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Photoinduced Electron Transfer in a New Bis(C_{60})−Phthalocyanine Triad

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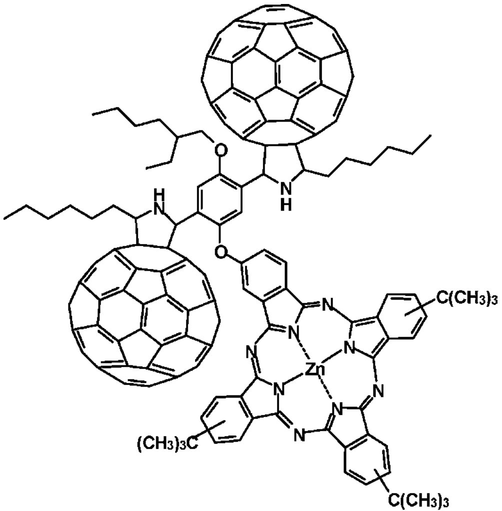
ABSTRACT



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A novel covalently linked bis([60]fullerene)−phthalocyanine triad is reported, exhibiting long-lived photoinduced charge separation both in solution and in the solid state. The first demonstration of a working solar cell using triad 1 as the active material is also presented.

Photoinduced electron transfer in organic molecules is an intensively investigated process in natural as well as in artificial systems.[1] In an attempt to understand and simulate some of the primary aspects of photosynthetic reaction centers, a great variety of synthetic donor−acceptor ensembles have been recently prepared, frequently featuring C_{60} as the acceptor component due to its three-dimensional structure and easily accessible reduction states in solution. These molecular dyads, composed of electron-donor and

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[1] (a) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001. (b) Balzani, V.; Credi, A.; Venturi, M. Photoinduced Charge Separation and Solar Energy Conversion. In *Molecular Devices and Machines: A Journey into the Nanoworld*; Balzani, V., Credi, A., Venturi, M., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 132−173.

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electron-acceptor units, will likely address the mechanistic details of electron transfer and develop photovoltaic devices and other technologies based on light-modulated data storage and retrieval.[2]

Phthalocyanines (Pc's),[3] structural analogues of porphyrins with unusual linear and nonlinear optical properties, are planar 18π-electron aromatic macrocycles perfectly suited for their integration in light energy conversion systems. They exhibit very high extinction coefficients around 700 nm (where the maximum of the solar photon flux occurs), rich redox chemistry, and semiconducting properties when appropriately self-assembled via $\pi-\pi$ stacking interactions. In the past few years, several examples of molecular[4] and supramolecular[5] architectures bearing Pc (or related compounds) and C_{60} units have been synthesized and studied. In particular, we recently reported efficient charge separation in strongly coupled phthalocyanine−fullerene dyads both in solution[6] and in the solid state.[7] Nevertheless, for effective use of such Pc−C_{60} dyads in photovoltaic applications, longer charge transfer state lifetimes are necessary to avoid recombination and increase the chances of positive and negative charges reaching the electrodes.

Long-lived charge-separated states have been achieved, in some cases, by incorporating a second donor or acceptor moiety to multicomponent arrays such as triads, tetrads and pentads. However, to the best of our knowledge, only one example of fullerene−phthalocyanine−fullerene triads has ever been reported.[8] To explore this new type of system, herein we describe the synthesis and photophysical properties of conjugate **1**, with two C_{60} spheres covalently attached to the phthalocyanine core. The suitability of bis([60]fullerene)−phthalocyanine **1** for solar cell applications has also been evaluated by the construction and characterization of photovoltaic devices that employ this compound as the active material.

Scheme 1 shows the synthetic methodology used to prepare bis([60]fullerene)−phthalocyanine **1**, which involves the in situ generation of azomethine ylides from the corresponding diformyl derivative **2** and [2 + 3] cycloaddition reaction with two equivalents of C_{60}.[9] Phthalocyanine **2** was synthesized in three steps from phthalonitrile **4** following the previously communicated procedure for the synthesis of Pc−C_{60} dyads.[4d]

