

Interlocked Bis(polyrotaxane) of Cyclodextrin–Porphyrin Systems Mediated by Fullerenes

Yu Liu,* Peng Liang, Yong Chen, Ying-Ming Zhang, Jian-Yu Zheng, and Hai Yue

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

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ABSTRACT: A nanometer-sized cyclodextrin–porphyrin–fullerene aggregate with an interlocked bis(polyrotaxane) structure is constructed from cyclodextrin–porphyrin conjugate and C₆₀, exhibiting the significant chiral and electrochemical behaviors due to the presence of numerous porphyrin and fullerene units.

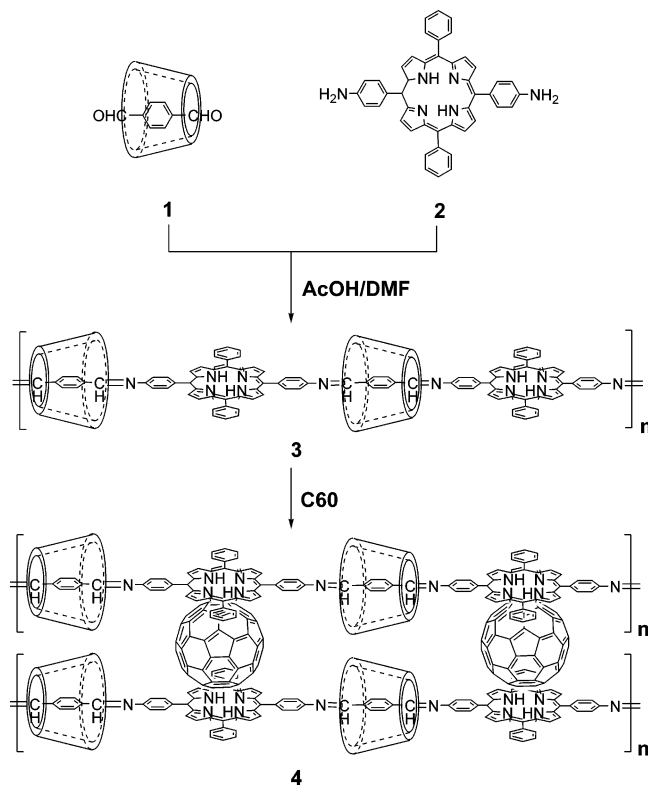
Introduction

Both porphyrins and fullerenes are important functional molecules possessing many fascinating physical, chemical, and biological properties.^{1,2} For example, multiporphyrin assemblies are reported able to be used as artificial photosynthetic reaction centers, light-harvesting antennas, electron- and/or energy-transfer molecular devices, molecular conductive wires, and optoelectronic devices.³ Moreover, possessing several unique properties, particularly in terms of electron donor or acceptor capability as well as photophysical and photochemical behaviors, fullerenes show many interesting magnetic, superconductive, and electrical functions.⁴ Therefore, one can hypothesize that, as an ideal donor–acceptor couple, the combination of porphyrin and fullerene, especially the nanometer-scaled porphyrin–fullerene systems, may bring a breakthrough in many fields of chemistry and material science. Recently, several sandwich-like porphyrin–fullerene conjugates have been reported.^{5–7} However, the nanometer-scaled porphyrin–fullerene aggregates are still rare.^{5,6d,7e} On the other hand, cyclodextrins have been successfully applied in the construction of nanometer aggregates, especially polyrotaxanes and polypseudorotaxanes, owing to their special capability of selectively binding a wide variety of model substrates.⁸ Herein, we wish to report an interlocked bis(polyrotaxane) with cyclodextrin–porphyrin conjugates as backbones and C₆₀ as linkers, which may open a new channel in the design and preparation of functional nanometer materials.

Results and Discussion

A polycondensation reaction of β -cyclodextrin/*p*-phthalaldehyde complex (**1**)⁹ with 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (**2**)¹⁰ gives the cyclodextrin–porphyrin conjugate **3** in 36% yield (Scheme 1). It should be noted that the complex **1** has a moderate stability in DMF,⁹ which may favor its further reaction with **2**. Moreover, because the formation of complex **1** through the inclusion complexation of cyclodextrins and *p*-phthalaldehyde is an equilibrium process, the dethreading of cyclodextrin is still possible. In the preparation and purification process, we make several attempts to avoid the dethreading of cyclodextrins. First, we add an excess amount of β -cyclodextrin in the reaction mixture, which

Scheme 1



will favor the formation of cyclodextrin/*p*-phthalaldehyde complex. Second, in the purification, the crude products are washed successively with chloroform and water, which will remove the unreacted materials, superfluous β -cyclodextrin, and possible byproducts (*p*-phthalaldehyde and *p*-phthalaldehyde/2 polymer without cyclodextrin) resulting from the dethreading of β -cyclodextrin because cyclodextrin and **1** are soluble in water while *p*-phthalaldehyde, **2**, and *p*-phthalaldehyde/2 polymer without cyclodextrin are soluble in chloroform. These attempts will efficiently avoid the unfavorable influence of the dethreading.

