Donor–Acceptor Hybrids

Tuning Optical and Electron Donor Properties by Peripheral Thio-Aryl Substitution of Subphthalocyanine: A New Series of Donor-Acceptor Hybrids for Photoinduced Charge Separation

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Abstract: Subphthalocyanine (SubPc), a unique ring-reduced member of the common phthalocyanines family, although known for its higher absorptivity, reveals narrow absorption with peak maxima around 570 nm thus limiting its utility in light-energy-harvesting applications. In the present study, by peripheral thio-aryl substitution of SubPc macrocycle, the spectral properties have been modulated to extend the absorption and emission well into the visible/near-IR region. Additionally, for α -ring-substituted derivatives, facile oxidation of SubPc was witnessed, thus making these derivatives better electron donors. Next, the preparation of donor-acceptor dyads containing the well-known electron acceptor C₆₀ connected to the central boron atom of SubPc was ac-

Introduction

Building donor-acceptor systems designed to mimic the photosynthetic reaction center events, and efficiently convert light energy into other forms (electricity or fuel) with the intermediate charge-separated state has been one of the goals of modern supramolecular chemistry.^[1-31] Various conjugated macromolecules including porphyrins, phthalocyanines, and BF₂-chelated dipyrromethenes (BODIPY) have been widely used as the primary building blocks because of their excellent photophysical and photochemical properties.^[32-37] Subphthalocyanine (SubPcs),^[38] a unique ring-reduced member of common phthalocyanine family with a bowl-shaped nonplanar structure, is a 14 π -electron aromatic compound composed of three N-fused diiminoisoindole units and an axial ligand around a tetra-coordinated boron atom. Because of the different π -conjugated skeleton, shape, and structure of SubPc from the commonly used porphyrins and phthalocyanines, these molecules show distinct optical and electronic properties. Consequently they have been utilized as organic functional materials in optoelectronic and light-energy-harvesting systems.^[39-52]

complished by making use of the 1,3-dipolar cycloaddition reaction. Control experiments and free-energy calculations using the redox and spectral data suggested that the observed fluorescence quenching of SubPc in these dyads is due to electron transfer. Accordingly, transient spectral studies performed both in polar and nonpolar solvents conclusively proved electron transfer to be the guenching mechanism in these dyads. The measured rate constants by fitting kinetic data revealed efficient charge separation and charge recombination processes, suggesting that these dyads could be useful materials for the construction of light-to-electricity or light-to-fuel production devices.

SubPcs display light absorption properties in the UV/Vis region in the context of solar energy conversion. In particular, they exhibit an intense absorption in the 570 nm region with the excitation coefficient in the order of $50\,000\,\text{m}^{-1}\,\text{cm}^{-1}$. The high electronic excitation energy, exceeding 2.0 eV, can thus be useful for promoting efficient exergonic electron-transfer processes. In addition, the rigid nonplanar SubPc core shows a small Stokes shift and low reorganization energy, useful to observe long-lived charge-separated states. Furthermore, the optoelectronic and light absorption features of SubPc can be finely tuned by varying their axial ligands and peripheral chemical modifications. In this regard, the axial halogen atom of SubPc can easily be replaced by oxygen nucleophiles, particularly phenol, and this has been a convenient reaction strategy for the axial modification and introduction of diverse functional groups to further enhance the stability and solubility of SubPcs.^[39–52]

Recently, significant efforts have been made to develop various types of near-infrared (near-IR) sensitizers due to their potential applications in various field in chemistry, physics, and biology.^[53] Near-IR sensitizers are especially important for lightenergy-harvesting applications for which sunlight carries over 50% of its radiation. Generally, porphyrins, phthalocyanines, and BODIPYs have been used to synthesize near-IR sensitizers after structural modifications and central metal-atom variations.^[54-57] Most of the phthalocyanines reveal their intense visible-band absorption around 650-700 nm.[35-37] Recently, it has been demonstrated that by introducing phosphorus(V) into the central cavity and peripheral substitution of electron-do-

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nating substituents (Group 16: S and Se), the phthalocyanine visible-band could be red-shifted beyond 1000 nm through synergistic effects.^[58] Inspired by this, in the present study, we have utilized the approach of peripheral modification of SubPc using six entities of electron-donor thiotolualyl and thionaphthyl groups. Such ring modification is expected not only to red-shift the absorption and emission, but also improve the electron donor ability of SubPc (facile oxidation). To verify this hypothesis, a new series of donor–acceptor dyads using fullerene (C_{60}) as an electron acceptor have been constructed and photoinduced electron-transfer events have been systematically investigated using steady-state and time-resolved emission, and transient absorption techniques operating at different time scales.

Figure 1 shows the structure of the dyads constructed using the peripherally modified SubPc using six entities of thio-aryl substituents. Here, the central SubPc macrocycle in each dyad bears a C₆₀ as an electron acceptor at the axial position connected through covalent bonding between B and O atom, while the α and β hydrogen atoms from the peripheral positions of SubPc macrocycle have been replaced either by thiotolualyl or thionaphthyl entities. For dyads 1 and 2, the six α hydrogen atoms of the SubPc macrocycle have been replaced by 4-thiotolualyl and 2-thionaphthyl substituents, respectively. For dyads **3** and **4**, the six β -hydrogen atoms of the SubPc macrocycle have been substituted either with 4-thiotolualyl or 2-thionaphthyl groups, respectively. Finally, for dyad 5, the six β-hydrogen atoms have been replaced by 1-thionaphthyl entities. The newly synthesized dyads, 1-5 along with their control compounds, 1c-5c (see Schemes 1 and 2 below for structures) have been fully characterized by NMR (¹H and ¹³C) spectroscopy, MALDI-TOF-mass spectrometry, absorption and emission spectroscopy, and electrochemistry. The dynamics of photoinduced electron-transfer processes within the dyads has been studied and confirmed by both femto- and nanosecond transient absorption spectroscopy in polar solvents.

Results and Discussion

Synthesis

The synthesis of all the derivatives have been achieved by following the procedure outlined in Schemes 1 and 2. Scheme 1 describes the procedure developed for the synthesis of SubPc- C_{60} dyads 1 and 2, in which the thio-aryl substituents are attached at the α -positions of the SubPc macrocycle. Scheme 2 describes the procedure developed for the synthesis of SubPc- C_{60} dyads 3–5, in which the thio-aryl substituents are attached at the β -positions of the SubPc macrocycle. Generally, the most convenient route for the synthesis of SubPc has been refluxing of target phthalonitrile in the presence of BX_3 (X = Cl or Br) to promote cyclotrimerization to form the SubPc macrocycle. Thus, for the modification of peripheral positions of the SubPc, the key step was to design and synthesize various substituted phthalonitriles as precursors. For dyads 1 and 2, first, 2,3-dicyanohydroquinone was tosylated to obtain 3,6-ditosylated phthalonitrile using tosyl chloride in the presence of triethylamine (TEA) and dimethylaminopyridine (DMAP). Next, the 3,6-ditosylated phthalonitriles were converted into the dithioaryl-substituted phthalonitriles 1a and 2a by the application of a base-catalyzed nucleophilic substitution reaction in the presence of 4-methylbenzenethiol and 2-naphthalenethiol, respectively. Next, compounds 1a and 2a were refluxed in the presence of BCl₃ in *p*-xylene for about an hour to obtain the respective SubPc-Cl 1b and 2b derivatives. The reactive chlorine atom in **1 b** and **2 b** was subsequently replaced by 4-formyl phenoxide group by the treatment of 4-hydroxybenzaldehyde in toluene to obtain compounds 1c and 2c, respectively. Finally, $\mathbf{1c}$ and $\mathbf{2c}$ were treated with $C_{\scriptscriptstyle 60}$ and sarcosine in toluene following standard Prato's 1,3-dipolar cycloaddition reaction of



Figure 1. Structures of newly synthesized SubPc $-C_{60}$ dyads with peripherally modified SubPc with thio-aryl entities. Structure of pristine SubPc used as control is also shown.

