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Silicon-Phthalocyanine-Cored Fullerene Dendrimers: Synthesis and Prolonged Charge-Separated States with Dendrimer Generations

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Abstract: Silicon-phthalocyanine-cored fullerodendrimers with up to eight fullerene substituents (SiPc–$n\,C_{60}$; $n=2$, 4, and 8) have been synthesized. Photophysical properties of newly synthesized SiPc–$n\,C_{60}$ have been investigated by time-resolved fluorescence and transient absorption analysis with pulsed laser light. Laser photolysis measurements suggest the occurrence of a charge-separation process from ^{1}SiPc* to the C_{60} subunits. The nanosecond transient absorption spectra in the near-IR region indicate that the lifetimes of the formed radical ion pairs are prolonged on the order of SiPc–$8\,C_{60}$ > SiPc–$4\,C_{60}$ > SiPc–$2\,C_{60}$, which may be related to the electron migration among the C_{60} subunits. The usefulness of SiPc–$n\,C_{60}$ as light-harvesting systems, evaluated as a ratio of the rates of charge recombination to those of charge separation, increases markedly with the dendrimer generation.

Keywords: charge transfer · dendrimers · photochemistry · phthalocyanines · silicon

Introduction

Studies on the energy- and electron-transfer processes in photosynthetic antenna proteins have undergone an enormous growth in recent years to develop artificial photosynthetic systems.[1] Various strategies have been employed to develop molecular electronic devices that use porphyrin arrays linked by covalent bonds,[2] self-assemblies,[3] dendrimers,[4] or polymers.[5] Phthalocyanines (Pc), structural analogues of porphyrins, with a strong absorption in the visible region (the Q band; $\lambda_{max} \approx 700$ nm), are highly versatile and stable chromophores with unique photophysical and photochemical properties that make them, alone or in combination with many other electro- and photoactive moieties, ideal building blocks for the construction of molecular materials with special electronic and optical properties.[6] Among the Pc derivatives, the axially substituted silicon phthalocyanines (SiPc) are of great interest because the axial substitutions make it possible to preclude undesirable aggregation in solution.[6] Furthermore, the axially substituted phthalocyanines with bulky dendritic subunits are known to produce glassy solids,[6–8] which allow the fabrication of the nonscattering films for practical-device applications.[6,8] However, despite such advantages, the number of axially substituted silicon phthalocyanines as multicomponent systems is still limited. A few elegantly designed dendrimers that incorporate a phthalocyanine core have been synthesized so far, and most photophysical and photochemical studies have been carried out with either metallic complexes or with a silicon derivative located within the central macrocycle.[7–10] Such dendrimers are known to produce glassy solids, which could be readily fabricated into nonscattering films for optical applications.

As photosynthetic models, phthalocyanine–fullerene systems have been mainly prepared covalently[11] or noncovalently[12] and are promising for efficient light harvesting. In

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the light of their particular electronic properties, fullerene derivatives appear to be superior electron acceptors owing to the low reorganization energy that results in rapid charge separation and rather slow charge recombination as a consequence of accessing the Marcus inverted region.[13] To the best of our knowledge, a phthalocyanine with more than two fullerene substituents had not been presented until we reported the first synthesis of silicon phthalocyanine with two axial fullerene substituents.[7] Dendrimers with fullerene cores have been widely studied,[14] whereas the synthesis of fullerene-rich dendrimers has been considered to a lesser degree, mainly because of the difficulties encountered in their synthesis, such as low solubility and limited chemical reactivity.[15]

In line with these aspects, herein we have for the first time designed and synthesized a series of silicon-phthalocyanine-cored fullerodendrimers bearing up to eight axial fullerene subunits (SiPc–$n\,C_{60}$; $n=2$ (**G1**), 4 (**G2**), and 8 (**G3**); see Scheme 1) and exclusively investigated their photophysical properties by employing steady-state and time-resolved techniques. The main advantage of such highly soluble dendrimers is the maintenance of prolonged charge-separated states between the phthalocyanine-donor and fullerene-acceptor components, in addition to the harvesting of a wide range of the solar-light spectrum.

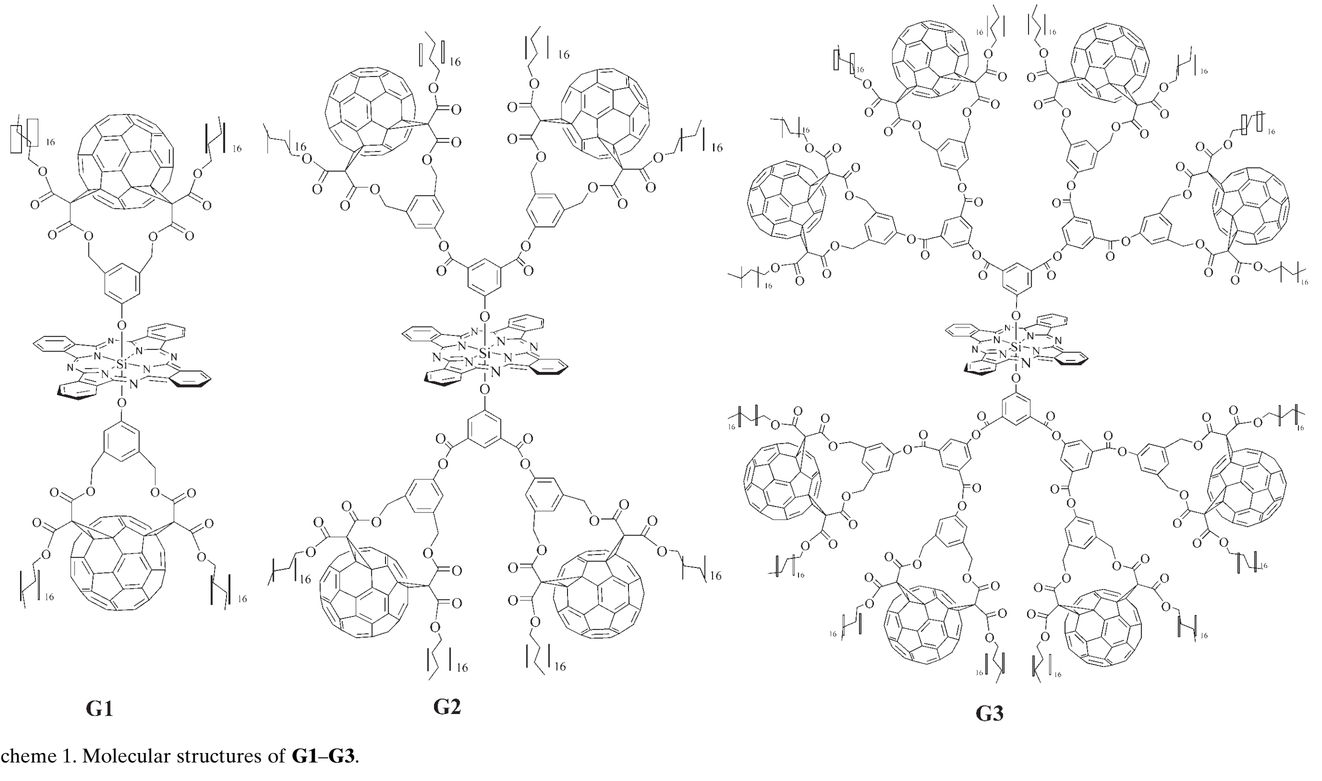
Results and Discussion

Synthesis: Since the first reported preparation of the peripherally four-fullerene-substituted porphyrin by Nierengarten et al.,[15a] we synthesized a silicon phthalocyanine with two axial fullerene substituents.[7] This success prompted us to synthesize phthalocyanine-cored fullerene dendrimers **G1**–**G3** with up to eight fullerene subunits.

