor Triads Based on Tetrathiafulvalene, Aluminum(III) Porphyrin and Naphthalenediimide

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Abstract: Two self-assembled supramolecular donor-acceptor triads consisting of Al^{III} porphyrin (AlPor) with axially bound naphthalenediimide (NDI) as an acceptor and tetrathiafulvalene (TTF) as a secondary donor are reported. In the triads, the NDI and TTF units are attached to Al^{III} on opposite faces of the porphyrin, through covalent and coordination bonds, respectively. Fluorescence studies show that the lowest excited singlet state of the porphyrin is quenched through electron transfer to NDI and hole transfer to TTF. In dichloromethane hole transfer to TTF dominates, whereas in benzonitrile (BN) electron transfer to NDI is the main quenching pathway. In the nematic phase of the liquid crystalline solvent 4-(n-pentyl)-4'-cyanobiphenyl (5CB), a spin-polarized transient EPR spectrum that is readily assigned to the weakly coupled radical pair TTF⁺⁺NDI⁻⁻ is obtained. The initial polarization pattern indicates that the charge separation

Keywords: aluminum electron transfer · photosynthesis · porphyrinoids · tetrathiafulvalene

occurs through the singlet channel and that singlet-triplet mixing occurs in the primary radical pair. At later time the polarization pattern inverts as a result of depopulation of the states with singlet character by recombination to the ground state. The singlet lifetime of TTF*+NDI- is estimated to be 200-300 ns, whereas the triplet lifetime in the approximately 350 mT magnetic field of the X-band EPR spectrometer is about 10 µs. In contrast, in dichloromethane and BN the lifetime of the charge separation is < 10 ns.

Introduction

In photosynthetic organisms, solar energy is converted into energy-rich compounds by a highly efficient light-induced multi-step electron-transfer reaction in the reaction center protein complexes that is coupled to a series of exogenous redox reactions.^[1] There is widespread interest in trying to mimic this process in artificial photosynthetic systems capable of converting solar energy into useful forms of energy.^[2] The main challenge in designing such systems is to bring to-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202995.

gether a photosensitizer and a series of redox-active components in a supermolecular complex capable of generating long-lived high-energy charge-separated states with high quantum yield. Optimizing the light-induced charge separation in donor-acceptor (D-A) complexes requires simultaneous optimization of factors such as the electron-accepting and -donating abilities and reorganization energies of the components as well as the electronic coupling between them. These factors can be varied by changing the number of components, the distance between them, their redox and optical properties, as well as their structures and orientation with respect to each other.

In recent years, many such donor-acceptor systems have been synthesized^[2m,3] and in most of them, one or more porphyrins adopt the role played by the chlorophylls in the natural systems. Porphyrins are an attractive choice for the photosensitizer because they strongly absorb light within the visible region, are often highly fluorescent, and have rich redox chemistry. More importantly, however, their optical and redox properties are also easily tunable.^[4] In combination with other redox-active species, especially electron acceptors, such as quinones and fullerenes, porphyrins have been used to produce a wide array of covalent and non-covalent D-A conjugates and supramolecular assemblies.^[2g, 3c, f,h, 5] Among the porphyrins, aluminum(III) porphyrin (AlPor) is unique, because it can form two different axial bonds that allow two different types of molecular compo-

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nents to be attached. Carboxylic acids react with the axial hydroxide group of AlPor-OH to form covalent ester linkages, whereas Lewis bases, such as pyridine and imidazole, form coordination bonds to the Al center, which is a Lewis acid.^[6] AlPor also has moderate oxidation and reduction potentials, and therefore could be used as a primary electron donor and/or acceptor.^[6h,7] This combination of properties

makes AlPor an ideal candidate for constructing multi-component D-A systems in which the electron-transfer pathway is perpendicular to the porphyrin plane. One advantage of such an arrangement is that the donor and acceptor sides of the complex are located on opposite faces of the porphyrin, which maximizes the spatial separation of the charges produced by the electron transfer. Moreover, the π^* orbital of the porphyrin resides in the same region of space as the axial ligands, which should increase the electronic coupling between the excited state of the porphyrin and the acceptor and, hence, promote electron transfer.

factors governing the electron transfer in axial triads. As the acceptor, we have chosen naphthalenediimide (NDI) because it is structurally very different from fullerene and has been used in porphyrin-based D–A complexes before.^[6d,8c,10] Attaching NDI covalently to AlPor gives the new axial dyad aluminum(III) porphyrin–naphthalenediimide (AlPor-Ph-NDI; Ph=phenyl) shown in Figure 1. This dyad can then be



Figure 1. Molecular components (AlPor-Ph-NDI and TTF-py or TTF-Ph-py) for construction of self-assembled axially connected vertical triads. The reference compound AlPor-Ph is also shown. TTF=tetrathiafulvalene.

There are a number of exam-

ples reported in the literature of D-A systems in which the direction of the electron transfer is axial to the porphyrin plane.^[3c,6d,f-h,8] Most of these axial systems show efficient electron transfer between the donor and acceptor components. However, the factors governing electron transfer in these types of complexes have not yet been fully explored. Recently, we reported the first supramolecular triads with an entirely axial electron-transfer pathway. The triads were based on AlPor with fullerene (C₆₀) covalently attached to Al^{III} and phenothiazine (PTZ) (or 2-methylthiophenothiazine (TPTZ)) coordinated to Al^{III} through an appended pyridine (py). We were able to show that excitation of the porphyrin led to an electron transfer to C_{60} followed by a hole transfer to PTZ (or TPTZ).^[6h] The electron-transfer rates and ΔG values for the forward and reverse electron transfer between AlPor and axially bound C₆₀ were found to lie very close to the Marcus curves determined for an equatorially bound zinc porphyrin-fullerene dyad,^[9] which suggested that the placement of the C₆₀ in the axial position did not lead to the expected increase in the electronic coupling. However, it is unclear whether this is a result of the unique properties of fullerene and whether other factors, such as the nature of the bridging group, may be critical in determining the coupling. Understanding the role of these factors is crucial if long-lived charge separation is to be achieved.

Here, we present the preparation and characterization of two AlPor-based triads in which the nature of the donor, the acceptor, and the bridging groups are varied to study the converted to a triad by coordinating a py-appended donor.

We have chosen tetrathiafulvalene as the secondary donor because of its strong electron-donating ability, which makes it an excellent candidate as a reductive electron guencher or hole acceptor in D-A systems.^[11] Despite its rich redox chemistry, there are only a few reports of TTF in porphyrincontaining D-A systems^[12] and very little is known about its efficiency as an electron donor when attached to a porphyrin through a coordination linkage.^[13] The resulting triads, TTF-py→AlPor-Ph-NDI and TTF-Ph-py→AlPor-Ph-NDI, are shown in Figure 2. In these triads four important variations have been introduced compared to the PTZ-AlPor-C₆₀ triads studied previously:^[6h] 1) TTF has a lower oxidation potential than PTZ or TPTZ and hence, the driving force for electron donation to the porphyrin cation AlPor⁺ or excited singlet state ¹AlPor^{*}) is greater, 2) NDI is a much smaller electron acceptor than C₆₀ and has a very different reorganization energy, 3) TTF is appended directly to the py unit to reduce the flexibility of the bridge and ensure a linear electron-transfer pathway, and 4) two different py-appended TTF donors have been prepared to allow the comparison of analogous complexes with different distances between the secondary donor and AlPor. We will show that efficient electron transfer occurs in the triads but that the lifetime of the charge-separated states is very strongly influenced by the nature of the solvent and is only weakly dependent on the length of the bridging group. We also present DFT calculations, which, along with the optical



Figure 2. Formation of self-assembled axially connected vertical supramolecular triads (R = phenyl).

spectra, indicate that the interaction of the lowest π^* orbital of the porphyrin with the bridge differs significantly, depending on whether it is covalently bound or coordinated to AlPor.

Results and Discussion

Synthesis: The assembly of the triads by coordination of pyappended TTF derivatives to the dyad AlPor-Ph-NDI is shown in Figure 2. Details of the synthetic procedure for AlPor-Ph-NDI and the TTF derivatives (TTF-py and TTF-Ph-py) are given in the Supporting Information. Briefly, AlPor-Ph-NDI was prepared in quantitative yield by condensation of 5,10,15,20-tetra(phenyl)porphyrinatoaluminum(III)hydroxide (AlPor-OH) with carboxylic acid functionalized NDI (NDI-Ph-COOH) (Scheme S2 in the Supporting Information) and the py-appended tetrathiafulvalene derivatives (TTF-py and TTF-Ph-py) were prepared by Stille and/or Suzuki coupling reactions.^[14] The synthesis and characterization of the reference compound, AlPor-Ph, is reported in the literature.^[6g]

The FAB mass spectrum of AlPor-Ph-NDI showed an intense molecular ion $[M]^+$ peak at m/z 1137 as well as a fragment ion peak at m/z 639 due to $[M-(NDI-Ph-COO)]^+$ formation. The molecular ion peaks of TTF-py and TTF-Ph-py were observed at m/z 281 and 357, respectively. Figure 3 shows a comparison of the ¹H NMR spectra of AlPor-Ph-NDI (Figure 3B) and the unbound ligand NDI-Ph-COOH (Figure 3A). The ring protons *a* and *b* of the benzoate spacer (see Figure 2 for the proton assignments) are shifted upfield in AlPor-Ph-NDI compared with unbound NDI-Ph-COOH as indicated in Figure 3. The signal of the naphthalic protons c and d, which appears as a singlet in unbound NDI-Ph-COOH, is split into two doublets with a small upfield shift in the dyad. The observed upfield shifts are due to the shielding effect of the porphyrin ring and the magnitude of the shift depends on the distance of the proton from the porphyrin ring. As shown in Figure 2, the protons in position a are closer to the AlPor ring than protons in position b and hence, they experience a larger shift. Similarly, protons c and dexhibit smaller shifts because they are further away from porphyrin ring.

