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Ultrafast Photoinduced Processes in Subphthalocyanine Electron Donor–Acceptor Conjugates Linked by a Single B–N Bond[||]

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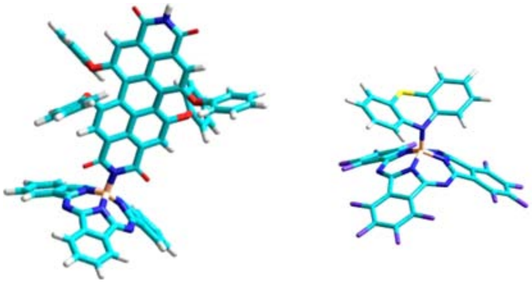
ABSTRACT



We have prepared two different subphthalocyanine conjugates by linking these macrocycles either to an electron-accepting perylene diimide or to an electron-donating phenothiazine through a single B–N covalent bond. The short spacing between the two active building blocks results in ultrafast photoinduced electron-transfer reactions.

The comprehension and optimization of a photoinduced electron transfer process is of paramount relevance for the development of efficient nature-mimicking photosynthetic systems.[1] We[2] and others[3] have recently demonstrated that subphthalocyanines (SubPcs)[4] are electronically versatile building blocks that may play the role of antenna units, electron donors, or electron acceptors in artificial photosynthetic systems. These roles are defined by the electronic character of the macrocycle, the electroactive partner,[2a–c,3f] and the nature of the spacer. The latter determines, moreover, the distance,[2d] the relative orientation,[2d] and the degree of electronic communication between the components.[2f,g] In the work presented herein,

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[||] In memory of our colleague and friend Christian G. Claessens.

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we have prepared and studied two different SubPc-based conjugates (Figure 1), in which the donors and acceptors are linked by a single B−N covalent bond without the intermediacy of a spacer. We have profited from recent synthetic advances in the activation of the axial position of SubPcs[5] to directly connect nitrogen nucleophiles to the boron atom. These are electron-poor and -rich units, such as perylene diimide (PDI) and phenothiazine (PTZ), respectively. The resulting conjugates differ in their ultrafast electron-transfer reactions, where the SubPcs play the corresponding role of electron donor or acceptor.

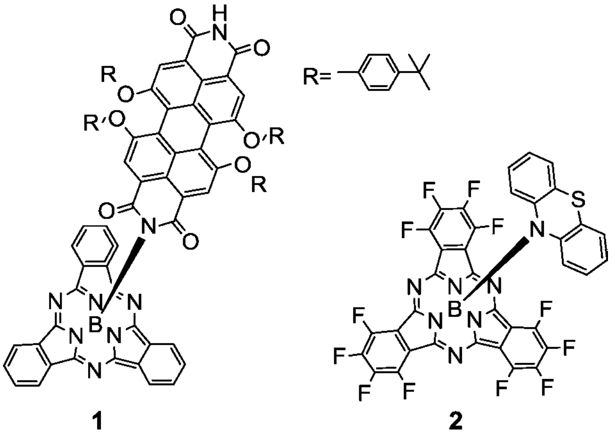
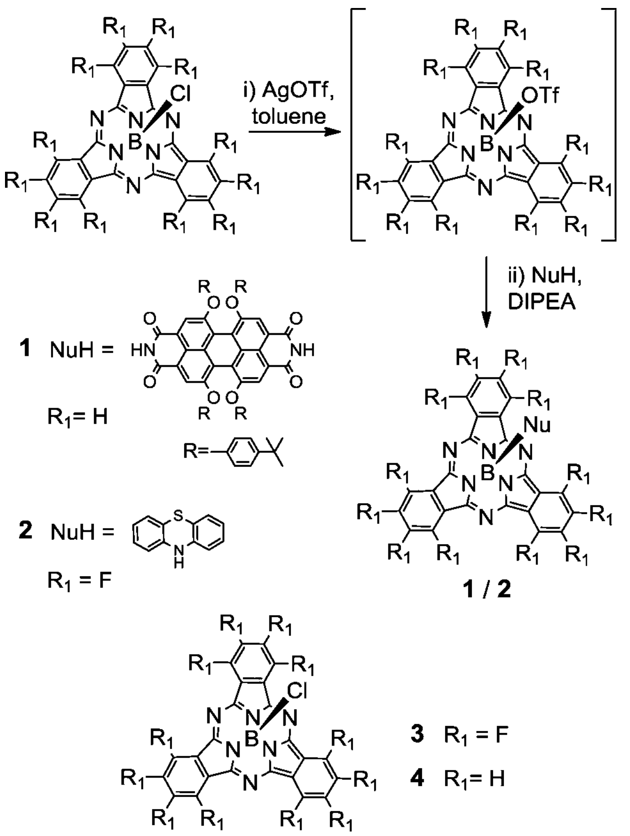


Figure 1. Chemical structure of **1** and **2**.