The ¹H NMR spectrum of **3** shows the appreciable signals at 8.77 ppm assigned to the azomethine protons¹¹ and at 7.94 ppm assigned to the phenylene protons of the *p*-phthalaldehyde units. As compared with those of the phenylene protons in free *p*-phthalaldehyde, the ¹H NMR signals of the phenylene protons in **3** show

* Corresponding author. E-mail: yuliu@nankai.edu.cn.

a downfield shift (ca. 0.05 ppm). Moreover, cyclodextrin's H-3 protons (interior protons of cyclodextrin cavity) also display an upfield shift (0.1 ppm) as compared with those of free cyclodextrin in the ^1H NMR spectrum of **3**. A comparison of the area of proton peaks shows that the ratio of phenylene protons (a molecule of *p*-phthaldehyde contains four phenylene protons) and β -cyclodextrin's C-H protons (a molecule of β -cyclodextrin contains 49 C-H protons) is 4.0:49.0, which indicates that **3** has a structure with one β -cyclodextrin cavity for each phenylene unit. These results reveal that the aromatic ring of *p*-phthaldehyde molecule must be located in the interior of cyclodextrin cavity, and the cyclodextrin units are threaded on the polymer backbone rather than free β -cyclodextrin,^{9,12} although it is still possible for some segments of phenylene devoid of any cyclodextrin cavities. In addition, the FT-IR spectrum of **3** shows a characteristic vibration band at 1652 cm^{-1} assigned to the C=N stretching vibration, and the elemental analysis data confirm the 1:1 condensation stoichiometry between **1** and **2**. Moreover, **3** gives several obvious induced circular dichroism (ICD) signals according to the porphyrin units located closed to the chiral cyclodextrin cavities. These results jointly verify the formation of polyrotaxane **3**. On the basis of GPC results and a Corey-Pauling-Koltun (CPK) molecular model study, we deduce that there should be more than 36 cyclodextrin-porphyrin units in **3**, and its possible length is larger than 140 nm. A further reaction of **3** with C_{60} in DMF gives the cyclodextrin-porphyrin-fullerene aggregate **4** in 42% yield, which can remain stable for several weeks when stored at a refrigeratory (4 °C). Besides the characteristic vibration bands at 1435, 1155, 576, and 526 cm^{-1} assigned to the C_{60} units in the FT-IR spectrum of **4**, UV/vis spectra also provide some evidences for the formation of **4**. That is, the UV spectrum of **2** shows four peaks at 424, 522, 564, and 657 nm and a shoulder at 598 nm, but the corresponding peaks in the UV spectrum of **3** appreciably shift to 422, 518, 555, 595, and 650 nm. After introducing C_{60} to **3**, these peaks further change to 422, 511, 551, 592, and 647 nm, accompanied by the appearance of two new strong maxima at 274 and 332 nm (assigned to C_{60}). In addition, the elemental analysis data indicate that the cyclodextrin:porphyrin: C_{60} molar ratio in **4** is 2:2:1. These phenomena jointly confirm an efficient association of **3** with C_{60} . The apparent association constant (K_{app}) of **3** with C_{60} is determined by a fluorescence titration experiment. By analyzing the fluorescence quantum yield of **3** with the addition of C_{60} according to a reported method,^{5-7,13} we obtain the apparent association constant between **3** and C_{60} as 7800 M^{-1} , which subsequently indicates a satisfactory stability of **4**.

The thermic stability of **4** is also investigated by means of TG analysis. The results show that the aggregate **4** dehydrates at the low temperature (below 120 °C) and starts to decompose at 285 °C. Significantly, **4** only loses 83.3% of its weight below 600 °C. In the control experiments, all of **1**, **2**, and **3** completely decompose below 600 °C, and C_{60} was reported to only decompose over 850 °C.¹⁴ Therefore, this result demonstrates that the content of C_{60} in **4** is 16.7%, which is basically consistent with calculated value (17.4%) from elemental analysis data.

