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Photoinduced Charge-Transfer States in Subphthalocyanine−Ferrocene Dyads

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Efficient conversion of light into other energy sources requires the effective formation of charge-separation (CS) states that exhibit long lifetimes and high energy content.[1] To this end, several approaches have been exploited in the last years. The most common of them is probably the design of complex multicomponent systems that separate the photogenerated charges over long distances, either by a cascade of sequential charge migration steps[2] or by dissociation of the charged components in supramolecular ensembles.[3] However, recent studies have demonstrated that there are still many optimizable parameters in simple donor-acceptor models that play a decisive role in the kinetics of charge separation and recombination. Among these, the approach of electronically decoupling the oxidized donor and the reduced acceptor is most notable.[4]

Subphthalocyanines (SubPcs)[5] are aromatic cone-shaped chromophores that present promising properties to be exploited in artificial photosynthetic systems:[6] (i) they are excellent antenna units that absorb in the 550−650 region with excitation energies above 2.0 V, (ii) they possess low reorganization energies,[7] and (iii) their redox characteristics may be tuned by the introduction of different peripheral substituents.[6b,d] Recent theoretical studies have shown that SubPc radical anions are stabilized by partial delocalization of the negative charge over the B−X axial bond.[8] Thus, when the macrocycle is reduced, the distance between the central boron atom and the adjacent axial atom increases, releasing a part of the electronic density by increasing the ionic character of the polar B−X bond.[9] Taking these properties in concert, we present here the first studies on the photoinduced electron-accepting ability of SubPcs in a series of dyads having a ferrocene (Fc) donor unit covalently attached through the axial position of the macrocycle. We will demonstrate that, despite the simplicity of the system, the photogenerated CS states possess an extraordinary stability, with lifetimes that reach 0.2 ms at 25 °C.

The synthetic pathway to SubPc-Fc dyads **1a**−**c** and reference SubPcs **2a**−**c**, bearing electron-withdrawing fluorine (**a**), nitro (**b**), and alkylsulfonyl groups (**c**) (Figure 1), involves a cyclotrimerization reaction of the corresponding phthalonitrile, followed by axial substitution of the chlorine atom in **3a**−**c** with the appropriate phenol derivative.[10,11] Compound **1a** crystallizes forming columns of Fc segregated by layers of SubPcs units that pack by π-π stacking between the donor phenoxy spacer and one of the electron-accepting diiminoisoindole units.[12]

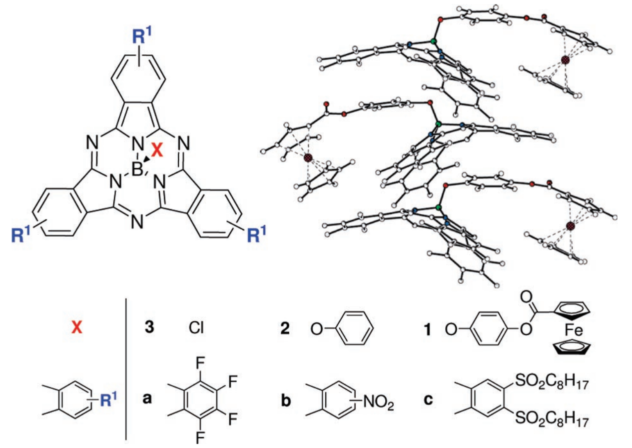

Figure 1. SubPc−Fc dyads **1a**−**c** and reference SubPc compounds **2a**−**c** and **3a**−**c**. Crystal structure and packing of SubPc−Fc **1a**.

