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Synthesis and Photoinduced Electron Transfer Studies of a Tri(Phenothiazine)–Subphthalocyanine–Fullerene Pentad

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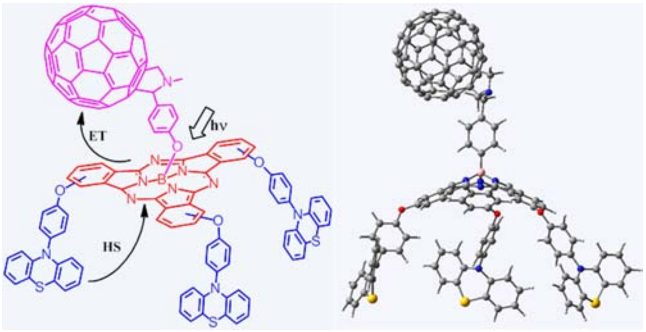
ABSTRACT



A novel donor–acceptor pentad featuring subphthalocyanine and fullerene as the primary electron donor and acceptor, and three phenothiazine entities as secondary hole transferring agents, have been newly synthesized and characterized as an photosynthetic reaction center model compound. Occurrences of ultrafast photoinduced electron transfer (PET) and slower charge recombination are witnessed in the pentad from the femtosecond and nanosecond transient absorption studies.

A molecular level understanding of multistep electron transfer processes, similar to that occurring in natural photosynthesis,[1] is fundamentally important for efficient conversion of light energy into electricity or fuels, and also building optoelectronic devices, in general.[2] The basic design involves organization of energetically well-aligned multimodular supramolecular systems to promote multistep electron transfer processes following a redox gradient thus ultimately generating long-lived charge separated states. In addition, the degree of electronic interactions between the entities controlled by their relative distance, orientation, and the nature of the linkages are key in governing the kinetics and mechanism of light induced electron transfer processes.[2] Using elegant supramolecular systems, a number of studies have probed one or more of these aspects of photoinduced electron transfer reactions. In majority these studies porphyrins/phthalocyanines have served as primary electron donors while fullerene, C_{60}, has served as an electron acceptor.[3] Fullerene, due to its low-reorganization energy demand in electron transfer, is well-known to generate long-lived charge separated states.[4]

Subphthalocyanines (SubPc) are 14 π-electron macrocycles made out of three 1,3-diiminoisoindole units N-fused

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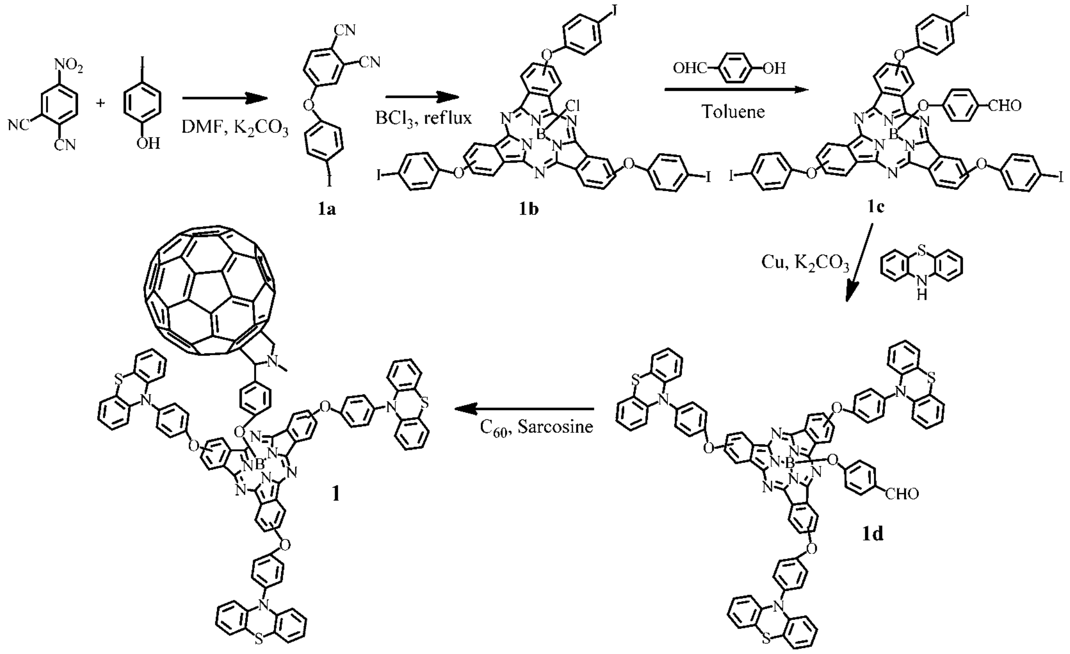
Scheme 1. Synthetic Methodology Developed for Pentad, **1**



