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Synthesis and Photophysical Studies of a New Nonaggregated C_{60}–Silicon Phthalocyanine–C_{60} Triad

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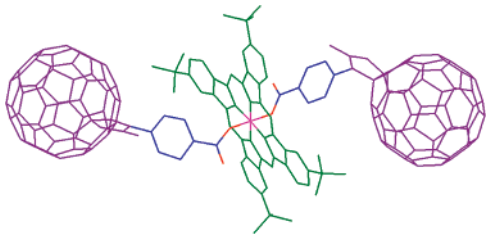
ABSTRACT



A C_{60}–SiPc–C_{60} triad showing no aggregation is synthesized and characterized. Photoexcitation of the triad results in formation of the charge-separated state by photoinduced electron transfer from the singlet excited state of the SiPc moiety to the C_{60} moiety. The charge-separated state has a lifetime of 5 ns in benzonitrile at 298 K.

Phthalocyanines (Pcs)[1] as electron donors as well as sensitizers are outstanding compounds for efficient photoinduced energy- and charge-transfer processes. Among all the Pcs, the silicon ones have gained great attention due to their high solubility in organic solvents without presenting aggregation phenomena, characteristics quite common in most of the peripherally substituted phthalocyanines. Thus, the possibility to link covalently different kinds of ligands in the Pc axial position avoids photoinactive aggregates in solution and allows tuning of the optical and electrochemical properties of the phthalocyanine.[2]

A large variety of phthalocyanine dyads with different photoactive electron acceptor moieties have been prepared.[3] One of the most attractive electron acceptor moieties to attach to the phthalocyanine is the [C_{60}]fullerene, mainly due to its high quantum efficiency and its low recombination speed.[4] Thus, a big assortment of molecular and supramolecular Pc–C_{60} dyads have been synthesized,[5] and their photoinduced electron-transfer processes have been studied.[5d,g−l,6]

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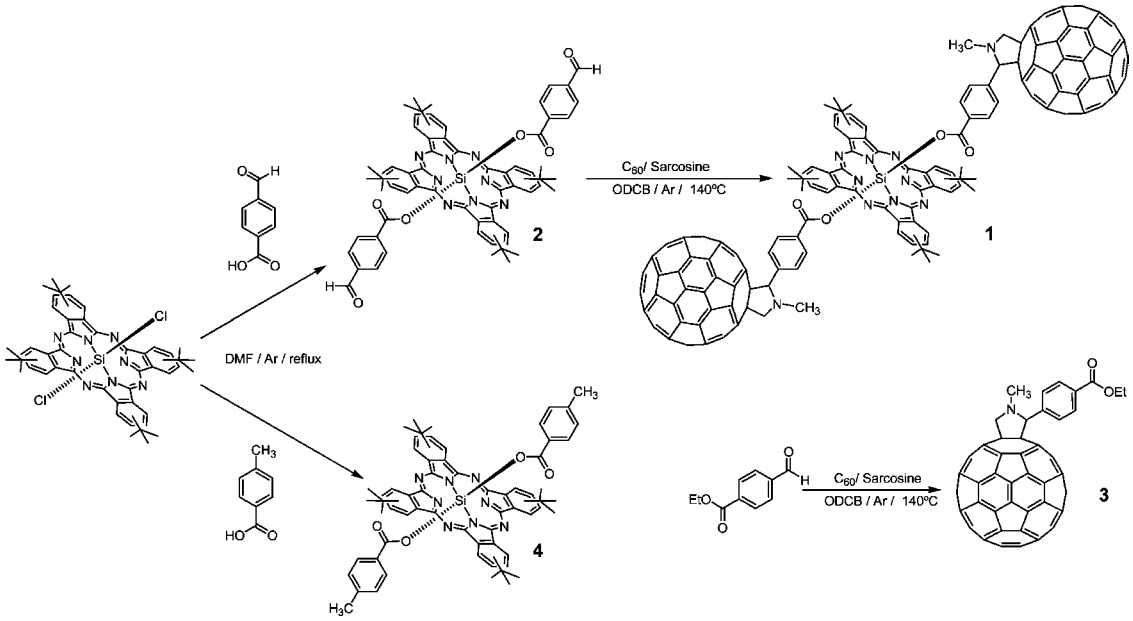
Scheme 1. Synthesis of C_{60}−SiPc−C_{60} Triad **1**, C_{60} Reference **3**, and SiPc Reference **4**



On the other hand, to the best of our knowledge, only a couple of C_{60}−Pc−C_{60} triads have been synthesized[7] so far, presumably due to the synthetic difficulties to prepare this kind of system. A silicon phthalocyanine with two axial fullerene substituents has been already reported.[7a,b] Recently, a novel bis([60]fullerene)−phthalocyanine triad has been synthesized exhibiting photoinduced charge separation both in solution and in the solid state.[7c] For effective use of such Pc−C_{60} derivatives in photovoltaic devices, the synthesis of new Pc−C_{60} derivatives that present longer lifetimes of charge-separated (CS) states should be pursued.

