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Enhanced Electron Transfer by Dendritic Architecture: Energy Transfer and Electron Transfer in Snowflake-Shaped Zn Porphyrin Dendrimers

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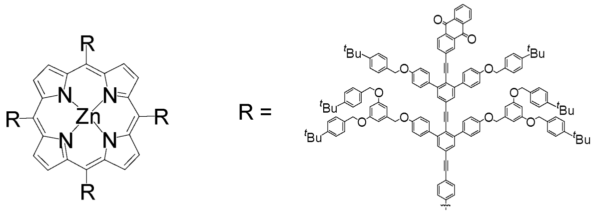
ABSTRACT



Photoinduced electron transfer was observed for the snowflake-shaped dendrimer with the Zn porphyrin core and anthraquinonyl terminals. Comparison of the electron-transfer efficiency of the dendrimer with the linear analogues indicates the advantage of the dendritic structure for the electron-transfer process.

Dendrimers have been extensively studied as promising candidates for a highly effective light-harvesting antenna in artificial photosynthesis.[1] Efficient exothermic energy transfer from branches into a core has been observed in many systems. However, fewer studies have been reported on the electron-transfer processes using harvested photoenergy.[2,3] In most cases, these studies involve dendrimers possessing an electron acceptor at the core and large numbers of electron donors at the peripheral ends of the branching chain or vice versa,[4] so that there are many different distances between electron donors and acceptors that impede the analysis. For this reason, the principle mechanism of how dendritic architecture influences the efficiency of electron transfer has not yet been established.

We have recently prepared a snowflake-shaped dendrimer that has a rigid conjugated oligomer network inside the flexible dendritic structure.[5] Here, we apply this structure to artificial photosynthesis by introducing an electron donor at the core and electron acceptors at the terminals of conjugated chains (Figure 1). This strategy is different from all the

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(1) (a) Newcome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*; VCH: Weinheim, Germany, 2001. (b) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and other Dendritic Polymers*; John Wiley & Sons: New York, 2002. (c) Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines −A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003; p 96.

(2) Some selected papers of dendrimers with light-harvesting properties: (a) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (b) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454. (c) Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895. (d) Kimura, M.; Shiba, T.; Yamazaki, M.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *J. Am. Chem. Soc.* **2001**, *123*, 5636. (e) Choi, M.-S.; Aida, T.; Yamazaki, T.; Yamazaki, I. *Chem.−Eur. J.* **2002**, *8*, 2668.

(3) Some selected papers of photoinduced electron transfer in dendrimers: (a) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978. (b) Rajesh, C. S.; Capitosti, G. J.; Cramer, S. J.; Moodarelli, D. A. *J. Phys. Chem. B* **2001**, *105*, 10175. (c) Capitosti, G. J.; Guerreo, C. D.; Binkley, D. E., Jr.; Rajesh, C. S.; Moodarelli, D. A. *J. Org. Chem.* **2003**, *68*, 247.

(4) For dendrimers with both light-harvesting and charge-separating systems, see: (a) Guldi, D. M.; Swartz, A.; Luo, C.; Gómez, R.; Segura, J. L.; Martín, N. *J. Am. Chem. Soc.* **2002**, *124*, 10875. (b) Qu, J.; Pschirer, N. G.; Liu, D.; Stefan, A.; Schryver, F. C. D.; Müllen, K. *Chem.−Eur. J.* **2004**, *10*, 528. (c) Thomas, K. R. J.; Thompson, A. L.; Sivakumar, A. V.; Bardeen, C. J.; Thayumanavan, S. *J. Am. Chem. Soc.* **2005**, *127*, 373. (d) Schryver, F. C. D.; Vosch, T.; Cotlet, M.; Van der Auwerare, M.; Müllen, K.; Hofkens, J. *Acc. Chem. Res.* **2005**, *38*, 514. (e) Nantalaksakul, A.; Dasari, R. R.; Ahn, T.-S.; Bardeen, C. J.; Thayumanavan, S. *Org. Lett.* **2006**, *8*, 2981.