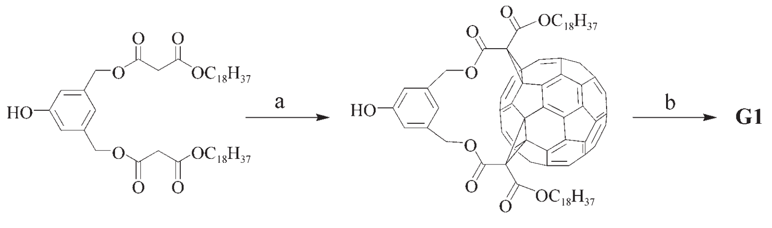
Our synthetic strategy for the dendritic fullerenes **G1**–**G3** consisted of preparing larger dendrimer arms or dendrons (**G*n*-OH**) and coupling several of these to a phthalocyanine core convergently. In the present context, the synthesis of the requisite dendrons was based upon a repetitive coupling/deprotection sequence that utilized silyl-protected phenols and dicarboxylic acids. Every step of the reaction sequence proceeded smoothly and efficiently to give a good-or-moderate yield of the product.

The compound **G1** was synthesized as depicted in Scheme 2. The starting compound bis(malonate) **1** was prepared in four steps from the commercially available 5-hydroxyisophthalic acid according to a method previously reported by us.[7] Reaction of **1** with C_{60} was based on the highly regioselective reaction developed by Diederich and co-workers,[16] which led to a macrocyclic bisadduct of C_{60} through a macrocyclization reaction of the carbon sphere with bis(malonate) derivatives in a double Bingel addition.[17] Treatment of C_{60} with **1**, iodine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded the bisadduct **G1-OH 2** in 34 % yield. The final reaction of bisadduct **2** with silicon phthalocyanine dichloride went smoothly in the presence of K_2CO_3 to produce **G1** in 27 % yield.

The structure of **G1** was confirmed by ^{1}H and ^{13}C NMR spectroscopic and MALDI-TOF mass-spectrometric analysis. The ^{1}H NMR spectrum is particularly informative, because the strong ring current of the Pc macrocycle helps to differentiate protons of similar type (see the Supporting In-



Scheme 1. Molecular structures of **G1**–**G3**.



1 **2 (G1-OH)**

Scheme 2. Synthesis of **G1**. Reagents and conditions: a) C_{60}, I_2, DBU, toluene, RT, 24 h (34 %); b) silicon phthalocyanine dichloride, K_2CO_3, toluene, reflux, 15 h (27 %).

formation). The ^{13}C NMR spectrum showed a set of signals for the C_{60} nucleus ($\delta = 136.85$–149.50 ppm), two carbonyl carbon atoms ($\delta = 162.37$ and 162.03 ppm), aromatic carbon atoms ($\delta = 113.91$–135.88 ppm), and aliphatic carbon atoms ($\delta = 14.33$–70.31 ppm). Further confirmation of the hybrid Pc–fullerene structure was obtained from the IR and UV/Vis spectra, which contain absorption bands that arise from the Pc and fullerene components. The MALDI-TOF mass spectrum showed peaks at m/z 2086.39 ([M^+−**G1-OH**-1]) as the basis peak and 1546.3767 (**G1-OH**-1). These results provided direct evidence for the structure of **G1**.

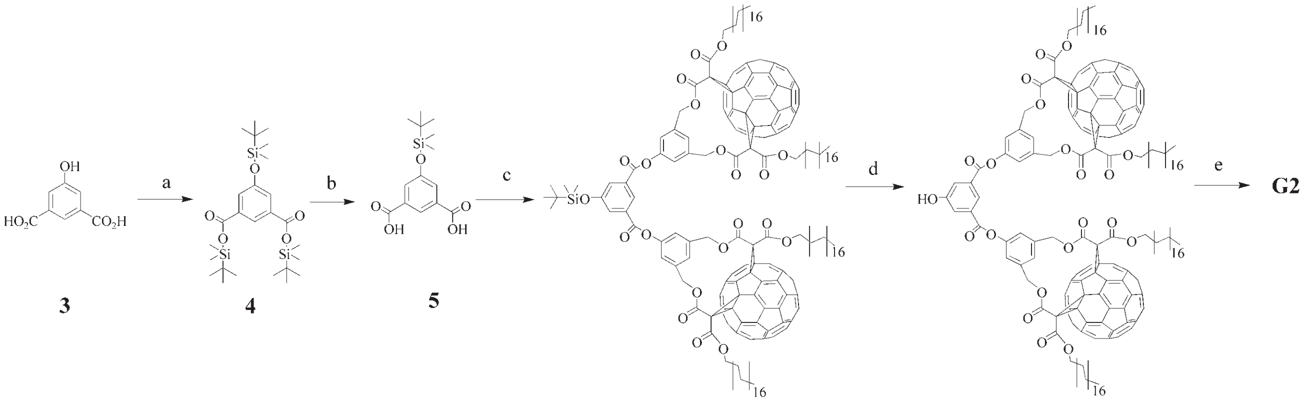
The preparation of **G2** is depicted in Scheme 3. According to the method developed by Corey and Venkateswarlu,[18] the hydroxy groups of 5-hydroxyisophthalic acid (**3**) were protected by reaction with *tert*-butyldimethylsilyl chloride to afford silyl-protected **4** in 94 % yield and then selectively deposited by glacial acetic acid/water (3:1)[19] to give diacid **5** in 89 % yield.

The reaction of **5** with a silyl-protected phenol group was carried out by a coupling reaction with **G1-OH** (**2**) under standard coupling conditions using dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and 1-hydroxy-1*H*-benzotriazole hydrate (HOBT) to afford silyl-protected **6** in 47 % yield. The silyl-protected phenol group in **6** was then deprotected with HF to give **G2-OH** dendron **7** in 97 % yield. Finally, **7** was coupled to the silicon phthalocyanine core in the presence of K_2CO_3 to produce the dendrimer **G2** with four fullerene subunits in 62 % yield.

^1H and ^{13}C NMR spectra were most useful for the characterization of **G2**. In spite of the increase in generation number, well-resolved resonance signals in the aliphatic and aromatic regions were present in both the ^1H and ^{13}C NMR spectra of **G2**, and distinct assignments could be made for the structure of **G2** (see the Supporting Information). Analogous to the **G1** fragmentation patterns, the MALDI-TOF mass spectrum also showed a basis peak at m/z 3781.10 ([M^+−**G2-OH**-1). These results gave good evidence for the structure of **G2**.