Comparison of the ¹H NMR spectrum of a 1:1 mixture of TTF-Ph-py and AlPor-Ph-NDI

(Figure 3D) with the spectra of AlPor-Ph-NDI (Figure 3B) and TTF-Ph-py (Figure 3C) confirms the expected coordination of the py group of TTF-Ph-py to the AlPor. In the triad complex, shielding due to the porphyrin ring current causes an upfield shift of the protons of the py moiety (protons e and f), of the phenyl spacer (protons g and h), and of the TTF unit (protons i and j). The pyridyl protons e and f display the greatest shift indicating that coordination occurs through the py group. On the other hand, protons a and b



Figure 3. ¹H NMR spectra of A) NDI-Ph-COOH, B) AlPor-Ph-NDI, C) TTF-Ph-py, and D) TTF-Ph-py \rightarrow AlPor-Ph-NDI (all samples 5.6 mm in CDCl₃). In the case of NDI-Ph-COOH few drops of CD₃OD were added to dissolve the sample. NMR solvent or solvent impurity peaks are indicated with an asterisk.

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of the bridging benzoate group between AlPor and NDI show an increased upfield shift when TTF-Ph-py coordinates. It is likely that the Al^{III} center lies out of the porphyrin plane when it is five-coordinate but that it moves closer to the porphyrin plane when it becomes six-coordinate and hence, the benzoate spacer also moves closer to the ring. Similar spectra are obtained for a 1:1 mixture of TTF-py and AlPor-Ph-NDI (data not shown) but with larger upfield shifts for the TTF protons as expected because the shorter spacer means they lie closer to the porphyrin ring.

UV/Vis absorption studies: The absorption spectra of AlPor-Ph-NDI and the reference compounds NDI-Ph and AlPor-Ph measured in dichloromethane shown in Figure 4.



Figure 4. UV/Vis absorption spectra of NDI-Ph (dotted line), AlPor-Ph (dashed line), and AlPor-Ph-NDI (solid line) in dichloromethane. The inset shows the absorption spectra of TTF-py and TTF-Ph-py in dichloromethane.

The absorption maxima and extinction coefficients (λ_{max} and $\log \varepsilon$) are included with the synthetic procedures given in the Supporting Information. The absorption spectrum of AlPor-Ph-NDI shows the typical very strong B-band (Soret band) at $\lambda = 415$ nm and a weak Q-band at $\lambda = 547$ nm from AlPor and weak π - π * bands at λ =342, 360, and 381 nm from NDI. The spectrum is essentially a superposition of the spectra of the individual chromophores indicating that in the covalently linked dyad there is little or no perturbation of the ground-state electronic structures of the chromophores. The py-appended TTF derivatives, which will be used to construct the self-assembled supramolecular triads, have relatively weak and very broad absorption bands (see inset in Figure 4) at $\lambda = 304$ (average of 285 and 323 nm bands) and $\lambda = 432$ nm for TTF-py, and at $\lambda = 299$ and 427 nm for TTF-Ph-py.

Figure 5 shows absorption titrations of AlPor-Ph-NDI with TTF-Ph-py in dichloromethane. The Q-band region was used to monitor the absorbance of the porphyrin in the titrations because the TTF-py absorption band (λ_{max} = 432 nm) and the AlPor Soret band (λ_{max} =415 nm) overlap. Upon adding TTF-py, the Q-bands of the porphyrin shift from λ =546 and 585 nm to λ =562 and 602 nm. An isosbes-



Figure 5. Titration of AlPor-Ph-NDI with TTF-Ph-py in dichloromethane. The inset shows the Benesi–Hildebrand plot of the absorbance change at $\lambda = 604$ nm. TTF-Ph-py was added up to 2.6×10^{-3} M in 20 µL (2.4×10^{-4} M) increments to 1 mL (6×10^{-5} M) of a solution of AlPor-Ph-NDI.

tic point is observed at $\lambda = 555$ nm, indicating complex formation. The observed shifts in the porphyrin bands are typical of axial coordination of nitrogen ligands to AlPor.[6b,h,15] Benesi-Hildebrand^[16] analysis (Figure 5, inset) gives a linear plot confirming that a 1:1 complex is formed and the slope yields the binding constant $K = 1.1 \times 10^3 \,\mathrm{M}^{-1}$. Similar spectral changes and similar binding constants were observed in titrations of TTF-py versus AlPor-Ph-NDI, py versus AlPor-Ph-NDI, TTF-py versus AlPor-Ph, TTF-Ph-py versus AlPor-Ph, and py versus AlPor-Ph (data not shown). The absence of any additional bands in these titrations suggests that perturbation of the electronic structures of the photo- and redox-active components due to formation of the complex is relatively small. However, compared to covalent attachment axial coordination causes a greater perturbation of the porphyrin. The same titrations were also performed in benzonitrile (BN), but because the solvent can also coordinate to the porphyrin (Ph–C \equiv N \rightarrow AlPor) complexation by the pyappended TTF does not lead to spectral shifts and the binding constants could not be determined. However, because py is a better Lewis base than BN, complex formation is expected.

Density functional modeling calculations: The geometries and electronic structures of the AlPor-Ph-NDI dyad and of the self-assembled dyads and triads were investigated by using B3LYP/3-21G*^[17] level DFT calculations similar to those carried out in previous studies of covalently linked and self-assembled donor–acceptor systems.^[3a,b,18] The optimized structures of the dyads and triads are shown in Figure 6 as well as Figures S7 and S8 in the Supporting Information. In the calculations, the 2-ethylhexyl chain of the NDI was truncated to simplify the optimization. This truncation is not expected to have any significant influence on the calculated geometry of the dyad AlPor-Ph-NDI. The centerto-center distances between the AlPor (Al center), the TTF unit, and the NDI moiety are summarized in Table S1 in the Supporting Information. The optimized structures also pro-



Figure 6. Frontier HOMO, HOMO-1, and LUMO of a) dyad AlPor-Ph-NDI, b) dyad TTF-Ph-py \rightarrow AlPor-Ph, and c) triad TTF-Ph-py \rightarrow AlPor-Ph-NDI calculated by ab initio B3LYP/3-21G* methods.

vide the radii of the AlPor, the NDI moiety, and the TTF unit, which are found to be $R_{AlPor} = 7.77$, $R_{NDI} = 6.85$, and $R_{\rm TTF}$ = 5.47 Å. As expected the HOMO and LUMO of AlPor-Ph-NDI (Figure 6a) are localized on the porphyrin macrocycle and the NDI unit, respectively, which implies that AlPor⁺-NDI⁻ is the lowest excited state of the complex. The computed gas-phase HOMO-LUMO gap is found to be 2.05 eV but this value drops to 1.71 eV if higher level calculations (e.g., B3LYP/6-31G(d,p)/6-311G+(d,p)) are performed. For the dyad TTF-Ph-py-AlPor-Ph (Figure 6b) the HOMO and LUMO are localized primarily on the TTF and AlPor units, again as expected. However, in both cases some delocalization onto the py bridge occurs. This delocalization is more pronounced in TTF-py-AlPor-Ph (Figure S8 in the Supporting Information), which does not have the phenyl group in the bridge. These HOMO and LUMO distributions suggest that excitation of the porphyrin, which removes an electron from the HOMO-1 orbital, would lead

to the migration of the hole to the TTF unit. In the case of the triad TTF-Ph-py \rightarrow AlPor-Ph-NDI (Figure 6c), the HOMO, HOMO -1, and LUMO are located on the TTF, AlPor, and NDI units as in the reference compounds. Thus, excitation of the porphyrin can be expected to result in migration of the electron to the LUMO on the NDI moiety and the hole to the HOMO on the TTF unit.

