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Construction of a Rigid Zn Porphyrin–C_{60} Dyad within Dendritic Structure: Dendrimer Effect on Singlet Energy Transfer

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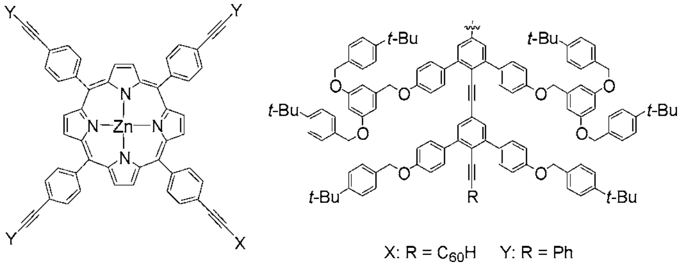
ABSTRACT



A snowflake-shaped Zn porphyrin dendrimer with a C_{60} terminal was prepared. Covalent linkage of the C_{60} unit results in significant quenching of the Zn porphyrin fluorescence mainly due to energy transfer from the Zn porphyrin core to the C_{60} terminal. Comparison of the energy-transfer efficiency with similar dendrons indicates that the dendritic structure considerably delays the energy-transfer rate.

Dendrimers with multiple functional groups have been extensively studied in the past decade because of a variety of promising applications.[1] We recently prepared a snowflake-shaped dendrimer comprising rigid, conjugated chains covered with flexible dendritic branching chains.[2] This arrangement allowed us to assemble various functional groups within the dendritic structure. It should be noted that the conjugated chains not only provide a scaffold for the construction of a well-designed and highly organized assembly but also serve as a mediator in both the electron- and energy-transfer processes.[3] However, it is not clear how the branching side chains and dendritic structure influence the conducting properties of the conjugated chain.[4] We have recently shown that the electron-transfer rate is enhanced by shielding of the conjugated chain with branching chains and also by assembly of the dendrons within the dendrimer.[2b] This unique shielding and dendrimer effect prompted us to construct a similar Zn porphyrin−C_{60} dyad within the dendritic structure (Figure 1). The C_{60} skeleton is a well-known energy and electron acceptor from the singlet excited state of Zn porphyrin.[5] Therefore, the study of Zn porphyrin−C_{60} dyads should provide information about the effect of the dendritic architecture on the energy- and/or electron-transfer processes.[6] Although multiple porphyrin−C_{60} dyads have been

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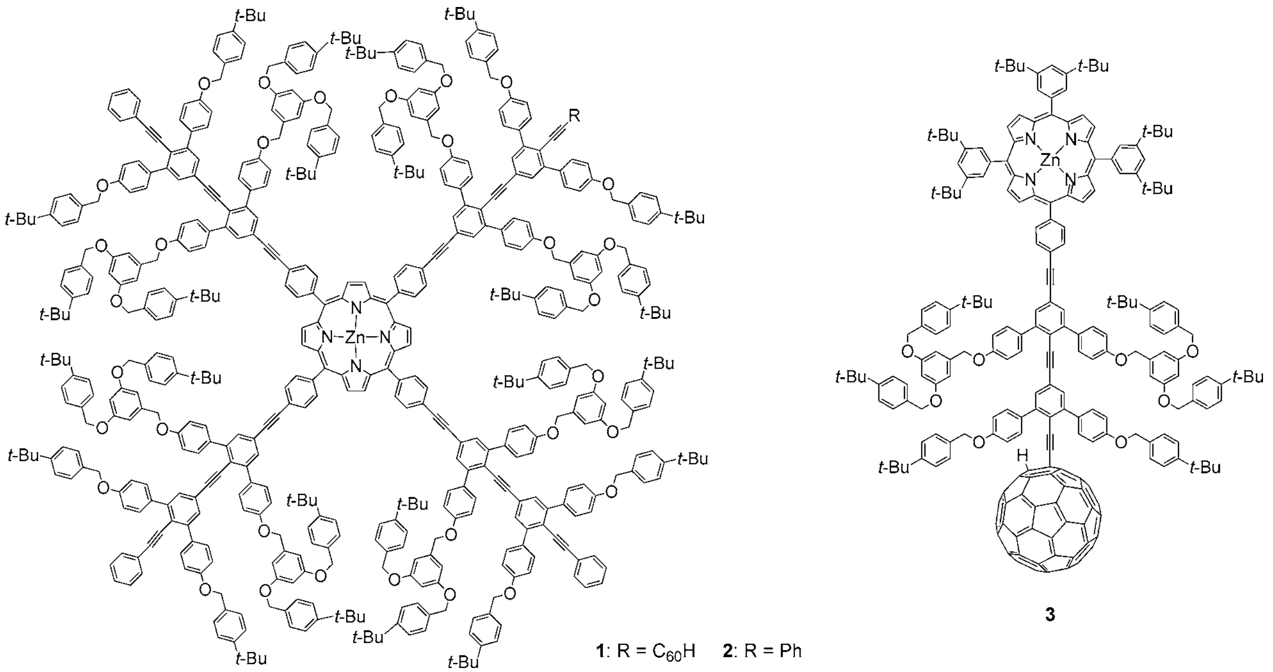

