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Construction of Snowflake-Shaped Dendritic Covalent Assemblies with Rigid Conjugated Networks

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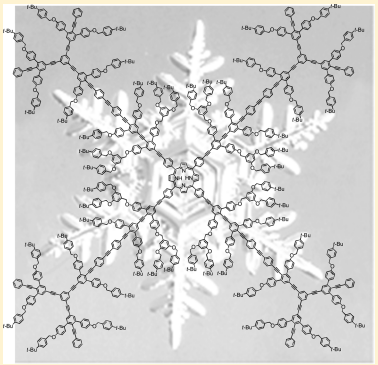
Supporting Information

ABSTRACT: A convergent method for the construction of shape-persistent nanoscale assemblies with conjugated backbones was developed. The copper-free Sonogashira coupling reaction was successfully applied to the formation of multiple covalent connections between conjugated terminals (iodide substituted aryl groups) of AB_2-type outer components and four conjugated terminals (acetylenic bonds) of an inner A_4-type core dendrimer. The conjugated networks in the starting components are expanded during the assembly process to afford nanoscale dendritic conjugated networks of the type $A_4(AB_2)_4$, which have a porphyrin core, and longer (3.9 or 4.5 nm) and shorter (1.6 nm) conjugated chains. Fluorescence measurements revealed that singlet energy is effectively transferred in the assemblies from peripheral benzyl ether units and conjugated chains to the free base porphyrin core.



INTRODUCTION

Organic synthesis is a versatile and reliable bottom-up method for building well-defined and highly sophisticated nanoscale architectures.[1] Dendrimers are one of the most attractive nanoscale macromolecular architectures because of their well-defined molecular size, shape, and arrangement of functional groups.[2] Therefore, the dendrimer architecture is often found in a variety of molecular devices and machines such as artificial photosynthetic systems,[3,4] bioinspired catalysts,[5] and molecular capsules.[6] In addition, dendrimers have been recognized as attractive modular building blocks for the construction of much larger and more complicated molecular systems where large numbers of specifically integrated molecular devices work cooperatively and synergistically to perform advanced functions.[7] Previously, Tomalia et al. reported covalent assemblies of polyamidoamine (PAMAM)-type dendrimers called "core-shell tecto(dendrimers)" in which several smaller dendrimers are covalently attached to the surface of a larger core dendrimer.[7a,b] Although higher molecular weight products were obtained by self-assembly and subsequent covalent bond formations, it is difficult to use this architecture as a scaffold for the construction of organized molecular systems, owing to the structural flexibility of PAMAM-type dendrimers and the wide size diversity of products. We have recently reported dendrimers containing rigid conjugated backbones within the dendritic side chains.[8,9] The rigid backbone serves as a scaffold for the construction of a well-designed assembly within the dendritic architecture and also serves as a mediator of both electron- and energy-transfer processes.[10] These advantages of dendritic architectures with conjugated backbones prompted us to develop a novel methodology for the construction of a larger covalent dendritic assembly with conjugated backbones using dendrimers as the key modular building blocks. In our preliminary report, we disclosed a method for the synthesis of a large dendritic porphyrin assembly (Scheme 1).[11] Although this method is undoubtedly effective for the synthesis of an $A_4(AB_3)_4$-type dendritic assembly, the yield (15%) could not be improved in spite of examination of various coupling conditions.

According to our experience, such low chemical yields are frequently encountered and are problematic in the preparation of larger sized dendrimers; poor yields may originate from poor encounter-probability and also steric interference between the two cross-coupling components. Therefore, it is quite important to develop a new general methodology which can be applied to the synthesis of larger dendrimers in good yields. We realized that the issue of poor yield can be improved by converting the couplers to "naked" couplers by extending the coupling terminals of the iodophenyl or acetylenic moieties or both. However, extension of the acetylenic moieties may facilitate not only cross-coupling but also dimerization.[12] For this reason, we examined the extension of the ethynylenephenylene iodide moiety, and using this substrate, we were able to prepare large dendritic assembly **1** in moderate yield (52%). Furthermore, we successfully prepared much larger dendritic assembly **2** in 17% yield. Assembly **2** has a square form with a diagonal distance of approximately 11 nm (Figure 1).[13] In this paper, we report the synthesis and photophysical properties of large dendritic assemblies **1** and **2**.

RESULTS AND DISCUSSION

Synthesis. First, we prepared relatively smaller $A_4(AB_2)_4$-type assembly **1** in order to optimize both the coupling

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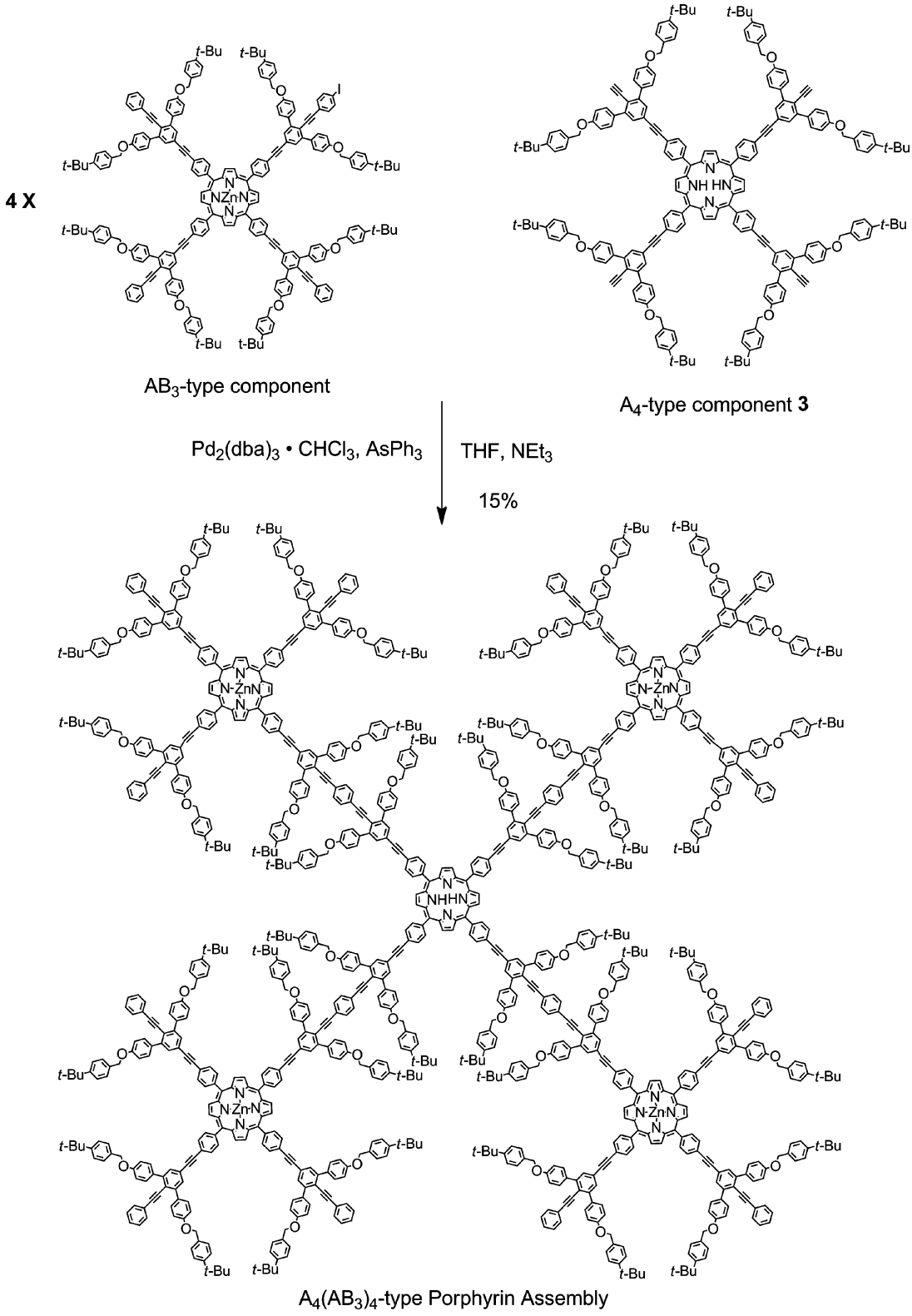
Scheme 1. Construction of a $A_4(AB_3)_4$-Type Covalent Dendritic Assembly with Conjugated Backbones



conditions and the molecular structures around the reactive sites in the starting dendritic compounds. Suitable starting materials for the construction of assembly **1** should be A_4-type core **3** and AB_2-type arm **4** (Scheme 2). A_4-type core **3** has a porphyrin center and four conjugated chains terminated by "shielded" ethynyl couplers that are embedded between 4-(4-*tert*-butylbenzyloxy)phenyl groups to suppress any undesired oxidative homo coupling reactions between the terminal ethynyl groups. The Y-shaped conjugated network inside AB_2-type arm **4** has an ethynylenephenylene iodide terminal. This extended terminal acts as a "naked" functional group to increase reactivity toward the acetylenic terminals of **3** in the Sonogashira coupling reaction.[14]