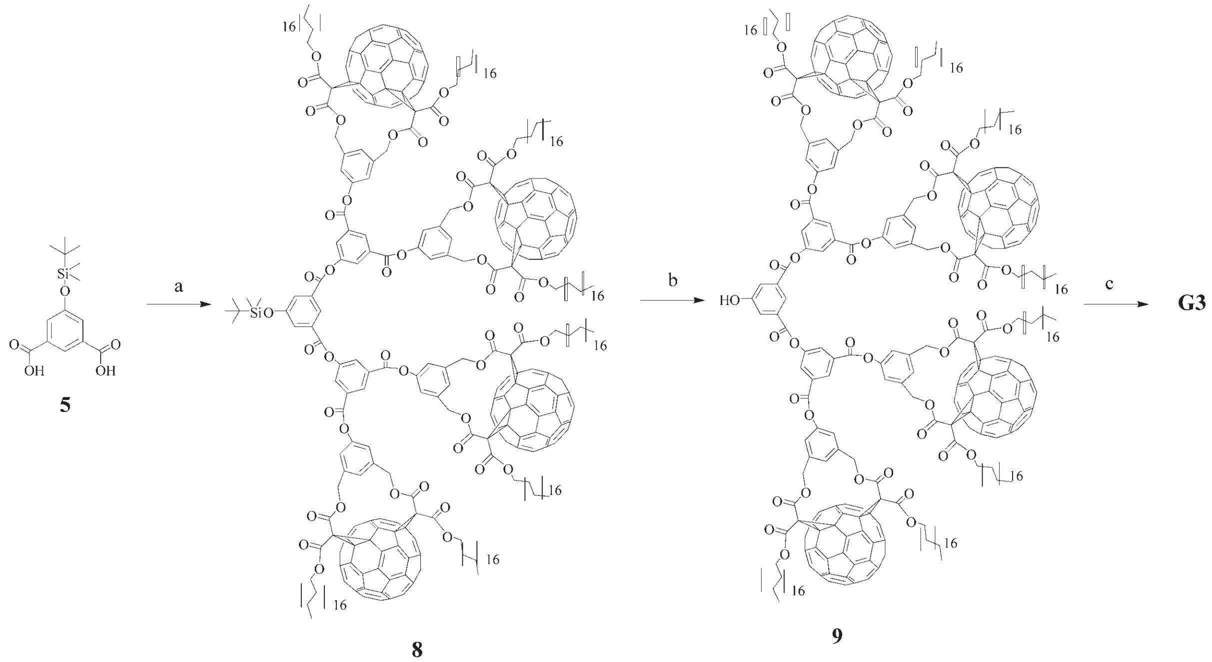
The synthesis of dendrimer **G3** with eight fullerene subunits is described in Scheme 4. Silyl-protected diacid **5** was coupled with the **G2-OH** dendron **7** in the presence of DCC, DMAP, and HOBT to give **8** in 57 % yield, and the silyl-protected phenol group of **8** was then deprotected with HF to afford the **G3-OH** dendron **9** with four fullerene subunits in 54 % yield. This dendron **G3-OH** (**9**) was coupled to the silicon phthalocyanine core to produce the **G3** dendrimer with eight fullerene subunits in 25 % yield.

The largest dendritic fullerophthalocyanine **G3** contains eight fullerene subunits and has a molar mass of 13978. The purity of **G3** was confirmed by thin-layer chromatography, ^1H and ^{13}C NMR spectroscopic, and MALDI-TOF mass-spectrometric analysis. Despite its macromolecular structure, the protons of the **G3** dendrimer showed clearly separated resonance signals in the aromatic and aliphatic regions. Owing to the highly symmetrical structure of **G3**, the ^{13}C NMR spectrum was simple, well resolved, and showed each set of the signals for the fullerene, carbonyl, aromatic, and aliphatic carbon atoms in the expected regions.



3 **4** **5** **6** **7**

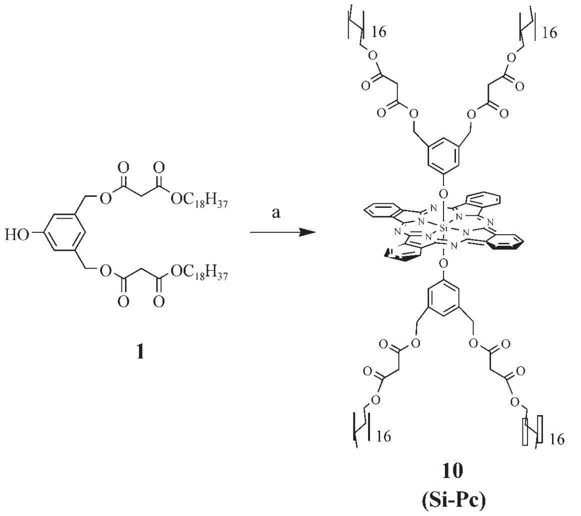
Scheme 3. Synthesis of **G2**. Reagents and conditions: a) *tert*-butyldimethylsilyl chloride, imidazole, DMF, 57 °C, 24 h (94 %); b) $THF/CH_3CO_2H/H_2O$ (1:3:1), RT, 3 h (89 %); c) **G1–OH** (**2**), DCC, DMAP, HOBT, $CHCl_3$, RT, 24 h (47 %); d) HF, THF, RT, 15 h (97 %); e) silicon phthalocyanine dichloride, K_2CO_3, [18]crown-6, toluene, reflux, 15 h (62 %). DMF = *N*,*N*,-dimethylformamide.



Scheme 4. Synthesis of **G3**. Reagents and conditions: a) **G2–OH** (**7**), DCC, DMAP, HOBT, $CHCl_3$, RT, 24 h (57%); b) HF, THF, RT, 15 h (54%); c) silicon phthalocyanine dichloride, K_2CO_3, [18]crown-6, toluene, reflux, 15 h (54%).

MALDI-TOF mass spectrum showed a signal at m/z 7169.67 ([M^+−**G3-OH**-1) and a basis peak at m/z 1096.31.

Silicon phthalocyanine (**SiPc**) **10** was also prepared as a reference compound in the electrochemical and photophysical characterization of Pc–fullerene dendrimers **G1**–**G3**. Bis(malonate) **1** was treated with silicon phthalocyanine dichloride under similar conditions as those for **G1** to produce dark blue **10** in 20% yield (Scheme 5).



Scheme 5. Synthesis of reference compound SiPc (**10**). Reagents and conditions: a) silicon phthalocyanine dichloride, K_2CO_3, [18]crown-6, toluene, reflux, 15 h (20%).

Cyclic voltammetry studies: The determination of the redox potentials of SiPc–$n\,C_{60}$ is important to evaluate the energetics of the electron-transfer processes. In benzonitrile (PhCN), the first oxidation potentials (E_{ox}) of the SiPc moieties of SiPc–$n\,C_{60}$ were located at 650–670 mV versus Ag/Ag$^+$ and are almost the same as SiPc (720 mV). The first reduction potentials (E_{red}) of the C_{60} moieties of SiPc–$n\,C_{60}$ were located at around −800 mV versus Ag/Ag$^+$. The driving forces for the charge recombination ($-\Delta G_{CR}$) and charge separation ($-\Delta G_{CS}$), calculated from the Rehm–Weller equations[20] (see Table 1) suggest an exothermic charge-separation process via ^{1}SiPc* to form SiPc$^{\bullet+}$–$C_{60}^{\bullet-}$-$(C_{60})_{n-1}$. On the other hand, quite small negative ΔG_{CS} values were calculated via $^1C_{60}$* in PhCN but not in toluene.