1: R = $C_{60}H$ **2**: R = Ph

3

Figure 1. Chemical structures of dendrimers **1** and **2** and dendron **3**.

successfully constructed at a dendrimer surface,[7] dendrimers containing a porphyrin core linked with a single C_{60} unit are unprecedented.[8] Here we report synthesis of a Zn porphyrin−C_{60} dyad within the snowflake-shaped dendrimer and a significant dendrimer effect, mainly on the singlet energy transfer.

Dendrimer **1** was synthesized according to Scheme 1. First, pyrrole and aldehydes **4**[9] and **5** were condensed under acidic conditions to give A_3B type porphyrin **6** in 10% yield. Porphyrin **6** was separated without any difficulty due to a polar 2-hydroxy-2-propyl group. After the incorporation of Zn metal ion, the selective removal of the 2-hydroxy-2-propyl protecting group in the presence of TMS groups[10] was achieved by refluxing Zn porphyrin **7** in toluene in the presence of sodium hydroxide to give Zn porphyrin **8** in 93% yield. Dendron **10** was obtained in 85% yield by the Sonogashira coupling reaction of Zn porphyrin **8** with TBS (*tert*-butyldimethylsilyl)-terminated dendron **9** that was prepared according to our reported procedure.[2] Removal of the TMS groups followed by the Sonogashira coupling reaction of dendron **11** with phenyl-terminated dendron **14**[11] gave dendrimer **12** in 40% yield (two steps). The TBS group in dendrimer **12** was removed by the treatment of TBAF in THF to afford dendrimer **13** in 84% yield. Finally, dendrimer **1** was obtained by the lithiation of the dendrimer **13** using LHMDS (lithium hexamethyldisilazane) in the presence of C_{60} in THF followed by protonation with TFA.[12] During the treatment of TFA, the Zn porphyrin unit was partially demetalated. The crude product was then heated with zinc acetate in chloroform to afford dendrimer **1** as a purple powder in 38% yield (two steps). Dendron **3** was obtained by a similar method (Scheme S3). Dendrimer **1** was soluble in various organic solvents such as chloroform, dichloromethane, THF, and toluene and unambiguously characterized by means of NMR, elemental analysis, and MALDI-TOF mass spectroscopy. Interestingly, the ^1H NMR spectra of **1** showed broad signals at room temperature probably because of the slow conformational change of the dendritic chain. Sharp well-resolved signals were obtained at 80 °C in tetrachloroethane-d_2.