Electrochemistry: Determination of the redox potentials of the compounds is important for evaluating the energetics of the electron-transfer reactions and possible electronic interactions between the constituents. Figure 7 shows the cyclic voltammograms of the dyad AlPor-Ph-NDI, its reference compounds AlPor-Ph and NDI-Ph as well as the triad components TTF-py and TTF-Ph-py in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP). The voltammogram for the dyad AlPor-Ph-NDI (Figure 7, bottom) is essentially a sum of the traces for the AlPor-Ph

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Figure 7. Cyclic voltammograms of TTF-py, TTF-Ph-py, NDI-Ph, AlPor-Ph, and AlPor-Ph-NDI in dichloromethane containing 0.1 M TBAP. All samples were measured with a scan rate of 100 mV s^{-1} , except TTF-py, which was measured with a scan rate of 500 mV s^{-1} .

and NDI-Ph references. Hence, the first two reduction processes at -0.55 and -1.00 V are assigned to the first and second reduction of the NDI unit and the third and fourth reduction processes at -1.16 and -1.54 V are the first and second reduction of the AlPor unit. The oxidation scan is virtually identical to that of AlPor-Ph and the observed two processes are assigned to the first and second oxidations of the porphyrin. As expected, the TTF derivatives show two processes corresponding to the first and second oxidation. The difference between the first oxidation potential of the donor and the first reduction potential of the acceptor corresponds to the HOMO-LUMO gap and is the energy of the charge-separated state E_{CS} . The free-energy changes for charge separation (ΔG_{CS}), charge recombination (ΔG_{CR}), and hole stabilization (ΔG_{HS}) are given by Equations (1) and (2):^[19]

$$\Delta G_{\rm CS} = E_{\rm CS} - E_{0-0} + G_{\rm S} \tag{1}$$

$$\Delta G_{\rm CR} = -E_{\rm CS} \tag{2}$$

where E_{0-0} is the singlet-state energy of AlPor (2.14 eV), estimated from the blue edge of the fluorescence spectrum at $\lambda = 579$ nm. G_s is the ion-pair stabilization and incorporates both the solvent-dependent Coulomb energy change upon ion-pair formation or recombination and the free energy of solvation of the ions [Eq. (3)]:

$$G_{\rm S} = e^2 / (4\pi\epsilon_0) [(1/(2R_+) + 1/(2R_-) - 1/R_{\rm D-A}) 1/\epsilon_{\rm S} - (1/(2R_+) + 1/(2R_-)) 1/\epsilon_{\rm R}]$$
(3)

where R_+ , R_- , and R_{D-A} are the donor radius, the acceptor radius, and the center-to-center distance between the donor and the acceptor, respectively; ε_s is the dielectric constant of the solvent used for the photophysical studies (9.1 and 26 for dichloromethane and BN, respectively); $\varepsilon_{\rm R}$ is the dielectric constant of the solvent used for measuring the redox potentials, in this case, dichloromethane.

By using the radii from the DFT calculations, $G_{\rm S}$ values of -0.14 and $-0.19 \,\text{eV}$ for AlPor⁺-NDI⁻ in dichloromethane and BN, respectively, are obtained. This leads to an energy of $1.28 \,\text{V}$ for AlPor⁺-NDI⁻ in dichloromethane, which is lower than the gas-phase value of $-1.71 \,\text{eV}$ calculated by DFT. This difference suggests that significant stabilization of the charges by the surrounding solvent occurs. By using, the energies obtained from the optical and electrochemical data, the energy-level diagram shown in Figure 8



Figure 8. Energy-level diagram for AlPor-Ph-NDI, TTF-py \rightarrow AlPor-Ph (E_{CS} =1.47 eV), TTF-Ph-py \rightarrow AlPor-Ph (E_{CS} =1.52 eV), TTF-py \rightarrow AlPor-Ph-NDI, and TTF-Ph-py \rightarrow AlPor-Ph-NDI in dichloromethane.

was constructed for the dyads and triads in dichloromethane. The free energy changes for charge separation obtained from Equation (1) are summarized in Table 1 and they suggest that the photoinduced electron transfer from ¹AlPor* to NDI and hole stabilization onto TTF as well as the electron shift to NDI are exothermic. The driving force of the hole shift ($\Delta G_{\rm HS}$) and electron shift ($\Delta G_{\rm ES}$) from AlPor⁺ and AlPor⁻ to TTF and NDI, respectively, are estimated from the difference of their corresponding ion-pair energies.

Fluorescence studies: The steady-state fluorescence spectra of the dyad AlPor-Ph-NDI and its reference compound AlPor-Ph were measured with the excitation $\lambda = 550$ nm in dichloromethane and BN. The only significant absorbance at $\lambda = 550$ nm is by the porphyrin and the concentration of the solution is the same for all of samples. Hence, the spectra (Figure 9A) reflect the fluorescence yield following excitation of the porphyrin. In each solvent, the band positions are the same for the dyad (Figure 9A, dashed lines) and the reference compound (Figure 9A, solid lines) but the fluorescence is quenched in the dyad. The positions and relative intensities of the bands differ in the two solvents BN and di-

Table 1. Energies of the charge-separated states (E_{CS}) and the free-energy	y changes of the electron transfer $(-\Delta G_{\rm CS})$, the hole shift $(-\Delta G_{\rm HS})$, and the
electron shift $(-\Delta G_{\rm ES})$ for the dyads and triads in dichloromethane. ^[a]	

Sample	E _{CS} (AlPor ⁺⁺ -NDI)	E _{CS} (TTF*+-NDI*-)	$E_{\rm CS} ({\rm TTF}^{+}-{\rm AlPor}^{-})$	$-\Delta G_{\rm CS}$ (¹ AlPor* \rightarrow AlPor'+-NDI'-)	$-\Delta G_{\rm CS}$ (¹ AlPor* \rightarrow TTF*+-AlPor*)	$-\Delta G_{\rm HS}$ (AlPor ⁺⁺ -NDI ⁻ \rightarrow TTF ⁺⁺ -NDI ⁻)	$\begin{array}{l} -\Delta G_{\rm ES} \\ ({\rm TTF^{+}-AlPor^{-}} \rightarrow \\ {\rm TTF^{+}-NDI^{-}}) \end{array}$
AlPor-Ph-NDI	1.28	_	_	0.86	_	-	-
TTF-py→ AlPor-Ph-NDI	1.28	0.96	1.47	0.86	0.67	0.32	0.51
$\begin{array}{l} TTF\text{-}Ph\text{-}py \rightarrow \\ AlPor\text{-}Ph\text{-}NDI \end{array}$	1.28	0.96	1.52	0.86	0.62	0.32	0.56

[a] $E_{\rm CS} = E_{1/2}(D^+/D) - E_{1/2}(A/A^-) + G_{\rm S}$, where $E_{1/2}(D^+/D)$ is the first oxidation potential of the donor, $E_{1/2}(A/A^-)$ is the first reduction potential of the acceptor, E_{0-0} is the singlet-state energy of AlPor (2.14 eV), $-\Delta G_{\rm HS} = E_{\rm CS}(AlPor^+-NDI^-) - E_{\rm CS}(TTF^+-NDI^-)$, and $-\Delta G_{\rm ES} = E_{\rm CS}(TTF^+-AlPor^-) - E_{\rm CS}(TTF^+-NDI^-)$. All energies are given in [eV].



Figure 9. Steady state fluorescence spectra. A) AlPor-Ph (solid lines) and AlPor-Ph-NDI (dashed lines) in dichloromethane and BN. The concentration is the same for all four spectra. B–D) Fluorescence titrations of AlPor-Ph-NDI with B) py, C) TTF-py, and D) TTF-Ph-py in dichloromethane. Py, TTF-py, or TTF-Ph-py were added up to 2.3×10^{-3} M in 20 µL (2.22×10^{-4} M) increments to 1 mL (6×10^{-5} M) of a solution of AlPor-Ph-NDI. The excitation wavelength is $\lambda = 555$ nm.

chloromethane, because BN coordinates to the Al center but dichloromethane does not. The observed fluorescence quenching suggests that the excited state of the porphyrin could be depopulated by processes such as energy and electron transfer between the components. Because there is no spectral overlap between the fluorescence bands of AlPor in the red part of the visible region (Figure 9) and the absorption bands of NDI in the ultraviolet (Figure 4), the yield of the energy transfer from the singlet excited state of AlPor (¹AlPor*) to NDI is expected to be negligible. On the other hand, the redox data (see Table 1) suggest that AlPor⁺⁺ -NDI⁻⁻ lies energetically below ¹AlPor* in both solvents. The free-energy change for charge separation (ΔG_{CS}) is found to be -0.86 and -0.91 eV in dichloromethane and BN, respectively. Consequently, electron transfer from ¹AlPor* to NDI is the more likely explanation for the quenching of the fluorescence of AlPor in AlPor-Ph-NDI.