Table 1. Selected Electrochemical and Photophysical Data for SubPcs **2a**−**c** and SubPc−Fc Dyads **1a**−**c**[a]

	$E_{1/2\,\mathrm{ox}}{}^{1\,b}$	$E_{1/2\,\mathrm{red}}{}^{1\,b}$	$\Phi_F{}^c$	$\tau_F{}^c$	$\lambda_{\max}{}^{S\,c}$	$\tau_S{}^c$	τ_{CS}
2a		−1057	0.4	1.8	735	3.0	
2b*C*$_3$		−1004	0.48	2.1	705	4.0	
2b*C*$_1$		−1013	0.37	2.0	705	3.5	
2c		−824	0.45	1.5	750	3.1	
1a	317	−1071	0.009	0.15	735	0.18	29[b]
						0.11[d]	43[d]
1b*C*$_3$	262	−1009	0.01	0.10	705	0.11	14[c]
						0.07[d]	55[b]
							61[d]
1b*C*$_1$	261	−998	0.01	0.11	705	0.13	[f]
1c	262	−883	0.005	[e]	750	0.06	231[d]
						0.06[d]	

[a] $E_{1/2}{}^1$: half-wave redox potentials in mV versus Fc/Fc$^+$. Φ_F: fluorescence quantum yields. τ_F: fluorescence lifetimes in ns. $\lambda_{\max}{}^S$: singlet maxima in nm. τ_S: singlet lifetime in ns. τ_{CS}: radical ion pair lifetime in μs. [b] In THF. [c] In toluene. [d] In benzonitrile. [e] Too fast for our 0.1 ns detection. [f] Not measured.

Dyads **1a**−**c** exhibit the typical reversible oxidation wave of the Fc group, which is positively shifted by 0.2−0.3 V versus Fc/Fc$^+$ (0 V). In the cathodic scan, as a general rule, the three series of SubPcs studied (**a**, **b**, and **c**) exhibit several reduction peaks, with an always reversible first one-electron reduction process around −1.0 V (Table 1). At more negative potentials, several processes (up to eight for **1c**) were observed. The different substituents placed on the axial and peripheral positions of the SubPc have an effect on the degree of reversibility of these processes (CVs shown in the SI).

The SubPc fluorescence in **2a**−**c** and **3a**−**c**, with quantum yields that are close to unity,[6] emerged as a powerful tool for the visualization and quantification of intramolecular deactivation processes in **1a**−**c**.[13] Notably, when comparing **1a**−**c** with **2a**−**c** or **3a**−**c**, about 100 times weaker SubPc fluorescence is seen (Table 1 and Figure S2). Important is the fact that, despite the strong

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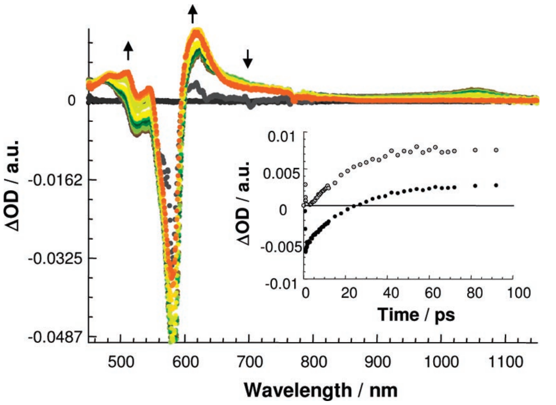

Figure 2. Differential absorption spectra (visible and near-infrared regions) obtained upon femtosecond photoexcitation (580 nm) of SubPc−Fc **1b**C_3 in THF (5.0×10^{-6} M) at room temperature with several time delays between 0 and 100 ps. Inset: time-absorption profiles of the spectra shown at 545 (filled circles) and 625 nm (hollow circles).

quenching, the overall fluorescence pattern remains essentially unchanged. This suggests that the change in quantum yields must be due to intrinsically faster singlet excited-state deactivations. In fact, fluorescence lifetime measurements reveal a significant shortening of the SubPc lifetimes, which are in the range of several nanoseconds in **2a**−**c** or **3a**−**c** and only about 100 picoseconds in **1a**−**c** (see Table 1 and Figure S3).[14]