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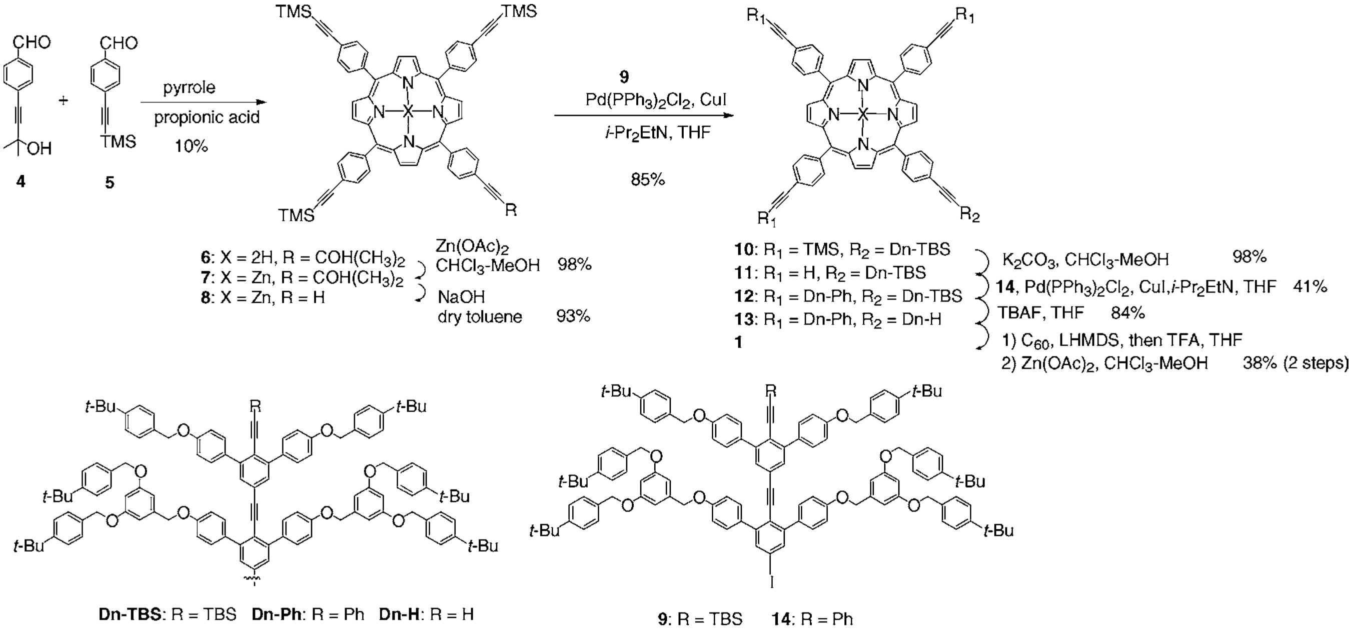
Scheme 1. Synthesis of Dendrimer **1**



The cyclic voltammogram of **1** in 1,2-dichloroethane showed two reversible reduction waves at −1.12 and −1.49 V vs Fc/Fc$^+$, assigned to the successive reduction of the C_{60} terminal (Table 1). The first reduction potential slightly shifts in the negative direction by 0.06 and 0.08 V compared with that of dendron **3** and 1-ethynyl-2-methyl[60]fullerene, respectively.[5c] Although broad oxidation waves were observed for dendrimers **1** and **2**, probably because of the slow electron-transfer rate between the encapsulated Zn porphyrin core and an electrode, dendron **3** showed sharp reversible Zn porphyrin oxidation waves at 0.25 and 0.59 V vs Fc/Fc$^+$ that are comparable to those of tetraphenyl Zn porphyrin (0.30, 0.60 V vs Fc/Fc$^+$). These results indicate that the linkage of the C_{60} unit and the Zn porphyrin core causes negligible electronic perturbation at each chromophore.

Table 1. Redox Potentials (V vs Fc/Fc$^+$) of Dendrimer **1** and Dendron **3**[a]

compd	$E_{1/2}^{\mathrm{Ox2}}$	$E_{1/2}^{\mathrm{Ox1}}$	$E_{1/2}^{\mathrm{Red1}}$	$E_{1/2}^{\mathrm{Red2}}$
1	*b*	*b*	−1.12	−1.49
3	0.59	0.25	−1.06	−1.44

[a] In 1,2-dichloroethane, 0.1 M $(C_4H_9)_4NClO_4$, 100 mV s^{-1}, Pt working electrode, SCE pseudo-reference electrode (Fc/Fc$^+$ = +0.48 V vs SCE). [b] Broad waves.