Figures 9B-D show fluorescence titrations of the AlPor-Ph-NDI dyad in the presence of increasing amounts of py, TTFpy, and TTF-Ph-py. The titrations were carried out in dichloromethane and the samples were excited at the isosbestic point ($\lambda = 555$ nm, see Figure 4). Upon addition of py to AlPor-Ph-NDI, (Figure 9B) a red shift of the fluorescence bands and a change in their relative intensities occurs. However, no quenching occurs and isosbestic points are observed in this fluorescence titration. In contrast, addition of TTF-py to AlPor-Ph-NDI (Figure 9C) leads to quenching of the fluorescence without any significant shift of the emission bands. Titration of

AlPor-Ph-NDI with TTF-Ph-py (Figure 9D) shows both quenching and a shift in the band positions. Corresponding titrations with AlPor-Ph instead of AlPor-Ph-NDI show a similar behavior (Figure S9 in the Supporting Information). The quenching without any shift of the band positions observed with TTF-py (Figure 9C) implies that the coordination complex TTF-py \rightarrow AlPor-Ph-NDI has negligible fluorescence. In contrast, TTF-Ph-py \rightarrow AlPor-Ph-NDI (Figure 9D) is fluorescent but its fluorescence is weaker than that of AlPor-Ph-NDI. Because coordination of AlPor-Ph and AlPor-Ph-NDI with py does not cause significant quenching, the strong quenching observed with TTF-py is not simply a result of coordination by the py group. More-

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over, control experiments in which AlPor-Ph was titrated against TTF without an appended py group (Figure S12 in the Supporting Information), showed only a small amount of fluorescence quenching. Stern-Volmer plots of the AlPor fluorescence monitored at $\lambda = 650$ nm (Figure S13 in the Supporting Information) give much larger slopes (K_{SV}) for TTF-py (1156 m⁻¹ vs. AlPor-Ph) and (454 m⁻¹ vs. AlPor-Ph-NDI) than for TTF without an appended py group $(48 \,\mathrm{m}^{-1}$ vs. AlPor-Ph). Because TTF cannot coordinate to AlPor in the absence of the py group, the latter K_{SV} value represents the contribution due to collisional quenching and we conclude that it plays only a minor role in the quenching seen with TTF-py. The most likely explanation for the increased quenching with py-appended TTF is an intramolecular hole transfer from ¹AlPor* to the TTF unit. This process is exothermic ($\Delta G = -0.67 \text{ eV}$) and has been observed in other systems in which TTF is attached axially to a porphyrin macrocycle.[8e,13] Insertion of an additional phenyl spacer between the TTF and py units is expected to decrease the electronic coupling and to slow down the hole transfer rate. Consistent with this expectation, the quenching is weaker in the titrations with TTF-Ph-py (Figures 9D and S9C in the Supporting Information).

Similar titrations were also carried out with BN as the solvent. In this case, the solvent coordinates to AlPor and therefore when AlPor-Ph is titrated with py no shift of the fluorescence bands or change in the intensity are observed (Figure S10A in the Supporting Information). In contrast, titration of AlPor-Ph with TTF-py or TTF-Ph-py, does lead to fluorescence quenching (Figures S10B and C in the Supporting Information) as would be expected if hole transfer from ¹AlPor* to TTF occurs. The amount of quenching in the BN titrations is low compared to those in dichloromethane, presumably because the large excess of BN competes with TTF-py (or TTF-Ph-py) for the Al coordination sites and the concentration of the coordination complex TTF-py \rightarrow AlPor-Ph (or TTF-Ph-py→AlPor-Ph) is lower. In contrast to the behavior in dichloromethane, titrations of AlPor-Ph-NDI with py, TTF-py, or TTF-Ph-py in BN (Figures S11 A-C in the Supporting Information) all show a small increase in the fluorescence intensity. This result suggests that coordination of py probably causes a slight slowing of the rate of electron transfer from ¹AlPor* to NDI. The absence of quenching in the titrations with TTF-py or TTF-Ph-py implies that in BN, the hole transfer from ¹AlPor^{*} to TTF is too slow to compete effectively with the electron transfer from ¹AlPor* to NDI.

To estimate the hole and the electron transfer rates between TTF, ¹AlPor*, and NDI, time-resolved fluorescence studies were carried out by using a time-correlated singlephoton-counting apparatus with excitation at $\lambda = 406$ nm. Figure 10 shows a comparison of the fluorescence decay time profiles of the triad TTF-py \rightarrow AlPor-Ph-NDI and its components monitored at $\lambda = 616$ nm in dichloromethane (top) and BN (bottom). The corresponding fluorescence lifetimes (τ_f) obtained by curve fitting with mono- and bi-exponential functions are summarized in Table 2. As is appa-



Figure 10. Fluorescence decay profiles 1) AlPor-Ph, 2) AlPor-Ph-NDI, 3) TTF-py \rightarrow AlPor-Ph, and 4) TTF-py \rightarrow AlPor-Ph-NDI in dichloromethane (top) and BN (bottom). The excitation wavelength is $\lambda = 406$ nm and the fluorescence was monitored at $\lambda = 616$ nm. The instrument response function (IRF) is also shown.

rent from Figure 10 (top) the lifetimes of the profiles in dichloromethane follow the order AlPor-Ph (trace 1) > AlPor-Ph-NDI (trace 2) > TTF-py \rightarrow AlPor-Ph (trace 3) > TTF-py \rightarrow AlPor-Ph-NDI (trace 4). For AlPor-Ph, the decay is monoexponential with a lifetime of $\tau_f = 5.70$ ns. The decay traces for the dyads are bi-exponential with a fast-decaying major component and a minor component that decays with approximately the same lifetime as in AlPor-Ph.

The fast, major components have been used to calculate the values of the rate constant of the quenching process (k_{a}) and the quantum yield (ϕ_{q}) as given in Table 2. If charge separation from AlPor to NDI is assumed to be responsible for the fluorescence quenching in AlPor-Ph-NDI then $k_q =$ $k_{\rm FT} = 1/\tau_{\rm FT}$ and the data for the dyad and reference compound with coordinated py give a value of $k_q = k_{ET} = 1.13 \times$ $10^9 \, \mathrm{s}^{-1}$ ($\tau_{\mathrm{ET}} \!=\! 880 \, \mathrm{ps}$) for the charge separation between AlPor and NDI in dichloromethane. For TTF-py-AlPor-Ph $k_{\rm q} = k_{\rm ET} = 4.12 \times 10^9 \, {\rm s}^{-1}$, which implies that the hole transfer to TTF occurs with a lifetime of 240 ps. Based on these two quenching rates, a lifetime of 180 ps is predicted for the fluorescence decay in the triad TTF-py→AlPor-Ph-NDI, which is very close to the observed lifetime of 174 ps. Thus, the data suggest that for TTF-py→AlPor-Ph-NDI in dichloromethane the reaction scheme is as follows [Eq. (4)]:

 $AlPor \xrightarrow{h\nu} {}^{1}AlPor^{* \xrightarrow{240 \text{ ps}}} TTF^{*+} - AlPor^{*- \xrightarrow{880 \text{ ps}}} TTF^{*+} - AlPor - NDI^{*-}$ (4)

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Sample	Solvent	$\tau_{\rm f} [{\rm ns}]^{[{\rm b}]} (A [\%])$	$k_q [imes 10^9 \mathrm{s}^{-1}]^{[\mathrm{c},\mathrm{d}]}$	$\phi_{\mathbf{q}} {\times} A$
A IDon Dh	dichloromethane	5.70 (100)	_	-
AIP0I-PII	BN	6.61 (100)	_	-
ave AlDon Dh	dichloromethane	5.66 (100)	-	-
py→AlPor-Pli	BN	6.62 (100)	-	-
AlDer Dh. NDI	dichloromethane	5.45 (21), 0.852 (79)	1.00	85×79
AIP0I-PII-INDI	BN	6.64 (22), 0.283 (78)	3.38	96×78
mu AlDer Dh NDI	dichloromethane	5.53 (24), 0.763 (78)	1.13	-
py→AlPor-Pn-NDI	BN	6.55 (28), 0.268 (76)	3.58	-
TTE av. AlDer Dh. NDI	dichloromethane	4.44 (8), 0.174 (92)	5.57	96×92
III-py→AlPoi-Pii-NDI	BN	6.25 (28), 0.231 (72)	4.18	96×72
TTE Dh. av AlDon Dh. NDI	dichloromethane	3.99 (8), 0.216 (92)	- 1.00 3.38 1.13 3.58 5.57 4.18 4.45 3.75 4.12 1.45 3.24	96×92
IIF-Pn-py→AlPor-Pn-NDI	BN	6.11 (20), 0.256 (80)	3.75	95×80
TTE av. AlDer Dh	dichloromethane	4.75 (18), 0.233 (82)	4.12	96×82
ПГ-ру→АРог-Рп	BN	6.22 (74), 0.623 (26)	1.45	90×26
TTE Dh. av. AlDon Dh	dichloromethane	4.08 (34), 0.293 (57)	3.24	94×57
III-FII-py→AlP0I-PII	BN	6.33 (63), 0.706 (37)	1.27	89×37

Table 2. Fluorescence lifetimes (τ_f) and their relative amplitudes (A), quenching rates (k_q), and quantum yields (ϕ_q) from time-resolved fluorescence data of the dyads and triads.^[a]

[a] Excitation wavelength $\lambda = 406$ nm, emission collected at $\lambda = 616$ nm. [b] Where two lifetimes are given, the shorter lifetime is a weighted average $[\tau = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)]$ of the two shortest lifetimes obtained from a tri-exponential fit. [c] $k_q = (1/\tau)_{dyad/triad} - (1/\tau)_{reference}$, $\phi_q = [(1/\tau)_{dyad/triad} - (1/\tau)_{reference}]/(1/\tau)_{dyad/triad}$ [d] If intramolecultricular fit is the second sec lar electron transfer is the dominant quenching mechanism $k_{a} = k_{\rm FT}$.