around a central boron atom.[5] Due to their synthetic versatality and interesting optical/photophysical properties, these show promise in their employment in organic photovoltaics as well as nonlinear optics and the development of artificial photosynthetic models.[5] Few donor–acceptor systems involving SubPc to probe photoinduced electron transfer have been reported in the literature.[6] Simple dyads involving SubPc covalently linked to fullerene revealed only singlet–singlet energy transfer to the fullerene entity instead of anticipated electron transfer to generate the charge separated species.[7] One can overcome this hurdle by modulating the electronic properites of SubPc by covalent attachment of a secondary electron donor group(s) while maintaining the same donor–acceptor distance as well as electrochemical and spectroscopic properties.[6] In the present study, we have designed such a pentad featuring covalently linked SubPc–C_{60} in which the SubPc is covalently linked to three easily oxidizable phenothiazine entities. The fullerene entity has been covalently linked to the SubPc unit using the central boron atom as shown in the abstract graphic. Due to a sequential electron/hole transfer mechanism, the easily oxidizable phenothizine entities are expected to promote and stabilize the charge separated states in this pentad.

Scheme 1 outlines the synthesis of the pentad while the synthetic details are given in the Supporting Information. This involved, first, the preparation of 4-(4-iodophenoxyl)-phthalonitrile, **1a**, from a reaction of 4-nitrophthalonitrile and 4-iodophenol. Next, **1b** was synthesized by condensation of **1a** and BCl_3 in *p*-xylene. The axial chloride in **1b** was subsequently replaced with the 4-formylphenoxyl group by treating the SubPc derivative with 4-hydroxybenzaldehyde in toluene to obtain compound **1c**. Next, **1c** was treated with phenothiazine in the presence of Cu and K_2CO_3 in 1,2-dichlorobenzene to obtain phenothiazine substituted SubPc, **1d**. Finally, **1d** was treated with C_{60} and sarcosine in toluene according to a standard Prato reaction of fulleropyrrolidine synthesis[8] followed by chromatographic purification to obtain the desired pentad, **1**. The newly synthesized pentad was fully characterized by NMR (^{1}H and ^{13}C), mass spectral, and electrochemical methods. The pentad was stored in the dark and was freshly purified prior to running spectral and photochemical measurements.

Figure 1a shows the absorption spectrum of **1** along with the control compounds. Chloro[2,9,16-tri(*tert*-butyl)-subphthalocyaninato]boron(III), SubPc, was used as a control (*tert*-butyl groups to increase solubility) revealing two bands at 314 and 567 nm, respectively. The presence of the three phenothiazine entities red-shifted the visible band by ca. 5 nm while the band located at 314 nm revealed an increase in absorbance along with spectral broadening due to the absorption of the phenothiazine entities in this wavelength range. The small red shift of the visible band is suggestive of weak intramolecular interactions between the phenothiazine and SubPc entities. Attachment of the fullerene entity revealed the weak signature band of fulleropyrrolidine at 430 nm in pentad **1**.

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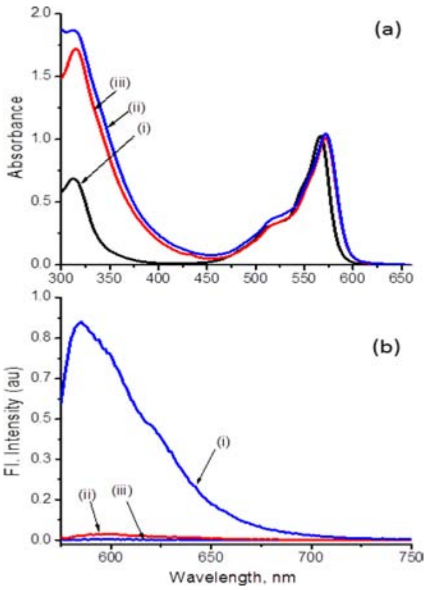

Figure 1. (a) Normalized absorption (visible band) and (b) fluorescence spectra of (i) pristine SubPc, (ii) **1d**, and (iii) **1** in benzonitrile. The sampes were excited at the visible band wavelength of the SubPc entity in the 570 nm range.