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Scheme 1. Synthetic scheme adopted for dyads 1 and 2.

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fullerene to obtain the desired compounds 1 and 2, respective-ly. $^{\left[59\right] }$

For the syntheses of dyads 3-5, the procedure outlined in Scheme 2 was adopted. Here, 4,5-difluoro phthalonitrile was used for the preparation of phthalonitrile precursors that were later used for the formation of SubPc macrocycles. By the application of a base-catalyzed nucleophilic substitution reaction in DMSO, treatment of 4,5-difluorophthalonitrile with 4-methylbenzenethiol, 2-naphthalenethiol and 1-naphthalenethiol lead to the isolation of compounds 3a, 4a, and 5a, respectively. The SubPc derivatives 3b, 4b, and 5b were synthesized by reacting the respective phthalonitrile with BCl₃ in *p*-xylene. This was followed by replacing the axial chloride with 4-formylphenoxide to obtain compounds 3c, 4c, and 5c. Finally, dyads 3, 4, and 5 were synthesized by reacting the corresponding aldehyde derivative with C₆₀ and sarcosine in toluene. Details of syntheses are given in the Experimental Section and the NMR (¹H and ¹³C) spectra and the MALDI mass spectra are given in the Supporting Information. The purity of the newly synthesized compounds was checked by thin-layer chromatography and were stored in dark to prevent any photodecomposition.



Scheme 2. Synthetic scheme adopted for dyads 3-5.

Optical absorption and emission studies

Figure 2a shows the normalized absorption spectra of dyads 1 and 3 along with their control compounds 1c and 3c, and tri(*tert*-butyl)boron subphthalocyanine chloride (SubPc), as a reference compound, in *o*-dichlorobenzene (DCB). Absorption bands of pristine SubPc were located at 572 and 320 nm, while in the spectra of peripherally modified SubPcs 1c and 3c redshifted absorption bands were located at 656 and 602 nm, respectively. This large change in absorption is presumably due to the induced electronic effects caused by electron-rich sulfur atoms of the thio-aryl entities. The dyads 1 and 3, which bear C_{60} on the top of the SubPc macrocycle, reveal absorption

maxima at 649 nm and 606 nm, respectively, in addition to the signature sharp band of fulleropyrrolidine at 432 nm. There was a significant increase in absorption in the 300 to 350 nm range due to various substituents and C₆₀ absorption in this region as shown in Figure 2a. The spectral features of 2c and **2** were similar to **1c** and **1** having substituents at the α -positions, while those of 4c and 5c were close to 3c, and of dyads **4** and **5** were close to **3** having substituents at the β -positions of SubPc macrocycle. The spectral data is listed in Table 1 while the spectra of dyads 2, 4 and 5 along with their control compunds is shown in Figure S1 in SI. It is important to note that the spectral perturbations were the highest for α -substituted derivatives while such effects were relatively less for β substituted derivatives likely due to better induced effects in the case of α -substituted derivatives. This could also be said for the peak width. For example, the full width at half maxima (FWHM) values of the visible band of SubPc, 3c and 1c were found to be 1183, 1090 and 2062 cm⁻¹, respectively. That is, peaks of 1c and 1 revealing higher spectral width compared to those of 3c and 3. The nature of the thio-aryl substituents, whether thiotolualyl or thionaphthyl for given type of ring substituion, had minimal influence on the spectral properties.

The steady-state fluorescence spectral studies of the newly synthesized SubPc derivatives along with their control compounds were performed in DCB as shown in Figure 2b for representative compounds, while the data for the entire series is given in Table 1 (see Figure S1b in the Supporting Information for fluorescence of **2**, **4**, **5** and corresponding control compounds). Complementary to the absorption properties, com-



Figure 2. a) Absorption and b) emission spectra of compounds 1 and 3 along with control compounds 1 c and 3 c, and the reference compound (SubPc) in DCB. The compounds were excited at the most intense visible band peak maxima of a given compound.

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Table 1. Spectral (absorption and fluorescence), electrochemical redox potentials,^[a] and free-energy change associated with electron transfer data of the investigated compounds in DCB.

Compound	λ_{abs} [nm]	$\lambda_{ m fl}$ [nm]	$ au^{ ext{[b]}}$ [ns]	$\Delta E_{00}^{[c]}$ [eV]	$\Phi_{f}^{[d]}$	$E_{\rm ox}$ [V]	$E_{\rm red}$ [V]	$-\Delta G_{ m CR}{}^{ m [e]}$ [eV]	$-\Delta G_{\rm CS}{}^{\rm [e]}$ [eV]
SubPc	568	582	1.86	2.13	0.25	0.59	-1.54	_	_
1c	656	691	1.53	1.80	0.07	0.49	-1.37	-	-
2 c	653	690	0.97	1.79	0.05	0.48	-1.38	-	-
3c	602	621	1.88	1.97	0.25	0.61	-1.34	-	-
4c	611	629	2.47	1.96	0.26	0.58	-1.32	-	-
5 c	607	625	1.63	1.97	0.17	0.59	-1-33	-	-
1	649	690	< 0.1	1.80	$< 5 \times 10^{-4}$	0.50	-1.44	1.61	0.19
2	653	692	< 0.1	1.79	$< 5 \times 10^{-4}$	0.48	-1.13	1.59	0.20
3	606	610	< 0.1	1.97	$< 10^{-4}$	0.62	-1.12	1.71	0.26
4	609	611	< 0.1	1.96	$< 10^{-4}$	0.59	-1.13	1.69	0.27
5	605	607	< 0.1	1.97	$< 10^{-4}$	0.60	-1.14	1.71	0.26

[a] In DCB containing 0.1 (TBA)ClO₄. [b] For SubPc 561 nm nanoLED, for 1 **c**, 2 **c**, 1 and 2 624 nm nanoLED and 2 **c**, 3 **c**, 4 **c**, 2, 3, and 4 561 nm nanoLED excitation sources were used. [c] ($\Delta E_{00} = (1240/\lambda_{abs} + 1240/\lambda_{fl})/2$) [d] SubPc was used as a standard [e] The free energy change for charge separation (ΔG_{cS}) from the singlet excited state of SubPc derivatives within the dyad was calculated using spectroscopic, and electrochemistry data following Rehm–Weller's approach, according to the following equations:^[61] $-\Delta G_{CR} = E_{ox} - E_{red} + \Delta G_{S}$ and $-\Delta G_{CS} = \Delta E_{00} - (-\Delta G_{CR})$ in which ΔE_{00} and ΔG_{S} correspond to the energy of singlet excited state of SubPc and electrostatic energy, respectively. E_{ox} and E_{red} represent the oxidation potential of the electron donor (SubPc) and the reduction potential of the electron acceptor (C_{60}), respectively. ΔG_{S} was calculated according to dielectric continuum model $\left(\Delta G_{s} = e^{2}/_{4\pi \epsilon_{0}}\left[\left(\frac{1}{2}R_{+} + \frac{1}{2}R_{-}\right)A\left(\frac{1}{\epsilon_{R}}\right) - \frac{1}{R_{CC}}\epsilon_{R}\right]\right)$. ϵ_{0} and ϵ_{R} are the vacuum permittivity and dielectric constant, respectively, of the solvent used for photochemical and electrochemical stance between boron and the center of fullerene is 9.2 Å).