The two electron donor−acceptor conjugates (**1** and **2**) were prepared by an axial ligand substitution reaction from the corresponding SubPcBCl *via* the generation of a SubPc-triflate intermediate (Scheme 1). Once the starting SubPcBCl is consumed and the activated triflate intermediate is formed, the nucleophile, namely perylene diimide or phenothiazine, is added *in situ* and the reaction is heated to reflux overnight. **2** was synthesized in 83% yield following this reported procedure.[5] To improve the reaction yield of **1**, we noted the necessity to use an excess of PDI **5** in $CHCl_3$, because of its low solubility in most of organic solvents. Only the monosubstituted **1** was obtained under these conditions. The axial substitution with imides (phthalimide) has been recently described by Bender et al. using SubPcBCl derivatives as precursors.[6] In our hands, this direct method produced only traces of **1** and a significant amount of decomposed material due to the high temperatures employed. On the contrary, the reaction *via* the SubPc-triflate increased the yield of **1** to 20% under milder conditions. The final products were characterized by ^{1}H and ^{13}C NMR, HR-MS, and UV−vis.

Scheme 1. Synthetic Route towards **1** and **2**



The structure and the HOMO and LUMO of **1** and **2** were calculated by DFT at the B3LYP/6-31G(d,p) level (Figure 2). From the redox potentials of each unit we could estimate the charge-transfer state energy levels for **1** (1.85 eV) and **2** (1.38 eV), which are in reasonable agreement with the computed values.

Turning to the electronic communication between SubPc and PDI/PTZ, ground state interactions were probed by means of steady state spectroscopy in a series of solvents of different polarity (Table 1). The effect of the solvent polarity on the absorption maxima is, however, minor. In particular, the absorption maxima at 567 and 571 nm for **1** and **2**, respectively, in tetrahydrofurane (THF), red-shifted by 5 nm when using chlorobenzene as solvent (Figure S8).

In complementary steady-state fluorescence experiments, we note a similar trend (Table 1). Here, the fluorescence maxima are bathochromically shifted from 593 and 576 nm for **1** and **2**, respectively, in THF, to 608 and 583 nm in chlorobenzene (Figure S9). The SubPc fluorescence quantum yields are impacted by the presence of either

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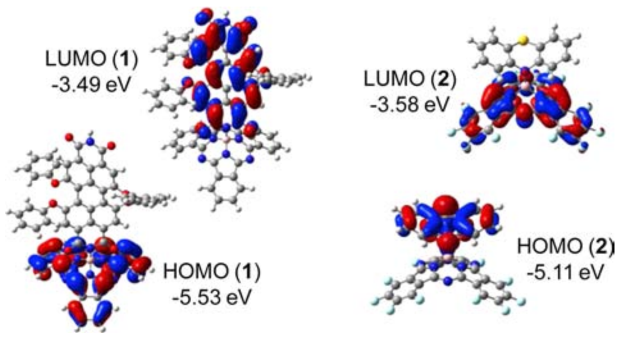

Figure 2. DFT-computed HOMO/LUMO orbitals of **1** and **2**.

Table 1. Spectroscopic Data of Conjugates **1**−**2** and SubPcs **3**−**4**

compd	solvent	λ_{abs} (nm)[a]	λ_{em} (nm)[b]	Φ[c]	τ_1, τ_2 (ns)[d]
1	1,4-dioxane	568	595	0.086	6.2, 1.1
	chlorobenzene	572	608	0.067	5.8, 1.4
	THF	567	593	0.099	6, 1.5
	DMF	570	602	0.08	5.9, 1.6
2	toluene	576	580	4.4×10^{-3}	0.1
	1,4-dioxane	572	579	1.7×10^{-3}	<0.1
	chlorobenzene	576	583	1.5×10^{-3}	<0.1
	THF	571	576	3×10^{-3}	<0.1
3[2h]				0.58	3.2
4[7]				0.25	3.1

[a] Absorption maxima. [b] Emission maxima. [c] Fluorescence quantum yields. Cresyl violet in methanol was used as standard (Φ = 0.54). [d] Fluorescence lifetime.

PDI or PTZ. Thus, the fluorescence quantum yields drop from 0.25 for SubPcBCl reference **4**,[7] to 0.067−0.099 for **1** and from 0.58 for F_{12}SubPcBCl **3**,[2h] to 1.5×10^{-3} to 4.4×10^{-3} for **2**. It is interesting that neither **1** nor **2** reveals a particularly strong solvent effect.