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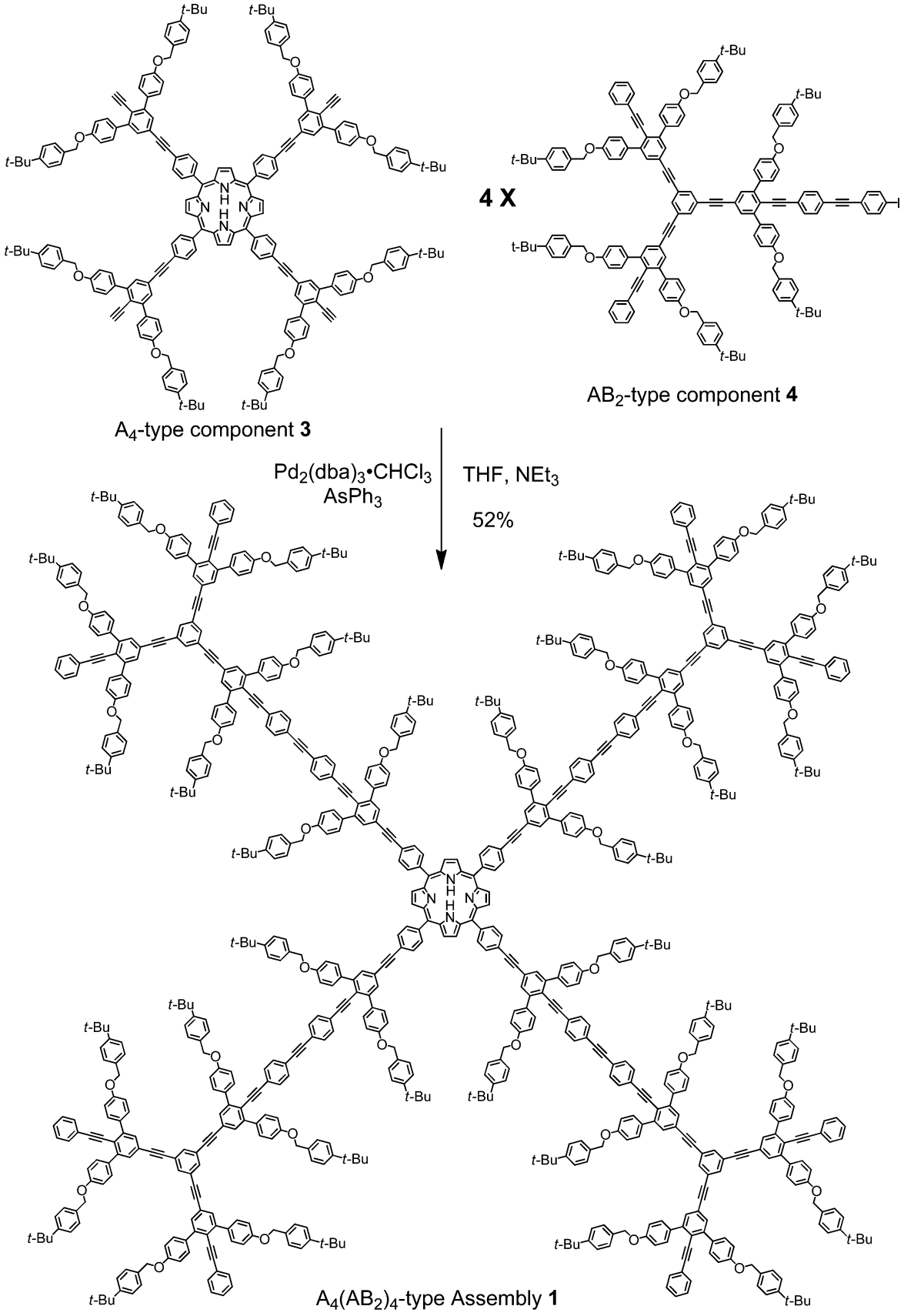
Scheme 2. Synthesis of $A_4(AB_2)_4$-Type Assembly 1



A_4-type core **3** was prepared according to our previous report.[11] AB_2-type arm **4** was synthesized according to the convergent method shown in Scheme 3. Triethynylbenzene **6** was obtained by selective removal of the TMS groups in AB_2-

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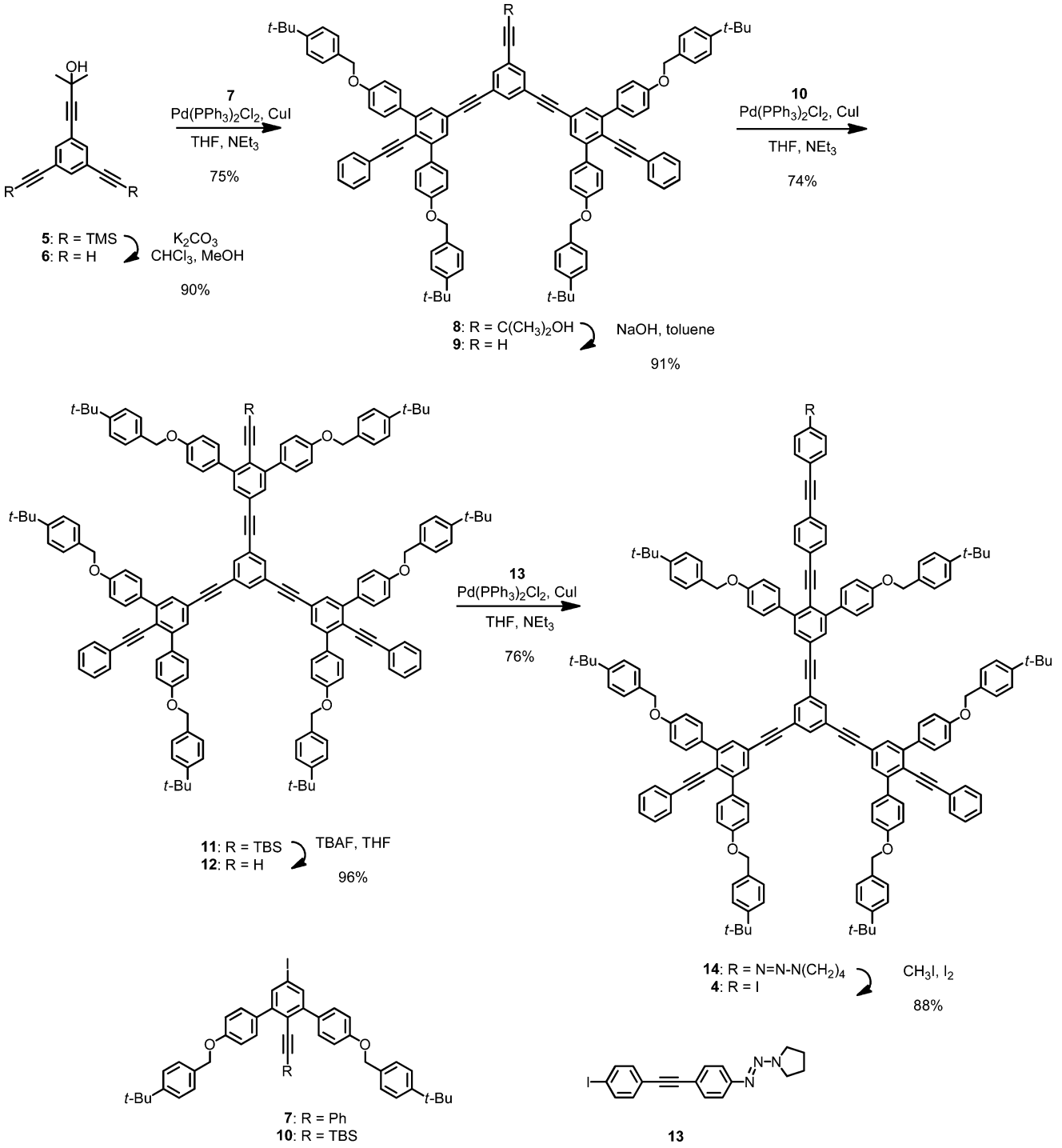
Scheme 3. Synthesis of AB_2-Type Arm 4