Transmission electron microscopy (TEM) and scanning tunneling microscopy (STM) experiments give

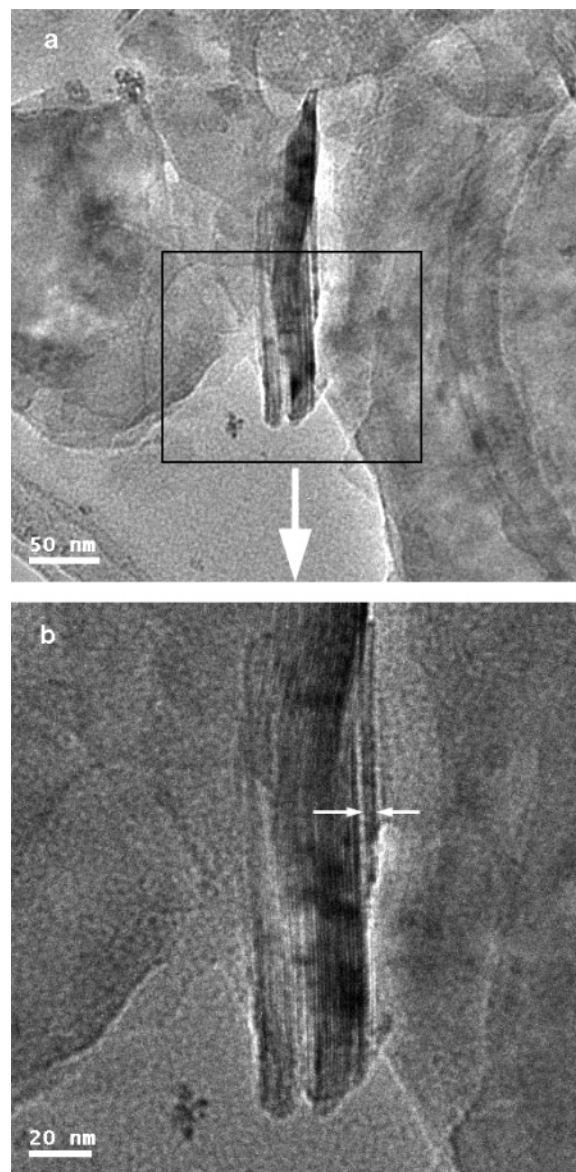


Figure 1. TEM images of **4**.

some visual information about the morphology of **4**. The TEM image (Figure 1) displays several linear structures with various lengths in the range 180–230 nm and a same width of 3.5 nm.

In addition, STM images give a fine structure of the aggregate **4**, which shows that the linear structure shown in TEM is actually an ordered double-lined array (total width 3.5 nm measured by STM) composed of many bright dots (Figure 2). The measured average distance between two adjacent bright dots in one line is ca. 2.3 nm (Figure 2), which is basically consistent with a sum of β -cyclodextrin's height (0.8 nm) and **2**'s diameter (1.5 nm). Moreover, the width (1.7 nm) and height (1.7 nm) of a bright dot are also similar to the outer diameter of β -cyclodextrin cavity (1.54 nm). Therefore, we can deduce that one bright dot should correspond to one β -cyclodextrin unit. In addition, the interval between two lines is also measured to be 1.7 nm.

Possessing electron acceptors (C_{60}) and donors (porphyrin) in one bis(polyrotaxane), the aggregate **4** exhibits the obvious electrochemical behavior. The cyclic voltammetric spectrum of **4** in a DMF solution of

