

Stepwise construction of a cross-shaped covalent assembly of dendrimers

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Abstract

A methodology for the stepwise construction of shape-persistent assemblies using snowflake-shaped dendrimers as the key modular building blocks was described. The Sonogashira coupling reaction of A_3B -type Zn-porphyrin with A_4 -type free-base porphyrin afforded a cross-shaped covalent assembly. Intramolecular singlet energy transfer from peripheral Zn-porphyrin core to a free-base porphyrin core was observed.

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In past decades, dendrimers have attracted considerable attention as nanoscale molecular materials due to their novel properties and many promising applications.¹ For example, the well-defined three-dimensional structure of dendrimers enable them to act as extremely attractive building blocks for the construction of the molecular-scale devices and machines where a huge number of functional groups are organized in a specific three-dimensional arrangement. Although several studies have been conducted on the assemblies of dendrimers, most of them employ flexible structures and/or isotropic assembling processes.² Therefore, these methods do not meet the criteria for the precise construction of rationally designed nanoscale architectures using dendritic building blocks. We have recently reported snowflake-shaped dendrimers containing rigid linearly conjugated backbones within the dendritic side chains.³ The rigid backbone serves as a scaffold for the construction of a well-designed assembly within the dendritic architecture and as a mediator in both electron- and energy-transfer processes.⁴ In this study, we propose a novel methodology for the stepwise construction of

shape-persistent assemblies using snowflake-shaped dendrimers as the key modular building blocks.

Our assembling method is based on the synthesis of snowflake-shaped dendrimers that possess the prerequisite structures to be extended to the designed structures (Fig. 1).³ Initially, dendrimers with A_4 - and A_3B -type connecting terminals with a flat square-arrangement were designed. These dendrimers could be covalently or non-covalently connected through the connecting terminals to furnish $A_4(A_3B)_4$ -type dendritic assemblies. According to predesigned architectures, the process of binding through the terminal rigid conjugated backbones ensures the formation of the shape-persistent⁵ $A_4(A_3B)_4$. Here, we report the

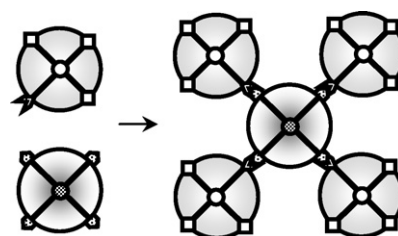


Fig. 1. Schematic representation of the method for the construction of the shape-persistent assembly of snowflake-shaped dendrimers through linkages between outer terminals of conjugated chains; white squares: inactive terminals, arrows: active terminals, black bold rods: conjugated chains.

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preparation of the cross-shaped covalent assembly **1** (Fig. 2) and the singlet energy transfer from a peripheral Zn-porphyrin unit to a central FB (free-base) porphyrin unit.⁶ These porphyrin units have similar structures to the previously reported snowflake-shaped dendrimers³ and served as model compounds of the corresponding dendrimers. Five porphyrin units in assembly **1** were fixed in a cross-shaped arrangement where the center-to-center distance between a central FB and a peripheral Zn-porphyrin is approximately 4.0 nm, as estimated by MM2 calculations.

The first precursor—A₄-type FB porphyrin **2**—was synthesized by the Sonogashira coupling reaction of FB porphyrin **4**⁷ with TBS (*tert*-butyldimethylsilyl)-terminated compound **5** under copper-free conditions⁸ to afford A₄-type porphyrin **6**; this was followed by the removal of the TBS protecting groups to afford **2** in 48% yield in two steps (Scheme 1). The second precursor—A₃B-type Zn-porphyrin **3**—was prepared from Zn-porphyrin **7**^{3c} by the repetition of the cross-coupling reaction and the transformation of the terminal functional groups as outlined in Scheme 2 to afford **3** in an 18% overall yield. The detailed procedures are described in Supplementary data.