Steady-state absorption studies: The absorption spectrum of the SiPc reference compound in toluene shows the B band at 352 nm, the Q band at 682 nm, and a shoulder at 615 nm (Figure 1). The absorption spectrum of SiPc–2C_{60} shows a red shift of the Q band at about 2 nm with respect to that of SiPc. The absorption bands of the C_{60} subunits were observed at 265 and 340 nm; thus, the absorption in the region 300–600 nm is significantly increased with an increasing number of attached C_{60} units. Interestingly, the red shift of the Q band is noted as the generation number of the dendritic C_{60} subunits increases: 684 (**G1**, SiPc–2C_{60}), 689 (**G2**, SiPc–4C_{60}), and 690 nm (**G3**, SiPc–8C_{60}). The surrounding C_{60} groups may interact with a SiPc unit in addition to the nearest C_{60} groups attached to the axial positions, thus causing the observed shift. In PhCN, the absorption spectra of

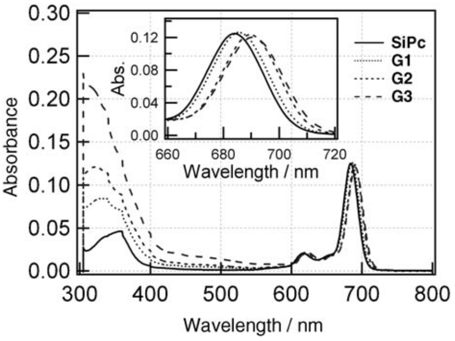


Figure 1. Steady-state absorbance spectra of SiPc–nC$_{60}$ in PhCN. Concentrations: 5×10^{-6} M.

the dendrimers SiPc–nC$_{60}$ show almost the same behavior as in toluene, although an additional red shift of the Q band of 1–2 nm was observed.

Steady-state fluorescence studies: The fundamental photophysical behavior of SiPc–nC$_{60}$ was investigated by using steady-state fluorescence in both toluene and PhCN (Figure 2). The peak maxima of the SiPc emission of SiPc–nC$_{60}$ revealed red shifts relative to the SiPc reference: 691 (**G1**, SiPc—2C$_{60}$), 684 (**G2**, SiPc–4C$_{60}$), and 697 nm (**G3**, SiPc–8C$_{60}$), which correspond to the red shifts of the absorption bands. In SiPc–nC$_{60}$, the SiPc emission bands are quenched by the fullerene subunits by approximately 83–86 % relative to that of the SiPc reference. It was observed that the emission quenching for the SiPc–4C$_{60}$ and SiPc–8C$_{60}$ was slightly higher relative to that of SiPc–2C$_{60}$. These observations suggest efficient quenching of the singlet excited state of the SiPc unit by the appended fullerene moieties, and such quenching increases with increasing the number of C$_{60}$ subunits. It may also be mentioned that the fluorescence peak of the C$_{60}$ unit at 720 nm was hidden by the strong emission that results from the SiPc unit because of the very low fluorescence quantum yield of C$_{60}$ ($\Phi_f = 6.0\times10^{-4}$).[21]

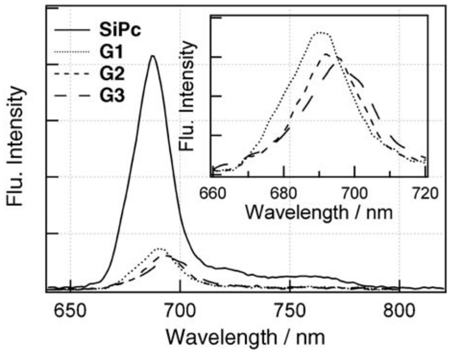


Figure 2. Steady-state fluorescence spectra of SiPc–nC$_{60}$ in toluene. Concentrations: 5×10^{-6} M.

Similar fluorescence spectral changes were observed in PhCN. The overall fluorescence quenching efficiency was increased by 10–20 % on changing the solvent from nonpolar toluene to polar PhCN. From this solvent dependence, we infer efficient electron-transfer quenching of the excited singlet state of the SiPc moiety (^{1}SiPc*) by the surrounding C$_{60}$ moieties.

Time-resolved studies: Time-resolved fluorescence measurements were performed to monitor the charge-separation process. Figure 3 shows the fluorescence decay–time profiles at 690 nm of SiPc—-2C$_{60}$ in toluene and PhCN along with pristine SiPc in toluene. The fluorescence time profile of pristine SiPc exhibited a single exponential decay with a lifetime (τ_{f0}) of 5.0 ns. The lifetimes (τ_f) of the SiPc moiety of SiPc–2C$_{60}$ were evaluated by curve fitting with single exponential functions of 1.79 and 2.08 ns in PhCN and toluene, respectively. Substantially similar fluorescence lifetimes of SiPc–nC$_{60}$ were observed (Table 1). These observations suggest the quenching of ^{1}SiPc* by the appended C$_{60}$ entities. The quenching is likely to occur by the charge-separation process via ^{1}SiPc* generating SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$. From the fluorescence lifetimes of ^{1}SiPc*, the rate constants (k_{CS}) and quantum yields (Φ_{CS}) of the charge-separation process of SiPc–nC$_{60}$ were estimated as listed in Table 1. Although the charge separation via ^{1}C$_{60}$* is energetically feasible, the estimation of both k_{CS} and Φ_{CS} via ^{1}C$_{60}$* is difficult as a result of the weak emission of C$_{60}$, which is hidden under the emission of SiPc.

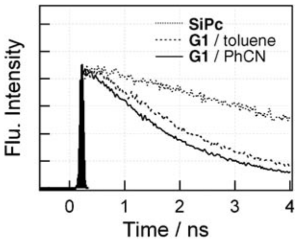


Figure 3. Fluorescence decay profiles of SiPc in toluene and **G1** in PhCN and toluene monitored at 690 nm; $\lambda_{ex} = 400$ nm.

The nanosecond transient studies that aimed to confirm the charge-separated states and follow the charge-recombination process were performed by the excitation of both the SiPc and C$_{60}$ moieties with 355-nm laser light, at which the absorption ratio of SiPc/C$_{60}$ is 80:20 for SiPc–2C$_{60}$; the partition of C$_{60}$ increases with the dendrimer generation. The transient spectra of SiPc–nC$_{60}$ in Ar-saturated PhCN exhibited the absorption bands of the SiPc$^{\bullet+}$ moiety at 740 and 860 nm and the characteristic band of the C$_{60}^{\bullet-}$ moiety at 1020 nm (Figure 4).[22,23] The assignment of the absorption bands for SiPc$^{\bullet+}$ at 740 and 860 nm was confirmed by the transient spectra of a mixture of SiPc and C$_{60}$ in PhCN (see the Supporting information) that exhibited a slow growth in the absorption bands of SiPc$^{\bullet+}$ at 740 and 860 nm and C$_{60}^{\bullet-}$ at 1080 nm,[24] accompanied by decays of the absorption bands of ^{3}SiPc* and ^{3}C$_{60}$* at 500 and 760 nm, respectively. Judging from the energy level of SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$ in

Table 1. Free-energy changes (ΔG_{CR} and ΔG_{CS}), fluorescence lifetimes of ^{1}SiPc* (τ_f), rates (k_{CS}), and quantum yields (Φ_{CS}) of the charge separation, rate of the charge recombination (k_{CR}), and lifetime of the radical ion pairs (τ_{RIP}) of SiPc–nC$_{60}$ in PhCN and toluene.[a]