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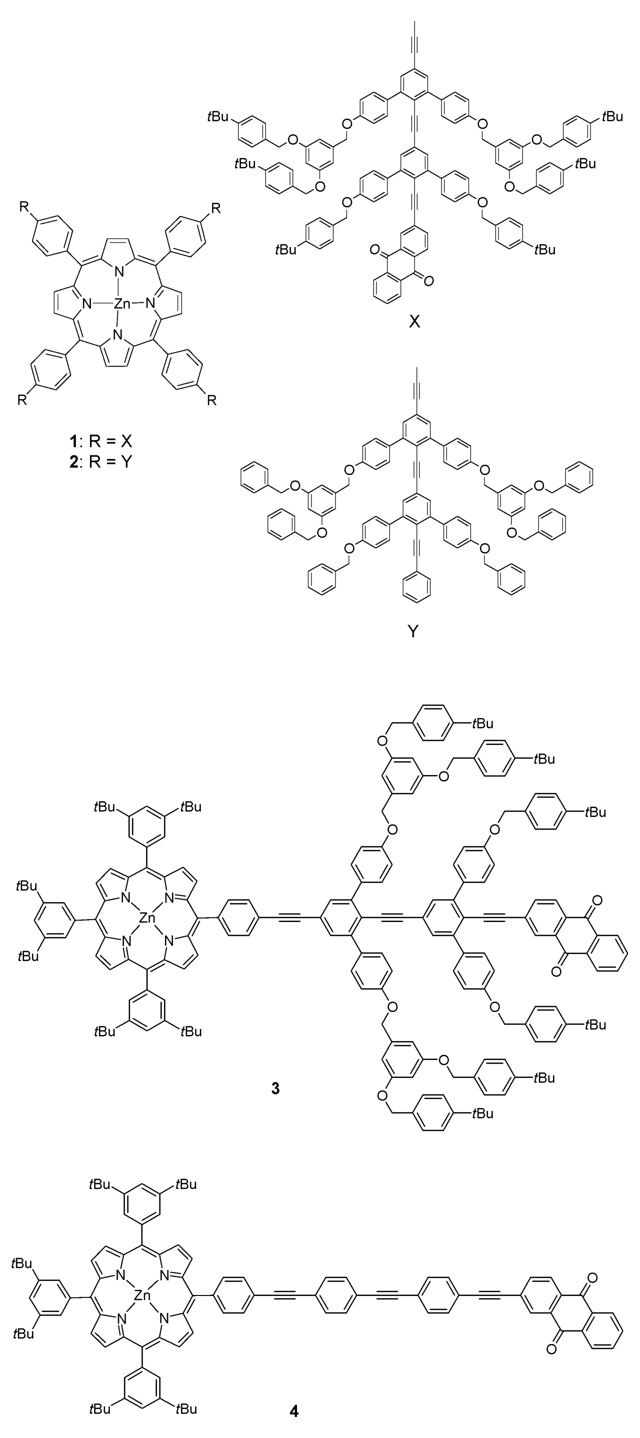
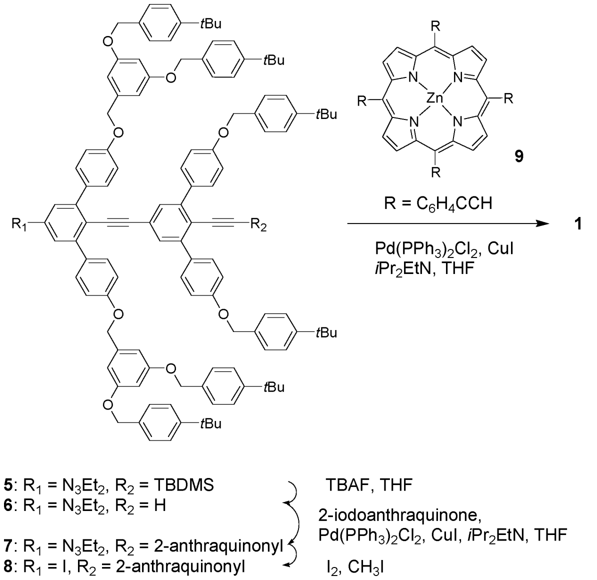