The synthesis of **1** was accomplished by the cross-coupling reaction of **2** with **3** in the following manner: **2** was reacted with 4 equiv of **3** under copper-free Sonogashira coupling conditions at 40 °C for 3 days;⁸ this was followed by repeated purification of the crude product by recycling GPC (gel permeation chromatography) to afford **1** as a purple solid in 15% yield. Compound **1** was soluble in various organic solvents such as chloroform, dichloromethane, THF, and toluene. The NMR signals assigned to the β -protons of the pyrrole rings in the FB porphyrin and Zn-porphyrins appeared at δ 8.91 (8 H) and 9.01 ppm (32 H), respectively. The molecular ion peak (MALDI-TOF-MS) was observed at $m/z = 16554$ (Calcd av mass: 16552).

The UV-vis absorption spectrum of **1** in THF showed characteristic bands for the porphyrin units (Soret band: $\lambda_{\max} = 433$ nm; Q-bands: $\lambda_{\max} = 519, 559, 601,$ and 649 nm) along with absorption bands due to the branched benzyl ether chains ($\lambda_{\max} = 291$ nm) and conjugated chains ($\lambda_{\max} = 346$ nm) (Fig. 3). The absorption bands are essentially a superposition of the spectra of the individual dendrimers **15** (Soret band: $\lambda_{\max} = 426$ nm; Q-bands: $\lambda_{\max} =$