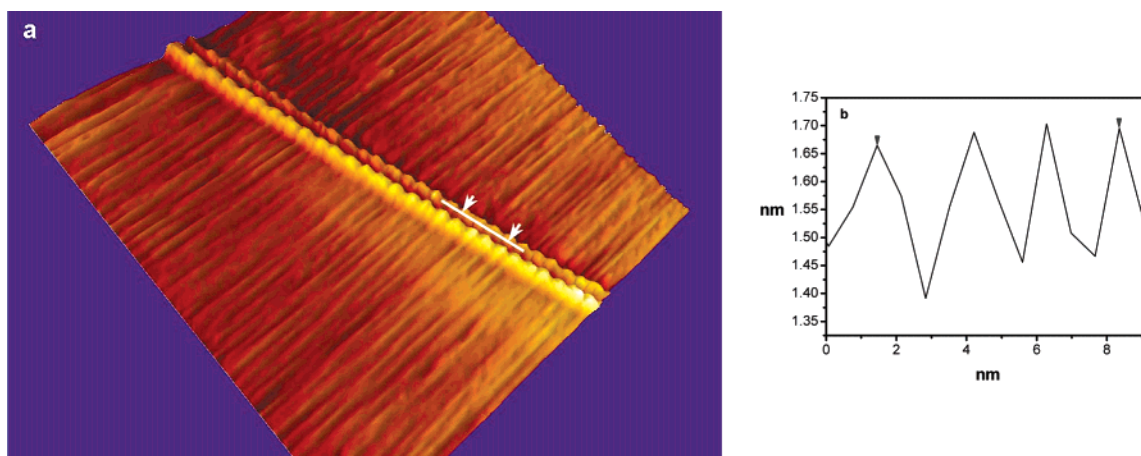


Figure 2. (a) STM images of **4** on HOPG a surface (tunneling current 1.0 nA). (b) Line profile of image shown in (a).

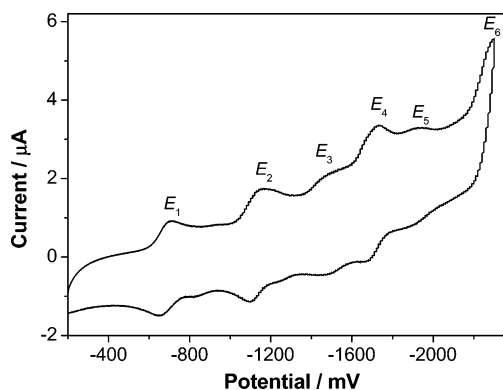


Figure 3. Cyclic voltammetric spectrum of **4** in DMF solution containing 0.1 M *n*-Bu₄NPF₆ at 50 mV/s.

(Bu₄N)PF₆ shows six reduction potentials at -835 , -1289 , -1625 , -1859 , -2064 , and -2422 mV vs Fc/Fc⁺ (Figure 3). Among them, four of the reductions (E_1 , E_2 , E_4 , E_6) correspond to the formation of the C₆₀'s mono-, di-, tri-, and tetraanions and two (E_3 and E_5) to porphyrin reductions. By comparing the first reduction potential of the C₆₀ unit in **4** (-835 mV) with that of free C₆₀ ($E = -770$ mV¹⁵ vs Fc/Fc⁺ in DMF), we deduce that C₆₀ becomes less subject to reduction upon complexation with **3**. This phenomenon verifies that a π -electronic interaction is operative between porphyrin rings and C₆₀ in **4**.

Interestingly, although either precursor **1** or porphyrin **2** displays very weak circular dichroism (CD) signals (-0.5 dm³ mol⁻¹ cm⁻¹ < $\Delta\epsilon$ < 0.5 dm³ mol⁻¹ cm⁻¹), the CD spectrum of **3** shows several obvious Cotton effect peaks in the range 370–450 nm (Figure 4b) assigned to the ICD of porphyrin units located close to the chiral cyclodextrin cavities. More interestingly, the CD spectrum of **4** shows tens of moderate and strong Cotton effect peaks in the range 270–500 nm (Figure 4b), which indicates a significant chirality of **4**. Considering the structural features of **4**, we deduce that this phenomenon may be mainly attributed to the proximity of many C₆₀ units to the chiral cyclodextrin cavities. Because C₆₀ is chromophoric but achiral and cyclodextrin is chiral but nonchromophoric, the proximity of C₆₀ to the cyclodextrin cavity will result in the ICD signals at the C₆₀ adsorption.¹⁶ Moreover, we also observe that **4** gives the reversed CD signals beyond 400 nm as compared with those of **3**. These negative CD signals beyond 400 nm may originate from C₆₀. Moreover, the change of the