type 1,3,5-triethynylbenzene **5**[15] using potassium carbonate. The Sonogashira coupling reaction of **6** and phenyl-terminated dendron **7**[16] gave **8**. Removal of the 2-hydroxy-2-propyl group from the ethynyl terminal was achieved upon the treatment of **8** with sodium hydroxide in toluene to afford **9**. Phenyl iodide **10**,[10a] containing a TBS-terminated alkyne, was coupled with **9** by the Sonogashira reaction to afford **11**. Expansion of the conjugated chain was achieved by the removal of the TBS group in **11** using TBAF followed by Sonogashira coupling with triazene **13**. Then, **14** was heated in iodomethane in the presence of iodine to afford AB_2-type arm **4**.[17]

The 4-fold coupling reaction of A_4-type core **3** and AB_2-type arm **4** was investigated under copper-free Sonogashira coupling conditions, that is, using the combination of $Pd(dba)_2{\cdot}CHCl_3$ and $AsPh_3$ in THF/triethylamine.[18] The reaction at room temperature gave only traces of assembly **1**, and when the reaction mixture was stirred at 40 °C for 24 h, assembly **1** was obtained in 12% yield. Elongation of the reaction time to 72 h resulted in considerable improvement of the yield of assembly **1** to 52% (Scheme 2). Although we used similar reaction conditions for the preparation of the closely related $A_4(AB_3)_4$-type assembly (Scheme 1), the isolated yield of the assembly was only 15%. These results suggest that the

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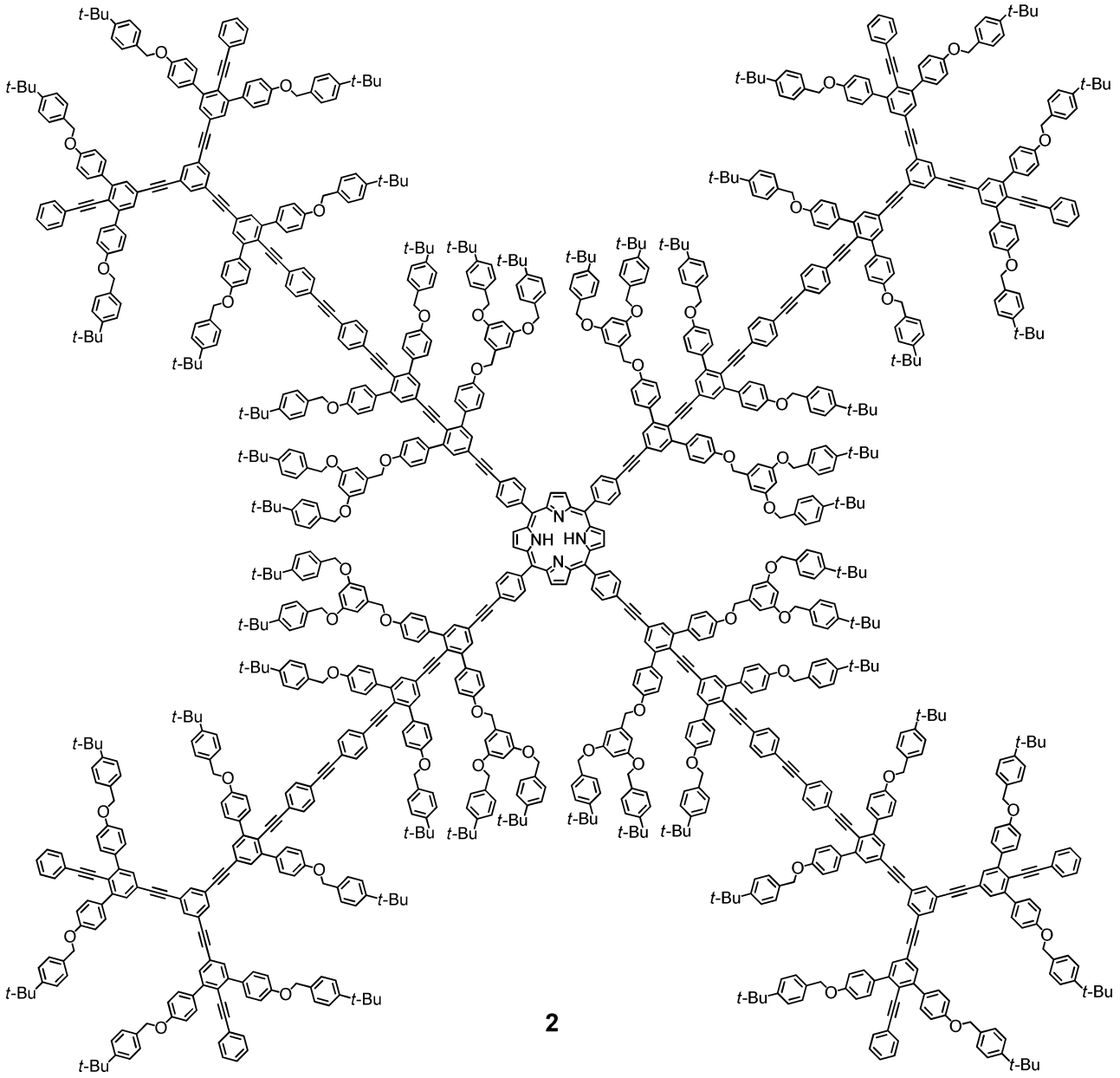

Figure 1. Molecular structure of $A_4(AB_2)_4$-type covalent dendritic assembly **2**.

reduction of steric hindrance around the iodide terminal of the conjugated chain in the "naked" coupler is crucial to obtaining higher yields of the coupling product.

Next, we turned our attention to preparing much larger assembly **2** from AB_2-type arm **4** and second generation dendrimer **15** (Figure 1, Scheme 3). Dendrimer **15** was synthesized according to Scheme 4 from dendron **16** which was prepared using the previously reported method.[10a,16] The coupling reaction of dendron **16** and A_4-type free-base porphyrin **17** under copper-free Sonogashira coupling conditions gave dendrimer **18**. The TBS groups at the ends of the conjugated chains in dendrimer **18** were removed with TBAF in THF to afford **15**. A mixture of dendrimer **15** and AB_2-type arm **4** was stirred at 45 °C for 3 days in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ and $AsPh_3$ in THF/triethylamine (5:1, v/v) to afford a purple solid. The MALDI-TOF mass spectrum of the solid product shows two intense ion peaks at m/z = 14170 and 16300. The peak at m/z = 16300 is reasonably assignable to desired assembly **2** (MW = 16299, calcd for $C_{1188}H_{1070}N_4O_{56}$). The peak at m/z = 14170 indicates the formation of T-shaped phenylated assembly **19** ($A_4(AB_2)_3$ type, MW = 14168, calcd for $C_{1030}H_{934}N_4O_{50}$) via phenyl group migration from triphenylarsine. The production of phenylated byproducts such as **19** is well-known and it is usually easy to remove such byproducts form palladium-catalyzed coupling reactions.[18,19] Gel permeation chromatography (GPC) should be an effective method for the separation of assemblies **2** and **19** owing to their large differences in molecular weight (ΔMW = 2130) and molecular shape. However, when separation of the mixture was attempted by GPC using chloroform as an eluent, only a single peak was observed in the elution profile, probably owing to the intense aggregation of assemblies **2** and **19** (Figure S1 in the Supporting Information). Fortunately, we found that addition of carbon disulfide and/or triethylamine effectively suppressed the formation of aggregates during the GPC separation. The GPC analysis of the mixture was