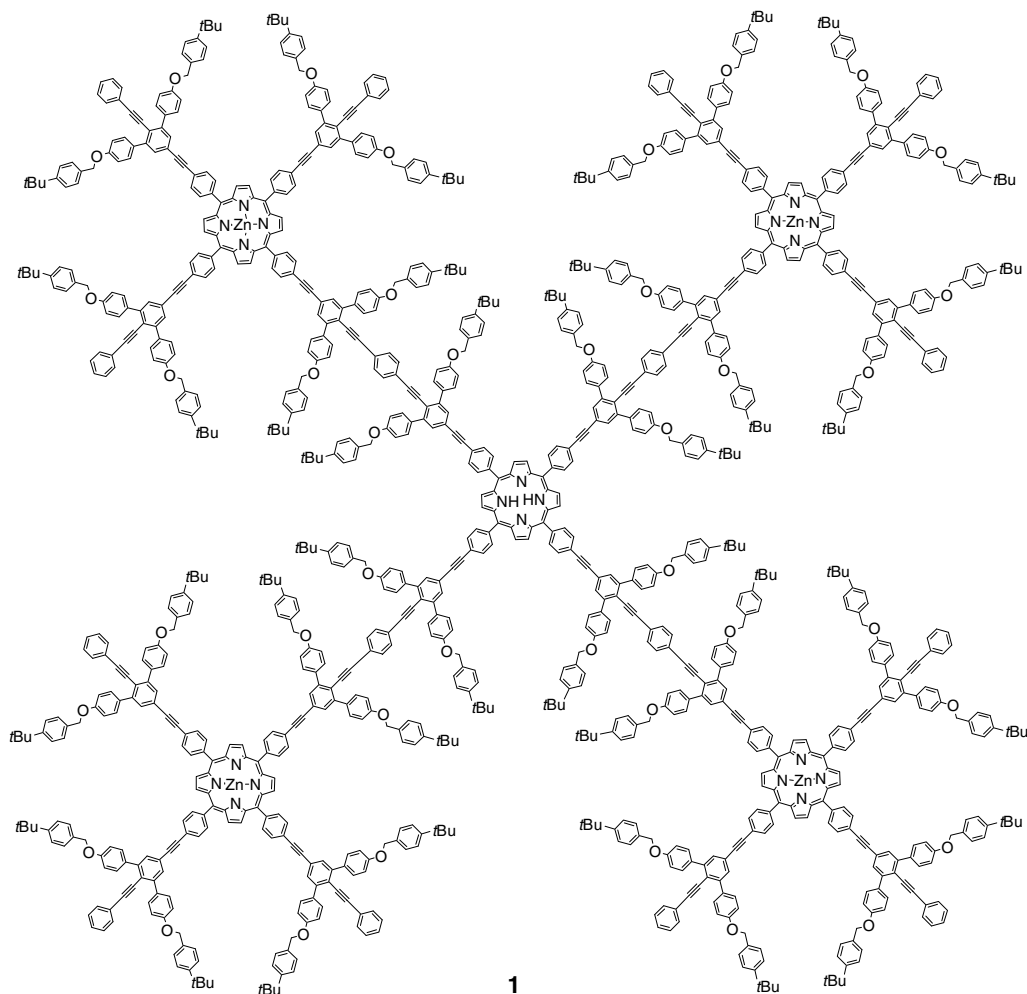
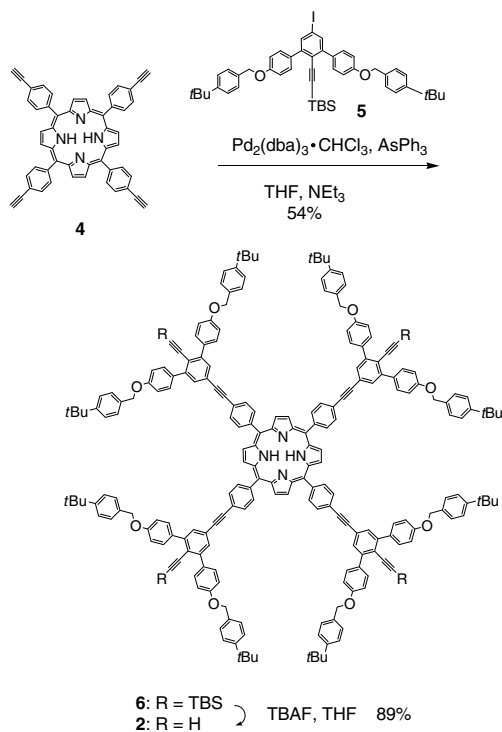
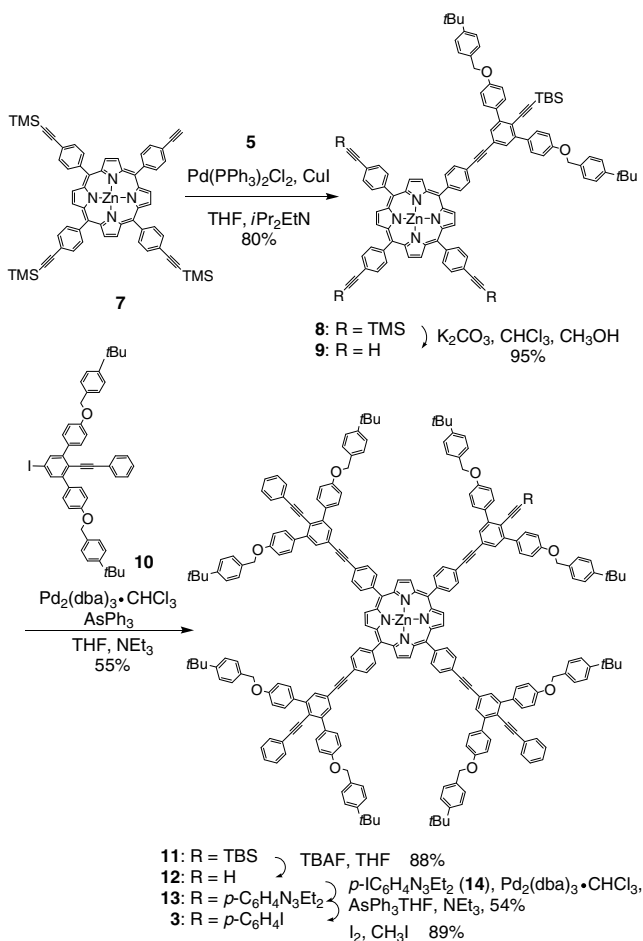
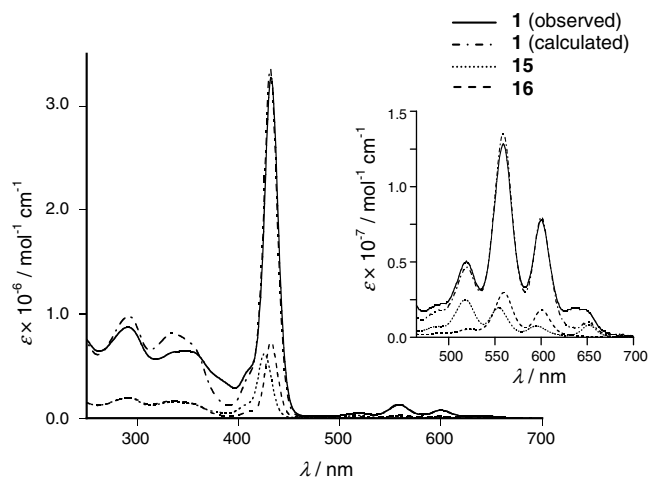
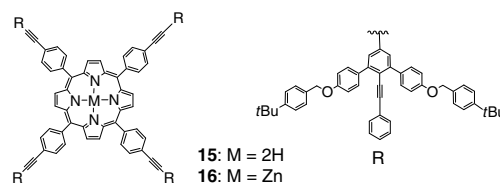