Compound	Solvent	$-\Delta G_{CR}$ [eV]	$-\Delta G_{CS}$ [eV]	τ_f [ns]	k_{CS} [s^{-1}]	Φ_{CS}	k_{CR} [s^{-1}]	τ_{RIP} [ns]
SiPc–2C$_{60}$ (**G1**)	PhCN	1.48	0.32	1.79	3.6×10^8	0.64	3.0×10^7	33
	toluene	1.70	0.10	2.08	2.8×10^8	0.58	7.0×10^7	13
SiPc–4C$_{60}$ (**G2**)	PhCN	1.46	0.34	2.18	2.7×10^8	0.58	6.7×10^6	149
	toluene	1.72	0.08	2.05	2.8×10^8	0.58	9.6×10^6	104
SiPc–8C$_{60}$ (**G3**)	PhCN	1.44	0.36	2.25	2.4×10^8	0.55	5.0×10^6	200
	toluene	1.74	0.06	1.96	3.1×10^8	0.60	6.3×10^6	160

[a] The driving forces for ΔG_{CR} and ΔG_{CS} were calculated by equations $-\Delta G_{CR}=e(E_{ox}-E_{red})+\Delta G_S$ and $-\Delta G_{CS}=\Delta E_{00}-(-\Delta G_{CR})$, in which ΔE_{00} is the energy of the 0–0 transition (1.80 and 1.76 eV for ^{1}SiPc* and ^{1}C$_{60}$*, respectively) and ΔG_S refers to the static energy. Calculation of this energy was carried by using $-\Delta G_S=e^2/(4\pi\varepsilon_0\varepsilon_R R_{CC})$ in PhCN and $-\Delta G_S=-(e^2/(4\pi\varepsilon_0))((1/(2R_+)+1/(2R_-)-(1/R_{CC})/\varepsilon_S-(1/(2R_+)+1/(2R_-))/\varepsilon_R)$ in toluene,[24] in which R_+ and R_- are radii of the radical cation (7.0 Å) and anion (4.2 Å), respectively; R_{CC} is the center–center distance between C$_{60}$ and SiPc (6.5 Å), which were evaluated from the optimized structure (see the Supporting Information); ε_R and ε_S refer to the solvent dielectric constants for the electrochemical and photophysical measurements, respectively; the k_{CS} and Φ_{CS} values via ^{1}SiPc* were calculated from the relation $k_{CS}=(1/\tau_f)-(1/\tau_{f0})$ and $\Phi_{CS}=k_{CS}/(1/\tau_f)$, in which τ_{f0} is the lifetime of the SiPc reference (5.0 ns).

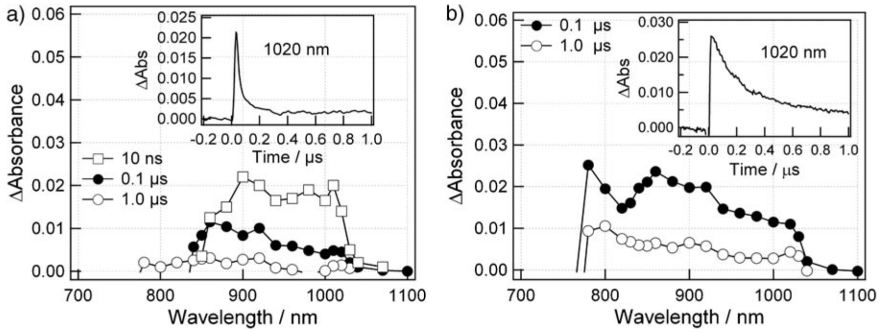


Figure 4. Nanosecond transient spectra of SiPc–2C$_{60}$ (left) and SiPc–8C$_{60}$ (right) in Ar-saturated PhCN; λ_{ex} = 355 nm. Inset: decay profile at 1020 nm.

PhCN, the charge-separation processes via ^{1}SiPc* (and also via ^{1}C$_{60}$*) are possible.

The characteristic band of the C$_{60}^{\bullet-}$ moiety was employed to determine the rate constants of the charge-recombination process (k_{CR}) of SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$, as the time profile of the absorption in the longest wavelength region may not be disturbed by the absorption tails of ^{3}SiPc* and ^{3}C$_{60}$*. In the case of SiPc–2C$_{60}$ (inset of Figure 4a), the decay showed major fast decay followed by the minor slow decay; such slow decay can be attributed to the absorption tails of the triplet states, in which ^{3}SiPc* may be generated through intersystem crossing via ^{1}SiPc* as a fraction of $(1-\Phi_{CS})$ and ^{3}C$_{60}$* after direct excitation. Thus, the fast decay was well fitted by the single-exponential function. Interestingly, in the case of SiPc–8C$_{60}$ (inset of Figure 4b), the decay seems to be fitted with a single exponential. An examination of Table 1 reveals slower k_{CR} with increasing number of C$_{60}$ units; that is, k_{CR}(SiPc–2C$_{60}$) > k_{CR}(SiPc–4C$_{60}$) > k_{CR}(SiPc–8C$_{60}$) (Table 1). From the k_{CR} values, the lifetimes (τ_{RIP}) of SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$ are evaluated as 33 (SiPc–2C$_{60}$), 149 (SiPc–4C$_{60}$), and 200 ns (SiPc–8C$_{60}$). From these findings, the τ_{RIP} value of SiPc–8C$_{60}$ is seven times longer than that of SiPc–2C$_{60}$, thus reflecting the role of dendritic C$_{60}$ subunits on prolonging the lifetime of SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$. Relative to a previously reported fullerene–tin porphyrin–fullerene triad linked by the axial coordination of tin porphyrin (Sn por-(C$_{60}$CHCOO)$_2$),[25] the prolonged lifetimes of the charge-separate state of SiPc–2C$_{60}$ in the present study are notable, which may reflect the effect of the SiPc donor ability and the bond character on increasing the τ_{RIP} value of SiPc–2C$_{60}$. Moreover, the τ_{RIP} values of the studied systems are extremely long relative to the reported axially substituted titanium Pc–C$_{60}$.[26]

In the case of SiPc–2C$_{60}$, as one side of the species is SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$, electron migration is impossible. However, for SiPc–4C$_{60}$ and SiPc–8C$_{60}$, these sides are SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$) and SiPc$^{\bullet+}$–C$_{60}^{\bullet-}$(C$_{60}$)$_3$, respectively; thus, it is possible for an electron to migrate to C$_{60}^{\bullet-}$-(C$_{60}$)$_{n-1}$ among the nearby (C$_{60}$)$_{n-1}$ subunits, thus resulting in such prolongation of the τ_{RIP} values. In separate experiments, the electron migration among the C$_{60}$ moieties of C$_{60}^{\bullet-}$(C$_{60}$)$_{n-1}$ can be supported by observing the steady-state absorption spectra of a solution of SiPc–nC$_{60}$ in tetrakis(dimethylamino)ethylene (TDAE), which is a strong electron donor.[27] For SiPc–2C$_{60}$, a new sharp absorption band appeared at 990 nm that can be clearly assigned to the isolated C$_{60}^{\bullet-}$ species (see the Supporting Information). This sharp absorption is quite similar to that observed in the transient absorption in Figure 4a. With an increasing number of C$_{60}$ subunits, the absorption peak of the C$_{60}^{\bullet-}$ unit generated by reduction with TDAE became broader and more similar to that in Figure 4b, thus reflecting the electron migration between the C$_{60}$ moieties.

The charge-separation process via ^{1}C$_{60}$* was confirmed by observing the nanosecond transient spectra of **G1**–**G3** in benzonitrile by 532-nm laser light (at which the absorption ratio of C$_{60}$/SiPc is 60:40), which shows that the partition of C$_{60}$ increases with the dendrimer generation. The spectra show similar characteristic peaks, as recorded by 355-nm laser light. The τ_{RIP} values were evaluated as 55, 111, and

280 ns for **G1**–**G3**, respectively. These values are almost the same as those obtained via ^{1}SiPc*.