Here, we will present the synthesis of new C_{60}−SiPc−C_{60} hybrids (**1**), showing no aggregation phenomena in solution, which are characterized by the close distance between the C_{60} and the Pc subunits. Such geometry is suitable for efficient *intramolecular* photoinduced electron transfer, which is also reported in this study.

Triad **1** was afforded by a double Prato reaction from the bis(4-formylbenzoate)silicon phthalocyanine **2** in 30% yield after purification by column chromatography. Phthalocyanine **2** was synthesized by reaction of *p*-formylbenzoic acid with (*tert*-butyl)$_4$PcSiCl$_2$ in 19% yield. The C_{60} and the SiPc reference compounds **3** and **4**, respectively, were synthesized as indicated in Scheme 1 (see Supporting Information). Compounds **1**−**4** were fully characterized by ^{1}H NMR, FT-IR, UV−vis, and MALDI-TOF-MS.[8] Figure 1 shows the ^{1}H NMR spectrum in $CDCl_3$ of the nonaggregated phthalocyanine **1**, where integration of the signals clearly indicates the presence of two fullerene units linked to the SiPc. Due to the effect of the strong ring current of the Pc, the signals of the pyrrolidine and benzoate protons of the triad **1** are upfield shifted when compared with those of the C_{60} derivative **3**:

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(8) Selected data for compound **1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.75−9.54 (8H, m), 8.42 (4H, d, J = 8.1 Hz), 6.67 (4H, br s), 5.20 (4H, br s), 4.62 (2H, d, J = 9.6 Hz), 4.26 (2H, s), 3.86 (2H, d, J = 9.6 Hz), 2.19 (6H, s), 1.83−1.75 (36H, m); UV/vis (CH_2Cl_2) λ_{max} (log ϵ) 695 (5.31), 664 (4.43), 624 (4.51), 360 (4.98), 334 (5.04), 255 (5.40); FT-IR (KBr) ν = 2954, 2902, 2865, 2777, 1687, 1612, 1527, 1281, 1080, 940, 758, 528 cm^{-1}; MALDI-TOF MS (dithranol) m/z 2556 [M$^+$].

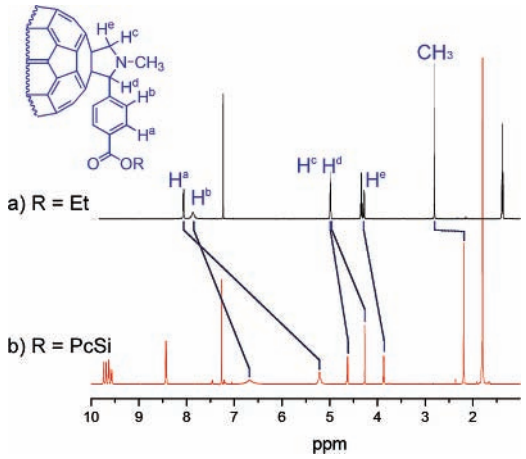


Figure 1. (a) ^{1}H NMR of the C_{60} derivative **3**. (b) ^{1}H NMR of C_{60}−PcSi−C_{60} triad **1**.

the signals corresponding to the benzoate protons move from 8.08 and 7.87 to 6.67 and 5.20 ppm; the pyrrolidine protons move from 4.98, 4.97, and 4.28 to 4.62, 4.26, and 3.86; and finally, the *N*-CH_3 protons move from 2.81 to 2.19 ppm.