Fig. 2. The chemical structure of cross-shaped covalent assembly **1** (C₁₁₉₆H₉₉₈N₂₀O₄₀Zn₄, MW: 16552). The distance between the terminal phenyl group and the diagonal phenyl group is approximately 12 nm.

Scheme 1. Synthesis of A₄-type FB porphyrin **2**.Scheme 2. Synthesis of A₃B-type FB porphyrin **3**.Fig. 3. Absorption spectra of **1**, **15**, and **16** measured in THF and simulated spectrum for **1** obtained from the absorption spectra of **15** and **16** ($\epsilon_{\text{sim}} = \epsilon_{15} + 4 \times \epsilon_{16}$).

518, 554, 595, and 652 nm) and **16** (Soret band: $\lambda_{\text{max}} = 432$ nm; Q-bands: $\lambda_{\text{max}} = 560$ and 600 nm). In fact, the observed spectrum (molar absorptivity (ϵ) scale) of **1** can be well simulated by the absorption of the components, $\epsilon_{15} + 4 \times \epsilon_{16}$, except for the region 300–400 nm where the conjugated chain shows absorption. These results indicate that there is a negligible electronic interaction between the FB porphyrin core and the peripheral Zn-porphyrin core in the ground state.



To evaluate the efficiency of singlet energy transfer from the peripheral Zn-porphyrin core to the central FB porphyrin core, the fluorescence of **1** was studied in degassed THF (Fig. 4). The quantum yield of fluorescence ($\lambda_{\text{max}}^{\text{em}} = 614, 657, \text{ and } 719$ nm) was determined as $\Phi_f = 0.057$ at the excitation wavelength of 571 nm where light is mainly absorbed by the Zn-porphyrin moieties with the absorption (I) ratio I (FB porphyrin moiety): I (Zn-porphyrin moiety) = 1:10.8, as determined from the molar absorptivity ratio of $\epsilon_{15}:\epsilon_{16} = 1:2.7$ at 571 nm. The observed fluorescence can be simulated as a linear combination of the normalized spectra ($\lambda_{\text{ex}} = 571$ nm) of **15** ($\lambda_{\text{max}}^{\text{em}} = 656$ and 720 nm, $\Phi_f = 0.121$) and **16** ($\lambda_{\text{max}}^{\text{em}} = 611$ and 658 nm, $\Phi_f = 0.040$), indicating that the fluorescence of **1** can be divided into two components with an emission area ratio of 1.57 (FB porphyrin):1 (Zn-porphyrin) (Fig. 4). Therefore, the chromophore-dependent quantum yields in **1** are determined as follows: $\Phi_{f\text{FB}}$ (FB porphyrin units in **1**) = $0.057 \times 1.57/2.57 \times 11.8/1.0 = 0.41$ and $\Phi_{f\text{Zn}}$ (Zn-porphyrin units in **1**) = $0.057 \times 1.0/2.57 \times 11.8/10.8 = 0.024$. $\Phi_{f\text{Zn}}$ (0.024) is smaller than Φ_{f16} (0.040), indicating