Figure 1. Chemical structures of snowflake-shaped Zn porphyrin dendrimers **1** and **2**, dendron **3**, and dyad **4**.

previous approaches; the advantages of this type of dendrimer are that (1) coupling of the dendritic antenna provides a versatile approach to various donor−acceptor (D−A) systems, (2) the distance between the electron donor and electron acceptors is fixed by the rigid conjugated chain, and (3) because of the symmetrical structure of the dendrimer the efficiency of the electron-transfer process can be directly compared between the dendrimers and their building blocks, providing important information about the relationship between the structures and the efficiency of electron-transfer processes. We report the preparation and photophysical properties of novel snowflake-shaped Zn porphyrin dendrimers **1** and **2** and related compounds **3** and **4** (Figure 1). We demonstrate enhanced electron transfer by dendritic architectures.

Scheme 1. Synthesis of Snowflake-Shaped Zn Porphyrin Dendrimer **1**



Dendrimer **1** was synthesized according to Scheme 1. First, dendron **5** was prepared by a method similar to that reported previously.[5] Dendron **7** was obtained in 78% yield (in two steps) by the removal of TBDMS groups in dendron **5** with TBAF followed by a Sonogashira coupling reaction with 2-iodoanthraquinone.[6] Dendron **7** was heated with iodine in iodomethane to give dendron **8** in 82% yield. A Sonogashira coupling reaction of Zn porphyrin core **9**[7] with dendron **8** afforded the desired dendrimer **1** in 36% yield as a purple powder. Dendrimer **2** was also obtained as a purple powder by a similar method.

Both dendrimers **1** and **2** were 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 ^{1}H NMR spectra of **1** and **2** showed broad signals at room temperature probably because of the slow conformational change of the dendritic chain. Sharp, well-resolved signals were obtained at higher temperature (at 135 °C for **1** and at 85 °C for **2**) in tetrachloroethane-d_2.

The UV−vis absorption spectrum of dendrimer **2** in THF showed characteristic bands for a Zn porphyrin unit (Soret band, $\lambda_{max} = 433$ nm; Q-bands: $\lambda_{max} = 563, 604$ nm) along with absorption bands due to the branched benzyl ether

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[6] Higgins, R. W.; Hilton, C. L.; Deodhar, S. D. *J. Org. Chem.* **1951**, *16*, 1275.

[7] Onisuka, K.; Kitajima, H.; Fujimoto, M.; Iuchi, A.; Takei, F.; Takahashi S. *Chem. Commun.* **2002**, 2576.

chains (λ_{max} = 286 nm) and the conjugated chains (λ_{max} = 372 nm) (Figure 2). The absorption of the porphyrin core exhibited a slight bathochromic shift compared to Zn tetraphenylporphyrin (Zn−TPP). Of particular interest, covalent linkages of the terminal anthraquinone chromophores resulted in slightly shifted and broadened bands [λ_{max} = 431 (Soret); 565, 609 (Q-bands) nm] compared to **2**. Such broadening was negligibly small for **3** and **4**. The shape of the Soret band was independent of the concentration in the range between 2.5×10^{-7} and 2.5×10^{-6} mol dm^{-3}. This result clearly rules out the possibility of the intermolecular aggregate formation (see Supporting Information, Figure S7). These spectral features suggest that there is a weak electronic interaction between the Zn porphyrin core and the four anthraquinone chromophores in the ground state for **1**.[8] The magnitude of the broadening of the absorption bands for **1** was dependent on solvents (THF (fwhm = 30 nm for the Soret band) ~ 1,4-dioxane (37) < DMF (43) ≈ benzonitrile (44)) (see Supporting Information, Figure S8), indicative of a CT-type electronic interaction in the ground state.