The absorption spectrum of the C_{60}−SiPc−C_{60} triad **1** in benzonitrile (PhCN) is a reasonable superposition of the spectra of the component chromophores making up the molecule (Figure 2a). Thus, there is no significant electronic

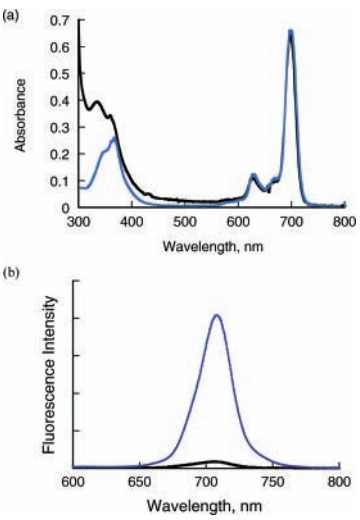


Figure 2. (a) Absorption spectrum of C_{60}−SiPc−C_{60} triad **1** (black line) with that of the reference compound (blue line) in deaerated PhCN at 298 K. (b) Fluorescence spectrum of C_{60}−SiPc−C_{60} triad **1** with the reference compound SiPc **4** in deaerated PhCN at 298 K.

interaction between the individual chromophores in their ground-state configuration. The cyclic voltammogram of C_{60}−SiPc−C_{60} triad **1** in deaerated PhCN containing 0.10 M Bu_4NPF_6 at 298 K in Figure 3a consists of two two-

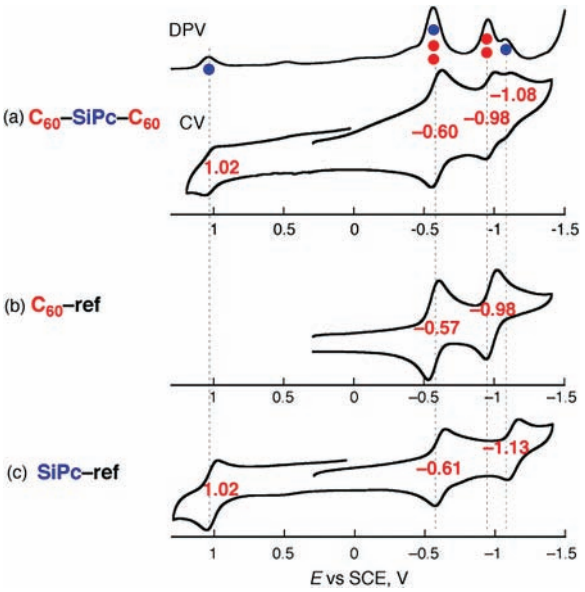


Figure 3. (a) Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of C_{60}−SiPc−C_{60} triad **1** in PhCN. Cyclic voltammograms of (b) C_{60}−ref **3** and (c) SiPc−ref **4** in PhCN.

electron reduction processes of C_{60} (red closed circles in Figure 3a; −0.60 and −0.98 V vs SCE), two one-electron reduction processes of SiPc (blue closed circles in Figure 3a; −0.60 and −1.08 V), and one-electron oxidation process of SiPc (red closed circle in Figure 3a; 1.02 V). These redox processes agrees well with those of the corresponding redox processes of the reference compounds (C_{60}−ref **3** in Figure 3b and SiPc−ref **4** in Figure 3c). This also indicates that there is no significant interaction between the SiPc and C_{60} units in C_{60}−SiPc−C_{60} triad **1**.

The photoexcitation of a deaerated PhCN solution containing **1** with 360 nm monochromatized light results in fluorescence with the emission maximum at 708 nm. The emission intensity is much smaller than that of the reference compound SiPc (Figure 2b). This indicates that the singlet excited state of SiPc is quenched efficiently by C_{60}. The quenching rate constant is determined to be 3.3×10^9 s^{-1} from the fluorescence quenching and the fluorescence lifetime of SiPc−ref **4** (9.0 ns). The fluorescence may occur by electron transfer from the singlet excited state ^{1}SiPc* to C_{60} in the triad. The free-energy change of photoinduced electron transfer (ΔG^0_{ET}) from the ^{1}SiPc* unit to the C_{60} unit in PhCN is determined to be −0.15 eV from the one-electron oxidation potential (1.02 V vs SCE), the excitation energy (S_1 = 1.77 eV) of the SiPc unit, and the one-electron reduction potential of the C_{60} unit (−0.60 V vs SCE) in C_{60}−SiPc−C_{60} triad **1**.

The occurrence of photoinduced electron transfer was confirmed by femtosecond laser flash photolysis measurements.[9] A deaerated PhCN solution containing C_{60}−SiPc−C_{60} triad **1** gave rise upon a 400 nm femtosecond laser pulse to transient absorption bands at 880 and 1000 nm due to the $SiPc^{\bullet+}$ and $C_{60}^{\bullet-}$ moiety, respectively. The absorption bands

due to $SiPc^{\bullet+}$ (880 nm) and $C_{60}^{\bullet-}$ (1000 nm) are quite distinct and well-separated. This clearly indicates the formation of the CS state.[10] From the rise in absorbance at 880 nm due to $SiPc^{\bullet+}$ in Figure 4b, the rate constant of formation of