Addition of a phenyl group to the bridge between TTF and AlPor causes only a slight decrease in the rate of the initial charge separation and the order of the steps remains the same (Table 2). In contrast, changing the solvent to BN (Figure 10, bottom), leads to a decrease of the electrontransfer lifetime to 280 ps $(k_a = k_{\rm ET} = 3.58 \times 10^9 \, {\rm s}^{-1})$ for AlPor-Ph-NDI (trace 2) and an increase in the hole-transfer lifetime to 690 ps $(k_q = k_{\rm HT} = 1.45 \times 10^9 \, {\rm s}^{-1})$ in TTF-py \rightarrow AlPor-Ph (trace 3). Thus, the data suggest that in BN the reaction scheme is as follows [Eq. (5)]:

$$AlPor \xrightarrow{h\nu} {}^{1}AlPor \xrightarrow{280 \text{ ps}} AlPor \xrightarrow{\bullet} {}^{-690 \text{ ps}} TTF \xrightarrow{\bullet} {}^{-AlPor-NDI}$$
(5)

Again, only a small increase in the hole-transfer lifetime is observed when the additional phenyl group in added to the bridge between TTF and the porphyrin. Although it is possible to deduce the lifetimes and the sequence of the initial charge separation events from the fluorescence data, they do not provide direct evidence for the charge-separated states or any information regarding their lifetimes. Hence, nanosecond transient absorbance measurements were also performed.

Transient absorption studies: Nanosecond transient absorption spectra of the dyads, triads, and their reference compounds in Ar-saturated dichloromethane and BN solutions were collected in the $\lambda = 400-800$ nm range by using $\lambda =$ 532 nm laser light to excite the AlPor moiety. For AlPor-Ph the absorbance difference spectrum exhibits the expected characteristic absorption increase at $\lambda = 470$ nm due to formation of the porphyrin triplet state (data not shown). From the decay of the absorption change at $\lambda = 470$ nm, the lifetime of ³AlPor^{*} was evaluated to be 32 µs. The transient spectra of the dyad AlPor-Ph-NDI also show the absorption band of the ³AlPor* moiety at $\lambda = 470 \text{ nm}$ (Figure S14 in the Supporting Information), but the intensity of the absorption change is a factor of two smaller and its lifetime is shorter (17 µs) compared to AlPor-Ph. Based on the energy level diagram, (Figure 8), exergonic electron transfer is possible from both the singlet and the triplet state of AlPor. However, additional absorption bands associated with the expected formation of AlPor⁺-NDI⁻ are not clearly seen. The most likely explanation for the absence of these bands is that charge recombination to the ground state is faster than the 10 ns instrument response time. The fact that the intensity of

the absorption change at $\lambda = 470$ nm is a factor of two smaller in the dyad is also consistent with the formation of a short-lived charge-separated state. The observed shorter lifetime of the triplet state could be the result of slow electron transfer from ³AlPor* to NDI, in addition to the singlet electron transfer, because the energy of the charge-separated state is lower than that of ³AlPor^{*} (Figure 8).

In the triads TTF-py-AlPor-Ph-NDI and TTF-Ph-py-> AlPor-Ph-NDI, absorbance changes due to TTF*+ are anticipated at $\lambda = 450$ and 600 nm (Figure S16 in the Supporting Information). Again, however, there is no clear evidence for the formation of the charge-separated states and only a further decrease in the triplet-state lifetime is seen. Thus, overall the transient absorbance data suggest that in dichloromethane or BN at room temperature the charge-recombination lifetimes of the states, AlPor⁺-NDI⁻, TTF⁺-AlPor⁻, and TTF⁺⁺-AlPor-NDI⁻⁻ are shorter than a few ns. Such behavior is consistent with that reported recently^[6d] for a similar dyad in which NDI is axially connected to the aluminum porphyrin through a flexible acetate spacer. By using ultrafast spectroscopy, the charge-separation and charge-recombination lifetimes of the dyad were found to be 8.1 and 120 ps, respectively, in dichloromethane solution at room temperature. The fluorescence data presented above, suggest that the charge separation is slower in AlPor-Ph-NDI, which has a benzoate spacer, than in the acetate-linked dyad reported in the literature.[6d]

Transient electron paramagnetic resonance studies: Transient electron paramagnetic resonance (TREPR) measurements of AlPor-Ph-NDI, TTF-py-AlPor-Ph, and TTF-Phpy-AlPor-Ph under the same conditions as used for the transient absorbance experiments (room temperature, dichloromethane and BN as solvents) did not show any signals. This observation is consistent with a rapid charge re-

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combination in the dyads. However, it is also possible that rapid motion and/or spin relaxation average the spectrum to zero in these solvents. Previous studies^[20] have shown that the charge-recombination rates in some donor–acceptor complexes are dramatically slowed down in partially ordered nematic liquid crystalline solvents. It has been proposed that this change in the electron-transfer rate occurs as a result of the anisotropic dielectric relaxation and rotational motion of the liquid crystalline solvent.^[20d,21] The high degree of light scattering of nematic phases precludes transient absorbance studies but such samples are well suited for TREPR experiments. Hence, we have measured the spin-polarized transient EPR spectra of the dyads and triads in the liquid crystal 4-(n-pentyl)-4'-cyanobiphenyl (5CB).

Figure 11 shows the TREPR spectrum for AlPor-Ph-NDI in the nematic phase of 5CB at room temperature taken



Figure 11. Room temperature (300 K) transient EPR spectrum of AlPor-Ph-NDI in liquid crystal 5CB. The spectrum shows the signal intensity 300 ns after the laser flash.

300 ns after the laser flash. A broad emission/absorption (E/ A) pattern that can be attributed to the triplet state of AlPor is observed along with a narrow E/A pattern consistent with the radical-pair triplet state ³(AlPor+-NDI-). The sign of the polarization, E/A or A/E, for a radical-pair triplet state is determined by which of the triplet sublevels is populated and by the sign of the splitting. In a strongly coupled radical pair with nearly pure singlet and triplet eigenstates, the splitting in the triplet state is approximately $(d+q^2/4J)$ where q is the difference of the resonance frequencies of the two radicals and d and J are the dipolar and exchange couplings between them, respectively. For AlPor⁺⁺ -NDI⁻⁻ in 5CB, we expect that $|d| \ge |q^2/4J|$. Hence, the splitting is dominated by the dipolar coupling. Singlet electron transfer followed by singlet-triplet mixing in the radical pair selectively populates the T_0 level and at a distance of 11 Å, the point dipole approximation predicts a dipolar coupling constant of D = -20 G. The combination of T₀ population and D<0 gives an E/A pattern as observed. The full

width of the radical-pair triplet spectrum is |2D| and the observed width of approximately 40 G is consistent with the distance between AlPor and NDI. Thus, together the fluorescence quenching and the transient EPR spectrum suggest that upon photoexcitation electron transfer from the excited singlet state of AlPor to the NDI unit occurs. The broad spectrum from the porphyrin triplet state is probably formed through intersystem crossing (ISC) because charge recombination to the porphyrin triplet state is energetically unfavorable. The two possible pathways to the porphyrin triplet state can be distinguished by the resulting polarization patterns and the observed pattern is consistent with an ISC. However, in the liquid crystalline solvent, the z component of the spectrum, which would have A/E polarization if the triplet state was formed by radical-pair recombination, is very weak because orientations with the z axis of the porphyrin parallel to the field have a low probability. Thus, although the triplet state is most likely formed by ISC, radical-pair recombination cannot be ruled out.

For the TTF-py \rightarrow AlPor-Ph and TTF-Ph-py \rightarrow AlPor-Ph dyads in 5CB at RT, only the spectrum of the porphyrin triplet is observed in TREPR measurements (data not shown). However, it is unclear whether this means that donation from TTF to ¹AlPor* is slower than the intersystem crossing, the lifetime of the charge separation is short or if only the singlet charge-separated state is populated.

Figure 12 shows the transient EPR spectrum of TTF-Phpy-AlPor-Ph-NDI in 5CB at room temperature. In a wide scan taken 300 ns after the laser flash (Figure 12a), the spectrum is dominated by a narrow four-line E/A/E/A pattern with a very weak, broad E/A pattern in the wings. The broad pattern is due to the AlPor triplet state and the narrow pattern is assigned to the weakly coupled radial pair TTF⁺⁺-NDI⁻⁻. The narrow pattern (Figure 12b) shows two anti-phase doublets centered at $g_{\text{eff}}=2.010$ and 2.0030. Qualitatively, these values are consistent with the expected gvalues for the TTF+ and NDI- radicals oriented in the liquid crystal. The sign of the polarization pattern is determined by the sign of the spin-spin coupling parameter a =J-d and whether the electron transfer occurs from the singlet state or the triplet state of the chromophore. At a distance of approximately 25 Å between the radicals the pointdipole approximation predicts a dipolar coupling constant of D = -0.167 mT. Thus, the sign of the dipolar splitting, d = $(D/3)(3\cos^2\theta - 1)$, depends on the sign of the order parameter $(3\cos^2\theta - 1)$. The long axis of the complex is expected to align along the field and thus the order parameter should be positive and therefore d should be negative. The value of Jis not known but it is expected to be small. Hence, we expect that a=J-d will be positive. Under these conditions, singlet electron transfer gives an E/A/E/A pattern^[22] as observed. Thus, the polarization pattern at early time (Figure 12b, solid line), leads to the conclusion that the radical pair TTF⁺-NDI⁻ is formed by singlet electron transfer.