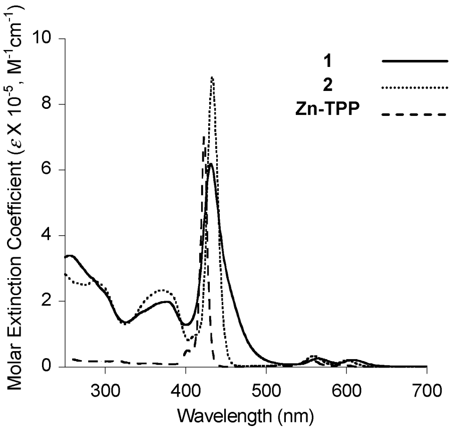

Figure 2. Absorption spectra of dendrimers **1** and **2** and Zn−TPP in THF.

To evaluate the efficiency of energy transfer from the branches (benzyl ether chain or conjugated oligomer) to the core (Zn porphyrin), the fluorescence of dendrimer **2** was studied. Direct excitation of the Zn porphyrin core (433 nm) in degassed THF gave strong fluorescence at 611 and 658 nm due to the Zn porphyrin unit. Sensitized excitation either of the branched benzyl ether chains (286 nm excitation with the quantum efficiency of Φ_F = 0.05) or of the conjugated chains (372 nm with Φ_F = 0.05) resulted in the same fluorescence patterns and efficiencies as direct excitation (Φ_F = 0.05), indicating highly efficient (~100%) intramolecular singlet energy transfer. These results establish that this system has the good light-harvesting property of the snowflake-shaped porphyrin dendrimers. No emission from either branched chains or conjugated chains was detected at all, whereas closely related showflake-shaped dendrimers without a porphyrin core showed strong emission from conjugated chains (Φ_F = 0.50 ~ 0.76).[5]

The fluorescence from the porphyrin core (431 nm excitation) is effectively quenched in the anthraquinone derivatives in polar solvents. Steady-state fluorescence spectra in degassed DMF of **1**−**4** are shown in Figure 3, where the spectra are normalized by the absorbance at the excitation wavelength. Dendrimer **2** revealed the highest intensity. The anthraquinone-linked dendrimer **1** showed the lowest fluorescence intensity, and the quenching efficiency was solvent-dependent [30% quenching (Φ_F = 0.04) in 1,4-dioxane (ϵ = 2.2), 69% quenching (Φ_F = 0.02) in THF (ϵ = 7.6), 90% quenching (Φ_F = 0.007) in benzonitrile (ϵ = 26), 98% (Φ_F = 0.001) quenching in DMF (ϵ = 37)]. Although **2**−**4** have fluorescence spectral shapes quite similar to Zn−TPP, a rather broad emission band was observed for the dendrimer **1** (see Supporting Information, Figures S11−13). The broad emission from **1** reflects the CT-type electronic interaction in the ground state evidenced by the absorption spectrum.

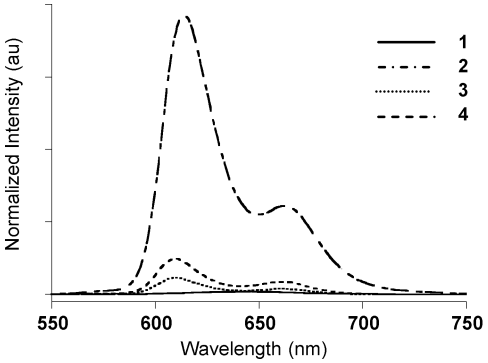

Figure 3. Fluorescence of anthraquinone-linked dendrimer **1**, dendrimer **2**, dendron **3**, and dyad **4** in degassed DMF (431 nm excitation). All the spectra were normalized to a constant absorbance at the excitation wavelength.

The energy transfer from the excited singlet porphyrin to anthraquinone is a highly endothermic process and should not be the origin of this quenching. On the other hand, the electron transfer from the excited singlet state of porphyrin to the anthraquinone is an exothermic process ($\Delta G = -16.5$ kcal mol^{-1}).[9] The fact that the quenching efficiency of **1** is strongly dependent on the solvent polarity also indicates that the electron-transfer mechanism is operative in the quenching process.

