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A Light-Harvesting Array Composed of Porphyrins and Rigid Backbones

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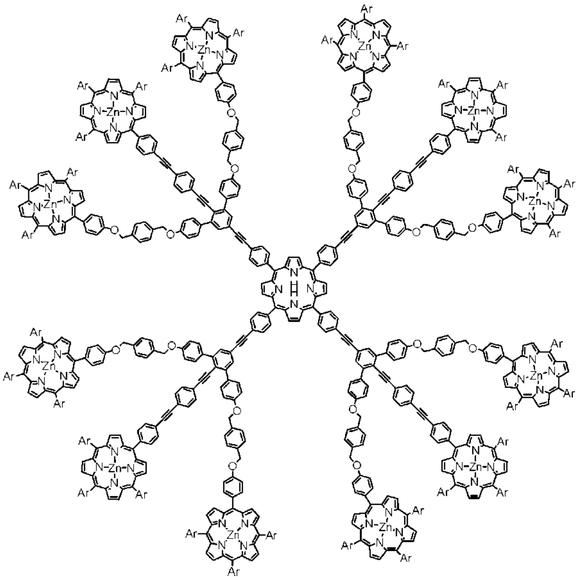
ABSTRACT



A light-harvesting array containing rigid backbones, peripherally positioned Zn-porphyrin terminals, and a free-base (Fb) porphyrin core was prepared by a convergent method where the Sonogashira coupling reaction was used in the key steps. Effective intramolecular singlet-energy transfer from the peripheral Zn-porphyrin units to the Fb porphyrin core was observed. The efficiency of the energy transfer was compared with those of reference compounds.

Many cyclic porphyrin assemblies have been reported as artificial light-harvesting antennae.[1] However, there are few such systems that can be applied to charge-separation to mimic the natural photosynthetic apparatus,[2] probably because of the synthetic difficulty of introducing antennae and charge separation moieties selectively in a system. Recently, we reported a unique convergent method for the synthesis of dendrimers having rigid backbones.[3] This architecture is useful for the construction of a well-defined charge-separating system inside a dendritic structure. The rigid backbone serves not only as a scaffold for the construction of a well-defined functional array but also as a conductive path in electron