Additionally, time-resolved fluorescence measurements were performed. In **1** and **2**, the fluorescence decays are biexponential, which contrast with the monoexponential decay seen for SubPcBCl references **3**[2h] and **4**.[7] In particular, **1** shows a long-lived component of around 6 ns, as well as a short-lived component of 1.5 ns. These lifetimes correlate with the nearly unquenched fluorescence of PDI (i.e., 6 ns)[8] and the F_{12}SubPcBCl **3**[2a] (i.e., 1.5 ns). In stark contrast, the fluorescence decay of **2** is dominated by a short-lived component of less than 0.1 ns, which is in accordance with a fast deactivation process.[9]

To shed light on the nature of the deactivation, that is, electron transfer and/or energy transfer, we turned to transient absorption spectroscopy. The transient absorption

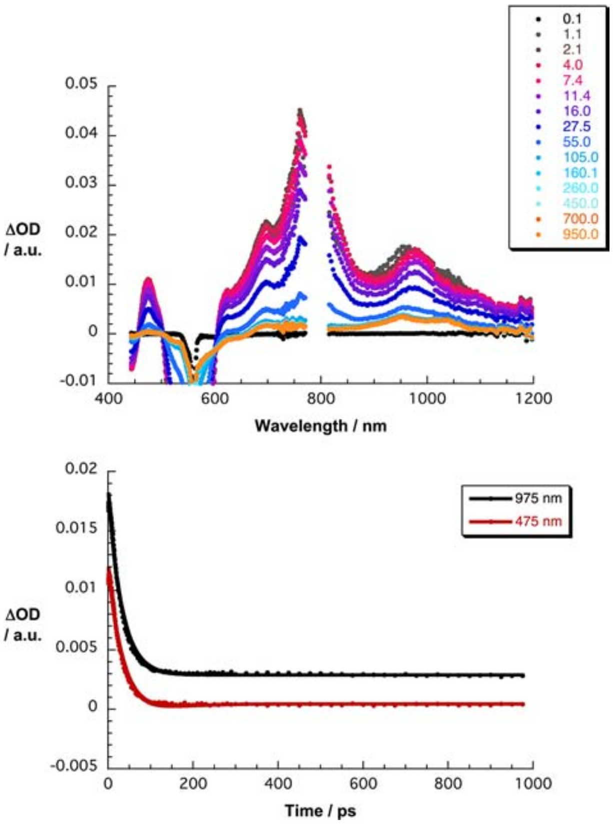

Figure 3. (Top) Differential absorption spectra obtained upon femtosecond flash photolysis (550 nm, 150 nJ) of **1** in THF with several time delays between 0.1 and 950 ps at rt; see figure legend. (Bottom) Time−absorption profile of the spectra at 475 and 975 nm monitoring the singlet excited state deactivation.

features of a SubPc reference infer its rapid singlet excited state formation with maxima at 430, 615, 755, 825, 910, and 1070 nm as well as minima at 515, 560, and 630 nm.[2h] The singlet excited state transforms into the corresponding triplet excited state, whose transient absorption spectrum maximizes at 460 and 645 nm and minimizes at 560 nm, with 1.5 ± 0.1 ns. In the case of a PDI reference,[8] the singlet excited state, as it is formed right after the laser pulse, includes a net decrease of the absorptions around 455, 580, and 615 nm and new absorptions at 730, 760, 965, and 1035 nm. The singlet transients produced upon photoexcitation decay with a lifetime of 4.5 ± 0.1 ns *via* an inefficient intersystem crossing to the corresponding triplet manifold.

In **1**, in line with the ground state absorption features, we note upon 387 or 550 nm excitation the SubPc and the PDI singlet excited states with features that include the following: maxima at 615, 755, 800, and 1100 nm and a minimum at 575 nm; maxima at 475, 700, and 1000 nm and a minimum at 440 nm, respectively (Figure 3). Both singlet excited states decay with lifetimes of 122 ± 2, 28.5 ± 0.8, and 7.4 ± 0.2 ps in chlorobenzene, THF, and DMF respectively. Notably, such similar kinetics for the SubPc and the PDI decay are in line with their nearly isoenergetic nature (i.e., 2.19 eV for SubPc versus 2.17 eV for PDI). It is,

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(9) A weak long-lived component of around 2.5 ns relates to an impurity level of SubPc.