pounds 1 c (λ_{ex} = 656 nm) and 3 c (λ_{ex} = 602 nm) along with reference compound SubPc ($\lambda_{ex} = 568$ nm) reveal emission at 691, 621 and 582 nm with fluorescence quantum yields ($\Phi_{\rm f}$) of 0.07, 0.25 and 0.25, respectively. That is, the most red-shifted emission in the case of 1c compared to 3c and SubPc were observed. The emission of 1c extends all the way to 800 nm. On the other hand, due to the presence of C₆₀, the emission of SubPc is quenched over 95% in case of dyads 1 and 3. Similar observations were also made for compounds 2, 4, and 5 along with their control compounds, 2c, 4c and 5c in DCB. That is, near-IR emission in the case of 2c (covering until 800 nm) and red-shifted emission in the case of 4c and 5c (emission extended to 750 nm), as a result of peripheral thio-aryl substitution was observed. Upon attaching the electron-acceptor fullerene, much of the emission was guenched revealing occurrence of excited state events in these donor-acceptor dyads.^[60] Changing the solvent to a slightly more polar benzonitrile revealed similar spectral trends. It should be mentioned here that direct excitation of SubPc in the dyads revealed no emission in the 720 nm range corresponding to ${}^{1}C_{60}^{*}$ suggesting singlet-singlet energy transfer may not be one of the quenching mechanisms.

Electrochemical studies and energy level diagram

The optical absorption and emission studies revealed that having thio-aryl substituents on either α or β positions of the SubPc macrocycle lowers the HOMO–LUMO gap, more so for the α -substituted derivatives. This could be a consequence of altering the HOMO and LUMO energy levels. In order to gain better understanding, electrochemical studies using differential pulse voltammetry (DPV) were performed. Figure 3 shows the DPVs in DCB containing 0.1 m (*n*Bu₄N)ClO₄ while the data of compounds **1**c–**5**c and dyads **1**–**5** along with pristine SubPc

without thio-aryl substituents are given in Table 1. The site of electron transfer for each redox couple, arrived by performing control experiments, is also labelled. Facile oxidation and reduction compared to that of pristine SubPc upon thio-aryl substitution was evident for the series of compounds. For **1 c** and **2 c**, having thio-aryl substituents at the α -positions, this effect was much more pronounced compared to those of **3 c**-**5 c**. That is, the oxidation potential was lowered by 110–120 mV while the reduction potential was lowered by 150–160 mV for **1 c**-**2 c** while for **3 c**-**5 c**, lowering of oxidation potential was less than 30 mV but the reduction potential was lowered as much as 200 mV (see Table 1). In essence, HOMO–LUMO gap followed the order **1**-**2** < **3**-**5** < SubPc, a trend that agreed well with the optical HOMO–LUMO gap.

As shown in Figure 3, in the case of the dyads 1-5, within the monitored potential window, there were no appreciate changes in the first, second, and third reduction potentials involving fullerene reductions, and these values agreed well with the reduction potentials of pristine fulleropyrrolidine. This observation suggests lack of intramolecular interactions between the fullerene and SubPc entities of the dyad, which are separated by over 9 Å.^[46] Notable changes were seen for the oxidation and reduction peaks corresponding to SubPc entity. The SubPc first oxidation potential followed the trend 1,2 < 3-5, while for SubPc reduction this trend was 3-5 < 1,2, similar to that observed for the series of control compounds 1 c-5 c. The HOMO-LUMO gap of the dyads, that is, the potential difference between the first oxidation potential of SubPc and first reduction potential of C₆₀, was also evaluated. A lower gap for dyads 1 and 2 (gap ca. 1.63 eV) compared to dyads 3-5 (gap ca.1.74 eV) was evident from such calculations.

An energy level diagram was established using the spectroscopic and electrochemical data, and the calculated freeenergy changes for charge separation and charge recombina-

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Figure 3. Differential pulse voltammograms of the indicated compounds (see Scheme 1 for structures) in DCB, 0.1 μ (*n*Bu₄N)ClO₄. Scan rate = 5 mV s⁻¹, pulse width = 0.25 s, pulse height = 0.025 V.

tion, according to Rehm-Weller approach^[61] (see Table 1 footnote for the pertinent equations). As can be seen in Figure 4, the energy levels indicating the singlet excited state of SubPc and charge-separated states in DCB were different for dyads 1 and 2 (green lines) than those of dyads 3-5 (shown by pink lines). The energy of the charge-separated state generated in dyads 3-5 is higher by about 0.1 eV than those generated by dyads 1–2, and are higher than the triplet excited state energy of both ${}^3\text{SubPc}^{*\,\text{[43]}}$ and ${}^3\text{C}_{60}{}^*\!.$ Under such conditions, the charge-separated state could return to the ground state by populating one of the triplet states. It may be mentioned here that the energy of the charge-separated state would be slightly lower (ca. 20 mV) in polar benzonitrile, due to different degrees of solvation of the charge-separated states. However, their relative positions with respect to the excited SubPc and C₆₀ levels (both singlet and triplet states) would not alter due to small change in magnitude of the energy levels caused by solvent polarity effects. In order to verify these predictions, and secure evidence of charge separation in these dyads in solvents of varying polarity, transient absorption studies at different time scales (femto- to millisecond) were performed as summarized in the following section.

Transient absorption studies

First, femtosecond transient spectral properties of peripherally functionalized SubPcs were performed in DCB and benzonitrile.



Figure 4. Energy level diagram showing different photochemical events occurring in the dyads 1–5 in DCB. Solid line: major process, dashed line: minor process.

Figure 5 shows transient spectra of SubPc derivatives in benzonitrile. The β -thioaryl-functionalized SubPcs, immediately after excitation (400 nm of 100 fs pulses), revealed transient peaks corresponding to singlet excited SubPc (see spectrum recorded at 25 ps delay time in Figure 5a and b). Compound **1c** revealed peaks at 522, 693, and 997 nm and a negative peak at 650 nm with contributions from ground-state bleaching and stimulated emission.

Similarly for compound **2c**, positive peaks were found at 502, 719, and 997 nm and the negative peak at 645 nm. At later times, decay of the positive peaks and recovery of the negative peak was accompanied by new peaks at 722 and 1194 nm for **1c** and at 509, 733 and 1184 nm for the case of **2c** was observed. These new peaks have been assigned to the triplet-state transitions of SubPc formed through an intersystem crossing process that was confirmed by performing nanosecond transient absorption studies (vide supra). Similar spectral features were observed in DCB also (see Figure S1 in the Supporting Information).