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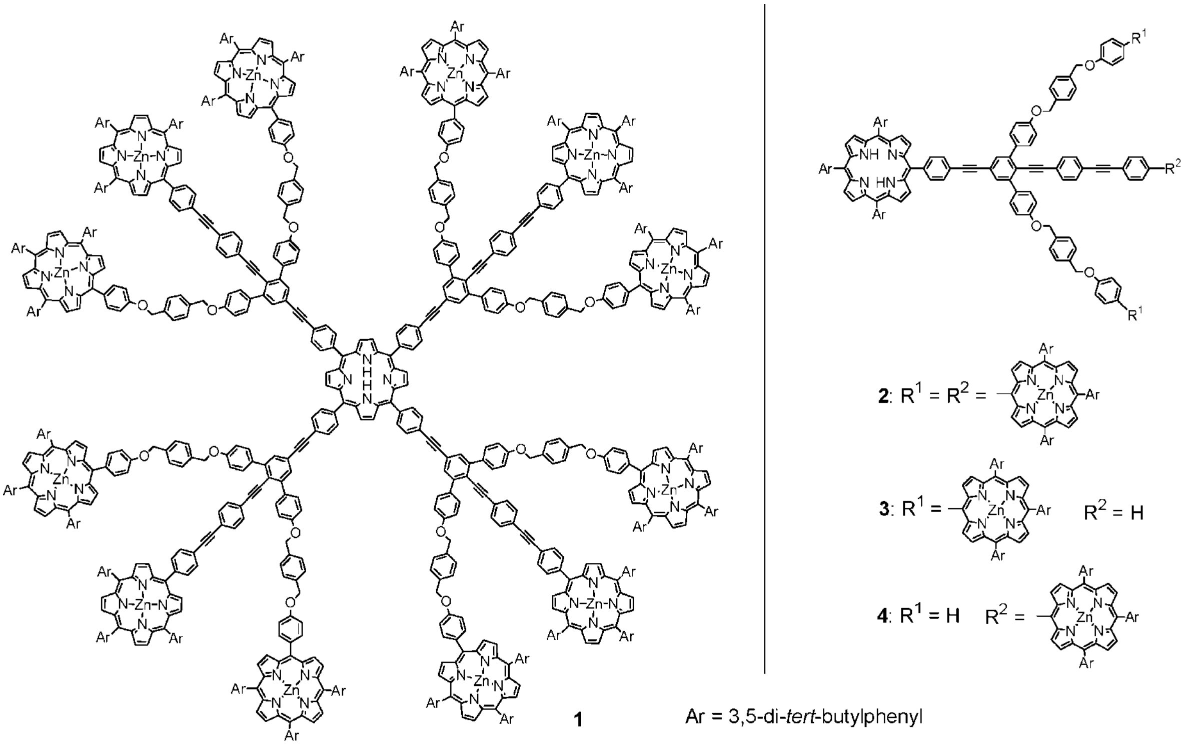
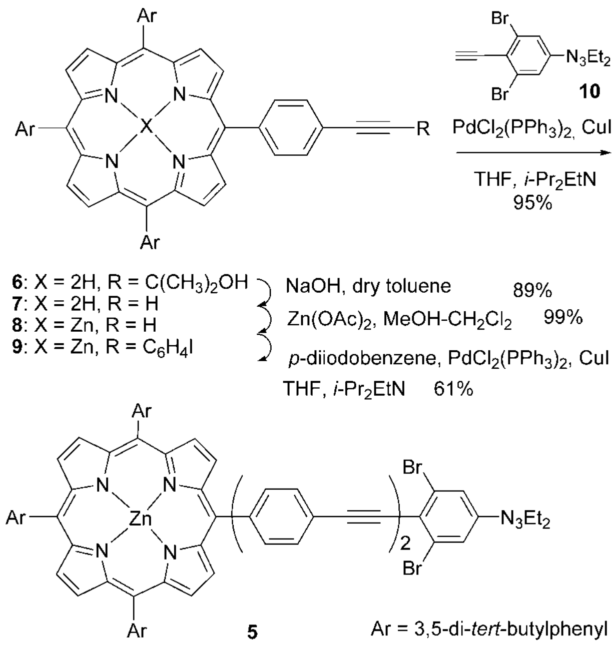


Figure 1. Chemical structures of a light-harvesting array **1** and reference compounds **2**−**4**.

transfer. Moreover, we have shown that these dendritic molecules with the rigid backbone are valuable building blocks for higher-ordered nanoscaled dendrimer assemblies.[4] Here, we applied this method for the preparation of a light-harvesting array **1** containing peripherally positioned Zn-porphyrin terminals, a free-base (Fb) porphyrin core, and rigid backbones. The abovementioned advantages of this architecture make **1** a highly attractive light-harvesting antenna. For elucidation of the effect of conjugated chains, the efficiency of the energy transfer in **1** was compared with those of reference compounds **2**−**4** (Figure 1).

A conjugated rigid chain **5** with a Zn-porphyrin unit on one terminal was synthesized from AB_3 type Fb porphyrin **6**, as shown in Scheme 1. Deprotection of the acetylenic unit in **6** under basic conditions followed by complexation with Zn metal afforded Zn porphyrin **8**[5] in 88% yield (2 steps). The extension of the conjugated chain was achieved by repetitively carrying out the Sonogashira coupling reaction of **8** to produce **5** in 58% yield (2 steps). A flexible chain **11** with a pinacol borate unit on one terminal and a Zn-porphyrin unit on the other terminal was obtained from 1,4-bis(bromomethyl)benzene (**12**), as shown in Scheme 2. The stepwise condensation of **12** first with pinacol arylborate **13** and then with Zn porphyrin **15**[6] afforded the flexible chain **11** in 51% yield (2 steps).

