

Accelerating charge transfer in a triphenylamine–subphthalocyanine donor–acceptor system†

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We have designed, synthesized and probed a dodecafluoro-subphthalocyaninato boron(III) unit, which bears a triphenylamine moiety in its axial position, as a novel electron donor–acceptor system.

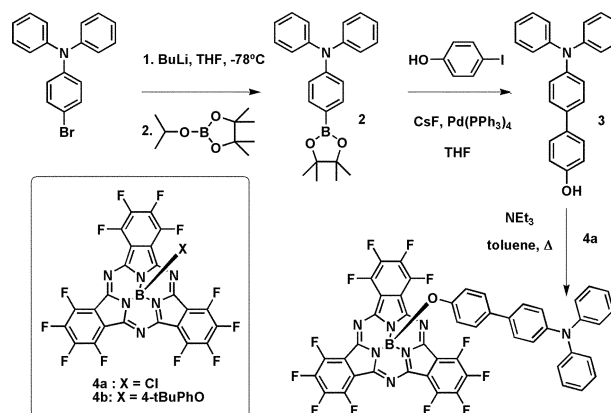
Designing, synthesizing and studying multicomponent electron donor–acceptor systems that efficiently separate photo-generated charges over long distances is a multidisciplinary field of research. It still requires substantial efforts—both theoretically and experimentally—to achieve performances that are typically seen in nature.¹ Among the broad range of possible categories of photoactive ensembles, the donor–acceptor approach is still the most widespread one. Subphthalocyanines (SubPcs),² non-planar 14 π -electron aromatic chromophores, have recently emerged as a platform for novel electron acceptor units. Importantly, they show great potential in artificial photosynthetic systems³—a consequence that is largely based on their outstanding light harvesting features (550–650 nm), their excitation energies above 2.0 V, and their low reorganization energies.⁴ On the other hand, triphenylamine (TPA), a large conjugated tertiary amine system, not only acts as a strong electron donor but may also stabilize the charge-transferred state.⁵

In the current work we have pursued an approach in which we have started with a theoretical survey to determine the frontier orbitals that are involved in the charge separation process in covalently linked subphthalocyanine–triphenylamine SubPc–TPA-systems. This was followed by the subsequent design, synthesis and finally characterization of dyad **1** (Scheme 1), especially in terms of charge transfer features. Indeed, a rapid charge transfer, evolving between the photo-excited SubPc and TPA fragments, has been confirmed in femtosecond transient absorption measurements.

The synthetic pathway to SubPc–TPA dyad **1**† (Scheme 1) involves the cyclotrimerization of the corresponding tetra-fluorophthalonitrile in the presence of boron trichloride to obtain SubPc **4a** followed by axial substitution of the axial chlorine atom with the corresponding phenol derivative **3**.⁶ Previously, pinacol borate **2**⁷ was obtained in a one-pot procedure from 4-bromotriphenylamine in 67% yield.⁸ Palladium-catalyzed Suzuki cross-coupling reaction between pinacol boronate **2** and 4-iodophenol in the presence of CsF and catalytic amounts of Pd(PPh₃)₄ in THF gave rise to phenol **3** in 54% yield.⁹ Substitution of the chlorine atom of chlorododecafluoro-subphthalocyanine **4a** with phenol **3** in toluene in the presence of stoichiometric amounts of NEt₃ gave SubPc–TPA dyad **1** in 45% yield.

According to TD-DFT calculations at the B3LYP/6-31G(d) level on ground-state geometries optimized at the same level of theory, three absorption bands are predicted at 882, 870 and 512 nm in SubPc–TPA **1** (Scheme 1). The former corresponds essentially to the HOMO–LUMO transition and does not lead to a charge-separation state and has negligible oscillator strength. The same applies to the second band which corresponds basically to the HOMO–LUMO+1 transition. The third band, however, corresponding to the SubPc Q band, has as dominant contribution the HOMO–1/LUMO+1 excitation leading to a clear charge-separation state (see Fig. 1) and presents a rather large oscillator strength (0.219), indicating that **1** should exhibit photoinduced charge separation behavior.