For β -thioaryl-substituted SubPcs the spectral features were almost similar. For **3c**, positive peaks at 482, 720 and 961 nm and a negative signal at 602 nm were observed. Decay of the positive peaks and recovery of the negative peak was accompanied by new weak spectral features at 551 and 653 nm, which could be attributed to ³SubPc* transitions. Similar spectral trends were also observed for other derivatives in both benzonitrile (see Figure 5c and d) and DCB (see Figure S2 in Supporting Information). In summary, successful excitation of SubPcs to initially populate the ¹SubPc* followed by the intersystem crossing process to populate the ³SubPc* state in the investigated solvents was observed.

The femtosecond transient absorption studies also provided evidence for the occurrence of photoinduced charge separation in these dyads. Figure 6a and b show the femtosecond transient spectra of α -substituted dyads **1** and **2** in benzonitrile. For dyad **1**, the transient peaks of the instantaneously formed ¹SubPc* decayed rapidly with the occurrence of new

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Figure 5. Femtosecond transient spectra of compounds 1 c-5 c at the indicated delay times in Ar-saturated benzonitrile.

peaks at 488, 710, 1005, 1126 and 1488 nm. Additionally, the recovery of the negative peak at 645 was much faster than that seen for **1c** in the same solvent. These observations support charge separation from the ¹SubPc* leading to the formation of SubPc⁺-C₆₀⁻⁻ charge-separated state. The transient peaks at 490, 710, 1126 and 1475 nm have been attributed to the presence of SubPc⁺⁺, while the 1005 nm peak was assigned to C₆₀⁻⁻.

Although different in peak intensity, since **1c** also had peaks in this spectral region, the spectra of **1** and **1c** at the same concentration and at a delay time of 100 ps (where charge separation was fully established) was compared, as shown in Figure 7a. Such comparison confirmed that the transient peaks observed for **1** in the spectral region of SubPc⁺⁺ (490, 710, 1126 and 1475 nm), while the 1005 nm peak was due to C_{60}^{--} (the noisy peak in the 730–800 nm range is due to extreme detector sensitivity and change of detectors from visible to near-IR). With time, peaks corresponding to the charge-separated state in Figure 6a and b decayed with the appearance of new peak at 1190 nm corresponding to the formation of ³SubPc^{*}. That is, population of the triplet excited state of ³SubPc^{*} by



Figure 6. Femtosecond transient absorption difference spectra of compounds 1-5 at the indicated delay times in Ar-saturated benzonitrile.

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Figure 7. Femtosecond transient difference absorption spectra of a) **1** (magenta) and **1 c** (wine) at a delay time of 100 ps, and b) **3** (magenta) and **3 c** (wine) at the delay time of 250 ps in Ar-saturated benzonitrile.

the radical ion-pair prior returning to the ground state as predicted by the energy level diagram in Figure 4 was witnessed.

For β -substituted SubPc-C₆₀ dyads charge separation from the singlet excited state of SubPc was also evident. That is, recovery of the depleted peak at 602 nm was much faster than that observed in the case of control SubPcs. In addition, the cation and anion radical peaks at their expected wavelength region were observed. Spectral data for dyads 3-5 in benzonitrile is shown in Figure 6c-e, while comparison of spectral data of 3 and 3c at a delay time of 250 ps is shown in Figure 7b. Such analysis clearly revealed SubPc⁺⁺ peak in the 660 nm range and C_{60} - peak at 1005 nm, confirming charge separation from ¹SubPc* in these dyads. The transient spectral data for dyads 1–5 in DCB is shown in Figure S3 in the Supporting Information, which also confirms charge separation in this solvent. The peaks corresponding to the charge-separated state decayed with time with the appearance of new peak in the 1165 nm range for 1 and 2, representing formation of ³SubPc* (see spectrum at 3 ns delay time). The kinetics of charge separation (k_{CS}) and charge recombination (k_{CR}) were evaluated by monitoring the growth the decay of the radical anion peak at 1005 nm, and are given in Table 2. The magnitude of k_{cs} indicated fast charge separation, while the k_{CR} was one-to-two orders of magnitude smaller than k_{CS} , a trend predicted for fullerene based donor-acceptor systems,^[13-25] and the expected solvent polarity trends within the experimental errors. In summary, successful occurrence of photoinduced electron transfer in peripherally modified with thioaryl entities SubPc axially bound to fullerene in polar solvent has been demonstrated.

In order to establish the return path of the charge-separated states of these dyads, nanosecond transient absorption studies

linked to C60.[a] Compound Solvent $k_{\rm CS} \, [{\rm s}^{-1}]$ $k_{\rm CR} \, [{\rm s}^{-1}]$ 3.4×10¹⁰ 1 1.5×10^{9} benzonitrile 2.4×10^{10} dichlorobenzene 9.3×10^{8} 5.9×10^{10} 1.3×10^{9} 2 benzonitrile dichlorobenzene 1.1×10^{10} 1.3×10⁹ 6.3×10^{10} 7.4×10^{8} 3 benzonitrile 6.0×10¹⁰ dichlorobenzene 2.1×10^{9} 1.5×10^{10} 7.5×10^{8} 4 benzonitrile 1.4×10^{10} 1.2×10^{9} dichlorobenzene 2.9×10¹⁰ 5 benzonitrile 2.4×10^{8} 1.4×10^{10} 4.3×10^{8} dichlorobenzene [a] Experimental uncertainty = \pm 10%.

Table 2. Kinetics of charge separation (k_{cs}) and charge recombination

 (k_{CR}) of the investigated α - and β -thioaryl substituted SubPc covalently

were performed. First, transient spectra of the control compounds 1c-5c were recorded; however, the transient signals were found to be weak implying inefficient population of ³SubPc* in these compounds. Next, the dyads **1–5** were excited using 550 nm excitation, in which only SubPc had major absorbance. As predicted from femtosecond transient data recorded at higher delay times, dyads 1 and 2 revealed peaks in the range of 508, 755, 996, and 1190 nm, and a negative peak at 650 nm corresponding to ³SubPc* (Figure 8a and b). For dyads 3-5 these peaks were in the 490, 730, and 990 nm range, and a negative peak at 610 nm corresponding to ³SubPc* (Figure 8c–e). These spectra were sufficiently different from that of fulleropyrrolidine, ${}^{3}C_{60}^{*}$, indicating the population of low-lying $^3\text{SubPc}^*$ instead of $^3\text{C}_{60}{}^*$ (see Figure 4 for energy level diagram). The signal intensities of ³SubPc* in both types of dyads, namely, α - or β -substituted, were better defined than those observed in 1c-5c. These results suggest that populating ³SubPc* by the process of charge recombination is much more efficient than by direct excitation. The decay time constants for the ³SubPc* signal in these dyads were in the range of 35-50 µs.

Conculsions

A series of SubPcs modified by peripheral substitution of thioaryl groups to improve their light-harvesting properties, namely, red-shifted absorbance and emission, have been newly designed and synthesized. Greater spectral modulation in the case of α -substituted SubPc derivatives compared to the β substituted derivatives was witnessed. Electrochemical studies revealed perturbation of both HOMO and LUMO levels and better electron-donor properties of thio-aryl-substituted SubPcs. Next, the modified SubPcs were successfully utilized to build donor-acceptor dyads through the central boron atom with the well known electron acceptor C₆₀. Both steady-state and time-resolved emission studies revealed quenching of SubPc in these dyads due to the occurrence of excited state events, and the free-energy calculations performed using spectroscopic and electrochemical redox data along with the control experiments suggested photoinduced charge separation

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Figure 8. Nanosecond transient difference absorption spectra of dyads 1–5 at the indicated delay times in Ar-saturated benzonitrile.

to be the likely quenching mechanism. Subsequent studies performed using transient absorption techniques operating at different time scales provided spectral proof of charge separation. Kinetic analysis of the data revealed ultrafast charge separation and relatively slow charge recombination in these dyads, properties relevant to solar energy harvesting. Further studies along these lines are in progress.