Scheme 1. Preparation of the Conjugated Chain



The Suzuki−Miyaura coupling reaction of the main chain **5** with the flexible chain **11** was carried out using cesium carbonate as a base to afford **16**in 82% yield.[7] The triazene

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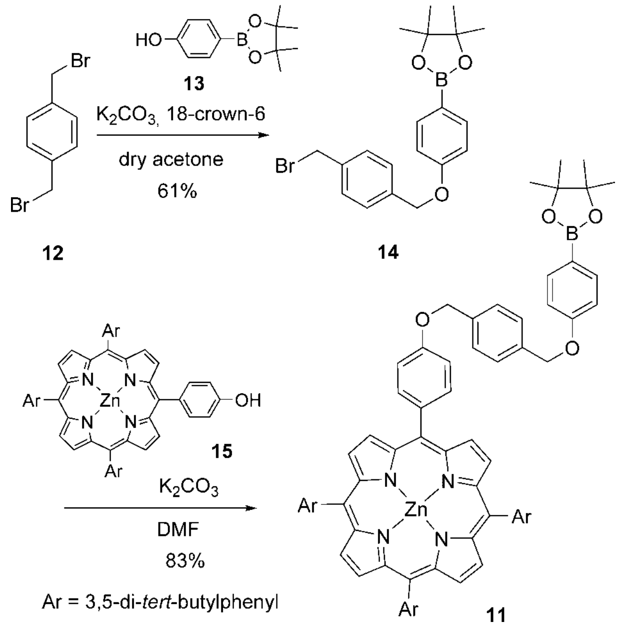
Scheme 2. Preparation of the Flexible Chain

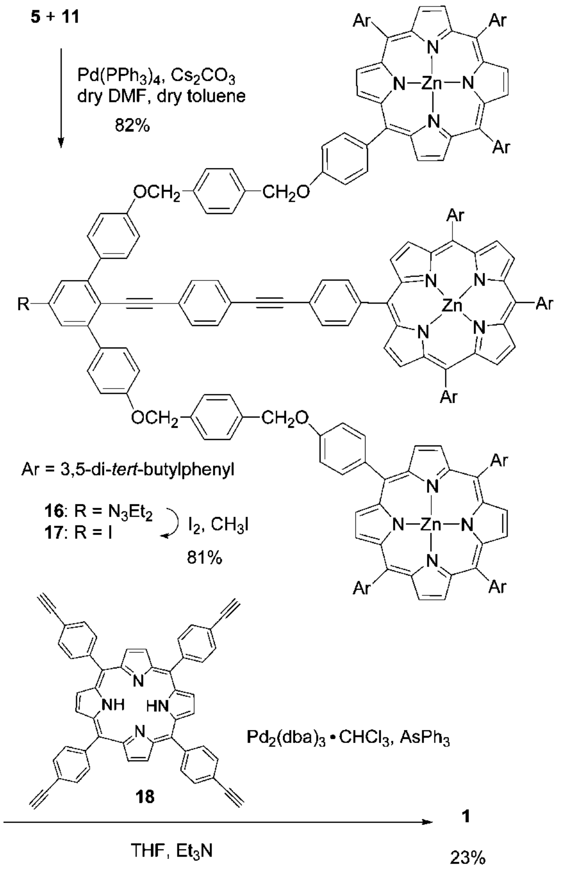


group in **16** was converted to an iodide group by heating with iodine in iodomethane (Scheme 3). Finally, a copper-free Sonogashira coupling reaction[8] of **17** with **18**[9] at 40 °C for 15 h, followed by a repeated purification of the crude product by recycling gel permeation chromatography (GPC) afforded **1** as a purple solid in 23% yield. The light-harvesting array **1** was soluble in various organic solvents such as hexane, dichloromethane, THF, and toluene and could be unambiguously characterized by NMR and MALDI-TOF mass spectroscopy.