Next we probed the SubPc references and the dyads in sets of transient absorption measurements with 150 fs (i.e., 580 nm) and 8 ns (i.e., 532 nm) laser pulses, which populate directly and exclusively the SubPc singlet excited state. In **2a**−**c** and **3a**−**c**, the following general picture unfolds: the initial singlet−singlet transitions (Figure S4) dominate the near-infrared region. Additional ground state bleaching evolves in the region that relates to the Q-band absorption. Both features are fairly long-lived, with lifetimes (1.5 ± 0.1−3.1 ± 0.2 ns) that are virtually identical to those determined from the fluorescence decay measurements. At the conclusion of the singlet decays, which refer to intersystem crossings (ISC) to the triplet manifolds, characteristic triplet excited-state spectra were noted. Figure S5 reveals, for example, a strong transient in the visible (∼440 nm), followed by ground-state bleaching of the Q-bands (∼580 nm) and a broad near-infrared transient (∼600−840 nm).

For **1a**−**c**, detecting the instantaneous grow-in of the near-infrared transitions affirms the successful SubPc excitation. Instead of seeing, however, the slow ISC dynamics, the singlet-singlet absorption (Figures 2 and S6) decays in the presence of the Fc donor unit with accelerated dynamics. Spectroscopically, the transient absorption changes, taken after the completion of the decay, bear no resemblance with the SubPc triplet excited state. In particular, the new transients reveal strong maxima at ∼640 nm, which match those of the one-electron reduced SubPc π-radical anions, produced in separate pulse radiolytic reduction experiments with SubPc references **2a**−**c** and **3a**−**c** (Figure S7).[15]

To examine the charge recombination dynamics, dyads **1a**−**c** were excited with 8 ns laser pulses. In this context, the spectral fingerprints of the SubPc π-radical anion (see Figures S8−S10) at 640 nm are useful probes. A close inspection of the radical ion pair lifetimes (Table 1) indicates that the charge recombination dynamics are located in the normal region of the Marcus parabola, despite the remarkably long lifetimes reaching 231 μs. This trend evolves from comparing (i) different electron acceptor moieties (i.e., **1a**, **1b**, and **1c**) and (ii) different solvent polarities (i.e., toluene, THF, and benzonitrile). Mainly structural reorganizations associated, for example, with the partial delocalization of the negative charge over the B−X axial bond are responsible for rather large reorganization energies.

These first studies on SubPcs as pure electron-accepting units demonstrate the great potential of these chromophores in artificial light-processing systems. Charge separation evolves from the singlet excited state (∼2.05 eV) to a stabilized radical ion pair (∼1.3 eV) whose recombination lifetime is among the longest reported for a dyad system.[4c] This stabilization is likely due to the particular characteristics of the axial polar B−X bond, which increases its length and ionic character upon SubPc reduction, and the donor−acceptor topology, which may prevent an efficient orbital overlap between the reduced SubPc LUMO and oxidized Fc HOMO.

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Supporting Information Available: Experimental procedures and complete structural characterization of SubPcs **2a**−**c** and **3a**−**c**, and SubPc−Fc dyads **1a**−**c**, along with ^{1}H NMR, ^{13}C NMR, and UV−vis spectra. CVs and redox potential data for **1a**−**c**, **2a**−**c**, and **3a**−**c**, crystal data for **1a**, and selected emission and transient absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) In the case of the **b** series, the two regioisomers (with C_3 and C_1 symmetry) were separated by column chromatography and characterized independently. See also: Claessens, C. G.; González-Rodríguez, D.; Torres, T.; Martín, G.; Agulló-López, F.; Ledoux, I.; Zyss, J.; Ferro, V. R.; García de la Vega, J. M. *J. Phys. Chem. B* **2005**, *109*, 3800−3806.

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(13) The fluorescence in the **a** series is slightly more energetic (2.08 eV) than in the **b** (2.03 eV) and **c** series (2.04 eV), a trend that matches the differences seen in the Q-band location.

(14) All fluorescence decay curves were best fitted by a single-exponential decay law and χ^2 values of at least 1.

(15) No spectral identification can be made for the radical cation of Fc, because it only shows a weak absorption maximum at 625 nm ($\epsilon = 500$ M^{-1} cm^{-1}).

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