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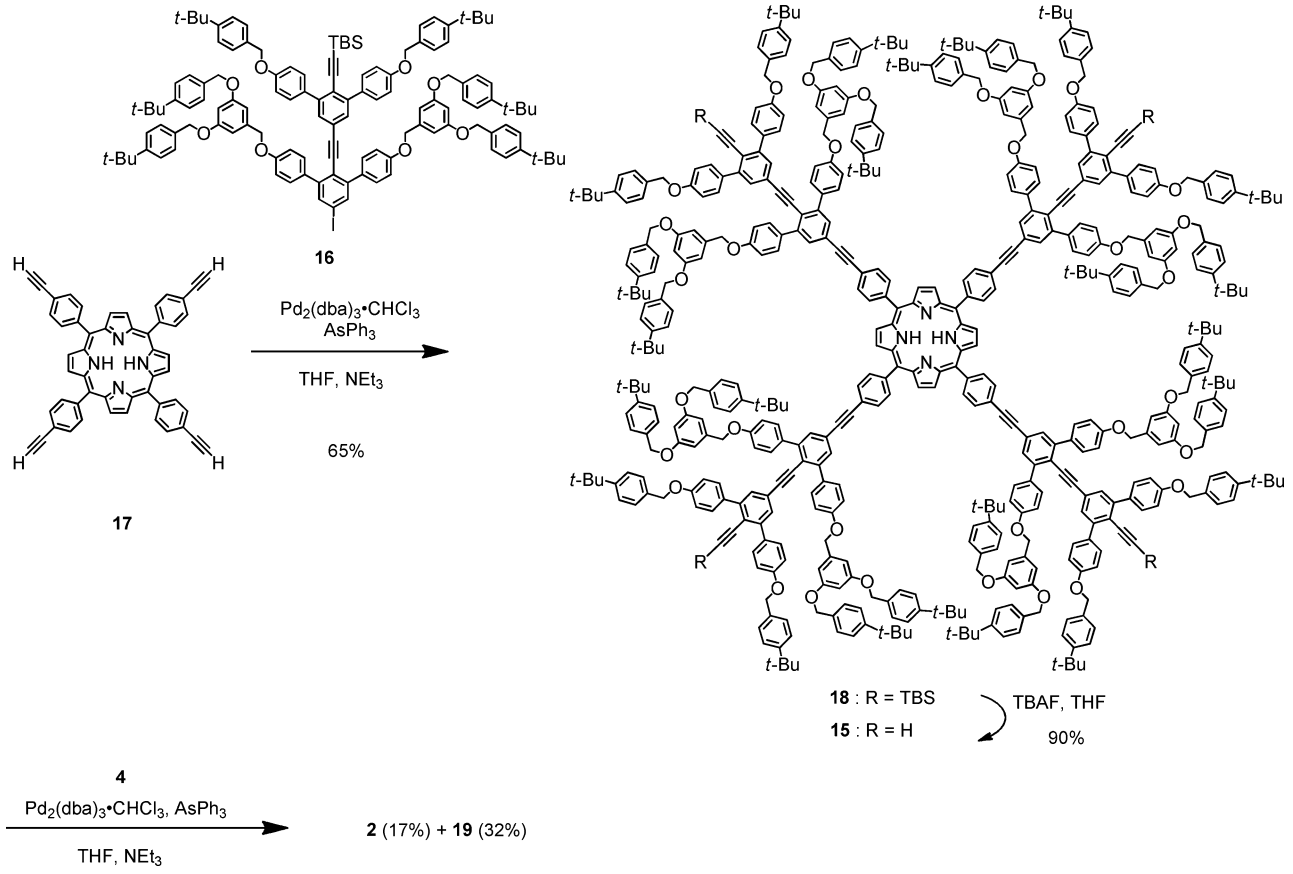
Scheme 4. Synthesis of Assembly 2



performed using chloroform containing various amount of carbon disulfide. As the result, two partially separated peaks were obtained when a 1:1 (v/v) mixture of chloroform and carbon disulfide was used as an eluent. These peaks had longer retention times relative to the peaks observed in the cases of other solvent mixtures, indicating that formation of the aggregate was effectively suppressed in the 1:1 (v/v) mixture of chloroform and carbon disulfide. The preparative separation was carried out using a 1:1:0.01 (v/v/v) chloroform−carbon disulfide−triethylamine mixture to afford assembly **2** in 17% yield and assembly **19** in 32% yield (Chart 1). These results clearly demonstrated that the suppression of aggregation is essential for the isolation of nanoscale assemblies with π-conjugated backbones.

Spectroscopic Characterization. The chemical structures of assemblies **1** and **2** were confirmed by means of NMR and MALDI-TOF mass measurement. Assembly **1** had a relatively simple NMR spectrum at room temperature in $CDCl_3$ resulting from its highly symmetric structure and a sharp molecular ion peak at m/z = 11846 (MW = 11845, calcd for $C_{876}H_{750}N_4O_{32}$) was observed in its mass spectrum (Figure S2, Supporting Information). While assembly **2** showed broad and unresolved NMR signals in $CDCl_2CDCl_2$ at room temperature, sharp and well-resolved signals were observed at 130 °C (Figure 2). This behavior is typical for large dendritic structures with rigid backbones and has been previously reported for a number of dendrimers.[8,10] Although NMR signals of the aromatic protons in the outer components and the core dendrimer were overlapped, three singlet peaks at 5.10, 5.00, and 4.98 ppm corresponding to benzyl protons were observed for assembly **2**. The peak at 5.10 ppm and the other singlet signals were assigned to the benzyl protons for the core and outer components, respectively, based on comparison of the spectra of AB_2-type arm **4** and dendrimer **15**. The observed integral ratio of these singlet peaks was 64:47 for **2** which is in good agreement with the expected values (64:48), confirming the 1:4 stoichiometry of the core and outer components in the assembly. A sharp molecular ion peak at m/z = 16300 for **2** further confirmed the formation of the desired assembly (Figure S3, Supporting Information).

The UV−vis absorption spectrum of assembly **2** in THF shows characteristic bands arising from the porphyrin skeleton (Soret band: λ_{max} = 430 nm (log ε = 5.78); Q-bands: λ_{max} = 525 (4.07), 562 (4.11), and 659 nm (3.66)) along with intense UV absorption bands due to the branched benzyl ether chains (λ_{max} = 289 nm (log ε = 5.63)) and conjugated chains (λ_{max} = 366 (5.54), 428 nm, (3.66)) (Figure 3). The intense UV absorption and characteristic absorption bands for the free base porphyrin unit were observed for assembly **19**. Assembly **1** also has characteristic absorption bands for the porphyrin core (λ_{max} = 427, 518, 555, 596, and 650 nm) in addition to the intense absorption of conjugated chains (364 nm) and benzyl ether chains (299 nm) (Figure S5, Supporting Information). The conjugated networks of assemblies **1** and **2** were constructed by shorter (1.6 nm) and longer phenyleneethynylene chains (3.9 nm for **1** and 4.5 nm for **2**) and porphyrin cores that were encapsulated by the benzyl ether chains. The absorption spectra indicated that the lowest singlet excitation energy levels decreased in the sequence of benzyl ether chains > shorter conjugated chains > longer conjugated chains > porphyrin core.