Phthalonitrile **4** was prepared through an ipso substitution to the nitro group of 4-nitrophthalonitrile with 2,5-dibromohydroquinone to afford phenoxyphthalonitrile **3** and subsequent alkylation with 2-ethyl-1-bromohexane (62% yield over the two steps). The crossover condensation of compound **4** with 3 equiv of 4-*tert*-butylphthalonitrile, in the presence of $ZnCl_2$ and *N*,*N*-dimethylaminoethanol (DMAE) as solvent, gave phthalocyanine **5** in 23% yield. A double Stille coupling over intermediate **5** using an excess of vinyl(tributyl)tin and $Pd(PPh_3)_4$ as catalyst, followed by the oxidation of the terminal alkenes of **6** with an $OsO_4/NaIO_4$ mixture in THF, gave the desired diformylphthalocyanine **2** (61% yield over the two steps). Finally, the reaction of diformylphthalocyanine **2** with 2 equiv of C_{60} in the presence hexylglycine at refluxing toluene gave the target triad **1** in 47% yield. Compounds **1**−**6** were fully characterized by NMR, FTIR, MALDI-MS, and UV/vis spectroscopy.[10]

The strong fluorescence transitions of zinc phthalocyanines generally serve as sensitive markers to visualize excited-state interactions such as electron transfer to covalently linked fullerene moieties.[6a] In particular, the fluorescence spectrum of the reference phthalocyanine **5** upon 670 nm excitation is compared in Figure 1 with those of triad **1** in different solvents. The fluorescence intensity observed for **1** is at least 80 times lower than that seen for **5**. For a given solution, the fluorescence response is known to be proportional to the intensity of the exciting light and the molar extinction coefficient. Since these parameters were kept constant, it is conceivable to attribute the decrease in fluorescence intensities to a reductive quenching of the ZnPc excited singlet state (1.8 eV) by the C_{60} unit via intramolecular electron transfer to afford $(ZnPc)^{\bullet+}-(C_{60})^{\bullet-}$ (1.24 eV).[11]

Femtosecond transient absorption spectroscopy was employed to follow the electron-transfer processes, that is,

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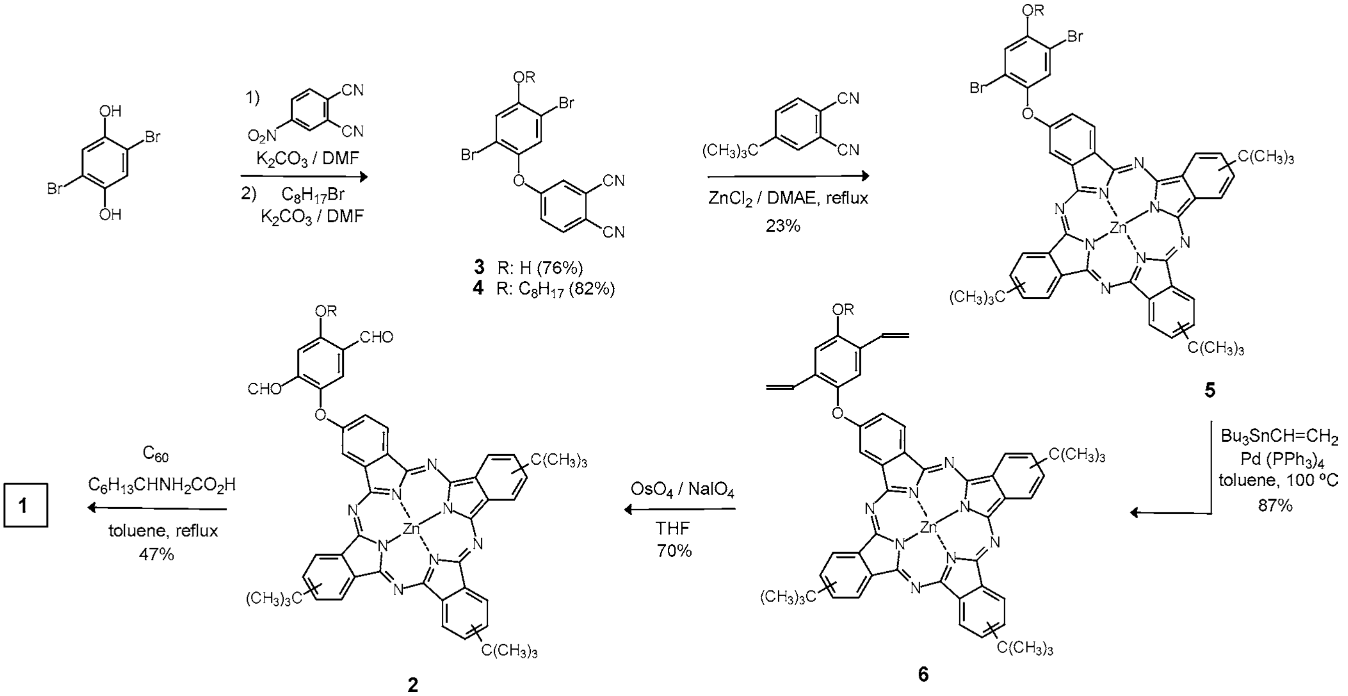
(10) Selected data for **1**: ^1H NMR (500 MHz, $CDCl_3$) δ 9.8−7.0 (br m, 14H; ArH), 5.4−4.6 (m, 4H; pyrrolidine), 4.1−3.8 (m, 2H; OCH_2), 2.0−0.8 (br m, 68H; CH, CH_2, CH_3 $(CH_3)_3$); UV/vis ($CHCl_3$) λ_{max} (log ϵ) 682 (5.13), 336 (5.01), 255 nm (5.27); FT-IR (KBr) ν 3413, 2955, 2871, 1613, 1512, 1463, 1380, 1192, 1085, 927, 744 cm^{-1}; HR MALDI-TOF MS *m/z* 2654.6328 [M^+], calcd for $C_{194}H_{86}N_{10}O_2Zn$ 2654.2626.