In the spectrum of a pure singlet-born radical pair, all four lines of the two anti-phase doublets are of equal intensity, that is, there is no net polarization of the radicals. How-



Figure 12. Room temperature (300 K) transient EPR spectra of TTF-Phpy \rightarrow AlPor-Ph-NDI in the nematic phase of the liquid crystal 5CB. a) Wide scan showing broad, very weak contribution from ³AlPor and intense narrow peaks from TTF⁺-AlPor-NDI⁻ 300 ns after the laser flash. b) Contribution from TTF⁺-AlPor-NDI⁻ on an expanded scale; solid line: 300 ns after the laser flash, dashed line: 1.1 µs after the laser flash. The arrow under the spectra indicates the field position of the transients shown in Figure 13.

ever, in the radical-pair spectrum in Figure 12b, emissive peak of TTF⁺ and the absorptive peak of NDI⁻ have greater intensity than the other two lines indicating net polarization of each radical. This net polarization is expected as a result of S-T₀ mixing during the sequential electron transfer in the triad. The sign of the net polarization is determined by the sign of the product $b_1q_1q_2$, where $b_1=2J_1+d_1$ is the non-secular part of the spin-spin coupling in the primary radical pair and q_1 and q_2 are the differences in the resonance frequencies in the primary and secondary radical pairs, respectively.^[22] The observed sign of the net polarization, E/A, implies that $b_1q_1q_2$ is positive. Because the fluorescence data indicate that the order of the two electron transfer steps is solvent dependent, the primary radical pair in 5CB could either be TTF+-AlPor- or AlPor+-NDI-. The sign of b_1 can be predicted for each of these possibilities based on the signs of q_1 and q_2 , which are known from the g factors of the radicals. If TTF+-AlPor- is the primary radical pair, then q_1q_2 is positive and, therefore, the spin polarization predicts that b_1 is positive. On the other hand, if AlPor⁺⁺-NDI⁻⁻ is the primary radical pair, then q_1q_2 is negative and the sign of the polarization implies that b_1 is negative. In both of the possible primary radical pairs, the exchange coupling J is expected to dominate the spin-spin coupling. Theoretical^[23] and experimental studies of bi-radicals^[24] and metal radical systems^[25] indicate that the sign of J should be negative. Therefore, AlPor⁺-NDI⁻ is the more likely candidate as the primary radical pair and the polarization pattern in Figure 12b (solid line) is most easily explained by the reaction sequence ¹AlPor^{*} \rightarrow AlPor^{*+}-NDI⁻ \rightarrow TTF^{*+}-NDI⁻. At later time, the spin polarization pattern decays and inverts (Figure 12b, dashed line). Such behavior has been observed in other donor–acceptor systems^[8d,26] and is usually the result of a spin-selective decay of the radical pair. Figure 13 shows the transients taken at



Figure 13. Signal decay and qualitative model of charge recombination in the triads. The transients were measured at the field position indicated by the arrow in Figure 12. The circles on the energy levels of the radical pair TTF⁺-NDI⁻ represent their relative populations.

the field position indicated by the arrow in Figure 12 along with a qualitative model that explains the signal decay. The diagram on the right of Figure 13 shows the spin states Ψ_{1-} Ψ_{4} of the weakly coupled radical pair TTF⁺⁺-NDI⁻⁻. The circles on the energy levels represent the population of the

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states. Initially, singlet electron transfer preferentially populates states Ψ_2 and Ψ_3 , which have S and T₀ character. Triplet electron transfer, spin relaxation, and/or microwave-induced transitions also place a small amount of population in states Ψ_1 and Ψ_4 , which are the pure triplet states T₊ and T_. As time progresses, states Ψ_2 and Ψ_3 are depopulated because the singlet recombination rate k_s is much higher than the triplet recombination rate $k_{\rm T}$. Thus, the signal inverts. Finally, the inverted signal decays due to a combination of spin relaxation and recombination. Kinetic fits of the transients (Figure 13, left) give lifetimes of 350 ns for the singlet recombination and 8.3 µs for the decay of the late signal. Similar results were also found for the shorter triad TTF-py \rightarrow AlPor-Ph-NDI (see Figure S17 in the Supporting Information). The singlet lifetime follows the expected trend and decreases from 350 to 200 ns when the phenyl spacer between the TTF and AlPor units is removed. The decay of the late signal on the other hand increases from 8.3 to 12 μ s probably as a result of differences in the T₁ relaxation rates in the two complexes.

Electronic coupling to axially bound ligands: For dichloromethane and BN, the electron transfer in the dyads and triads can be discussed in terms of the classical Marcus equation, which assumes non-adiabatic electron transfer (ET). The longitudinal dielectric relaxation times of the solvent (0.33 and 6.9 ps, for dichloromethane and BN, respectively)^[27] are much shorter than the electron-transfer lifetimes estimated from the fluorescence quenching and hence, the non-adiabatic assumption should be valid in these solvents. Previous studies have shown that the reorganization energy for electron transfer from ZnPor^{*} to NDI is $\lambda =$ $(1.4\pm0.3) \text{ eV}^{[10f]}$ in polar solvents. In AlPor-Ph-NDI, the free energy differences for charge separation and recombination are found to be -0.86 and -1.28 eV, respectively in dichloromethane. By using these values, the classical Marcus equation gives activation energies of 52 meV for the forward reaction but only 2.5 meV for the back reaction. Consistent with these estimates, competition between intersystem crossing and charge separation occurs during the forward reaction and long-lived charge separation is not observed for AlPor-Ph-NDI in dichloromethane. For the hole transfer from ¹AlPor^{*} to TTF, the reorganization energy is not known but it is expected to be similar to or slightly larger than that of the electron transfer from ¹AlPor* to NDI. The driving force for the hole transfer (-0.64 eV) is therefore considerably smaller than the reorganization energy, which places the reaction in the normal region of the Marcus curve. The driving force for recombination of TTF⁺⁺-AlPor⁻⁻ is close to $-\lambda$ and again long-lived charge separation is not expected.

In the case of the triads TTF-py \rightarrow AlPor-Ph-NDI and TTF-Ph-py \rightarrow AlPor-Ph-NDI, competition between hole transfer to TTF and electron transfer to NDI exists. Based on the activation energies, electron transfer to NDI is expected to be the faster process. The fluorescence data in BN (Figure 10, bottom) agree with this expectation, however, in

dichloromethane (Figure 10, top) they indicate that the hole transfer to TTF is faster. Thus, there appears to be a subtle balance of factors that changes the relative order of the rates in different solvents. One possible reason for this can be seen in the results of the DFT calculations. The orbitals presented in Figure 6b show that when py-appended TTF coordinates, the LUMO of AlPor, which is a π^* orbital, is delocalized onto the axially coordinated py bridge and away from the covalently bound phenyl group on the opposite face of the porphyrin. In the triads, the effect of this delocalization should be to weaken the coupling between the LUMO of AlPor and the LUMO of NDI and to stabilize the TTF⁺⁺-AlPor⁻⁻ state. It is likely that these effects compensate for the difference in driving force between the two reactions and leave them with similar rates. Because both the electronic coupling and the activation energy depend on the nature of the solvent it is not surprising that the relative order of the rates should change in different solvents. The reorganization energy for charge separation/recombination between TTF and NDI has been estimated to be between 0.8 and 1.0 eV in BN.^[28] This range of values gives activation energies in the vicinity of 100 meV for recombination of the final charge-separated state TTF*+-AlPor-NDI*- in the triads. Because there is little or no spatial overlap between the HOMO and LUMO in the triads (Figure 6c) the electronic coupling between TTF⁺⁺ and NDI⁻⁻ should be small and long-lived charge separation is expected. However, in dichloromethane and BN, TTF+-AlPor-NDI- is probably not observed because the back reactions of the initial charge-separated states AlPor'+-NDI'- and TTF'+-AlPor'lie near the top of the Marcus curve and recombination out competes formation of the secondary radical pair.