A first set of electrochemical and photophysical experiments was conducted to establish the optical markers of the radical



Scheme 1 Synthesis of subphthalocyanine–TPA dyad **1**.

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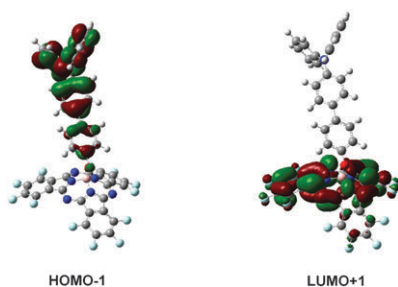


Fig. 1 Electron density plots associated with the HOMO–1 and LUMO+1 orbitals of SubPc–TPA dyad **1**.

ions involved in photoinduced charge separation processes (Fig. S18 in ESI[†]). In particular, we tested the one-electron reduction of the SubPc reference **4b**¹⁰ (in a deoxygenated toluene–acetone–2-propanol solvent mixture) and the one-electron oxidation of the TPA reference **3** (in oxygenated dichloromethane). In the oxidation experiments a major peak is noted, with a maximum at 460 nm, and on onset of broad absorption, which seems to extend out into the near-infrared. Notably, the latter band is extremely broad and is likely to reflect the delocalization of the positive charge. Radiolytic reduction of reference SubPc **4b**, on the other hand, leads to the following features: a transient maximum at 490 nm that is followed by a sharp bleaching of the ground state between 510 and 610 nm. Moreover, a series of sharp transient peaks in the range between 800 and 900 nm complete the spectral features. It should be noted that this feature is unique for perfluorinated SubPc derivatives such as **4b**.¹¹

Additional experiments by means of cyclic voltammetry further underline these data. (1) these studies confirmed the ease of reduction and oxidation of SubPc and TPA references, **4b** and **3**, respectively. The following redox potentials were established in these experiments: $E_{1/2}(\mathbf{4b}/\mathbf{4b}^{\bullet-}) = -1.06$ V vs. Fc/Fc⁺; $E_{1/2}(\mathbf{3}/\mathbf{3}^{\bullet+}) = 0.55$ V vs. Fc/Fc⁺. (2) When adding the potentials of the first SubPc **4b** reduction and the first TPA **3** oxidation an energy of the radical ion pair of 1.61 eV was estimated.[§]

Next, we tested the SubPc reference **4b** and SubPc–TPA **1** in steady-state and time-resolved fluorescence experiments. As Fig. 2 illustrates, common to both compounds is a distinct fluorescence pattern, which includes a strong *0–0 maximum around 580 nm ($E_{\text{singlet}} = 2.16$ eV) followed by a set of *0–1, *0–2, etc. transitions in the form of poorer resolved shoulders at 600, 620 and 660 nm. Such features are essentially a mirror image to the ground-state absorption (*i.e.*, 0–*0 at 573 nm). Different are, however, the fluorescence quantum yields, which are 0.31 for the SubPc reference **4b** and 1.2×10^{-3} for SubPc–TPA **1** in toluene. This corresponds to an overall quenching of at least 250. Importantly the SubPc fluorescence quantum yield depends primarily on the solvent polarity: toluene > anisole > THF. In time-resolved fluorescence measurements, that is, probing the SubPc fluorescence deactivation in the SubPc reference **4b** and in SubPc–TPA **1** at 580 nm, reveal for **4b** a strictly mono-exponential decay from which we derived a fluorescence lifetime of 1.6 ns. Not surprising is the observation that no appreciable SubPc fluorescence was registered for **1**, that lies outside of a time