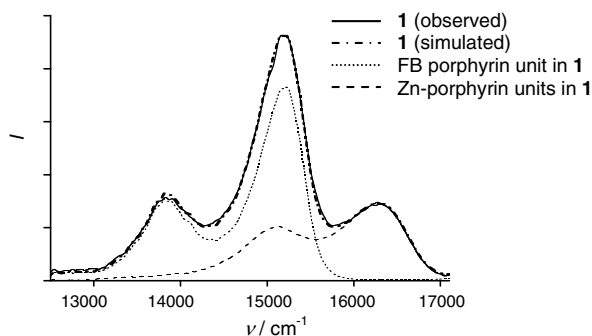
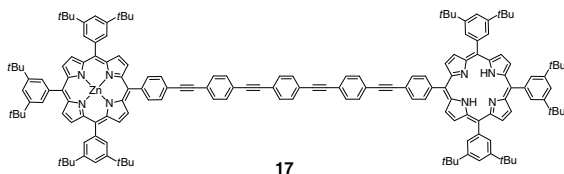


Fig. 4. Fluorescence ($\lambda_{\text{exc}} = 571 \text{ nm}$) spectrum of **1** measured in THF and simulated spectrum for **1** obtained from the normalized spectra of **15** and **16** ($I_{\text{sim}} = 0.28 \times I(\mathbf{15}) + 2 \times I(\mathbf{16})$).

40% quenching in **1**. Φ_{f1FB} (0.41) is 3.4 times higher than Φ_{f15} (0.121); this is consistent with an efficient energy transfer.^{9,10} Energy transfer mechanisms in donor–acceptor systems bridged with oligo(phenylene–ethylene)s have been investigated by both experimental and theoretical methods. These works showed a significant contribution of through-bond interaction to the energy transfer rate that allowed effective long-range energy transfer.^{4d}

Comparison of the efficiency of the energy transfer in **1** with a dyad **17** may clarify the effect of the dendritic structure. The fluorescence spectrum of **17** measured in THF ($\lambda_{\text{max}}^{\text{em}} = 606, 653 \text{ and } 723 \text{ nm}$, $\Phi_{\text{f}} = 0.065$) can be divided into FB porphyrin and Zn–porphyrin components with an emission area ratio of 2.02:1. According to the same procedure as above, the chromophore-dependent quantum yields in **17** are calculated as $\Phi_{\text{f17FB}} = 0.17$ and $\Phi_{\text{f17Zn}} = 0.028$. Φ_{f1Zn} (0.028) indicates 30% quenching of Zn–porphyrin fluorescence in **17**. The energy transfer in **17** is less effective than in **1**. This result showed the dendritic structure of **1** is advantageous for efficient light harvesting.



In summary, we have developed a facile methodology for the stepwise construction of shape-persistent assemblies with rigid conjugated backbones. Snowflake-shaped dendrimers can serve as ‘dendritic atoms’ in the presented assembling process. Namely, each dendrimer has its own valency and directionality for bonding besides individual functionalities. The method was successfully applied for the preparation of cross-shaped covalent assemblies of snowflake-shaped porphyrins. The fluorescence from the Zn–porphyrin cores in **1** was partially quenched due to the energy transfer to the central FB porphyrin core. The efficiency of energy transfer may be improved by the incorporation of a suitable chromophore into a connecting site. Since many snowflake-shaped porphyrins as well as dendri-

mers with varied properties and geometries of the connecting units are accessible, the presented studies provide a powerful tool for the construction of a variety of complex but precisely designed nanoscale architectures.

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Supplementary data

Detailed synthetic procedure and spectral data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.008.

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- At 571 nm excitation, the ratio of the number of excited states of Zn–porphyrin–FB porphyrin = 10.8:1. If all the excited states of Zn–porphyrins are transferred to the FB porphyrin, the number of excited states of FB porphyrin increases by up to 11.8 times after the energy transfer. The observed Φ_{f1FB} (3.4 times Φ_{f15}) corresponds to the energy transfer from 29% of the excited Zn–porphyrin. The efficiency is slightly less than that of observed for 40% quenching of the Zn–porphyrin moiety, thereby suggesting a partial non-emissive quenching in the Zn porphyrin moiety in **1**.