The transient absorption spectra in Ar-saturated toluene (Figure 5) show similar characteristic peaks to those in PhCN. Therefore, the fluorescence quenching can also be mainly attributed to charge separation from ^{1}SiPc* to C_{60}. The k_{CR} and τ_{RIP} values were similarly evaluated as listed in Table 1: 13, 104, and 160 ns (SiPc–2 C_{60}, SiPc–4 C_{60}, and SiPc–8 C_{60}, respectively). Although this order is the same as that in PhCN, each value is shorter than the corresponding one in PhCN, which is not in agreement with the prediction of the Marcus inverted region.[28] This behavior suggests therefore that the direction of the charge recombination in toluene is not the same as that in PhCN; namely, that it is possible that charge recombination directs to the triplet states in toluene but to the ground state in PhCN.

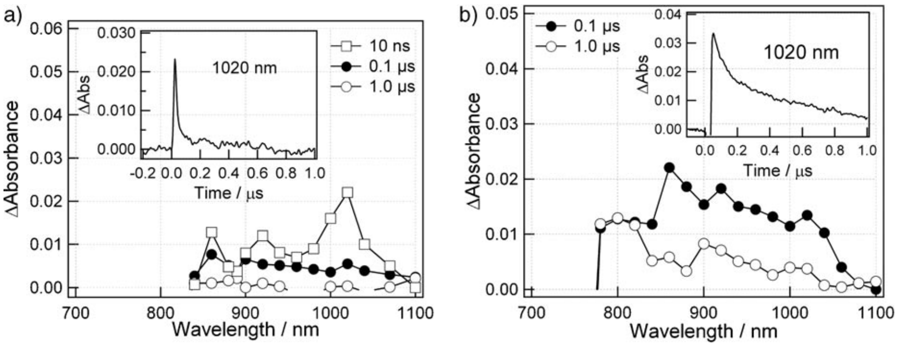


Figure 5. Nanosecond transient spectra of SiPc–2 C_{60} (left) and SiPc–8 C_{60} (right) in Ar-saturated toluene; λ_{ex} = 355 nm. Inset: decay profile at 1020 nm.

Figure 6 shows energy-level diagrams that summarize the observed photoinduced events in the SiPc–n C_{60} species in PhCN and toluene. The fluorescence quenching pathway is mainly through electron transfer from ^{1}SiPc* to the covalently bonded C_{60} entity in both solvents. The charge recombination of $\mathrm{SiPc}^{\bullet+}$–$\mathrm{C}_{60}^{\bullet-}(\mathrm{C}_{60})_{n-1}$ may direct to the ground state of SiPc–$n$$C_{60}$ in PhCN, whereas charge recombination may produce ^{3}SiPc* and $^3C_{60}$* in toluene.

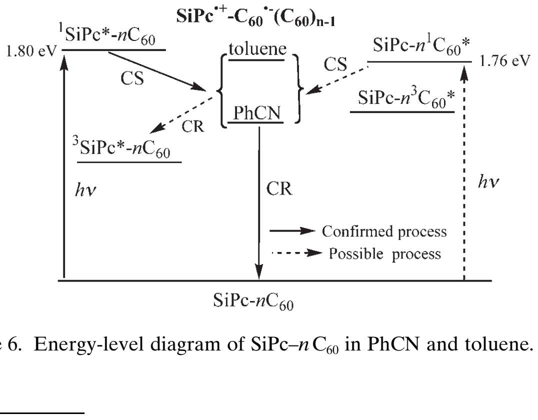


Figure 6. Energy-level diagram of SiPc–n C_{60} in PhCN and toluene.

Conclusion

We have explored a novel strategy to prepare silicon-phthalocyanine-cored fullerodendrimers with up to eight fullerene subunits (SiPc–n C_{60}; n = 2, 4, and 8). The steady-state and time-resolved measurements indicate a charge-separation process from ^{1}SiPc* to the fullerodendrimer moieties in both benzonitrile and toluene. The collected data support that the stabilization of the formed radical ion pairs is achieved for multiple C_{60} subunits on one side of the SiPc moiety, which may be related to the electron migration among the C_{60} subunits. The rates of charge recombination in SiPc–n C_{60} are slower than those of charge separation by about two orders of magnitude, thus suggesting that these SiPc–n C_{60} dendrimers could be useful as components in light-harvesting systems. Furthermore, such the usefulness of SiPc–n C_{60} units as light-harvesting systems, evaluated as a ratio of the rate of charge recombination to that of charge separation, increases markedly with the dendrimer generation.

Experimental Section

Materials and instruments: The reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed using dry glassware in a nitrogen atmosphere. Analytical TLC analysis was carried out on Merck 60 F_{254} silica gel plates and column chromatography was performed on Merck 60 silica gel (230—400 mesh). The melting points were determined on an Electrothemal IA 9000 series melting-point apparatus and were uncorrected. The NMR spectra were recorded on a Varian Mercury 400 (400 MHz) spectrometer with trimethylsilane as the reference signal. The FT-IR spectra were recorded on a Nicolet 550 spectrophotometer with KBr disks. MALDI mass spectra were obtained on a VGAutoSpec spectrometer using ditranol as the matrix.

G1–OH (2): Bis(malonate) **1**[7] (600 mg, 0.72 mmol), I_2 (228 mg, 1.80 mmol), and DBU (0.59 mL, 3.93 mmol) were added to a solution of fullerene (520 mg, 0.72 mmol) in toluene (500 mL). The reaction mixture was stirred at room temperature for 24 h, and the fullerene starting material was eliminated by flash chromatography on silica gel with toluene. The crude product was subjected to chromatography on silica gel with MeOH/$CHCl_3$ (1:50) as the eluant followed by a second chromatographic run on silica gel with THF/hexane (2:5) as the eluant. The fraction collected at R_f = 0.2 was evaporated to give **G1-OH** (0.40 g, 34 %) as a reddish-brown solid. M.p. 190 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (s, 1 H, ArH), 6.70–6.80 (s, 2 H, ArH), 5.80 (d, 2 H, CH_2), 4.40 (t, 4 H, CH_2), 1.70 (m, 4 H, CH_2), 1.30 (m, 60 H, CH_2), 0.90 ppm (t, 6 H, CH_3); IR (KBr): $\tilde{\nu}$ = 3412, 2921, 2851, 1748, 1723, 1450, 1237 cm^{-1}.