Scheme 1. Synthesis of Bis([60]fullerene)−Phthalocyanine **1**



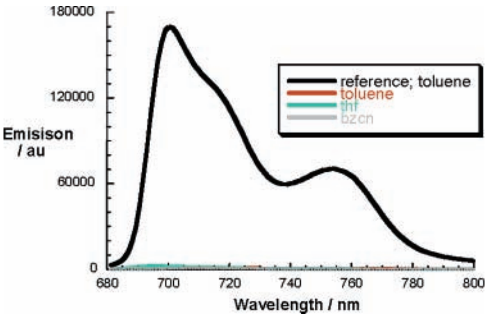


Figure 1. RT fluorescence spectra of **5** in toluene (black) and **1** in several solvents recorded with solutions that exhibit optical absorptions of 0.5 at the 670 nm excitation wavelength.

charge separation from the photoexcited chromophore to the electron accepting fullerene and charge recombination within the metastable $(\mathrm{ZnPc})^{\bullet +}-(\mathrm{C}_{60})^{\bullet -}$ radical pair. After 680 nm excitation, which directs most of the illuminating light in **1** to the phthalocyanine core, the characteristic features of the singlet excited state of ZnPc evolves despite the presence of the two C_{60} moieties. Transient bleaching between 605 and 705 nm, with minima at 615 and 680 nm, is flanked by new absorptions that center at 550 and 740 nm.

Furthermore, a significant acceleration of the decay kinetics was observed, instead of the slow intersystem crossing which converts, in the ZnPc reference **5**, the initial singlet excited-state into the corresponding triplet manifold with a rate constant of $2.6 \times 10^8\ \mathrm{s}^{-1}$. The kinetics, as derived at several wavelengths in the 400 to 1200 nm region, yielded rates of 6.2×10^{10}, 8.6×10^{10}, and $1.5 \times 10^{11}\ \mathrm{s}^{-1}$ in toluene, anisole, and THF, respectively. These values are in good quantitative correlation with the steady-state fluorescence quenching (see above).

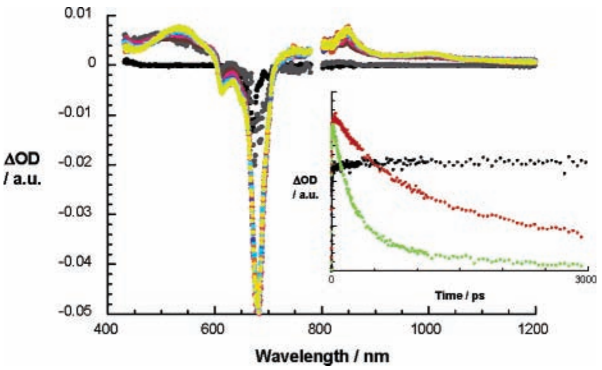


Figure 2. Femtosecond transient absorption spectra (visible and near-infrared region) obtained upon laser flash photolysis (680 nm) of **1** (ca. 1.0×10^{-5} M) in deoxygenated toluene with several time delays between 0 and 3000 ps at room temperature, indicating the formation of the ZnPc π-radical cation and the C_{60} π-radical anion absorption. Inset: time-absorption profiles at 1000 nm following photolysis of **1** in toluene (black), anisole (red), and THF (green).

Key features of the new product are transitions at 535, 850, and 1000 nm (Figure 2), which correspond to the one-electron oxidized $\mathrm{ZnPc}^{\bullet +}$ and one-electron reduced $\mathrm{C}_{60}{}^{\bullet -}$.[6a]

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(11) The energy of the excited states and the charge-separated state of triad **1** have been calculated on the base of its electrochemical data. Cyclic and Osteryoung square wave voltammograms are provided in the Supporting Information.