The excitation energy gradient is helpful for enhancing the efficiency of excitation energy transfer from outer units to the

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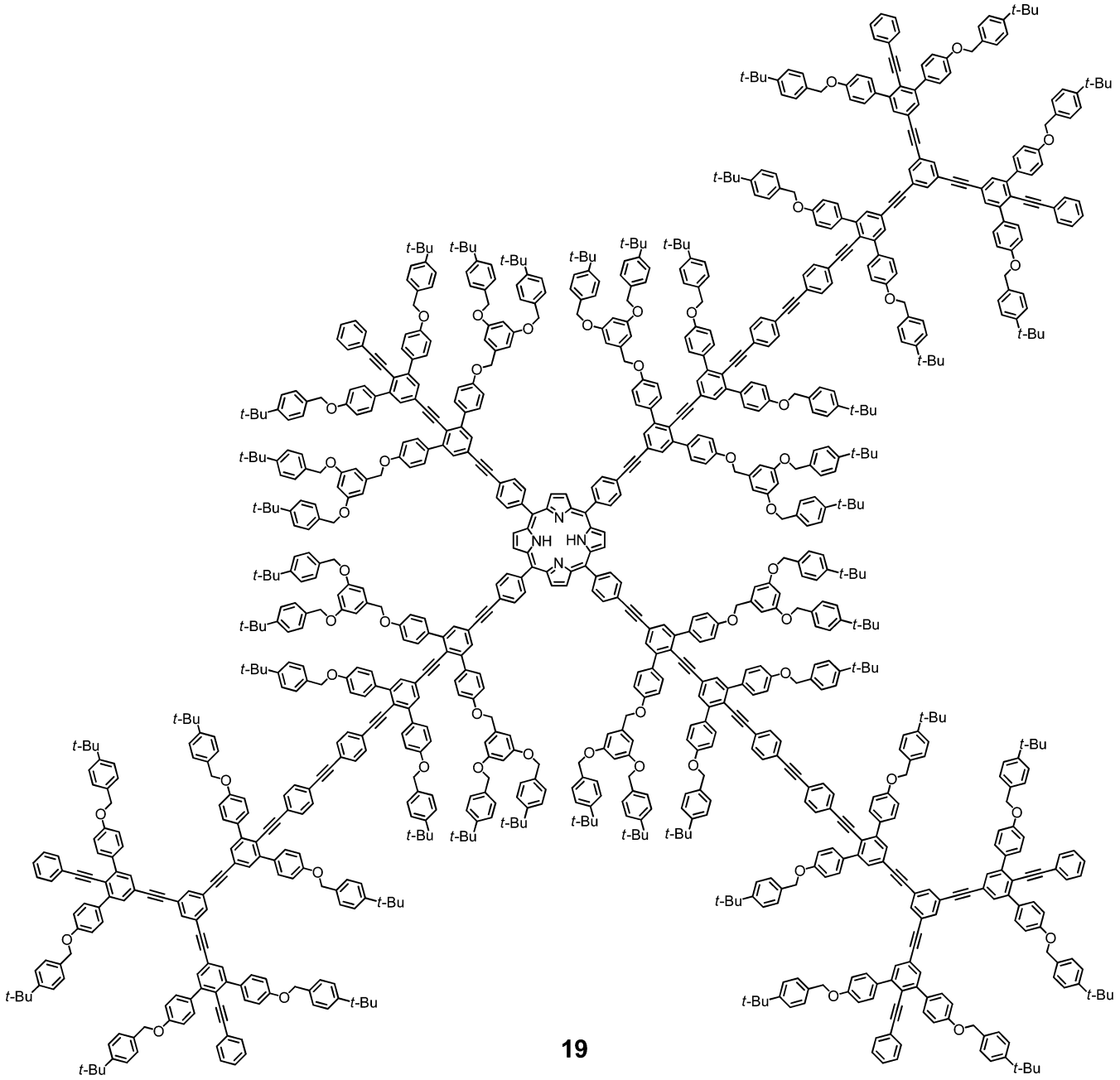
Chart 1



19

porphyrin core.[4,10] To evaluate the efficiency of singlet energy transfer from the outer units to the central porphyrin core, the fluorescence spectrum of assembly **2** was measured in degassed THF at different excitation wavelengths (Figure 4). Excitation at 430 nm, where light is mainly absorbed by the porphyrin core,[10d,20] results in characteristic fluorescence at 666 and 725 nm with the quantum yield of Φ_f = 0.109 (Figure 4c). Under excitation of the benzyl ether chains at 299 nm, a value at which both the conjugated chain and the porphyrin core have only weak absorption, an intense fluorescence of the porphyrin core with the quantum yield of Φ_f = 0.078 appeared with almost complete fluorescence quenching of the benzyl ether chains as shown in Figure 4a, suggesting efficient singlet energy transfer from excited benzyl ether chains to the porphyrin core (quantum efficiency: 72%). Furthermore, excitation of the conjugated chain (λ_{em} = 364 nm) also induced porphyrin fluorescence with the quantum yield Φ_F = 0.073, indicating 72% quantum efficiency for energy transfer (Figure 4b). The excitation spectrum of assembly **2** monitored by porphyrin emission at 650 nm further supports the efficient excitation energy transfer from benzyl ether chains and conjugated chains to the porphyrin core (Figure S6, Supporting Information).

The quantum efficiencies of intramolecular singlet energy transfer in assemblies **1** and **19** were similarly evaluated by means of fluorescence spectroscopy in THF (Figures S7 and S8, Supporting Information). Assembly **1** has quantum efficiencies of 78% and 86% in the energy transfer from benzyl ether and conjugated chains to the porphyrin core, respectively. On the other hand, quantum efficiencies of the energy transfer from benzyl ether and conjugated chains to the porphyrin core in assembly **19** are both 93%. These results indicate that efficient intramolecular singlet energy transfer takes place both

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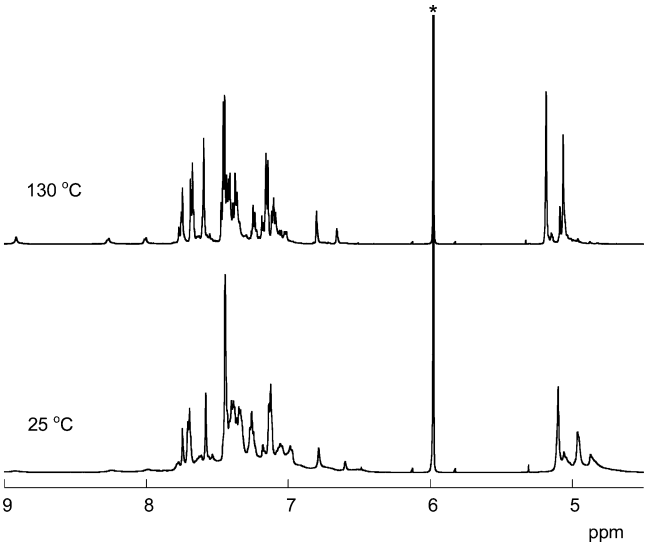

Figure 2. 600 MHz VT ^{1}H NMR spectra of assembly **2** in $CDCl_2CDCl_2$ (*, solvent).

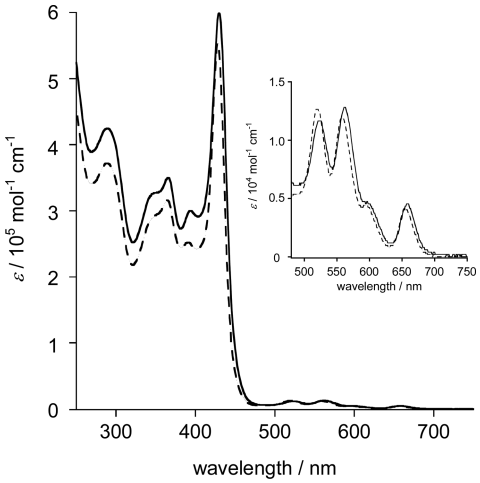

Figure 3. UV−vis spectra of assemblies **2** (solid line) and **19** (dashed line) in THF.

from the benzyl ether chains and the conjugated chains to the porphyrin core in assemblies **1** and **2**.