Experimental Section

Chemicals

Buckminsterfullerene (C_{60} ; +99.95%) was from SES Research (Houston, TX). All other reagents were from Aldrich Chemicals (Milwaukee, WI), while the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetra-*n*-butylammonium perchlorate, (*n*Bu₄N)ClO₄, used in electrochemical studies was from Fluka Chemicals.

Synthesis peripherally modified SubPc-C₆₀ dyads

3,6-Ditosylated phthalonitrile: 3,6-Dihydroxyphthalonitrile (1.5 gm, 9.3 mmol), *p*-toluenesulfonyl chloride (3.8 gm, 20 mmol), triethylamine (2.78 mL, 20 mmol), and 4-(dimethylamino)pyridine (244 mg, 2 mmol) were dissolved in dichloromethane (DCM; 300 mL) and stirred for overnight under nitrogen at room temperature. After evaporation of the reaction solvent, the crude compound was re-dissolved in DCM (200 mL) and first washed with saturated sodium bicarbonate solution (100 mL), and then with water (100 mL). The organic layer was collected and dried over sodium sulfate. After removing the solvent, the crude compound was purified over silica column. The desired compound was eluted by with DCM:hexanes (70:30, v/v) ratio. Yield: 65 %; ¹H NMR (CDCl₃: 400 MHz): δ = 2.52 (s, 6H; methyl-Hs), 7.42 (d, *J* = 7.2 Hz, 4H; Ar-H), 7.82 (s, 2H; Ar-H), 7.85 ppm (d, 4H; Ar-H).

3,6-Dithioethertolyl phthalonitrile: 3,6-Ditosylated-phthalonitrile (1 g, 2.23 mmol), 4-methylbenzenethiol (530 mg, 4.26 mmol), and

potassium carbonate (2.9 g, 21.3 mmol) were dissolved in DMSO (30 mL) under nitrogen for 48 h. Then the reaction mixture was poured into ice water to get the organic precipitate out. The precipitate was obtained by filtration and dissolved in DCM (200 mL) then washed with water (2×100 mL). The organic layer was collected and dried over sodium sulfate. Thus obtained organic layer was evaporated to obtain the desired compound, which was used for next reaction without further purification after being confirmed by NMR spectroscopy. Yield: 75%; ¹H NMR (CDCl₃: 400 MHz): δ = 2.42 (s, 6H; methyl-Hs), 6.87 (d, *J* = 6.3 Hz, 2H; Ar-H), 7.22 (s, 4H; Ar-H), 7.37 ppm (d, *J* = 6.8 Hz, 4H; Ar-H).

4,5-Dithioethertolyl phthalonitrile: 4,5-Difluorophthalonitrile (500 mg, 3.04 mmol), 4-methylbenzenethiol (758 mg, 6.1 mmol), and potassium carbonate (4.14 g, 30 mmol) were dissolved in DMSO (25 mL) under nitrogen for 48 h. Then the reaction mixture was poured into ice water (200 mL) to get the organic precipitate out. The precipitate was obtained by filtration and dissolved in DCM (150 mL) then washed with water (2×100 mL). The organic layer was collected and dried over sodium sulfate. Thus obtained organic layer was evaporated to obtain the desired compound which was used for next reaction without further purification after being confirmed by NMR spectroscopy. Yield: 68%; ¹H NMR (CDCl₃: 400 MHz): δ = 2.40 (s, 6 H; methyl-Hs), 6.84 (s, 2 H; Ar-H), 7.26 (d, J = 6.8 Hz, 4H; Ar-H).

3,6-Dithioether-2-naphthyl phthalonitrile: 3,6-Ditosylated phthalonitrile (1 g, 2.23 mmol), 2-naphthalenethiol (721 mg, 4.5 mmol), and potassium carbonate (3.1 gm, 23 mmol) were dissolved in DMSO (30 mL) under nitrogen for 48 h. Similar procedure was used for the purification process as described for compound 4,5-dithioethertolyl phthalonitrile as in above. Yield: 55%; ¹H NMR (CDCl₃: 400 MHz): δ = 6.86 (s, 2 H; Ar-H), 7.41 (dd, 2 H; Ar-H), 7.47 (m, 4 H; Ar-H), 7.81 (m, 6 H; Ar-H), 8.03 ppm (s, 2 H; Ar-H).

4,5-Dithioether-2-naphthyl phthalonitrile: 4,5-Difluorophthalonitrile (500 mg, 3.04 mmol), 2-naphthalenethiol (1.05 g, 6.5 mmol), and potassium carbonate (4.48 g, 32.5 mmol) were dissolved in DMSO (30 mL) under nitrogen for 48 h. Similar procedure was used for the purification process as described for compound 4,5-dithioethertolyl phthalonitrile as in above. Yield: 65%; ¹H NMR (CDCl₃:

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400 MHz): δ = 7.05 (s, 2H; Ar-H), 7.51 (dd, 2H; Ar-H), 7.64 (m, 4H; Ar-H), 7.88 (dd, 2H; Ar-H), 7.94 (dd, 2H; Ar-H), 8.01 (d, *J* = 7.2 Hz, 2H; Ar-H), 8.16 ppm (s, 2H; Ar-H).

4,5-Dithioether-1-naphthyl phthalonitrile: 4,5-Difluorophthalonitrile (500 mg, 3.04 mmol), 1-naphthalenethiol (1.05 g, 6.5 mmol), and potassium carbonate (4.48 g, 32.5 mmol) were dissolved in DMSO (30 mL) under nitrogen for 48 h. Similar procedure was used for the purification process as described for compound 4,5-dithioethertolyl phthalonitrile as in above. Yield: 55%; ¹H NMR (CDCl₃: 400 MHz): δ = 6.68 (s, 2 H; Ar-H), 7.64 (m, 6 H; Ar-H), 8.01 (m, 4 H; Ar-H), 8.12 (d, *J* = 7.3 Hz, 2 H; Ar-H), 8.26 ppm (m, 2 H; Ar-H).

3,6-Hexthioethertolyl-SubPc-CHO (1 c): 3,6-Dithioethertolyl phthalonitrile (500 mg, 1.34 mmol) was refluxed with BCl₃ solution (5 mL) for an hour under nitrogen. After cooling the reaction mixture the solvent was evaporated to obtain a purple crude subphthalocyanine compound. Without further purification, thus obtained crude compound was mixed with 4-hydroxy benzaldehyde (300 mg, 2.45 mmmol) and dissolved in dry toluene (5 mL) and refluxed for 18 h under nitrogen. After cooling the reaction mixture the solvent was evaporated to obtain the crude compound. Thus obtained crude product was washed with water:methanol mixture (80:20 v/ v ratio; 100 mL) and extracted with DCM. The organic layer was collected and dried over sodium sulfate. After evaporation of the organic solvent, the purple crude product was obtained and purified over a silica column. The desired compound was eluted by DCM. Yield: 20%; ¹H NMR (CDCl₃: 400 MHz): $\delta = 2.38$ (m, 18H; methyl-Hs), 5.5 (d, 2H; Ar-H), 6.95 (m, 6H; Ar-H), 7.24 (m, 12H; Ar-H), 7.34 (m, 2H; Ar-H), 7.65 (m, 12H; Ar-H), 9.66 ppm (s, 1H; -CHO).