Time-resolved pulse radiolytic oxidation and reduction experiments with the individual building blocks (i.e., ZnPc and C_{60}) provides unambiguous evidence for the formation of the radical pair $(ZnPc)^{\bullet+}-(C_{60})^{\bullet-}$ in triad **1**.

Within our femtosecond time domain (i.e., up to 3.2 ns) we only noted appreciable decays of the radical pair in anisole (i.e., 2200 ps) and THF (i.e., 360 ps). On the contrary, in toluene the radical pair features were stable. Thus, complementary nanosecond transient absorption experiments were employed to analyze the charge-recombination dynamics in toluene. Interestingly, the transitions at 840 and 1000 nm are still observed, which confirms the stability of the photoproduct. Fitting the decay dynamics of $ZnPc^{\bullet+}$ and $C_{60}{}^{\bullet-}$ to a first-order rate law, a lifetime of 21 ns was derived for the radical ion pair $(ZnPc)^{\bullet+}-(C_{60})^{\bullet-}$ in toluene. This value is a magnitude longer than those measured for structurally related Pc−C_{60} dyads.[6]

For photovoltaic applications, the photophysical behavior in the solid state is decisive. Figure 3 shows the photoinduced absorption (PIA) spectrum of a drop cast film of triad **1**.

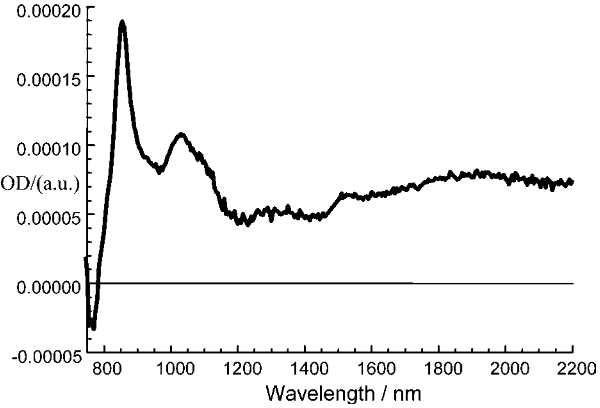

Figure 3. Photoinduced absorption spectrum of **1** in a thin solid film at 80 K.

The sample was excited by a diode laser at 664 nm with a modulation frequency of 73 Hz. As shown in Figure 3, the PIA spectrum shows a peak around 855 nm, a broad peak around 1050 nm, and a bleaching at 785 nm. The peak at 1050 nm has been assigned to the absorption of the fullerene anion,[12] while the peak at 855 nm is related to the phthalocyanine cation. Both absorptions are also present in solution. Finally, the broad and unstructured features at wavelengths longer than 1400 nm are, in accordance with the PIA spectrum obtained for a phthalocyanine−fullerene dyad solid film by Loi et al.,[7] tentatively assigned to charge separation. However, a detailed interpretation of these features is not available yet.

The lifetime of the charge separated state was studied by analyzing the chopper frequency dependence of the in-phase and out-of-phase PIA signal at the phthalocyanine cation absorption band at 855 nm, and fitting the data with a dispersive recombination model (see the Supporting Information).[13] The fit reveals an average lifetime of 1 ms, which is around five times longer than that for the previously reported Pc−C_{60} dyad.[7] This increased lifetime provides the opportunity to use the material as the active layer in photovoltaic devices.

Additionally, preliminary solar cells built with triad **1** as the active material were fabricated by spin casting from chlorobenzene solution (see the Supporting Information). In the dark, the device shows diode behavior. Under white light illumination at 100 mW cm^{-2}, an open circuit voltage of 320 mV and a short circuit photocurrent of 0.3 mA cm^{-2} have been measured. These moderate values together with a fill factor of 25% indicate charge transport problems, which might be improved by optimizing device parameters like film thickness, film casting conditions and morphological features.

In summary, it has been shown that bis([60]fullerene)−phthalocyanine **1** can harvest photons with wavelengths up to the infrared region, and efficiently convert them into long-lived charge carriers for solar energy conversion. Although the overall photocurrent and therefore the conversion efficiency is only moderate, the device's optimization is being investigated in order to improve the transport of charges to the electrodes.

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Supporting Information Available: Experimental procedures, full characterization of compounds **1**−**6**, the MALDI-TOF spectrum of triad **1**, ^{1}H NMR and UV/vis spectra of compounds **1**, **2**, **5**, and **6**, the time dependence of the PIA signal for bis([60]fullerene)−phthalocyanine **1**, electrochemistry of triad **1**, and current−voltage features of a solar cell built with triad **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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