In summary, we report a novel methodology for the construction of nanoscale shape-persistent covalent assemblies with rigid conjugated backbones using dendrimers as modular building blocks. "Naked" and "shielded" couplers were incorporated at the ends of conjugated chains in order to improve the efficiency of the coupling reaction. The method was successfully applied to the construction of cross-shaped assembly **2**. The T-shaped assembly **19** was formed as a major byproduct via phenyl group migration under the copper-free Sonogashira coupling conditions. In general, the separation of these products (**2** and **19**) should be easy because of the large difference in their molecular weights. However, a possible strong tendency for aggregation between these products impeded the GPC separation. These results indicate that not only the preparation, but also purification of large dendrimers requires new approaches that are unique to nanoscale assemblies. The cross-shaped assemblies **1** and **2** exhibited superior UV light absorption and the absorbed photoenergy was effectively funneled to the central porphyrin core. The

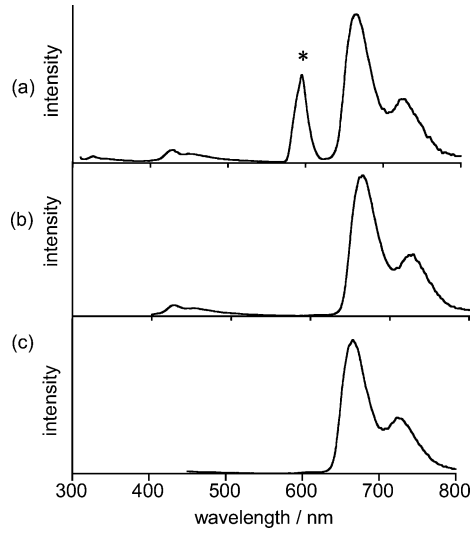

Figure 4. Florescence spectra of assembly **2**, excitation of (a) benzyl ether chains (λ_{ex} = 299 nm, *; the intense peak at 598 nm is the scattered overtone of excitation light), (b) conjugated chains (λ_{ex} = 364 nm), and (c) porphyrin core (λ_{ex} = 430 nm).

dendrimers can serve as "dendritic atoms" in the present assembly process; that is, each dendrimer has its own valency and directionality for bonding in addition to its own individual functionalities. Since various dendrimers with a variety of properties and geometries are accessible as connecting groups, the present study provides a powerful tool for the construction of a broad range of precisely designed nanoscale architectures.

EXPERIMENTAL SECTION

4-[3,5-Bis(2-ethynyl)phenyl]-2-methyl-3-butyn-2-ol (6). To the solution of **5**[15] (3.50 g, 9.92 mmol) in chloroform (250 mL) and methanol (250 mL) was added potassium carbonate (7.10 g, 51.4 mmol). The mixture was stirred for 1 h at room temperature and filtered. After the solvent was evaporated under reduced pressure, the resulting solid was dissolved in dichloromethane. The solution was washed with brine and dried over anhydrous sodium sulfate. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to afford **6** (1.86 g, 90%) as a white solid: mp 79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, J = 1.6 Hz, 1H), 7.50 (d, J = 1.6 Hz, 2H), 3.09 (s, 2H), 1.99 (s, 1H), 1.61 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 135.1, 123.5, 122.8, 95.2, 81.7, 80.3, 78.5, 65.5, 31.3; IR (KBr) 3296, 3277, 2988, 2934, 1582, 1150, 947, 878, 667, 638 cm^{-1}; MS (FAB+) m/z 208 (M^+); HRMS calcd for $C_{15}H_{12}O$ 208.0889, found 208.0877.

General Procedure for Sonogashira Coupling Reactions. Before beginning the reactions, all solid samples were dried in vacuo and THF, triethylamine, and ethyldiisopropylamine were deaerated by bubbling nitrogen or argon. An oven-dried vessel was charged with an aryl iodide, a terminal alkyne, and metal catalysts [$Pd(PPh_3)_2Cl_2$ (or $Pd(PPh_3)_4$) and CuI ($Pd_2(dba)_3{\cdot}CHCl_3$ and $AsPh_3$ for copper-free conditions)]. The vessel was evacuated and backfilled with nitrogen or argon three times. To the vessel, THF and an amine were added in this order. The mixture was stirred at room temperature or 60 °C. After filtration, the solvent was evaporated and the resulting residue was purified by column chromatography on silica gel. Eluents and other slight modifications are described below for each material.

Dendron 8. According to the general procedure, **6** (115 mg, 0.55 mmol), **7**[16] (988 mg, 1.27 mmol), $Pd(PPh_3)_2Cl_2$ (38 mg, 0.054 mmol), and CuI (21 mg, 0.11 mmol) in triethylamine (4 mL) and THF (40 mL) were reacted at 80 °C overnight. The crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:2) to afford **8** (622 mg, 75%): yellow powder; mp 154−155 °C;

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^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.61 (m, 9H), 7.55 (m, 2H), 7.51 (m, 4H), 7.43 (m, 16H), 7.23−7.18 (m, 6H), 7.11−7.05 (m, 12H), 5.11 (s, 8H), 2.01, (s, 1H), 1.62 (s, 6H), 1.34 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.1, 144.7, 134.3, 133.9, 132.9, 131.14, 130.97, 130.8, 128.3, 128.2, 128.1, 127.5, 125.6, 123.9, 123.6, 123.5, 122.3, 120.5, 114.2, 97.4, 95.1, 90.5, 89.4, 89.2, 80.6, 70.0, 65.6, 34.6, 31.40, 31.36; IR (KBr) 2961, 1609, 1506, 1232, 1177, 833 cm^{-1}; MS (FAB+) m/z 1514 (MH^+); HRMS calcd for $C_{111}H_{100}O_5$ 1512.7571, found 1512.7566. Anal. Calcd for $C_{111}H_{100}O_5{\cdot}H_2O$: C, 87.02; H, 6.71. Found: C, 86.84; H, 6.56.

Dendron 9. Dendron **8** (500 mg, 0.33 mmol) and sodium hydroxide powder (132 mg, 3.30 mmol) in dry toluene (50 mL) were refluxed under argon overnight. The solvent was evaporated and the crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **9** (437 mg, 91%) as yellow powder: mp 166−167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.68 (m, 1H), 7.65 (d, J = 8.8 Hz, 8H), 7.62 (d, J = 1.7 Hz, 2H), 7.52 (s, 4H), 7.44 (m, 16H), 7.25−7.18 (m, 6H), 7.13−7.07 (m, 12H), 5.12 (s, 8H), 3.12 (s, 1H), 1.33 (s, 36H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.1, 144.8, 134.7, 133.9, 132.9, 131.1, 131.0, 130.8, 128.2, 128.1, 127.5, 125.6, 123.9, 123.4, 123.0, 122.2, 120.5, 114.1, 97.4, 90.6, 89.21, 89.19, 81.9, 78.5, 69.6, 34.6, 31.3; IR (KBr) 2961, 1609, 1593, 1578, 1506, 1244, 1177, 1109, 1015, 876, 833, 754, 689 cm^{-1}; MS (FAB+) m/z 1456 (M^+); HRMS calcd for $C_{108}H_{94}O_4$ 1454.7152, found 1454.7136.

TBS Acetylene 11. According to the general procedure, **9** (600 mg, 0.41 mmol), **10**[10a] (470 mg, 0.57 mmol), $Pd(PPh_3)_2Cl_2$ (29 mg, 0.041 mmol), and CuI (8 mg, 0.042 mmol) in triethylamine (5 mL) and THF (50 mL) were reacted at 65 °C overnight. The crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **11** (653 mg, 74%) as a yellow powder: mp 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.63 (m, 11H), 7.55 (d, J = 8.5 Hz, 4H), 7.52 (s, 4H), 7.47 (s, 2H), 7.44 (m, 24H), 7.42−7.38 (m, 4H), 7.23−7.19 (m, 6H), 7.11−7.09 (m, 12H), 7.01 (d, J = 8.5 Hz, 2H), 5.12 (s, 8H), 5.08 (s, 4H), 1.34 (s, 36H), 1.33 (s, 18H), 0.74 (s, 9H), −0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.6, 151.1, 151.0, 145.4, 144.7, 134.3, 134.0, 133.9, 132.9, 132.8, 131.1, 131.0, 130.8, 130.7, 128.2, 128.1, 127.5, 127.4, 125.58, 125.55, 124.0, 123.5, 122.3, 120.6, 120.5, 114.2, 104.3, 102.2, 97.4, 90.53, 90.46, 89.4, 89.2, 70.00, 69.95, 34.6, 31.4, 26.0, 16.6, −5.0; IR (KBr) 2957, 1609, 1506, 1362, 1223, 1177, 1109, 1015, 827, 754 cm^{-1}; MS (FAB+) m/z 2146.5 (M^+); HRMS (FAB+) m/z calcd for $C_{156}H_{148}O_6Si$ 2145.1045, found 2145.1045.