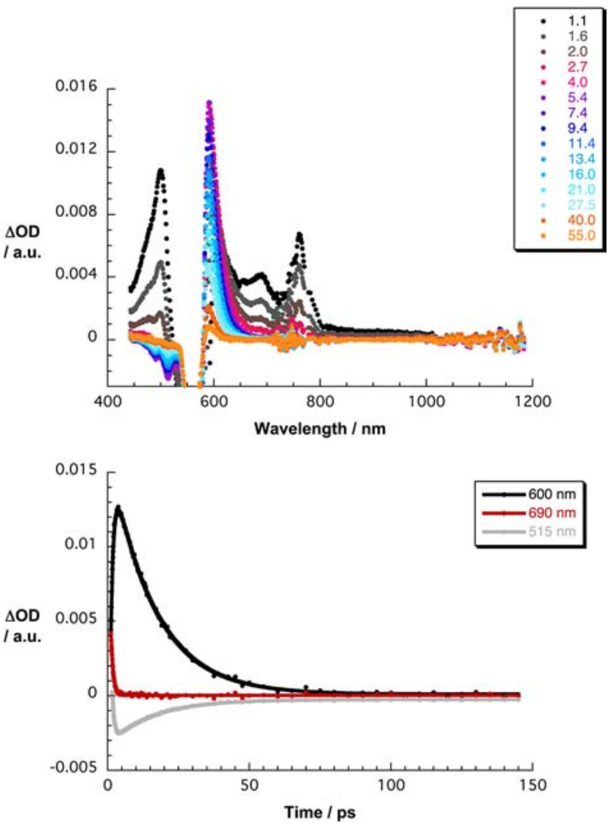

Figure 4. (Top) Differential absorption spectra obtained upon femtosecond flash photolysis (550 nm, 150 nJ) of **2** in THF with several time delays between 1.1 and 55 ps at rt; see figure legend. (Bottom) Time–absorption profile of the spectra at 515, 600, and 690 nm, monitoring the forward electron transfer and back electron transfer.

however, the triplet excited state of PDI that results from a fast deactivation of the two singlet excited states rather than SubPc$^{\bullet+}$–PDI$^{\bullet-}$. Please note that an energy transfer is unlikely to happen due to identical singlet excited state energies. Taking the aforementioned into concert, we conclude that SubPc$^{\bullet+}$–PDI$^{\bullet-}$ is semistable and that the back electron transfer must be significantly faster than the forward electron transfer. In other words, the overall kinetics are ruled by the rate-determining step.

Owing to weak absorption of PTZ, the spectral features that are seen immediately upon excitation of **2** at 387 or 550 nm are almost superimposable with those recorded for the SubPc singlet excited state (Figure 4). The lifetime of the SubPc singlet excited state is, however, impacted by the presence of PTZ. In fact, formation of a new transient develops as a result of the rapid decay of the SubPc singlet excited state (i.e., 1.7 ± 0.2 ps in toluene, 1.5 ± 0.2 ps in chlorobenzene, and 1.1 ± 0.1 ps in THF), which replaces the much slower intersystem crossing to the triplet excited state. The new transient lacks, however, resemblance with the SubPc triplet excited state. In this context, minimum at 595 nm and minima at 490, 515, 530, 560, and 570 nm bear great resemblance with the pulse radiolytic findings when reducing SubPc.[2] The 520 nm maximum[10] seen for PTZ$^{\bullet+}$ in pulse radiolytical oxidation is, however, masked by the SubPc$^{\bullet-}$ related features. Nevertheless, the aforementioned suggests involvement of the SubPc singlet excited state in an intramolecular electron transfer, occurring between the photoexcited SubPc and the singlet ground state of PTZ, which are driven by a thermodynamic driving force of 1.38 eV to afford SubPc$^{\bullet-}$–PTZ$^{\bullet+}$. From multiwavelength analyses, that is, monitoring the SubPc$^{\bullet-}$/PTZ$^{\bullet+}$ fingerprints, we have derived the back electron transfer dynamics as 16 ± 2 ps in toluene, 18 ± 2 ps in chlorobenzene, and 16 ± 2 ps in THF.

In summary, we have prepared two novel SubPc-based electron donor–acceptor conjugates, in which the SubPc unit functions either as an electron donor or as an electron acceptor. The latter depends, on one hand, on the peripheral substitution and, on the other hand, on the nature of the axial electroactive partner (i.e., perylene diimide versus phenothiazine). The different building blocks have been connected through a single boron–nitrogen bond. Spectroscopic investigations of the conjugates confirmed the suitability of nitrogen-based linkers for efficient photoinduced electron transfer processes in SubPc-based systems.

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Supporting Information Available. Synthesis, NMR, MS, and absorption/emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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