G1: K_2CO_3 (15 mg, 0.015 mmol) and **2** (144 mg, 10.093 mmol) in toluene (45 mL) were stirred under nitrogen for 0.5 h. Silicon phthalocyanine dichloride (28 mg, 0.046 mmol) and 18-crown-6 (4 mg, 0.015 mmol) were added to this reaction mixture. The reaction mixture was cooled to room temperature after heating at reflux for 15 h, and the solvent was evaporated. The crude product was subjected to chromatography on silica gel with $CH_3CN/CHCl_3$ (1:45) as the eluant. The fraction collected at $R_f=0.9$ was evaporated to give **G1** (45 mg, 27%) as a green solid. M.p. >353 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.65$ (m, 8H, SiPc ArH), 8.40 (m, 8H, SiPc ArH), 5.85 (s, 2H, ArH), 4.50 (d, 4H, CH_2), 4.15 (t, 8H, CH_2), 3.70 (d, 4H, CH_2), 2.30 (s, 4H,ArH), 1.10–1.60 (m, 128H, CH_2), 0.90 ppm (t, 12H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta=162.37$, 162.03, 149.50, 148.93, 148.27, 147.24, 147.04, 145.78, 145.45, 145.38, 145.35 145.07, 144.92, 144.87, 144.73, 144.31, 144.07, 143.96, 143.90, 143.58, 143.39, 143.31, 142.91, 142.62, 141.84, 140.96, 140.71, 139.46, 136.85, 135.88, 135.17, 135.14, 134.41, 131.32, 123.76, 115.30, 113.91, 70.31, 67.02, 66.72, 65.65, 48.99, 32.05, 29.85, 29.81, 29.75, 29.63, 29.57, 29.51, 29.12, 28.36, 25.78, 22.85, 14.33 ppm; IR (KBr): $\nu=2921$, 2850, 1749, 1596, 1525, 1461, 1234 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}=260$, 330, 352, 615, 656, 684 nm; MS (MALDI-TOF): *m*/*z* 2086.39 [M^+−**G1-OH**-1), 17485.17, 1546.38 (**G1-OH**-1), 1284.11, 1096.08.

Bis(*tert*-butyldimethylsilyl)-5-(*tert*-butyldimethylsiloxy)isophthalate (4): This compound was prepared according to reported procedures[19] in 94% yield. M.p. 38–39 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.27$ (t, 1H, ArH), 7.70 (d, 2H, ArH), 1.03 (s, 18H, CH_3), 0.99 (s, 9H, CH_3), 0.39 (s, 12H, CH_3), 0.23 ppm (s, 6H, CH_3); IR(KBr): $\tilde{\nu}=2956$, 2859, 1708, 1598, 1255 cm^{-1}.

5-(*tert*-Butyldimethylsiloxy)isophthalic acid (5): This compound was prepared according to reported procedures[19] in 89% yield. M.p. 44–46 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=13.37$ (s, 2H, CO_2H), 8.15 (t, 1H, ArH), 7.61 (d, 2H, ArH), 1.01 (s, 9H, CH_3), 0.27 ppm (s, 6H, CH_3); IR (KBr): $\tilde{\nu}=3500$–2500 (CO_2H), 2956, 2859, 1700, 1596, 1282 cm^{-1}.

6: Compound **2** (295 mg, 0.19 mmol), DCC (40 mg, 0.19 mmol), DMAP (24 mg, 0.19 mmol), and HOBT (26 mg, 0.19 mmol) were added to a solution of **5** (29 mg, 0.10 mmol) in $CHCl_3$ (70 mL). The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was evaporated to dryness, and the crude product was subjected to chromatography on silica gel with CH_2Cl_2 as the eluant. The fraction collected at $R_f=0.9$ was evaporated to yield **6** (153 mg, 47%). M.p. 114–117 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.60$ (s, 1H, ArH), 7.90 (s, 2H, ArH), 7.50 (s, 2H, ArH), 7.20 (s, 4H, ArH), 5.81 (d, 4H, CH_2), 5.20 (d, 4H, CH_2), 4.30 (t, 8H, CH_2), 1.20–1.70 (m, 128H, CH_2), 1.10 (s, 9H, CH_3), 0.90 (t, 12H, CH_3), 0.30 ppm (s, 6H, CH_3); IR (KBr): $\tilde{\nu}=2921$, 2850, 1749, 1598, 1461, 1232, 1197 cm^{-1}.

G2-OH (7): An excess amount of HF (50% solution, 2.2 g) was added to a solution of **6** (151 mg, 0.045 mmol) in THF (25 mL), and the reaction mixture was stirred at room temperature for 15 h. The solvent was evaporated and washed with water to eliminate the excess HF. The crude product was subjected to chromatography on silica gel with CH_2Cl_2 as the eluant, and the fraction collected at $R_f=0.5$ was evaporated to afford **G2-OH** (142 mg, 97%) as a black solid. M.p. 107 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.59$ (s, 1H, ArH), 7.90 (s, 2H, ArH), 7.50 (s, 2H, ArH), 7.20 (s, 4H, ArH), 5.80 (d, 4H, CH_2), 5.20 (d, 4H, CH_2), 4.30 (t, 8H, CH_2), 1.10–1.70 (m, 128H, CH_2), 0.90 ppm (t, 12H, CH_3); IR(KBr): $\tilde{\nu}=3434$, 2921, 2850, 1749, 1598, 1461, 1294, 1232, 1201 cm^{-1}.

G2: K_2CO_3 (9 mg, 0.061 mmol) and **7** (190 mg, 0.058 mmol) were stirred in toluene (30 mL) under nitrogen at room temperature for 0.5 h. Silicon phthalocyanine dichloride (16 mg, 0.026 mmol) and [18]crown-6 (3 mg, 0.011 mmol) were added to this reaction mixture. The reaction mixture was cooled to room temperature after heating at reflux for 15 h and filtered. The filtrate was evaporated and the resulting residues were isolated by chromatography on silica gel with $CH_3CN/CHCl_3$ (1:45) as the eluant. The fraction collected at $R_f=0.8$ was evaporated to give **G2** (115 mg, 62%) as a green solid. M.p. >375 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.70$ (m, 8H, SiPc ArH), 8.38 (m, 8H, SiPc ArH), 7.50 (s, 4H, ArH), 7.40 (s, 2H, ArH), 6.70 (s, 8H, ArH), 5.80 (d, 8H, CH_2), 5.20 (d, 8H, CH_2), 4.45 (t, 16H, CH_2), 3.50 (s, 4H, ArH), 1.10–1.80 (m, 256H, CH_2), 0.90 ppm (t, 24H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta=162.68$, 162.56, 149.72, 147.43, 146.07, 145.98, 145.67, 145.66, 145.54, 145.29, 145.13, 145.10 144.95, 144.50, 144.29, 144.19, 144.08, 143.95, 143.73, 143.49, 143.23, 141.24, 140.96, 140.01, 138.02, 137.95, 136.03, 135.75, 135.55, 134.68, 131.95, 128.50, 124.68, 124.02, 120.01, 119.03, 70.99, 67.85, 67.05, 49.79, 32.03, 29.83, 29.78, 29.75, 29.48, 29.34, 26.06, 22.82, 14.29 ppm; IR (KBr): $\tilde{\nu}=2921$, 2850, 1749, 1592, 1461, 1336, 1292, 1234, 1195 cm^{-1} ; UV/Vis ($CHCl_3$): $\lambda_{max}=259$, 318, 354, 618, 657, 689 nm; MS (MALDI-TOF); *m*/*z*: 3781.10 [M^+−**G1-OH**-1), 2087.63, 765.15, 557.11.

8: **G2-OH** (**7**) (228 mg, 0.07 mmol), DCC (15 mg, 0.07 mmol), DMAP (9 mg, 0.07 mmol), and HOBT (10 mg, 0.07 mmol) were added to a solution of **5** (9 mg, 0.03 mmol) in $CHCl_3$ (80 mL). The reaction mixture was stirred at room temperature for 24 h and the insoluble residue filtered. The solvent was evaporated and the crude product was subjected to chromatography on silica gel with ethyl acetate/$CHCl_3$ (1:60) as the eluant. The fraction collected at $R_f=0.9$ was evaporated to give **8** (116 mg, 57%) as a black solid. M.p. 94–97 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.98$ (s, 2H, ArH), 8.70 (s, 1H, ArH), 8.38 (s, 4H, ArH), 7.98 (s, 2H, ArH), 7.50 (s, 4H, ArH), 7.21 (s, 8H, ArH), 5.80 (d, 8H, CH_2), 5.28 (d, 8H, CH_2), 4.40 (t, 16H, CH_2), 1.20–1.80 (m, 256H, CH_2), 1.10 (s, 9H, CH_3), 0.90 (t, 24H, CH_3), 0.30 ppm (s, 6H, CH_3); IR (KBr): $\tilde{\nu}=2921$, 2850, 1749, 1598, 1461, 1292, 1232, 1201 cm^{-1}.