Terminal Acetylene 12. To the solution of **11** (50 mg, 0.023 mmol) in THF (5 mL) was added 1.0 M TBAF in THF (0.030 mL, 0.030 mmol) and stirred at room temperature overnight. The reaction was quenched by water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **12** (45 mg, 96%) as a yellow powder: mp 206−207 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.63 (m, 11H), 7.55 (d, J = 8.8 Hz, 4H), 7.52 (s, 4H), 7.47 (s, 2H), 7.43 (s, 16H), 7.42−7.37 (m, 8H), 7.23−7.19 (m, 6H), 7.11−7.04 (m, 16H), 5.12 (s, 8H), 5.08 (s, 4H), 3.07 (s, 1H), 1.34 (s, 36H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.1, 145.8, 144.8, 134.3, 133.90, 133.87, 132.9, 132.6, 131.2, 131.0, 130.8, 130.7, 128.2, 128.1, 127.6, 127.5, 125.60, 125.58, 124.1, 124.0, 123.5, 122.8, 122.3, 120.6, 119.3, 114.22, 114.18, 97.4, 90.6, 90.1, 89.6, 89.4, 89.2, 86.7, 82.2, 76.7, 70.0, 69.9, 34.6, 31.4; IR (KBr) 2959, 2905, 2866, 1609, 1506, 1464, 1294, 1231, 1177, 1015, 831, 818 cm^{-1}; MS (FAB+) m/z 2032.9 (M^+); HRMS (FAB+) m/z calcd for $C_{150}H_{134}O_6$ 2031.0180, found 2031.0179. Anal. Calcd. for $C_{150}H_{134}O_6{\cdot}H_2O$: C, 87.85; H, 6.68. Found: C, 87.54; H, 6.57.

Triazene 13. According to the general procedure, 1-[2-(4-ethynylphenyl)diazenyl]pyrrolidine[21] (200 mg, 0.678 mmol), 1,4-diiodobenzene (670 mg, 2.03 mmol), $Pd(PPh_3)_4$ (39 mg, 0.034 mmol), and CuI (13 mg, 0.068 mmol) in triethylamine (5 mL) and toluene (25 mL) were reacted at 40 °C overnight. The crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **13** (303 mg, 73%) as a yellow powder: mp 182−183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 3.80 (bs, 4H), 2.04 (bs, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 137.4, 133.0, 132.4, 123.2, 120.4, 119.0, 93.7, 91.5, 88.3, 50.9, 46.3, 23.8; IR (KBr) 2964, 2870, 1497, 1421, 1398, 1319, 1263, 1223, 1132, 1003, 843, 820 cm^{-1}; MS (FAB+) m/z 401.37 (M^+); HRMS (FAB+) m/z calcd for $C_{18}H_{16}N_3I$ 401.0389, found 401.0370.

Triazene 14. According to the general procedure, **12** (40 mg, 0.020 mmol), **13** (470 mg, 0.57 mmol), $Pd(PPh_3)_2Cl_2$ (1.0 mg, 0.0014 mmol), and CuI (0.5 mg, 0.0026 mmol) in triethylamine (2 mL) and THF (4 mL) were reacted at 65 °C overnight. The crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **14** (35 mg, 76%) as a yellow powder: mp 258 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 15H), 7.53 (s, 6H), 7.48−7.43 (m, 26H), 7.39 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.24−7.19 (m, 6H), 7.12−7.08 (m, 16H), 7.02 (d, J = 8.3 Hz, 2H), 5.13 (m, 12H), 5.12 (s, 4H), 2.04 (bs, 4H), 1.34 (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.74, 158.70, 151.4, 151.1, 144.8, 144.7, 134.3, 133.90, 132.93, 132.85, 132.4, 131.3, 131.2, 131.0, 130.8, 129.3, 128.23, 128.19, 128.1, 127.53, 127.50, 125.60, 125.58, 125.3, 123.99, 123.97, 123.5, 123.3, 122.9, 122.5, 122.3, 120.5, 120.4, 119.2, 114.19, 114.16, 97.4, 92.1, 91.1, 90.6, 89.6, 89.4, 89.24, 89.1, 70.0, 34.61, 34.60, 31.4, 23.8; IR (KBr) 2961, 2926, 2868, 1609, 1506, 1396, 1315, 1244, 1177, 1015, 831; MS (FAB+) m/z 2306.0 (M^+). Anal. Calcd for $C_{168}H_{149}N_3O_6$: C, 87.50; H, 6.51; N, 1.82. Found: C, 87.42; H, 6.56; N, 1.88.

Arm 4. To a thick-walled oven-dried screw-cap tube was added **13** (18 mg, 0.0078 mmol), iodine (2.2 mg, 0.0087 mmol), and iodomethane (0.5 mL). The tube was flushed with nitrogen or argon, sealed, and heated at 80 °C overnight. The mixture was cooled to room temperature and quenched with water. The solution was extracted with dichloromethane. The extract was washed with sodium thiosulfate and brine and dried over anhydrous sodium sulfate. After filtration the solvent was evaporated. The crude material was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **4** (16 mg, 88%) as yellow powder: mp 250−251 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.63 (m, 17H), 7.53 (bs, 6H), 7.44 (s, 24H), 7.34 (d, J = 8.6 Hz, 2H), 7.24−7.21 (m, 10H), 7.11−7.08 (m, 16H), 7.03 (d, J = 8.3 Hz, 2H), 5.12 (m, 12H), 1.34 (s, 54H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 158.7, 151.13, 151.11, 144.9, 144.8, 137.6, 134.3, 133.90, 133.87, 133.1, 132.9, 132.8, 131.4, 131.16, 131.16, 131.0, 130.8, 128.2, 127.53, 127.50, 125.6, 124.0, 123.5, 122.5, 122.3, 120.5, 114.20, 114.18, 97.4, 97.0, 94.5, 91.9, 90.6, 90.1, 89.4, 89.2, 77.2, 70.0, 34.6, 31.4; IR (KBr) 2961, 2926, 1609, 1508, 1246, 1177, 1016, 831, 820 cm^{-1}; MS (FAB+) m/z 2332.8 (M^+). Anal. Calcd for $C_{164}H_{141}IO_6{\cdot}H_2O$: C, 83.72; H, 6.13. Found: C,83.75; H, 6.05.

Assembly 1. An oven-dried vessel was charged with **3** (10.2 mg, 0.0034 mmol), **4** (34.6 mg, 0.0148 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.73 mg, 0.0017 mmol), and $AsPh_3$ (5.0 mg, 0.0163 mmol). The vessel was evacuated and backfilled with argon three times. To the vessel were added THF (3.0 mL) and triethylamine (0.6 mL). The mixture was stirred at room temperature or 40 °C for 3 days. After filtration, the solvent was evaporated, and the resulting residue was purified by column chromatography on silica gel (dichloromethane) and then recycling preparative GPC (JAIGEL-3H and -2H columns, $CHCl_3$) to afford the assembly **1** (21 mg, 52%) as a purple solid: mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 8H), 8.21 (m, 8H), 7.93 (m, 8H), 7.75−7.57 (m, 76H), 7.55−7.49 (m, 20H), 7.48−7.37 (m, 128H), 7.37−7.31 (m, 24H), 7.23−7.16 (m, 32H), 7.16−6.96 (m, 94H), 5.15−5.11 (m, 64H), 1.35 (m, 288H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.9, 151.19, 151.16, 145.1, 145.0, 144.9, 134.3, 134.12, 134.09, 133.21, 133.16, 133.1, 131.4, 131.2, 131.10, 131.06, 130.93, 130.87, 128.2, 128.10, 128.06, 127.49, 127.47, 125.62, 125.60, 125.59, 124.2, 123.6, 122.8, 122.4, 120.8, 120.5, 114.5, 114.4, 114.4, 97.6, 90.7, 89.5, 89.4, 77.2, 70.2, 34.7, 34.7, 31.6, 31.4, 22.7, 14.1; IR (KBr) 2961, 2905, 2866, 1607, 1506, 1227, 1175, 1015, 831 cm^{-1}; MS (MALDI-TOF) m/z 11846 (M^+). Anal. Calcd for $C_{876}H_{750}N_4O_{32}{\cdot}2CHCl_3$: C, 87.27; H, 6.27; N, 0.46. Found: C, 87.52; H, 6.41; N, 0.58.