The fluoresence spectral features of **1** and the control compounds are shown in Figure 1b. Pristine SubPc when excited at 567 nm revealed a fluorescence band at 584 nm with a shoulder type band at 624 nm. Interestingly, for both **1d** and **1** when excited at the peak maxima of the visible band corresponding to SubPc excitation and not the phenothiazine substituents, the emission band was found to be highly quenched, more so for **1** (95% quenching for **1d** and 98% quenching for **1**). Under these excited state conditions, no emission of fulleropyrrolidine in the 720 nm range was observed suggesting energy transfer from the ^{1}SubPc* to fullerene is not a quenching mechanism.

Figure 2 shows the cyclic voltammograms of **1**; the site of electron transfer corresponding to different redox active entities of the pentad were deduced from additional experiments involving control compounds used in Figure 1. The first reversible anodic process of **1** occurred at 0.70 V vs Ag/AgCl corresponding to the oxidation of the phenothiazine entities. The higher currents for this process compared to other redox processes as a result of three entities were also supportive of this assigment. The second irreversible anodic process located at 0.98 V vs Ag/AgCl was due to oxidation of the SubPc of **1**. On the cathodic side, the first reversible reduction corresponding to C_{60} was located at -0.60 V vs Ag/AgCl whereas the second reduction around -1.02 V was overlapped with the second reduction of C_{60} and the first reduction of SubPc entities. At more negative and positive potentials, additional irreversible redox processes were also observed.

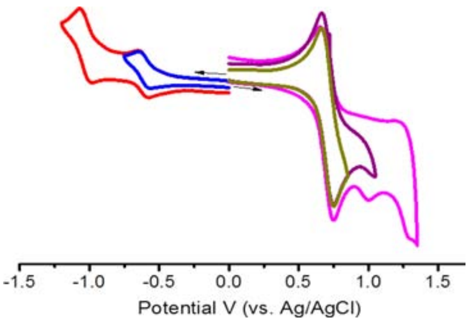

Figure 2. Cyclic voltammograms of **1**, at different switching potential to show the reversibility, in benzonitrile containing 0.1 M (TBA)ClO_4. Scan rate = 100 mV/s.

Further, geometry optimizations of the triad were performed using the B3LYP/3-21G(*) model.[9] Owing to the flexible linkages, more than one conformer of the two regioisomers was possible. However, as shown in Figure 3a, the most stable isomer was one in which the SubPc and the three phenothiazine entities formed a half-cage type structure leaving the fullerene on the top. Moving one of the phenothiazine units close to fullerene yielded a structure that did not reveal significant interactions with the fullerene (Figure 3b). In agreement with the electrochemistry results, the HOMO was found to be on one of the phenothiazine entities while the LUMO was found to be on the fullerene entity (Figure 3c and d).

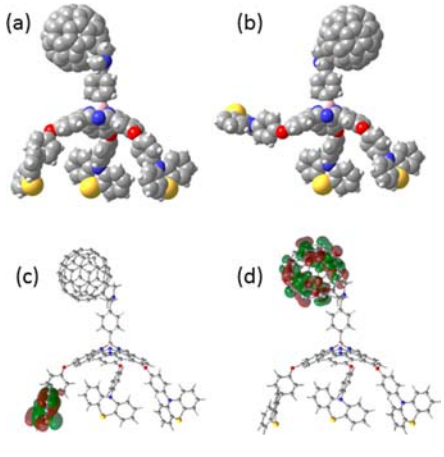

Figure 3. B3LYP/3-21G(*) optmized structures (a and b in two forms) and the HOMO and LUMO of the triad, **1**.

Using the redox, spectral, and computational data, free-energy calculations for the occurrence of photoinduced electron transfer from ^{1}SubPc* (E_{0-0} = 2.1 eV) to C_{60} and a hole transfer from $SubPc^{\bullet+}$ to phenothiazine in **1** were performed using Rehm–Weller's approach.[10] These calculations revealed that the formation of PHZ–$SubPc^{\bullet+}$–$C_{60}{}^{\bullet-}$ and

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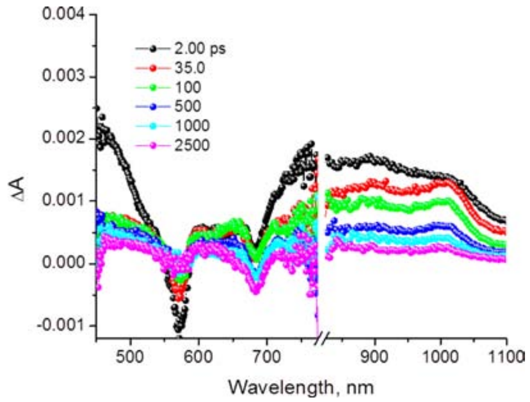

Figure 4. Femtosecond transient absorption spectra of **1** in benzonitrile at different time intervals. λ_{ex} = 400 nm.