4,5-Hexthioethertolyl-SubPc-CHO (3 c): 4,5-Dithioethertolyl phthalonitrile (500 mg, 1.34 mmol) was used and followed the same method as described for **1 c**. Yield: 30 %; ¹H NMR (CDCl₃: 400 MHz): δ = 2.50 (s, 18H; methyl-Hs), 5.3 (d, 2H; Ar-H), 7.25 (m, 14H; Ar-H), 7.45 (d, 12H; Ar-H), 8.35 (s, 6H; Ar-H), 9.60 ppm (s, 1H; -CHO).

3,6-Dithioether-2-naphthyl SubPc-CHO (2 c): 3,6-Dithioether-2-naphthyl phthalonitrile (500 mg, 1.12 mmol) was used and followed the same method as described for **1 c**. Yield: 20%; ¹H NMR (CDCl₃: 400 MHz): δ = 5.40 (d, 2 H; Ar-H), 7.10 (s, 6 H; Ar-H), 7.45 (m, 14 H; Ar-H), 7.70 (dd, 12 H; Ar-H), 7.80 (dd, 12 H; Ar-H), 8.25 (s, 6 H; Ar-H), 9.60 ppm (s, 1 H; -CHO).

4,5-Dithioether-2-naphthyl SubPc-CHO (**4c**): 4,5-Dithioether-2-naphthyl phthalonitrile (500 mg, 1.12 mmol) was used and followed the same method as described for **1c**. Yield: 25%; ¹H NMR (CDCl₃: 400 MHz): δ = 5.20 (d, 2 H; Ar-H), 7.08 (d, 2 H; Ar-H), 7.40 (m, 18 H; Ar-H), 7.65 (m, 18 H; Ar-H), 7.82 (s, 6 H; Ar-H), 8.35 (s, 6 H; Ar-H), 8.40 (d, 6 H; Ar-H), 9.50 ppm (s, 1 H; -CHO).

4,5-Dithioether-1-naphthyl SubPc-CHO (5 c): 4,5-Dithioether-1-naphthyl phthalonitrile (500 mg, 1.12 mmol) was used and followed the same method for **1c**. Yield: 20%; ¹H NMR (CDCl₃: 400 MHz): δ = 5.10 (d, 2 H; Ar-H), 7.08 (d, 2 H; Ar-H), 7.55 (m, 18H; Ar-H), 7.75 (d, 6 H; Ar-H), 7.98 (d, 6 H; Ar-H), 8.55 (m, 12 H; Ar-H), 9.40 ppm (s, 1 H; -CHO).

3,6-Hexthioethertolyl SubPc-C₆₀ (1): Compound 1 c (90 mg, 0.07 mmol), C₆₀ (151 mg, 0.21 mmol), and sarcosine (31 mg, 0.35 mmol) were mixed and refluxed in toluene (60 mL) for 12 h. After cooling, the solvent was evaporated to obtain the purple crude product, which was purified over a silica column. The desired compound was eluted by toluene:ethylacetate (90:10 v/v). Yield: 45%; ¹H NMR (CDCl₃: 400 MHz): δ = 2.35 (m, 18H; methyl-Hs), 2.55 (s, 3H; fulleropyrrolidine methyl-H), 3.91 (d, *J* = 7.8 Hz, 1H; fulleropyrrolidine-H), 4.40 (s, 1H; fulleropyrrolidine-H), 4.70 (d, *J* = 7.4 Hz, 1H; fulleropyrrolidine-H), 5.40 (m, 2H; Ar-H), 6.71 (m, 6H; Ar-H), 6.85 (d, 2H; Ar-H), 7.15 (m, 12H; Ar-H), 7.20 (d, 2H; Ar-H),

7.48 ppm (m, 12 H; Ar-H); ¹³C NMR (CDCl₃, 400 MHz): δ = 24.92, 25.02, 125.45, 125.98, 127.05, 128.11, 128.64, 29.70, 130.23, 130.76, 134.95, 135.50 (m), 136.08, 137.60, 138.7, 140.80 (m), 143.52, 144.56 (m), 151.95 ppm (m); MS MALDI-TOF: *m/z* calcd: 1999.18; found: 1126–1130 [*M*–Phenoxy–C₆₀].

4,5-Hexthioethertolyl SubPc-C₆₀ (3): Compound 3 c (90 mg, 0.07 mmol), $C_{\rm 60}$ (151 mg, 0.21 mmol), and sarcosine (31 mg, 0.35 mmol) were mixed and refluxed in toluene (60 mL) for 12 h. After cooling, the solvent was evaporated to obtain the purple crude product, which was purified over a silica column. The desired compound was eluted by toluene:ethylacetate (90:10 v/v). Yield: 50%; ¹H NMR (CDCl₃: 400 MHz): $\delta = 2.40$ (m, 18H; methyl-Hs), 2.55 (s, 3H; fulleropyrrolidine methyl-H), 4.01 (d, J = 7.2 Hz, 1H; fulleropyrrolidine-H), 4.50 (s, 1 H; fulleropyrrolidine-H), 4.75 (d, J = 7.6 Hz, 1H; fulleropyrrolidine-H), 5.25 (m, 2H; Ar-H), 7.15 (d, 2H; Ar-H), 7.25 (m, 12H; Ar-H), 7.43 (m, 12H; Ar-H), 8.25 ppm (m, 6H; Ar-H); ^{13}C NMR (CDCl₃, 400 MHz): $\delta\!=\!24.96,\;42.88,\;70.65,\;71.60,\;122.65$ (m), 127.65, 129.15, 129.65, 130.15, 130.65, 132.65, 134.50, 135.65 (m), 138.15 (m), 139.15, 140.15 (m), 141.20, 141.75 (m), 143.65, 144.58 (m), 145.70, 149.15, 151.65, 152.35, 154.65 ppm; MS MALDI-TOF: *m*/*z* calcd: 1999.18; found: 1126–1131 [*M*–Phenoxy–C₆₀].

3,6-Dithioether-2-naphthyl SubPc-C₆₀ (2): Compound 2c (90 mg, 0.06 mmol), C_{60} (130 mg, 0.18 mmol), and sarcosine (27 mg, 0.30 mmol) were mixed and refluxed in toluene (60 mL) for 12 h. After cooling, the solvent was evaporated to obtain the purple crude product, which was purified over a silica column. The desired compound was eluted by toluene:ethylacetate (90:10 v/v). Yield: 40%; ¹H NMR (CDCl₃: 400 MHz): $\delta = 2.57$ (s, 3 H; fulleropyrrolidine methyl-H), 3.91 (d, J = 7.5 Hz, 1H; fulleropyrrolidine-H), 4.42 (s, 1H; fulleropyrrolidine-H), 4.75 (d, J = 7.2 Hz, 1H; fulleropyrrolidine-H), 5.42 (m, 2H; Ar-H), 6.75 (s, 6H; Ar-H), 7.15 (m, 2H; Ar-H), 7.40 (m, 12H; Ar-H), 7.70 (m, 24H; Ar-H), 8.20 ppm (d, 6H; Ar-H). ¹³C NMR (CDCl₃, 400 MHz): δ = 25.59, 42.60, 70.44, 125.25, 162.50 (m), 126.95 (m), 127.69 (m), 128.19, 128.56, 128.94, 129.25, 131.69, 132.81, 133.56 (m), 134.44 (m), 140.94, 1443.81, 149.94 ppm; MS MALDI-TOF: m/z calcd: 2215.38; found: 2215.9 [M], 1342-1347 [M-Phe $noxy-C_{60}$].