Dendrimer 18. According to the general procedure, **16** (25 mg, 0.0351 mmol), **17** (299 mg, 0.155 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (22 mg, 0.021 mmol), and $AsPh_4$ (52 mg, 0.170 mmol) in triethylamine (3

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mL) and THF (15 mL) were reacted at 40 °C overnight. The crude material was purified by column chromatography on silica gel (CH_2Cl_2) and then recycling preparative GPC (JAIGEL-3H and -2H columns, $CHCl_3$) to afford **18** (180 mg, 65%) as a purple powder: mp 185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.89 (bs, 8H), 8.22 (d, J = 8.0 Hz, 8H), 7.94 (d, J = 8.0 Hz, 8H), 7.95−7.71 (m, 24H), 7.47 (d, J = 8.5 Hz, 16H), 7.46−7.30 (m, 96H), 7.10−7.06 (m, 24H), 6.94 (d, J = 8.5 Hz, 16H), 6.73 (d, J = 2.0 Hz, 16H), 6.56 (t, J = 2.0 Hz, 8H), 5.00 (s, 16H), 4.97 (s, 32H), 4.87 (s, 16H), 1.30 (m, 216H), 0.70 (s, 36H), −0.14 (s, 24H), −2.73 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.3, 158.6, 158.5, 151.0, 150.9, 145.0, 145.0, 139.4, 134.7, 134.0, 133.7, 133.1, 132.8, 131.1, 130.9, 130.7, 130.3, 130.1, 127.6, 127.5, 125.52, 125.46, 123.1, 120.2, 119.9, 119.7, 114.3, 114.1, 106.2, 104.5, 101.9, 101.6, 97.3, 91.2, 91.1, 90.5, 70.03, 69.96, 69.8, 34.6, 31.4, 31.3, 26.0, 16.6, −5.0; IR (KBr) 2963, 2905, 2965, 1604, 1504, 1458, 1363, 1296, 1247, 1180, 1151, 1109, 1013, 831, 540 cm^{-1}; MS (MALDI-TOF) m/z 7931.3 ((M + H)$^+$). Anal. Calcd. for $C_{556}H_{556}N_4O_{32}Si_4{\cdot}2CH_2Cl_2$: C, 82.75; H, 7.09; N, 0.69. Found: C, 83.02; H, 7.10; N, 0.82.

Dendrimer 15. To the solution of **18** (120 mg, 0.015 mmol) in THF (15 mL) was added 1.0 M TBAF in THF (0.075 mL, 0.075 mmol) and the mixture stirred at room temperature overnight. The reaction was quenched with water and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) to afford **15** (101 mg, 90%) as a purple solid: mp 202 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ (ppm) 8.86 (bs, 8H), 8.20 (d, J = 8.0 Hz, 8H), 7.93 (d, J = 8.0 Hz, 8H), 7.69−7.67 (m, 24H), 7.46 (d, J = 8.6 Hz, 16H), 7.47−7.29 (m, 96H), 7.09−7.06 (m, 24H), 6.96 (d, J = 8.6 Hz, 16H), 6.72 (d, J = 2.0 Hz, 16H), 6.56 (t, J = 2.0 Hz, 8H), 4.99 (s, 16H), 4.96 (s, 32H), 4.89 (s, 16H), 2.97 (s, 1H), 1.30 (m, 216H), −2.70 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.5, 158.9, 158.8, 151.1, 151.0, 145.6, 145.2, 139.5, 136.2, 134.1, 134.0, 133.3, 132.8, 131.2, 131.0, 130.64, 130.57, 130.2, 130.0, 127.58, 127.55, 126.1, 125.52, 125.48, 124.0, 123.7, 123.5, 120.2, 119.9, 119.9, 117.9, 114.6, 114.3, 106.5, 101.9, 88.4, 70.2, 70.1, 70.0, 34.6, 31.41, 31.39; IR (KBr); 2961, 2905, 2868, 1607, 1506, 1458, 1364, 1294, 1244, 1177, 1151, 1109, 1016, 966, 831, 540 cm^{-1}; MS (MALDI-TOF MS) m/z 7474.3 ((M + H)$^+$). Anal. Calcd for $C_{532}H_{510}N_4O_{32}{\cdot}2CH_2Cl_2$: C, 83.93; H, 6.78; N, 0.73. Found: C, 84.04; H, 6.81; N, 0.84.

Assembly 2. An oven-dried vessel was charged with **4** (32 mg, 0.0132 mmol), **15** (17.0 mg, 0.0022 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (1.4 mg, 0.00135 mmol), and $AsPh_3$ (3.4 mg, 0.0111 mmol). The vessel was evacuated and backfilled with nitrogen or argon three times. To the vessel were added THF (2.5 mL) and triethylamine (0.5 mL). The mixture was stirred at 40 °C for 3 days. After filtration, the solvent was evaporated, and the resulting residue was purified by column chromatography on silica gel (dichloromethane) and then recycling preparative GPC (JAIGEL-4H and -3H columns, $CHCl_3$−CS_2−triethylamine, 1:1:0.01) to afford the assembly **2** (6.3 mg, 17%) as a purple solid and **19** (10.7 mg, 32%) as a purple solid. **2**:[22] mp >300 °C; ^{1}H NMR (600 MHz, $CDCl_2CDCl_2$, 130 °C) δ (ppm) 8.83 (br, 8H), 8.19 (br, 8H), 7.92 (m, 8H), 7.69−7.64 (m, 32H), 7.61−7.57 (m, 56H), 7.56−7.51 (m, 44H), 7.47−7.23 (200H), 7.21−7.11 (m, 32H), 7.11−6.92 (m, 112H), 6.71 (bs, 16H), 6.57 (bs, 8H), 5.10 (s, 48H), 5.00−4.94 (m, 64H), 1.35−1.24 (m, 432H); IR (KBr) 2922, 2851, 1508, 1458, 1244, 1113, 1026, 835 cm^{-1}; MS (MALDI-TOF) m/z 16299 (M$^+$). **19**:[22] mp >300 °C; ^{1}H NMR (600 MHz, $CDCl_2CDCl_2$, 130 °C) δ (ppm) 8.83 (bs, 8H), 8.22 (bs, 8H), 7.97 (m, 8H), 7.70−7.65 (m, 30H), 7.61−7.57 (m, 45H), 7.53−7.50 (m, 34H), 7.40−7.24 (m, 174H), 7.18−7.13, (m, 24H), 7.12−6.91 (m, 94H) 6.72 (bs, 16H), 6.57 (bs, 8H), 5.10 (s, 36H), 5.00 (s, 16H), 4.98 (s, 48H), 1.36−1.24 (m, 432H); IR (KBr) 2961, 2866, 1607, 1508, 1458, 1244, 1177, 1016, 833 cm^{-1}; MS (MALDI-TOF) m/z 14172 (M$^+$).

Electronic and Emission Spectra Measurement. Electronic and emission spectra were recorded using 1 cm quartz cuvettes. The solution with an optical density around 0.1 at the Soret band was used for the fluorescence measurement. For the investigation of energy-transfer efficiency, fluorescence quantum yields are relative to zinc tetraphenylporphyrin or quinine as the external standards.[23]

■ ASSOCIATED CONTENT

Supporting Information

GPC elution profile, NMR spectra, MALDI-TOF spectra, and photophysical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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