Achieving long-lived charge separation: In the nematic phase of 5CB the solvent dynamics change dramatically compared to dichloromethane and BN and this clearly has a pronounced effect on the lifetime of the charge separation, as has been observed in a number of other systems.^[20] In particular, the higher viscosity and ordering of the nematic phase result in much slower and highly anisotropic dielectric relaxation compared to dichloromethane and BN. In liquid crystals, which are structurally similar to 5CB, the component of the molecular dipole along the director is known to relax with a lifetime of approximately 100 ns, whereas the relaxation lifetime of the perpendicular component is about 1 ns.^[29] For such slowly relaxing solvents, the pre-exponential term in the Arrhenius ET rate equation is predicted to be proportional to the solvent relaxation rate^[30] because the slow reorganization of the solvent dipoles impedes the formation of the transition state from which the electron transfer occurs. Thus, slower ET is expected in 5CB because of this effect. However, recent studies^[20d,21] point to a more complex situation in liquid crystalline solvents. An important feature of such solvents is the correlation of the motion of the solvent molecules over relatively long distances. It is these correlated motion that leads to the partial ordering of the solvent and restrict the rotational motion of solutes.^[31]

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This restriction of the rotational motion leads to anisotropy in the solvation energy, which in turn affects the ET rates. Further, if the reorientation of the solvent occurs on a timescale similar to that of the electron transfer, the contribution of the solvation energy to the activation barrier for electron transfer is predicted to be much lower than its thermodynamic value.^[21] For the dyads and triads studied here, the relative importance of these solvent effects is not known but together they increase the lifetime of the charge-separated states by at least an order of magnitude in 5CB compared to the isotropic solvents dichloromethane and BN. Further extension of the lifetime of the charge-separated states is achieved by exploiting the spin selectivity of the charge recombination in a magnetic field.

Conclusion

The results presented above show that self-assembled triads capable of step-wise, light-induced charge separation can be constructed by coordinating py-appended TTF derivatives with the AlPor-Ph-NDI dyad. It is well known that hydrogen bonds mediate electron transfer better than analogous covalent bonds.^[32] In AlPor-based triads, a similar comparison can be made between axial coordination bonds versus axial covalent bonds. The observation that donation by TTF and electron transfer to NDI have similar rates suggests that the two types of bonding have similar efficiencies in mediating electron transfer. However, a better comparison could be made if an analogous system was constructed with the acceptor bound to AlPor through the py linker. The DFT calculations also suggest that more efficient electron transfer might be obtained with this arrangement because the LUMO of the porphyrin is delocalized onto the py bridge. Currently, we are exploring these ideas and are preparing similar triads with different arrangements and structures for the donors and acceptors.

Acknowledgements

We thank Prof. Gonzalo Cosa, Department of Chemistry, McGill University for access to the nanosecond laser flash photolysis setup and Prof. Doug Bruce at Brock University for use of the time-resolved fluorescence instrument. This work was supported by Discovery Grants from Natural Sciences and Engineering Research Council Canada to A.v.d.E. and D.B.

Moore, Chem. Soc. Rev. 2009, 38, 25-35; i) K. Kalyanasundaram, M. Graetzel, Curr. Opin. Biotechnol. 2010, 21, 298-310; j) G.F. Moore, G. W. Brudvig, Annu. Rev. Condens. Matter Phys. 2011, 2, 303-327; k) D. G. Nocera, Acc. Chem. Res. 2012, 45, 767-776; l) A. Magnuson, M. Anderlund, O. Johansson, P. Lindblad, R. Lomoth, T. Polivka, S. Ott, K. Stensjo, S. Styring, V. Sundstrom, L. Hammarstrom, Acc. Chem. Res. 2009, 42, 1899-1909; m) M. R. Wasielewski, Acc. Chem. Res. 2009, 42, 1910-1921.

- [3] a) F. D'Souza, S. Gadde, D. M. S. Islam, C. A. Wijesinghe, A. L. Schumacher, M. E. Zandler, Y. Araki, O. Ito, J. Phys. Chem. A 2007, 111, 8552-8560; b) F. D'Souza, S. Gadde, M. E. Zandler, K. Arkady, M. E. El-Khouly, M. Fujitsuka, O. Ito, J. Phys. Chem. A 2002, 106, 12393-12404; c) F. D'Souza, O. Ito, Chem. Commun. 2009, 4913-4928; d) F. D'Souza, C. A. Wijesinghe, M. E. El-Khouly, J. Hudson, M. Niemi, H. Lemmetyinen, N. V. Tkachenko, M. E. Zandler, S. Fukuzumi, Phys. Chem. Chem. Phys. 2011, 13, 18168-18178; e) S. L. Gould, G. Kodis, R. E. Palacios, L. de La Garza, A. Brune, D. Gust, T. A. Moore, A. L. Moore, J. Phys. Chem. B 2004, 108, 10566-10580; f) D. M. Guldi, Chem. Soc. Rev. 2002, 31, 22-36; g) H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. P. Luo, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 2001, 123, 6617-6628; h) H. Imahori, Y. Mori, Y. Matano, J. Photochem. Photobiol. C 2003, 4, 51-83; i) P. V. Kamat, J. Phys. Chem. C 2007, 111, 2834-2860; j) P. A. Liddell, G. Kodis, J. Andreasson, L. de La Garza, S. Bandyopadhyay, R. H. Mitchell, T. A. Moore, A. L. Moore, D. Gust, J. Am. Chem. Soc. 2004, 126, 4803-4811; k) J. Y. Liu, M. E. El-Khouly, S. Fukuzumi, D. K. P. Ng, Chem. Eur. J. 2011, 17, 1605-1613; l) C. Luo, D. M. Guldi, H. Imahori, K. Tamaki, K. Sakata, J. Am. Chem. Soc. 2000, 122, 6535-6551; m) M. D. Ward, Chem. Soc. Rev. 1997, 26, 365-375.
- [4] K. M. S. a. R. G. K. M. Kadish in Handbook of Porphyrin Science, World Scientific, Singapore, 2010.
- [5] a) D. Gust, T. A. Moore, Top. Curr. Chem. 1991, 159, 103-151; b) D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 1993, 26, 198-205; c) M. R. Wasielewski, Chem. Rev. 1992, 92, 435-461.
- [6] a) T. Aida, S. Inoue, Acc. Chem. Res. 1996, 29, 39-48; b) G. J. E. Davidson, L. H. Tong, P. R. Raithby, J. K. M. Sanders, Chem. Commun. 2006, 3087-3089; c) Y. Hirai, T. Aida, S. Inoue, J. Am. Chem. Soc. 1989, 111, 3062-3063; d) E. Iengo, G. D. Pantos, J. K. M. Sanders, M. Orlandi, C. Chiorboli, S. Fracasso, F. Scandola, Chem. Sci. 2011, 2, 676-685; e) G. A. Metselaar, J. K. M. Sanders, J. de Mendoza, Dalton Trans. 2008, 588-590; f) P. K. Poddutoori, P. Poddutoori, B. G. Maiya, T. K. Prasad, Y. E. Kandrashkin, S. Vasil'ev, D. Bruce, A. van der Est, Inorg. Chem. 2008, 47, 7512-7522; g) P.K. Poddutoori, A. S. D. Sandanavaka, T. Hasobe, O. Ito, A. van der Est, J. Phys. Chem. B 2010, 114, 14348-14357; h) P.K. Poddutoori, A. S. D. Sandanayaka, N. Zarrabi, T. Hasobe, O. Ito, A. van der Est, J. Phys. Chem. A 2011, 115, 709-717.
- [7] P. P. Kumar, B. G. Maiya, New J. Chem. 2003, 27, 619-625.
- [8] a) N. Armaroli, G. Marconi, L. Echegoyen, J. P. Bourgeois, F. Diederich, Chem. Eur. J. 2000, 6, 1629-1645; b) M. A. Fazio, A. Durandin, N. V. Tkachenko, M. Niemi, H. Lemmetyinen, D. I. Schuster, Chem. Eur. J. 2009, 15, 7698-7705; c) S. Fukuzumi, Y. Kashiwagi, J. Porphyrins Phthalocyanines 2007, 11, 368-374; d) A. G. Moiseev, P. K. Poddutoori, A. van der Est, Appl. Magn. Reson. 2012, 42, 41-55; e) P. K. Poddutoori, A. Dion, S. J. Yang, M. Pilkington, J. D. Wallis, A. van der Est, J. Porphyrins Phthalocyanines 2010, 14, 178-187; f) D. I. Schuster, P. Cheng, P. D. Jarowski, D. M. Guldi, C. P. Luo, L. Echegoyen, S. Pyo, A. R. Holzwarth, S. E. Braslavsky, R. M. Williams, G. Klihm, J. Am. Chem. Soc. 2004, 126, 7257-7270.
- [9] H. Imahori, K. Tamaki, D. M. Guldi, C. P. Luo, M. Fujitsuka, O. Ito, Y. Sakata, S. Fukuzumi, J. Am. Chem. Soc. 2001, 123, 2607-2617.
- [10] a) S. J. Langford, M. J. Latter, C. P. Woodward, Photochem. Photobiol. 2006, 82, 1530-1540; b) N. Banerji, S. V. Bhosale, I. Petkova, S. J. Langford, E. Vauthey, Phys. Chem. Chem. Phys. 2011, 13, 1019-1029; c) Y. Mori, Y. Sakaguchi, H. Hayashi, J. Phys. Chem. A 2002, 106, 4453-4467; d) S. Wallin, C. Monnereau, E. Blart, J. R. Gankou, F. Odobel, L. Hammarstrom, J. Phys. Chem. A 2010, 114, 1709-1721; e) L. Flamigni, M. R. Johnston, L. Giribabu, Chem. Eur. J. 2002, 8, 3938-3947; f) H. Imahori, H. Yamada, D. M. Guldi, Y.