PHZ$^{\bullet+}$–SubPc–C$_{60}^{\bullet-}$ (PHZ = phenothiazine) are both exothermic with ΔG_{CS} values of −0.54 and −0.80 eV, respectively.

Evidence for photoinduced electron transfer can be secured by performing time-resolved transient absorption studies wherein signature bands of electron transfer products, *viz*., the cation and anion radical ions are sought out.[3] Time-evolution of these bands can also provide the kinetics of charge separation and charge recombination, and the extent of charge stabilization in the pentad. The one-electron reduced product of fulleropyrrolidine, one of the species of photoinduced electron transfer, is known to exhibit a characteristic band around 1000 nm. In order to identify the spectral features of the cation formed from the phenothiazine–SubPc part of the pentad, chemical oxidation of **1** and the control compounds was performed using nitrosyl tetrafluoroborate as an oxidizing agent. As shown in Figure S1, chemical oxidation of phenothiazine revealed bands at 442 and 525 nm with weak bands in the 650–900 nm range. Oxidation of **1d** also revealed these bands in the spectral range. The oxidation of the phenothiazine entity over SubPc confirms its ease of oxidation as discussed earlier.

Femtosecond and nanosecond transient spectral studies were performed to secure evidence of photoinduced electron transfer. Upon 400 nm femtosecond excitation of **1**, the instantaneous formation of ^{1}SubPc* was observed indicating successful SubPc excitation (Figure 4).[11] The formation of the PHZ$^{\bullet+}$–SubPc–C$_{60}^{\bullet-}$ charge separated state from the initial ^{1}SubPc* was witnessed from the C$_{60}^{\bullet-}$ band at 1020 nm and PHZ$^{\bullet+}$ in the 525 and 650 nm range. Bleaching of the 565 nm band, corresponding to the ground state absorption of SubPc that was recovered with time, was also observed. The radical ion peaks, after reaching a maximum, started decaying due to a charge recombination process. Interestingly, as predicted for fullerenes,[4] this recombination process was much slower than the charge separation process with considerable radical peak intensities lasting over 3 ns, the time window of the instrument.

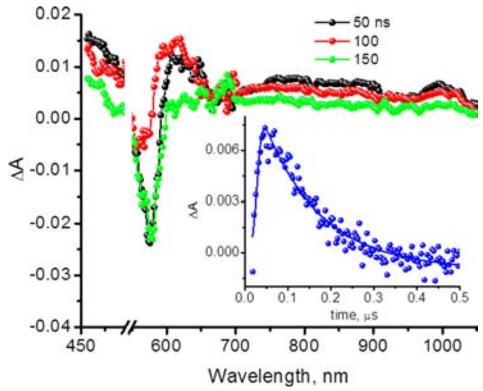

Figure 5. Nanosecond transient spectra of **1** at different time intervals in deaerated benzonitrile, λ_{ex} = 532 nm. The figure inset shows time profile of the C$_{60}^{\bullet-}$ band at 1000 nm.

In order to evaluate the lifetime of the final charge separated state, nanosecond transient absorption studies were performed by exciting the sample at 532 nm, corresponding to SubPc in **1**. As predicted, we were able to observe the radical ions peaks (Figure 5), and by monitoring the decay of the C$_{60}^{\bullet-}$ band at 1000 nm, the rate of charge recombination, k_{CR}, was evaluated to be 5.4 × 10^6 s^{-1} that resulted in a lifetime of the radical ion pair, τ_{RIP}, of 185 ns. This value compares with a value of 100 ns reported earlier for a structurally similar, tris(triphenylamine) substituted SubPc–C$_{60}$ pentad.[11a] The better τ_{RIP} can be attributed to the improved hole transferring ability of phenothiazine (compared to triphenylamine) in the present pentad. Further studies along these line are in progress in our laboratory.

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Supporting Information Available. Synthesis details, experimental section, and spectra of chemically oxidized phenothiazine and **1d** in benzonitrile, ^{1}H and ^{13}C NMR, and MALDI-Mass of selected compounds. This material is free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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