4,5-Dithioether-2-naphthyl SubPc-C₆₀ (4): Compound 4c (90 mg, 0.06 mmol), C₆₀ (130 mg, 0.18 mmol), and sarcosine (27 mg, 0.30 mmol) were mixed and refluxed in toluene (60 mL) for 12 h. After cooling, the solvent was evaporated to obtain the purple crude product, which was purified over a silica column. The desired compound was eluted by toluene:ethylacetate (90:10 v/v). Yield: 40%; ¹H NMR (CDCl₃: 400 MHz): $\delta = 2.55$ (s, 3H; fulleropyrrolidine methyl-H), 4.01 (d, J = 7.4 Hz, 1H; fulleropyrrolidine-H), 4.50 (s, 1H; fulleropyrrolidine-H), 4.75 (d, J = 7.6 Hz, 1H; fulleropyrrolidine-H), 5.25 (m, 2H; Ar-H), 7.13 (m, 6H; Ar-H), 7.23 (m, 8H; Ar-H), 7.42 (dd, 6H; Ar-H), 7.52 (m, 6H; Ar-H), 7.72 (m, 6H; Ar-H), 7.81 (d, 6H; Ar-H), 7.92 (m, 6H; Ar-H), 8.40 ppm (m, 6H; Ar-H); ¹³C NMR (CDCl₃, 400 MHz): $\delta = 21.34$, 39.9, 68.26, 123.9, 124.27, 125.37, 126.77 (m), 127.65, 127.95 (m), 128.15, 129.05, 129.27 (m), 29.52 (m), 130.4, 130.65, 131.54, 131.77, 132.77, 134.02, 137.92, 140.15, 140.52, 141.65 (m), 145.02 (m), 145.90 (m), 150.27 ppm; MS MALDI-TOF: m/ z calcd: 2215.38; found: 2215.2 [M], 1342–1347 [M–Phenoxy–C₆₀].

4,5-Dithioether-1-naphthyl SubPc-C₆₀ (**5**): Compound **5c** (90 mg, 0.06 mmol), C₆₀ (130 mg, 0.18 mmol), and sarcosine (27 mg, 0.30 mmol) were mixed and refluxed in toluene (60 mL) for 12 h. After cooling, the solvent was evaporated to obtain the purple crude product, which was purified over a silica column. The desired compound was eluted by toluene:ethylacetate (90:10 v/v). Yield: 35%; ¹H NMR (CDCl₃: 400 MHz): δ = 2.40 (s, 3 H; fulleropyrrolidine methyl-H), 4.01 (d, *J* = 6.9 Hz, 1 H; fulleropyrrolidine-H), 4.45 (s, 1 H; fulleropyrrolidine-H),

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5.10 (m, 2H; Ar-H), 7.15 (m, 2H; Ar-H), 7.55 (m, 18H; Ar-H), 7.77 (m, 6H; Ar-H), 7.91 (d, 6H; Ar-H), 7.98 (m, 6H; Ar-H), 8.10 (s, 6H; Ar-H), 8.35 ppm (d, 6H; Ar-H); MS MALDI-TOF: *m/z* calcd: 2215.38; found: 2215.4 [*M*], 1342–1348 [*M*–Phenoxy–C₆₀].

Spectral measurements

The UV/Vis spectral measurements were carried out with a Shimadzu Model 2550 double monochromator UV/Vis spectrophotometer. The fluorescence emission was monitored by using a Varian Eclipse spectrometer. A right-angle detection method was used. The ¹H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Differential pulse voltammograms were recorded on an EG&G PAR-STAT electrochemical analyzer using a three electrode system. A platinum button electrode was used as the working electrode. A platinum wire served as the counter electrode and an Ag/AgCI electrode was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using nitrogen gas.

Femtosecond pump-probe transient spectroscopy

Femtosecond transient absorption spectroscopy experiments were performed using an ultrafast femtosecond laser source (Libra, Coherent Inc), incorporating a diode-pumped, mode-locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into a harmonic generator that produced second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of a white-light continuum. In the present study, the second harmonic 400 nm excitation pump was used in all experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Nanosecond laser flash photolysis

The studied compounds were excited by a Opolette HE 355 LD pumped by a high energy Nd:YAG laser with second and third harmonics OPO (tuning range 410–2200 nm, pulse repetition rate 20 Hz, pulse length 7 ns) with powers of 1.0–3 mJ per pulse. The transient absorption measurements were performed using a Proteus UV/Vis/NIR flash photolysis spectrometer (Ultrafast Systems, Sarasota, FL) with a fibre optic delivered white probe light and either a fast rise Si photodiode detector covering the 200–1000 nm range or a InGaAs photodiode detector covering 900–1600 nm range. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing Tektronix oscilloscope.

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Keywords: electron transfer • fullerenes • subphthalocyanines • spectral tuning