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www.chemeurj.org These are not the final page numbers! **77**



^[1] R. E. Blankenship, Molecular Mechanisms of Photosynthesis, Blackwell Science, Oxford, 2002.

^[2] a) B. Albinsson, J. Martensson, J. Photochem. Photobiol. C 2008, 9, 138-155; b) J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, Inorg. Chem. 2005, 44, 6802-6827; c) J. Barber, Chem. Soc. Rev. 2009, 38, 185-196; d) S. V. Bhosale, C. H. Jani, S. J. Langford, Chem. Soc. Rev. 2008, 37, 331-342; e) M. E. El-Khouly, O. Ito, P. M. Smith, F. D'Souza, J. Photochem. Photobiol. C 2004, 5, 79-104; f) S. Fukuzumi, Eur. J. Inorg. Chem. 2008, 1351-1362; g) D. Gust, T.A. Moore, A. L. Moore, Acc. Chem. Res. 2001, 34, 40-48; h) M. Hambourger, G.F. Moore, D.M. Kramer, D. Gust, A.L. Moore, T.A.

Endo, A. Shimomura, S. Kundu, K. Yamada, T. Okada, Y. Sakata, S. Fukuzumi, *Angew. Chem.* **2002**, *114*, 2450–2453; *Angew. Chem. Int. Ed.* **2002**, *41*, 2344–2347.

- [11] J. L. Segura, N. Martin, Angew. Chem. 2001, 113, 1416–1455; Angew. Chem. Int. Ed. 2001, 40, 1372–1409.
- [12] a) G. Kodis, P.A. Liddell, L. de La Garza, A.L. Moore, T.A. Moore, D. Gust, J. Mater. Chem. 2002, 12, 2100-2108; b) P. A. Liddell, G. Kodis, L. de La Garza, J. L. Bahr, A. L. Moore, T. A. Moore, D. Gust, Helv. Chim. Acta 2001, 84, 2765-2783; c) J. Becher, T. Brimert, J. O. Jeppesen, J. Z. Pedersen, R. Zubarev, T. Bjornholm, N. Reitzel, T. R. Jensen, K. Kjaer, E. Levillain, Angew. Chem. 2001, 113, 2565-2568; Angew. Chem. Int. Ed. 2001, 40, 2497-2500; d) H. C. Li, J. O. Jeppesen, E. Levillain, J. Becher, Chem. Commun. 2003, 846-847; e) K. A. Nielsen, E. Levillain, V. M. Lynch, J. L. Sessler, J. O. Jeppesen, Chem. Eur. J. 2009, 15, 506-516; f) Y. B. Liu, C. Y. Wang, M. J. Li, S. F. Lv, G. Q. Lai, Y. J. Shen, J. Porphyrins Phthalocyanines 2007, 11, 729-735; g) M. Di Valentin, A. Bisol, G. Agostini, P.A. Liddell, G. Kodis, A.L. Moore, T.A. Moore, D. Gust, D. Carbonera, J. Phys. Chem. B 2005, 109, 14401-14409; h) S. Sadaike, K. Takimiya, Y. Aso, T. Otsubo, Tetrahedron Lett. 2003, 44, 161-165; i) S. Saha, L. E. Johansson, A. H. Flood, H. R. Tseng, J. I. Zink, J. F. Stoddart, Small 2004, 1, 87-90.
- [13] X. W. Xiao, W. Xu, D. Q. Zhang, H. Xu, H. Y. Lu, D. B. Zhu, J. Mater. Chem. 2005, 15, 2557–2561.
- [14] a) Y. L. Wang, D. L. Frattarelli, A. Facchetti, E. Cariati, E. Tordin, R. Ugo, C. Zuccaccia, A. Macchioni, S. L. Wegener, C. L. Stern, M. A. Ratner, T. J. Marks, *J. Phys. Chem. C* 2008, *112*, 8005–8015; b) S. Bouguessa, A. K. Gouasmia, S. Golhen, L. Ouahab, J. M. Fabre, *Tetrahedron Lett.* 2003, *44*, 9275–9278.
- [15] S. V. Zaitseva, S. A. Zdanovich, T. A. Ageeva, O. A. Golubchikov, *Russ. J. Gen. Chem.* 2001, 71, 132–136.
- [16] H. A. Benesi, J. H. Hildebrand, J. Am. Chem. Soc. 1949, 71, 2703– 2707.
- [17] Gaussian 98 (Revision A.11.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakr-zewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dap-prich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Ra-ghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-

Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2002.

- [18] a) F. D'Souza, G. R. Deviprasad, M. E. Zandler, M. E. El-Khouly, M. Fujitsuka, O. Ito, *J. Phys. Chem. A* 2003, *107*, 4801–4807; b) F. D'Souza, P. M. Smith, S. Gadde, A. L. McCarty, M. J. Kullman, M. E. Zandler, M. Itou, Y. Araki, O. Ito, *J. Phys. Chem. B* 2004, *108*, 11333–11343.
- [19] a) D. Rehm, A. Weller, Ber. Bunsen Gesell. 1969, 73, 834–839; b) D.
 Rehm, A. Weller, Isr. J. Chem. 1970, 10, 259–271.
- [20] a) K. Hasharoni, H. Levanon, J. Phys. Chem. 1995, 99, 4875-4878;
 b) L. E. Sinks, M. R. Wasielewski, J. Phys. Chem. A 2003, 107, 611-620;
 c) G. P. Wiederrecht, W. A. Svec, M. R. Wasielewski, J. Phys. Chem. B 1999, 103, 1386-1389;
 d) L. Sinks, M. J. Fuller, W. H. Liu, M. J. Ahrens, M. R. Wasielewski, Chem. Phys. 2005, 319, 226-234;
 e) M. Di Valentin, A. Bisol, G. Agostini, M. Fuhs, P. A. Liddell, A. L. Moore, T. A. Moore, D. Gust, D. Carbonera, J. Am. Chem. Soc. 2004, 126, 17074-17086.
- [21] V. Kapko, D. V. Matyushov, J. Phys. Chem. B 2006, 110, 13184– 13194.
- [22] Y. E. Kandrashkin, K. M. Salikhov, A. van der Est, D. Stehlik, *Appl. Magn. Reson.* **1998**, *15*, 417–447.
- [23] A. H. Goldberg, D. A. Dougherty, J. Am. Chem. Soc. 1983, 105, 284–290.
- [24] M. D. E. Forbes, G. L. Closs, P. Calle, P. Gautam, J. Phys. Chem. 1993, 97, 3384–3389.
- [25] P. K. Poddutoori, M. Pilkington, A. Alberola, V. Polo, J. E. Warren, A. van der Est, *Inorg. Chem.* 2010, 49, 3516–3524.
- [26] M. Jakob, A. Berg, E. Stavitski, E. T. Chernick, E. A. Weiss, M. R. Wasielewski, H. Levanon, *Chem. Phys.* 2006, 324, 63–71.
- [27] G. Grampp, S. Landgraf, K. Rasmussen, J. Chem. Soc. Perkin Trans. 2 1999, 1897–1899.
- [28] X. F. Guo, Z. H. Gan, H. X. Luo, Y. Araki, D. Q. Zhang, D. B. Zhu, O. Ito, J. Phys. Chem. A 2003, 107, 9747–9753.
- [29] a) M. Davies, R. Moutran, A. H. Price, M. S. Beevers, G. Williams, J. Chem. Soc. Faraday Trans. 2 1976, 72, 1456–1458; b) S. Urban, B. Gestblom, W. Kuczynski, S. Pawlus, A. Wurflinger, Phys. Chem. Chem. Phys. 2003, 5, 924–928.
- [30] M. J. Weaver, G. E. Mcmanis, Acc. Chem. Res. 1990, 23, 294-300.
- [31] a) A. J. van der Est, P. B. Barker, E. E. Burnell, C. A. Delange, J. G. Snijders, *Mol. Phys.* **1985**, *56*, 161–169; b) A. J. van der Est, M. Y. Kok, E. E. Burnell, *Mol. Phys.* **1987**, *60*, 397–413.
- [32] P. J. F. De Rege, S. A. Williams, M. J. Therien, Science 1995, 269, 1409–1413.

Received: August 22, 2012 Published online: ■■ ■, 0000

Chem. Eur. J. 0000, 00, 0-0

Long live the charge separation: New biomimetic donor-acceptor triads have been constructed by taking advantage of the ability of aluminum in Al^{III} porphyrin to form axial covalent and coordination bonds with carboxylic acids and Lewis bases, respectively (see figure; NDI = naphthalenediimide, TTF = tetrathiafulvalene). Upon light excitation the triads undergo sequential electron transfer and by using a liquid crystalline solvent and high magnetic field, the lifetime of the charge separation can be extended into the microsecond range.



Artificial Photosynthesis -

P. K. Poddutoori,* N. Zarrabi, A. G. Moiseev, R. Gumbau-Brisa, S. Vassiliev, A. van der Est*...

Long-Lived Charge Separation in Novel Axial Donor–Porphyrin– Acceptor Triads Based on Tetrathiafulvalene, Aluminum(III) Porphyrin and Naphthalenediimide