G3-OH (9): An excess of HF (50% solution, 2.2 g) was added to a solution of **8** (116 mg, 0.017 mmol) in THF (25 mL), and the reaction mixture was stirred at room temperature for 15 h. The solvent was evaporated and washed with water to eliminate excess HF. The crude product was subjected to chromatography on silica gel with ethyl acetate/$CHCl_3$ (1:60) as the eluant, and the fraction collected at $R_f=0.5$ was evaporated to yield **9** (61 mg, 54%) as a black solid. M.p. 120 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.98$ (s, 2H, ArH), 8.65 (s, 1H, ArH), 8.39 (s, 4H, ArH), 8.00 (s, 2H, ArH), 7.55 (s, 4H, ArH), 7.21 (s, 8H, ArH), 5.80 (d, 8H, CH_2), 5.25 (d, 8H, CH_2), 4.38 (t, 16H, CH_2), 1.10–1.80 (m, 256H, CH_2), 0.90 ppm (t, 24H, CH_3); IR(KBr): $\tilde{\nu}=3434$, 2919, 2850, 1747, 1598, 1292, 1232, 1201 cm^{-1}.

G3: K_2CO_3 (4 mg, 0.029 mmol) and **9** (127 mg, 0.019 mmol) in toluene (40 mL) were stirred under nitrogen at room temperature for 0.5 h. Silicon phthalocyanine dichloride (4.5 mg, 0.007 mmol) and [18]crown-6 (1 mg, 0.004 mmol) were added to this reaction mixture, which was cooled to room temperature after reflux for 15 h. The insoluble solids were filtered, the filtrate was evaporated, and the crude product was subjected to chromatography on silica gel with $CH_3CN/CHCl_3$ (1:45) as the eluant. The fraction collected at $R_f=0.9$ was evaporated to produce **G3** (25 mg, 25%) as a dark green solid. M.p. >400 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.65$ (m, 8H, SiPc ArH), 8.90 (s, 2H, ArH), 8.35 (m, 8H, SiPc ArH), 7.80 (s, 8H, ArH), 7.55 (s, 8H, ArH), 7.50 (s, 4H, ArH), 7.30 (s, 16H, ArH), 5.75 (d, 16H, CH_2), 5.30 (d, 16H, CH_2), 4.35 (t, 32H, CH_2), 3.60 (s, 4H, ArH), 1.00–1.80 (m, 512H, CH_2), 0.90 ppm (t, 48H, CH_3); ^{13}C NMR($CDCl_3$): $\delta=162.65$, 162.56, 150.25, 149.72, 148.46, 148.18, 147.37, 147.18, 145.95, 145.79, 145.54, 145.15, 144.94, 144.39, 144.19, 143.98, 143.64, 143.33, 143.16, 142.86, 142.10, 141.12, 140.88, 139.74, 138.61, 137.41, 136.06, 135.71, 135.12, 128.46, 124.12, 119.82, 70.68, 67.44, 66.92, 49.33, 45.28, 36.08, 32.03, 30.52, 29.84, 29.73, 29.49, 29.29, 28.63, 26.01, 22.83, 14.30, 6.77, 3.90 ppm; IR (KBr): $\tilde{\nu}=2919$, 2848, 1749, 1598, 1461, 1430, 1292, 1232, 1199 cm^{-1}; UV/Vis ($CHCl_3$): $\lambda_{max}=259$, 319, 356, 364, 619, 658, 690 nm; MS (MALDI-TOF) for $C_{960}H_{682}N_8O_{90}Si$ ($M_r=13797.77$); *m*/*z*: 7169.67 [M^+−**G3-OH**-1], 3780.33, 2086.78, 1096.31.

SiPc (10): K_2CO_3 (52 mg, 0.375 mmol) and **1** (290 mg, 0.35 mmol) were stirred in toluene (45 mL) under nitrogen at room temperature for 0.5 h. Silicon phthalocyanine dichloride (100 mg, 0.163 mmol) and [18]crown-6 (15 mg, 0.0543 mmol) were added to this reaction mixture, which was cooled to room temperature after heating to reflux for 15 h. The insoluble solids were removed by filtration, the filtrate was evaporated, and the crude product was subjected to chromatography on silica gel with $CH_3CN/CHCl_3$ (1:30) as the eluant. The fraction collected at $R_f=0.45$ was evaporated to afford SiPc (70 mg, 20%) as a deep blue solid. M.p. 320 °C (decomp); ^1H NMR (400 MHz, $CDCl_3$): $\delta=9.60$ (m, 8H, SiPc ArH), 8.35 (m, 8H, Si–Pc ArH), 5.65 (s, 2H, ArH), 3.95 (t, 8H, CH_2), 3.80 (s, 8H, CH_2), 3.00 (s, 8H, CH_2), 2.30 (s, 4H, CH_2), 1.00–1.50 (m, 128H, CH_2), 0.85 ppm (t, 12H, CH_3); IR (KBr): $\tilde{\nu}=2917$, 2850, 1781, 1731, 1594, 1469, 1336 cm^{-1} ; UV/Vis ($CHCl_3$): $\lambda_{max}=356$, 613, 653, 683 nm; MS (MALDI-TOF) for $C_{132}H_{186}N_8O_{18}Si$ ($M_r=2201.02$); *m*/*z*: 1370.76 [M^+−**1**—1], 869.38, 809.40.

Electrochemical measurements: The redox values were measured by using the differential pulse voltammetry (DPV) technique with a BAS

CV-50W Voltammetric Analyzer. A platinum disk electrode was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. All measurements were carried out in different solvents containing 0.1 M $(n\mathrm{Bu})_4\mathrm{NClO}_4$ as the supporting electrolyte. Scan rate = 0.1 $\mathrm{V\,s^{-1}}$.

Steady-state optical measurements: Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube with high sensitivity in the 700–800-nm region.

Laser flash photolysis: The picosecond time-resolved fluorescence spectra were measured by a single-photon counting method using a second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physica; Tsunami 3950 L2S, 1.5 ps fwhm (fwhm = full width half maximum) and a streakscope (Hamamatsu Photonics) equipped with a polychromator as the excitation source and detector, respectively. Lifetimes were evaluated with software attached to the equipment. The nanosecond transient absorption measurements in the near-IR region were measured by laser-flash photolysis, and 355-nm and 532-nm light from a Nd:YAG laser (Spectra-Physics and Quanta-Ray GCR-130; 6-ns fwhm) was used as the excitation source. The monitoring lights from a pulsed Xe lamp were detected through a Ge-avalanche photodiode module. The samples were held in a quartz cell (1 × 1 cm) and were deaerated by bubbling argon gas through the solution for 20 min.[29]

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[29] The ^{1}H NMR and ^{13}C NMR spectra of SiPc–nC$_{60}$, MO calculations of SiPc–C$_{60}$, electrochemistry measurements, and transient spectra of **G2** in PhCN and toluene are available in the Supporting Information.

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