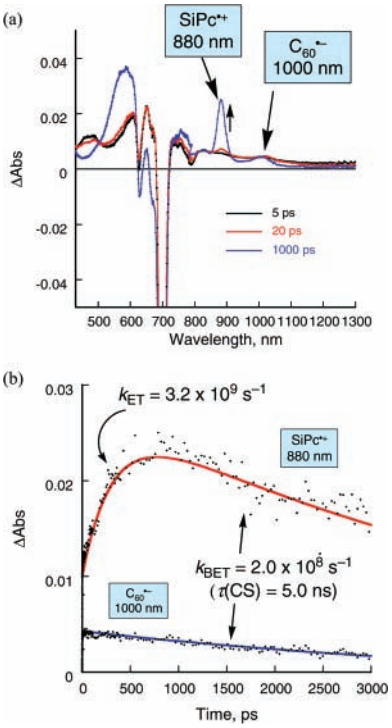
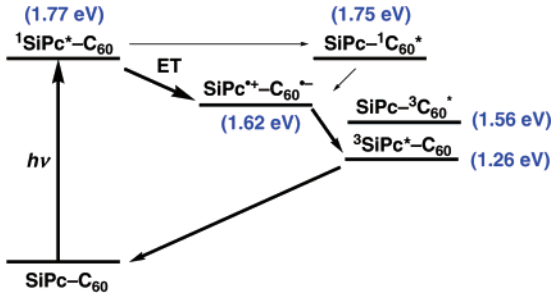


Figure 4. (a) Transient absorption spectra of C_{60}−SiPc−C_{60} triad **1** (1.0×10^{-5} M) in deaerated PhCN at 298 K after laser excitation at 400 nm. (b) Time profiles of absorbance at 880 and 1000 nm.

$SiPc^{\bullet+}$ in the triad is determined to be 3.2×10^9 s^{-1}, which agrees well with the fluorescence quenching rate constant (3.3×10^9 s^{-1}). This indicates clearly that *intramolecular* electron transfer from ^{1}SiPc* to C_{60} occurs in the triad to produce the charge-separated state, $C_{60}^{\bullet-}$−$SiPc^{\bullet+}$−C_{60} (or C_{60}-$SiPc^{\bullet+}$−$C_{60}^{\bullet-}$). At 1000 nm, the decay of ^{1}SiPc* is overlapped with the rise of $C_{60}^{\bullet-}$. The lifetime of the CS state in PhCN is determined to be 5.0 ns from the decay of absorbance at 880 and 1000 nm. This is the longest CS lifetime ever reported for electron donor−acceptor molecules of phthalocyanine in a polar solvent.[11]

Although the CS state was observed by femtosecond laser flash photolysis measurements (Figure 4), the CS state was not detected, but instead the triplet−triplet absorption band due to ^{3}SiPc* ($\lambda_{max} = 530$ nm) was observed at microsecond time scale in the transient absorption spectrum obtained upon nanosecond laser pulse excitation (355 nm) of a deaerated PhCN solution of C_{60}−SiPc−C_{60} triad **1**. This indicates that the back electron transfer in the CS state affords the triplet excited state rather than the ground state because the triplet energy is lower than the CS state.[12] The energy diagram is summarized in Scheme 2, where one C_{60} unit is omitted for

Scheme 2



clarity. Although the energy of the triplet excited state of C_{60} (SiPc−$^3C_{60}$*, 1.56 eV)[13] is also lower than the energy of the CS state, the back electron transfer to the lower energy triplet of SiPc (^{3}SiPc*−C_{60}, 1.26 eV)[12] may be much faster than to SiPc−$^3C_{60}$*.

In conclusion, the newly synthesized C_{60}−SiPc−C_{60} triad, which shows no aggregation in solution with a long wavelength absorption ($\lambda_{max} = 700$ nm), undergoes efficient *intramolecular* photoinduced electron transfer to afford the CS state in PhCN.

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.), and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC.

(10) This shows sharp contrast to the observation of the broad absorption bands with no distinct absorption maxima in other SiPc−$n$$C_{60}$ (n = 2, 4, 8) compounds that decay much more slowly than the present case.[7a]

(11) In a nonpolar solvent (toluene), a bis([60]fullerene)−phthalocyanine triad (ref 7b) has been reported to afford a CS lifetime of 21 ns.

(12) The triplet energy (1.26 eV) of SiPc was determined from the phosphorescence spectrum of SiPc−ref in 2-MeTHF/ethyliodide (1:1 v/v).

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