Interestingly, dendron **3** has a lower quenching efficiency than the anthraquinone-linked dendrimer **1** but a higher

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(8) A similar spectral feature was reported for some porphyrins with conjugated chains at all meso positions. (a) Yen, W.; Lo, S.; Kuo, M.; Mai, C.; Lee, G.; Peng, S.; Yeh, C. *Org. Lett.* **2006**, *8*, 4239. (b) Li, B.; Li, J.; Fu, Y.; Bo, Z. *J. Am. Chem. Soc.* **2004**, *126*, 3430.

(9) The ΔG value was determined using the Rehn−Weller equation. The dendrimer **1** gave significantly broad redox waves due to the slow electron-transfer rate between the encapsulated porphyrin core and an electrode. Redox potentials of the dendron **3** ($E_{red} = -0.806$ V vs SCE and E_{ox} = 0.744 V vs SCE) in 1,2-dichloroethane were used for the calculation.

quenching efficiency (2.2 times in DMF) than dyad **4**, clearly indicating that (1) the presence of the flexible chain covering the conjugated chain effectively enhances the quenching and (2) the dendrimer structure has higher quenching efficiency (2.6 times) than the dendron structure; as a result, (3) anthraquinone dendrimer **1** has a much higher (5.9 times) quenching ability than the uncovered dyad **4**. The quantum yields of the fluorescence are determined as 7.4×10^{-2} for **2**, 3.7×10^{-3} for **3**, 8.2×10^{-3} for **4**, and 1.4×10^{-3} for **1**. This is the first set of experimental data clearly establishing how the dendrimer architecture is relevant to the electron-transfer process. Importantly, the ratio of quenching efficiency (**3**:**4**) was found to be solvent dependent: the higher the solvent polarity, the higher the quenching efficiency (1.0 (1,4-dioxane), 1.1 (THF), 1.7 (benzonitrile), and 2.2 (DMF)). It is probable that the higher quenching efficiency of **1** may be partly due to this covering effect and also partly due to the CT-type electronic interaction in the ground state probably reflecting the higher number (four) of anthraquinone terminals.

It may be of interest to compare the present results with the recently reported flexible D−A system linked by polymethylene chains (typically $n = 7$, 8) reported by Mallouk and co-workers. They reported that encapsulation of the flexible chain by β-cyclodextrin molecules slows the electron transfer from the excited ruthenium trisbipyridyl to the viologen moiety in sharp contrast to the present study.[10] In their flexible system, the electron transfer may occur at various D−A distances; encapsulation of the chain spacer certainly interrupts short electron-transfer pathways, giving a slower rate of the electron transfer. The present system has a rigid D−A structure, and the electron transfer would occur by a through-bond mechanism at a constant distance. The enhanced electron transfer by covering the conjugated chain with flexible benzyl ether chains may be related to the conformational effect of oligo(phenylene-ethynylene) moieties, where hydrophobic interaction between polybenzyl ether chains favors a planar conformation.[11] This conformational effect leads to different values for the through-bond D−A coupling strength.

In summary, we prepared and characterized novel snowflake-shaped Zn porphyrin dendrimers, where highly efficient (∼100%) intramolecular singlet energy transfer providing a good light-harvesting property is attained. Steady-state fluorescence measurement showed the highly effective quenching for the dendrimer with anthraquinonyl terminals by the electron-transfer mechanism. Comparison of the electron-transfer efficiency of **1** with the linear analogues clearly demonstrates that (1) covering of the conjugated chain enhances the electron transfer in the dendron system and (2) assembly of the dendrons into the dendrimer also enhances the electron transfer partly because of the charge-transfer interaction. The enhanced electron transfer by covering of the conjugated chain is a new important finding that may be general and characteristic to the molecular assembly systems. Further studies involving the kinetics using laser flash photolysis of the present system as well as clarification of the origin of the covering effect for the present and other electron-transfer systems are in progress in our laboratory.

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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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[10] Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.; Mallouk, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 4786.

[11] The prolonged conjugation in the covered dendrons can be supported in the related compounds in polar solvents (see Supporting Information, Figure S9).