The UV−vis absorption spectrum of **1** in THF showed characteristic bands for both the Fb and Zn-porphyrin units (Soret band: λ_{max} = 426 nm (log ε = 6.90); Q-bands: λ_{max} = 518, 557, 596, and 650 nm) along with absorption bands due to the conjugated chains (λ_{max} = 346 nm) (Figure 2). The absorption bands of **1** are essentially superimposed on the spectra of components **17** (Soret band: λ_{max} = 425 nm; Q-bands: λ_{max} = 595 and 557 nm) and **19**[4] (Soret band: λ_{max} = 426 nm; Q-bands: λ_{max} = 518, 554, 595, and 652 nm). In fact, the observed spectrum (molar absorptivity (ε) scale) of **1** can be effectively simulated by the absorption of the components, $4 \times \varepsilon_{17} + \varepsilon_{19}$. These results indicate that there is a weak electronic interaction between the Fb porphyrin core and the peripheral Zn-porphyrin units in the ground state.

To evaluate the efficiency of the singlet-energy transfer from the peripheral Zn-porphyrin unit to the Fb porphyrin core, the fluorescence of **1** was measured in degassed THF (Figure 3). The quantum yield of fluorescence (λ^{em}_{max} =

Scheme 3. Preparation of the Light-Harvesting Array



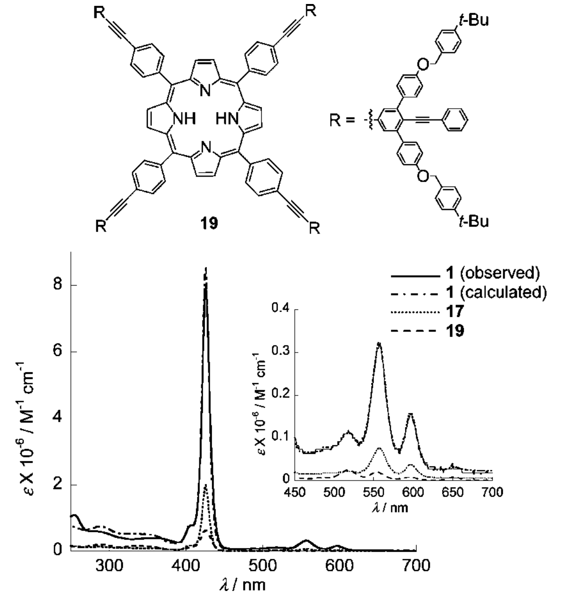


Figure 2. Absorption spectra of **1**, **17**, and **19** measured in THF and simulated spectrum for **1** obtained from the absorption spectra of **17** and **19** ($\varepsilon_{sim} = 4 \times \varepsilon_{17} + \varepsilon_{19}$).

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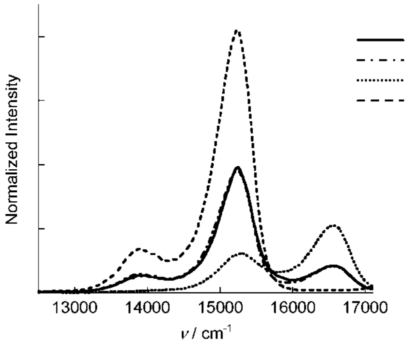

Figure 3. Fluorescence spectra of **1**, **17**, and **19** measured in THF and simulated spectrum for **1** obtained from the normalized spectra of **17** and **19** ($I_{\text{sim}} = 0.38 \times I_{17} + 0.41 \times I_{19}$ with an area ratio of S_{19}:S_{17} = 2.73:1).