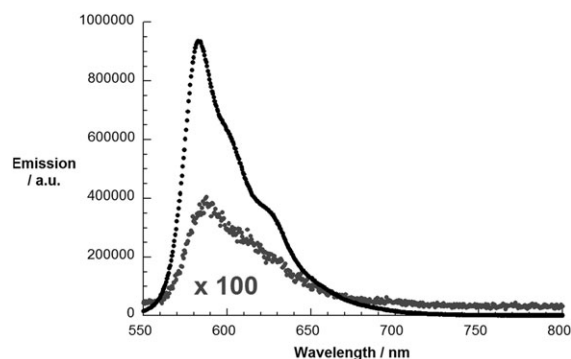


Fig. 2 Room-temperature fluorescence spectra of SubPc **4b** (black) and SubPc–TPA dyad **1** (grey) in toluene recorded with solutions that exhibit optical absorption of 0.5 at the 530 nm excitation wavelength.

resolution of approximately 0.1 ns. In fact, considering the fluorescence quantum yields of **4b** and **1** we can extrapolate the fluorescence lifetime for **4b** as ~ 3 ps. The presence of the electron donor TPA thus causes a rapid intramolecular deactivation of the SubPc fluorescence (*i.e.*, $\gg 10^{10}$ s⁻¹). A possible rationale implies an exothermic transformation of the SubPc singlet excited state (2.16 eV) into an intramolecular radical ion pair state (1.61 eV). Interestingly, such a fast charge transfer contrasts the behavior seen in a comparable SubPc–ferrocene (Fc) conjugate, where charge separation occurs with $\sim 10^{10}$ s⁻¹ to generate a similarly energetic SubPc^{•-}–Fc^{•+} (~ 1.4 eV).³

Conclusive information about the photoproducts came from transient absorption spectroscopy. In particular, with the help of femtosecond laser pulses (*i.e.*, 580 nm) the fate of the SubPc singlet excited state was probed in the SubPc reference **4b** and in SubPc–TPA **1**. Following, for instance, the time evolution of the characteristic singlet excited state features of SubPc is a convenient approach toward identifying spectral features of the resulting photoproducts (*i.e.*, triplet excited state in SubPc and radical ion pair state in SubPc–TPA dyad **1**) and determining absolute rate constants for these intramolecular decays.

The differential spectrum recorded immediately after the laser pulse for the SubPc reference **4b** gives rise to the instantaneous formation (*i.e.*, $> 1 \times 10^{12}$ s⁻¹) of a transient species, which exhibits the following characteristics: maxima at 415 and 770 nm and minima at 525 and ~ 575 nm (Fig. S19 in ESI[†]). The minima are a good reflection of the ground-state absorption maxima. These spectral attributes are indicative of the SubPc singlet excited state— $E_{\text{singlet}} = 2.16$ eV. This decays slowly (9.1×10^8 s⁻¹) to the energetically lower-lying triplet excited state *via* intersystem crossing— $E_{\text{triplet}} = 1.45$ eV. Kinetically, an important aspect is that the intersystem crossing goes well in hand with the lifetimes derived in the fluorescence experiments. Spectroscopically, the newly formed features include maxima at 455 and 611 nm, which are further accompanied by a strong transient bleach in the region of the ground state absorption (*i.e.*, 510–590 nm). Complementary nanosecond experiments helped to corroborate these transient changes and their oxygen sensitive nature through generation of singlet oxygen (not shown).

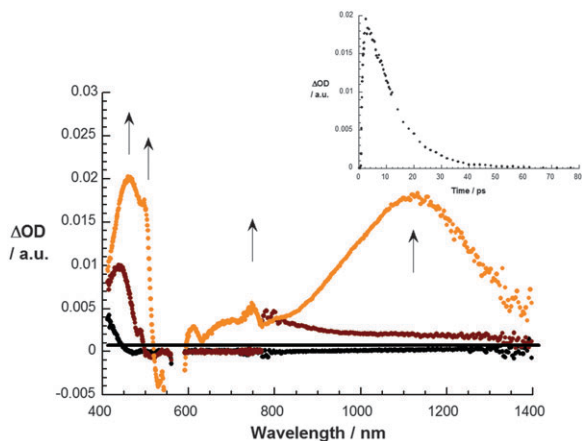


Fig. 3 Differential absorption spectrum (visible and near-infrared) obtained upon femtosecond flash photolysis (580 nm, 150 nJ) of SubPc-TPA **1** in nitrogen-saturated toluene with time delays of 0 ps (black spectrum), 1 ps (red spectrum) and 5 ps (orange spectrum) at room temperature. Inset: time-absorption profiles of the spectra at 500 nm, monitoring the formation and decay of the radical ion pair state.