The UV−vis absorption spectrum of dendrimer **1** in DMF showed characteristic bands for a Zn porphyrin unit (Soret band: $\lambda_{\max} = 435$ nm, Q-bands: $\lambda_{\max} = 564, 606$ nm) along with absorption bands due to the branched benzyl ether (around 285 nm) and conjugated ($\lambda_{\max} = 365$ nm) chains (Figure 2). Although the Zn porphyrin absorption of dendrimer **1** slightly shifts to a longer wavelength region relative to dendron **3**, the dendrimer **2** has absorption identical to that of dendrimer **1**. Neither a significant shift nor a change in the spectral shape was observed. A weak absorption of the C_{60} unit throughout the visible region was not clearly observed because of the spectral overlapping. Overall, these spectral features suggest that there is an insignificant electronic interaction between the Zn porphyrin core and the C_{60} terminal in the ground state for **1** and **3**.

Excitation of the Zn porphyrin core in dendrimer **1** in DMF resulted in a typical Zn porphyrin fluorescence with emission maxima at 615 and 660 nm, as in the case of dendrimer **2**

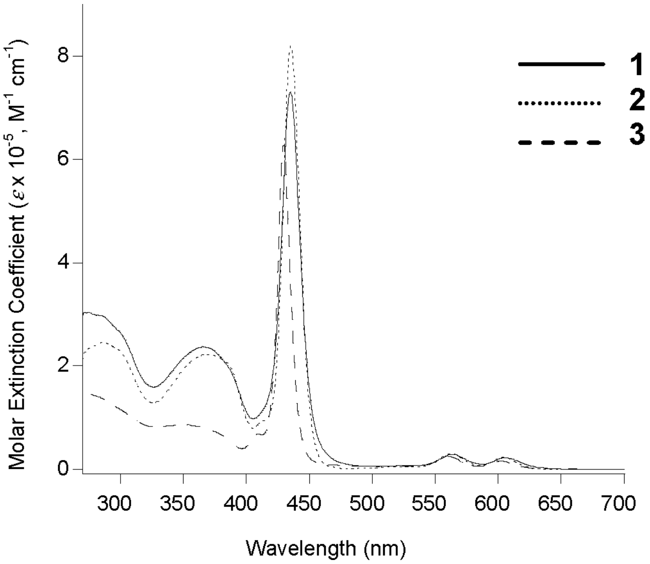


Figure 2. Absorption spectra of **1**, **2**, and **3** in DMF.

Table 2. Photophysical Data of **1**, **2**, and **3** in DMF

compd	λ_{max} Soret band	λ_{max} Q-bands	$\lambda^{em}{}_{max}$	Φ_F
1	435	564, 606	615, 660	0.028
2	436	563, 604	614, 659	0.074
3	430	562, 602	609, 661	0.015