- [1] D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 2009, 42, 1890-1898.
- [2] D. Gust, T. A. Moore, A. L. Moore, Acc. Chem. Res. 2001, 34, 40-48.
- [3] M. R. Wasielewski, Acc. Chem. Res. 2009, 42, 1910-1921.
- [4] D. M. Guldi, G. M. A. Rahman, V. Sgobba, C. Ehli, Chem. Soc. Rev. 2006, 35, 471–487.
- [5] D. I. Schuster, K. Li, D. M. Guldi, C. R. Chim. 2006, 9, 892-908.
- [6] G. Gottari, O. Trukhina, M. Ince, T. Torres, Coord. Chem. Rev. 2012, 256, 2453–2477.
- [7] K. Dirian, M. A. Herranz, G. Katsukis, J. Malig, L. Rodriquez-Perez, C. Romero-Nieto, V. Strauss, N. Martin, D. M. Guldi, *Chem. Sci.* 2013, 4, 4335–4353.
- [8] J. L. Sessler, C. M. Lawrence, J. Jayawickramarajah, Chem. Soc. Rev. 2007, 36, 314–325.
- [9] S. Fukuzumi, K. Ohkubo, F. D'Souza, J. L. Sessler, Chem. Commun. 2012, 48, 9801–9815.
- [10] T. Umeyama, H. Imahori, Energy Environ. Sci. 2008, 1, 120-133.
- [11] T. Hasobe, Phys. Chem. Chem. Phys. 2010, 12, 44-57.
- [12] H. Imahori, T. Umeyama, K. Kei, T. Yuta, Chem. Commun. 2012, 48, 4032–4045.
- [13] C. B. KC, F. D'Souza, Coord. Chem. Rev. 2016, 322, 104-141.
- [14] F. D'Souza, O. Ito, Chem. Commun. 2009, 4913-4928.
- [15] M. E. El-Khouly, O. Ito, P. M. Smith, F. D'Souza, J. Photochem. Photobiol. C 2004, 5, 79-104.
- [16] F. D'Souza, O. Ito, Chem. Soc. Rev. 2012, 41, 86-96.
- [17] F. D'Souza, O. Ito, *Molecules* 2012, 17, 5816-5835.
- [18] S. Fukuzumi, Org. Biomol. Chem. 2003, 1, 609–620.
- [19] S. Fukuzumi, Bull. Chem. Soc. Jpn. 2006, 79, 177-195.
- [20] S. Fukuzumi, Phys. Chem. Chem. Phys. 2008, 10, 2283-2297.
- [21] S. Fukuzumi, T. Kojima, J. Mater. Chem. 2008, 18, 1427-1439.
- [22] S. Fukuzumi, T. Honda, K. Ohkubo, T. Kojima, Dalton Trans. 2009, 3880– 3889.
- [23] S. Fukuzumi, K. Ohkubo, J. Mater. Chem. 2012, 22, 4575-4587.
- [24] M. E. El-Khouly, S. Fukuzumi, F. D'Souza, ChemPhysChem 2014, 15, 30– 47.
- [25] N. S. Lewis, D. G. Nocera, Proc. Natl. Acad. Sci. USA 2006, 103, 15729– 15735.
- [26] J. A. Turner, Science 1999, 285, 687–689.
- [27] J. Barber, Chem. Soc. Rev. 2009, 38, 185-196.
- [28] G. D. Scholes, G. R. Fleming, A. Olaya-Castro, R. V. Grondelle, Nat. Chem. 2011, 3, 763 – 774.
- [29] P. V. Kamat, J. Phys. Chem. C 2007, 111, 2834-2860.
- [30] S. Fukuzumi, Eur. J. Inorg. Chem. 2008, 1351-1362.
- [31] S. Fukuzumi, Y. Yamada, J. Mater. Chem. 2012, 22, 24284-24296.
- [32] F. D'Souza, K. M. Kadish, Eds., Handbook of Carbon Nanomaterials, World Scientific, Volumes 1–8, Singapore, 2011, 2012, 2014 and 2016.
- [33] K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam **1972**.
- [34] The Porphyrin Handbook Vol. 1-20 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, CA, 2000.
- [35] Phthalocyanine Materials: Structure, Synthesis and Function (Ed.: N.B. McKeown), Cambridge University Press, Cambridge, 1998.
- [36] Phthalocyanine: Properties and Applications (Eds.: C. C. Leznoff, A. B. P. Lever), VCH, Weinheim, 1993.
- [37] G. Bottari, G. de La Torre, D. M. Guldi, T. Torres, Chem. Rev. 2010, 110, 6768-6816.
- [38] C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, Chem. Rev. 2002, 102, 835–853.
- [39] C. Romero-Nieto, J. Guilleme, J. Fernandez-Ariza, M. S. Rodriquez-Morgade, D. Gonzalez-Rodriguez, T. Torres, D. M. Guldi, *Org. Lett.* 2012, 14, 5656–5659.

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- [40] D. González-Rodríguez, E. Carbonell, D. M. Guldi, T. Torres, Angew. Chem. Int. Ed. 2009, 48, 8032 – 8036; Angew. Chem. 2009, 121, 8176 – 8180.
- [41] D. González-Rodríguez, E. Carbonell, G. de Miguel Rojas, C. A. Castellanos, D. M. Guldi, T. Torres, J. Am. Chem. Soc. 2010, 132, 16488-16500.
- [42] D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, L. Echegoyen, Org. Lett. 2002, 4, 335–338.
- [43] D. González-Rodríguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz, L. Echegoyen, J. Am. Chem. Soc. 2004, 126, 6301–6313.
- [44] D. González-Rodríguez, T. Torres, M. A. Herranz, L. Echegoyen, E. Carbonell, D. M. Guldi, *Chem. Eur. J.* 2008, 14, 7670–7679.
- [45] I. Sánchez-Molina, C. G. Claessens, B. Grimm, D. M. Guldi, T. Torres, *Chem. Sci.* 2013, 4, 1338–1344, and referenced cited therein.
- [46] C. B. KC, G. N. Lim, M. E. Zandler, F. D'Souza, Org. Lett. 2013, 15, 4612– 4615.
- [47] C. B. KC, G. N. Lim, F. D'Souza, Angew. Chem. Int. Ed. 2015, 54, 5088– 5092; Angew. Chem. 2015, 127, 5177–5181.
- [48] R. Cantu, H. B. Gobeze, F. D'Souza, J. Porphyrins Phthalocyanines 2016, in press, DOI: 10.1142/S1088424615500947.
- [49] V. Bandi, F. P. D'Souza, H. B. Gobeze, F. D'Souza, Chem. Commun. 2016, 52, 579-581.
- [50] C. B. KC, G. N. Lim, F. D'Souza, Asian J. Chem. 2016, 11, 1246-1256.
- [51] K. L. Mutolo, E. I. Mayo, B. P. Rand, S. R. Forrest, M. E. Thompson, J. Am. Chem. Soc. 2006, 128, 8108–8109.

- [52] R. Pandey, A. A. Gunawan, K. A. Mkhoyan, R. J. Holmes, Adv. Funct. Mater. 2012, 22, 617–624.
- [53] Near-Infrared Dyes for High Technology Applications (Eds.: S. Daehne, U. Resch-Genger, O. S. Wolfbeis) NATO ASI Series, Vol 52, Springer, 1997.
- [54] A. Dualeh, J. H. Delcamp, M. K. Nazeeruddin, M. Grätzel, Appl. Phys. Lett. 2012, 100, 173512.
- [55] E. Arunkumar, A. Ajayaghosh, Chem. Commun. 2005, 5, 599.
- [56] V. Bandi, S. K. Das, S. G. Awuah, Y. You, F. D'Souza, J. Am. Chem. Soc. 2014, 136, 7571.
- [57] V. Bandi, H. B. Gobeze, F. D'Souza, *Chem. Eur. J.* 2015, *21*, 11483–11494.
 [58] T. Furuyama, K. Satoh, T. Kushiya, N. Kobayashi, *J. Am. Chem. Soc.* 2014,
- 136, 765 776.
- [59] M. Maggini, G. Scorrano, M. Prato, J. Am. Chem. Soc. 1993, 115, 9798– 9799.
- [60] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd ed., Springer, Singapore, 2006.
- [61] D. Rehm, A. Weller, Isr. J. Chem. 1970, 8, 259-271.
- [62] D. M. Guldi, P. V. Kamat in *Fullerenes* (Eds.: K. M. Kadish, R. S. Ruoff), Wiley, New York, **2000**, Chapter 5, pp. 225–281.

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FULL PAPER

Donor–Acceptor Hybrids

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— Tuning Optical and Electron Donor **Properties by Peripheral Thio-Aryl** Substitution of Subphthalocyanine: A New Series of Donor-Acceptor Hybrids for Photoinduced Charge Separation



Supramolecular electron transfer: A

new series of dyads comprised of structurally modified (to extend the absorption and singlet emission in to near-IR region) subphthalocyanine covalently linked to fullerene, as light energy harvesting capable functional materials is synthesized and occurrence of photoinduced electron transfer is demonstrated (see figure).