Regarding the femtosecond transient absorption measurements of dyad **1**, immediately, after the laser excitation, the strong singlet-singlet absorption of the SubPc grows in instantaneously (*i.e.* 10^{12} s^{-1}). This confirms that, despite the presence of TPA, the SubPc singlet excited state is successfully formed. Instead of seeing, however, the slow intersystem crossing dynamics, as we have discussed in the context of the SubPc reference **4b**, the singlet-singlet absorptions decay ($1 \times 10^{12} \text{ s}^{-1}$) in the presence of the electron donating TPA via an intramolecular charge transfer reaction to yield $\text{SubPc}^{\bullet-}\text{-TPA}^{\bullet+}$.

Spectroscopic proof for the radical ion pair formation was obtained from the features developing in parallel with the disappearance of the SubPc singlet-singlet absorption in the visible and the near-infrared, which are exemplified in Fig. 3. In the visible region, two sharp absorptions correspond to the one-electron oxidized $\text{TPA}^{\bullet+}$ (460 nm) and to the one-electron reduced $\text{SubPc}^{\bullet-}$ (495 nm). We noted, on the other hand, in the near-infrared region fine-structured peaks in the 700–800 nm range and a 1100 nm maximum, which resemble the signatures of the one-electron reduced $\text{SubPc}^{\bullet-}$ and the one-electron oxidized $\text{TPA}^{\bullet+}$, respectively. In other words, the transient features all the spectroscopic markers that were found in the electrochemical and radiolytical assays.

Both radical ion pair attributes are only short lived and start to decay on the picosecond time scale. To examine the charge-recombination dynamics all of the spectral fingerprints are useful probes. Important is the fact that their decays resemble each other and give rise to kinetics that obey a clean unimolecular rate law. The lifetimes range from 17 ps (toluene) to 9 ps (THF) and 7 ps (benzonitrile).

In view of these studies it can be concluded that dodecafluorosubphthalocyanine is an excellent electron-acceptor unit which, when covalently linked in its axial position to a

triphenylamine moiety through a rigid phenylene spacer, undergo fast photoinduced electron transfer.

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Notes and references

† SubPc-TPA dyad **1** was isolated as a purple solid. Mp $>250 \text{ }^\circ\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ 7.15 (t, 4H), 7.14 (d, 2H), 6.99 (d, 2H), 6.98 (d, 2H), 6.95 (d, 2H), 6.93 (d, 2H), 5.32 (d, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ 154.9, 147.8, 146.7, 138.4, 135.0, 133.4, 129.9, 129.3, 127.9, 127.4, 124.3, 124.2, 122.8, 117.9, 115.7 ppm. ^{19}F NMR (470.5 MHz, CDCl_3): δ -147.38 (m, 6F), -136.65 (m, 6F) ppm. ^{11}B NMR (160.5 MHz, CDCl_3): δ -15.1 (s) ppm. MS (FAB, *m*-NBA): m/z = 947.2 $[\text{M}]^+$, 611.1 $[\text{M} - \text{axial group}]^+$. HRMS calc. for $\text{C}_{48}\text{H}_{18}\text{BF}_{12}\text{N}_7\text{O}$: 947.1474; found, 947.1454. UV-Vis (CHCl_3): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 571 (4.6), 552 (sh), 531 (sh), 310 (4.4). FT-IR (KBr): ν/cm^{-1} 3031, 2925, 1534, 1485, 1318, 1032, 881, 680. Anal. Calc. for $\text{C}_{48}\text{H}_{18}\text{BF}_{12}\text{N}_7\text{O}$: C, 60.85; H, 1.91; N, 10.35. Found: C, 60.71; H, 2.00; N, 10.26%.

§ The corresponding experiments with SubPc-TPA **1** yield an energy of 1.68 eV.

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