and dendron **3** (Table 2). The fluorescence from the Zn porphyrin core was effectively quenched for dendrimer **1** ($\Phi_F = 0.028$) relative to that of dendrimer **2** ($\Phi_F = 0.074$) as shown in Figure 3, where all the spectra were normalized by the absorbance at the excitation wavelength. No apparent C_{60} emission was detected around 700 nm. In dyads **1** and **3**, both the electron and the singlet energy transfers from the excited Zn porphyrin core to the C_{60} terminal are exothermic processes in DMF ($\Delta G = -1.16$ and -0.33 eV for **1**, respectively).[13] The observed weaker fluorescence for **1** and **3** may reflect both electron- and energy-transfer processes in comparable weight or in one of the processes predominantly. It has been well-established that solvent polarity has strong effects selectively on the electron-transfer process.[14] To differentiate the electron- and energy-transfer processes revealed in the fluorescence intensity, we investigated the solvent effect on the fluorescence intensity. The free energy change in the electron-transfer process was estimated by applying the Weller approximation.[13] Obviously, the free energy values are much more negative in polar solvents: $\Delta G = -0.13$ in 1,4-dioxane ($\epsilon = 2.2$), -0.91 in THF ($\epsilon = 7.6$), and -1.13 eV in benzonitrile ($\epsilon = 26$). However, the efficiency of fluorescence quenching for dendrimer **1** was almost constant for these solvents: 39% quenching ($\Phi_F = 2.3 \times 10^{-2}$) in 1,4-dioxane; 33% quenching ($\Phi_F = 2.3 \times 10^{-2}$) in THF; 39% quenching ($\Phi_F = 3.5 \times 10^{-2}$) in benzonitrile; and 38% ($\Phi_F = 2.8 \times 10^{-2}$) quenching in DMF ($\epsilon = 37$). These results undoubtedly indicate that the major quenching mechanism in dendrimer **1** is not the electron transfer but the energy transfer from the excited Zn porphyrin core to the C_{60} terminal. The poor fluorescence quantum yield of the C_{60} skeleton[5c] and the possible electron-transfer process from the excited C_{60} unit are consistent with no emission from the C_{60} terminal.[15]

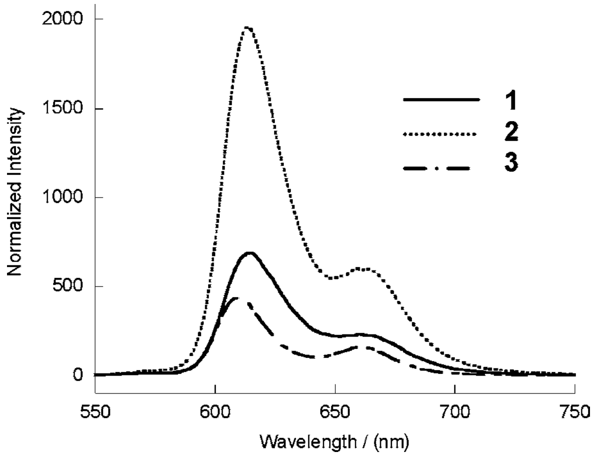


Figure 3. Florescence of **1**, **2**, and **3** in degassed DMF (431 nm excitation). All the spectra were normalized to a constant absorbance at the excitation wavelength.

Interestingly, the intensity of the fluorescence of dendron **3** is several times smaller than that of dendrimer **1** for all solvents ($\Phi_F = 6.5 \times 10^{-3}$ in 1,4-dioxane; 1.1×10^{-2} in THF; 2.3×10^{-2} in benzonitrile; and 1.5×10^{-2} in DMF for **3**). This result suggests that energy transfer from the singlet excited state of the Zn porphyrin core to the C_{60} terminal is somewhat retarded by the dendritic structure.

We have previously clarified that the electron-transfer rate is enhanced by the dendritic structure for the similar Zn porphyrin dendrimer with four anthraquinolyl terminals.[2b] Therefore, the dendrimer architecture effect on energy transfer is in sharp contrast to that of electron transfer. Further photophysical studies involving kinetics using laser flash photolysis of these dendrimers may disclose the detailed mechanism of the dendrimer effect.

In summary, we successfully incorporated a Zn porphyrin$-C_{60}$ dyad within the dendritic assembly by applying the snowflake-shaped dendrimer. The Zn porphyrin fluorescence is quenched in consequence of the covalent linkage of the C_{60} terminal. The intramolecular energy transfer from the excited singlet state of the Zn porphyrin core to the C_{60} terminal was shown to be a major contributing mechanism for the quenching. Comparison of the fluorescence quenching between dendrimer **1** and the model dendron **3** revealed an interesting dendrimer effect, namely, that dendrimer **1** has a lower quenching efficiency in the energy-transfer process than dendron **3** in all the solvents examined.

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Supporting Information Available: Detailed synthetic procedure and NMR, UV−vis−NIR, and emission spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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