604, 656, and 717 nm) was determined to be $\phi_{\text{f}} = 0.077$ at an excitation wavelength of 557 nm, where the light was mainly absorbed by Zn-porphyrin moieties with the absorption (I) ratio, $I_{\text{Zn-porphyrin moiety}}$:$I_{\text{Fb porphyrin moiety}}$ = 16.2:1, as determined from the molar absorptivity ratio of $\varepsilon_{\mathbf{17}}$:$\varepsilon_{\mathbf{19}}$ = 4.05:1 at 557 nm. The observed fluorescence can be effectively simulated as a linear combination of the normalized spectra of **17** ($\lambda^{\text{em}}_{\text{max}}$ = 604 and 653 nm, $\phi_{\text{f17}} = 0.050$) and **19** ($\lambda^{\text{em}}_{\text{max}}$ = 656 and 720 nm, $\phi_{\text{f19}} = 0.121$), indicating that the fluorescence of **1** can be divided into two components with an emission area ratio of 2.73 (Fb porphyrin):1 (Zn-porphyrin) (Figure 3). Thus, the emission quantum yields were determined to be $\phi_{\text{f1Fb}} = 0.077 \times 2.73/3.73 = 0.056$ and $\phi_{\text{f1Zn}} = 0.077 \times 1.0/3.73 = 0.021$ for emissions from the Fb porphyrin and Zn-porphyrin chromophores in **1**, respectively. These values can be compared to the calculated quantum yields without energy transfer, $\phi_{\text{f1Fb}}(0\%\text{ET})_{\text{calc}}$ and $\phi_{\text{f1Zn}}(0\%\text{ET})_{\text{calc}}$ estimated from ϕ_{f17}, ϕ_{f19}, and the absorption fraction ratio (16.2:1) at 557 nm in **1**; $\phi_{\text{f1Fb}}(0\%\text{ET})_{\text{calc}} = \phi_{\text{f19}}(0.121) \times 1.0/17.2 = 0.0070$ and $\phi_{\text{f1Zn}}(0\%\text{ET})_{\text{calc}} = \phi_{\text{f17}}(0.050) \times 16.2/17.2 = 0.047$. The comparison of ϕ_{f1Zn} (0.021) with $\phi_{\text{f1Zn}}(0\%\text{ET})_{\text{calc}}$ (0.047) suggests 55% quenching due to the singlet-energy transfer from Zn-porphyrin to Fb porphyrin chromophores in **1**. The degree of amplification of the Fb porphyrin emission is estimated as follows. Assuming that α% of the excited Zn-porphyrin is converted to the excited Fb porphyrin, the quantum yield $\phi_{\text{f1Fb}}(\alpha\%\text{ET})_{\text{calc}}$ is estimated as $\phi_{\text{f19}}(0.121) \times [1 + 16.2 \times (\alpha/100)]/17.2$. The observed ϕ_{f1Fb} (0.056) can be reproduced by using a quenching efficiency value of α = 43. The small value of the quenching efficiency (α = 43) as compared to 57% quenching, estimated from the intensity of the Zn-porphyrin chromophore, may be ascribed to the partial deactivation of the excited state of the Zn-porphyrin chromophore before energy transfer to Fb porphyrin within **1**.

The efficiency of the energy transfer in **1** was compared to those in reference compounds **2**−**4**. The fluorescence spectra of **2**−**4** were measured in THF, and the quantum yields of Zn-porphyrin emission were determined as described above: $\phi_{\text{f2Zn}} = 0.016$, $\phi_{\text{f3Zn}} = 0.011$, and $\phi_{\text{f4Zn}} = 0013$. The degree of quenching of Zn-porphyrin fluorescence was estimated as 53% (**2**), 41% (**3**), and 45% (**4**) by comparison with the fluorescence quantum yields of appropriate reference compounds (see Supporting Information). Compound **2**, which is a quarter of the cyclic assembly, has a quenching efficiency comparable to that of **1**, indicating that each wedge unit plays an independent role in the energy transfer. The wedge **4** showed a quenching efficiency modestly higher than that of **3**, indicating the limited effect of the conjugated chain on the energy transfer efficiency, probably due to a small electronic coupling between the bridging chain and the Zn-porphyrin terminal. Interestingly, the light-harvesting array **1** as well as the wedge **2** have quenching efficiencies higher than those of wedge **3** and **4**. These results indicate a certain level of cooperative effect of Zn-porphyrin units in **1** and **2** that is advantageous for effective light harvesting.

In conclusion, we prepared a light-harvesting array containing the Fb porphyrin core, Zn-porphyrin terminals, and the rigid backbones. Effective singlet-energy transfer was observed from the peripheral Zn-porphyrin units to the Fb porphyrin core. Thus, this array was shown to be an important building block for the construction of a biomimicking light-harvesting system. The construction of such a light-harvesting system is currently under progress in our laboratory.

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Supporting Information Available: Detailed synthetic procedure and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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