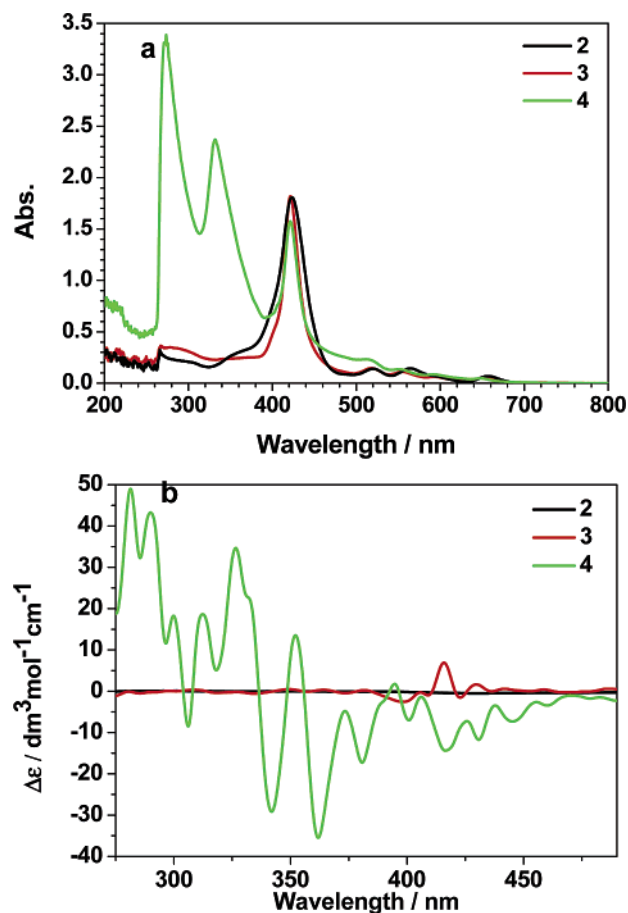


Figure 4. (a) UV spectra of and (b) circular dichroism spectra of **2** (1.2×10^{-5} M), **3** (1.2×10^{-5} M, calculated as porphyrin units), and **4** (1.2×10^{-5} M, calculated as porphyrin units) in DMF at 298 K.

orientation (related to the cyclodextrin axis) of porphyrin units in **3** upon association with C₆₀ may also contribute to the reversed CD signals to some extent.

In conclusion, we successfully construct an interlocked bis(polyrotaxane) mediated by fullerenes. The introduction of cyclodextrins efficiently protects the C=N bonds in both the cyclodextrin–porphyrin conjugate and the bis(polyrotaxane) and thus enables their satisfactory stabilities. Superior to its precursors **1–3**, this bis(polyrotaxane) exhibits the significant chiral and electrochemical behaviors. Benefiting from the fascinating functions of porphyrin and fullerene, the bis(polyrotax-

ane) will meet its future application in many fields of chemistry and biology.

Experimental Section

General. β -Cyclodextrin of reagent grade (Shanghai Reagent Factory) was recrystallized twice from water and dried in vacuo at 95 °C for 24 h prior to use. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under a reduced pressure prior to use. *p*-Phthaldehyde were commercially available and used without further purification. The β -cyclodextrin/*p*-phthaldehyde complex (**1**)⁹ and 5,15-bis(4-aminophenyl)-10,20-diphenylporphyrin (**2**)¹⁰ were synthesized according to the reported procedures.

Transmission electron microscopy (TEM) experiments were performed using a Philips Tacnai G² 20 S-TWIN microscope operating at 200 kV. TEM samples (1.0×10^{-4} M) were prepared by depositing a drop of the suspension onto a holey carbon grid or by placing a drop of the solution onto a carbon-coated copper grid. STM experiments were performed by using a Nanosurf instrument (Switzerland) with a Pt–Ir tip and were carried out with a sample bias voltage of +300 mV. All images were recorded in the constant-current mode. A DMF solution of sample **4** was prepared at a diluted concentration of 2×10^{-5} M and dripped onto a freshly prepared highly ordered pyrolytic graphite surface at room temperature. The sample was then dried in a vacuum for 2 h. All measures were performed in air at room temperature. Thermogravimetric (TG) analyses were obtained by using a RIGAKU standard type spectrometer. The samples were put into platinum pans, which were hung in the heating furnace. The weight percentage of material remaining in the pan was recorded, while the temperature was increased from room temperature to 600 °C at a heating rate of 20 °C/min. Nitrogen was used as the purge gas. Circular dichroism (CD) and UV–vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a JASCO J-715S spectropolarimeter or a Shimadzu UV-2401PC spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C. Fluorescence spectra were recorded in a conventional quartz cell ($10 \times 10 \times 45$ mm) at 25 °C on a JASCO FP-750 fluorescence spectrometer with the excitation and emission slits of 5 nm width. The cyclic voltammetry (CV) measurements were performed on a BAS Epsilon electrochemical analyzer in a deoxygenated DMF solution containing 0.10 M *n*-Bu₄NPF₆ as a supporting electrolyte at 298 K (50 mV s⁻¹). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO₃ (0.01 M AgNO₃) reference electrode and recalculated against internal Fc/Fc⁺.

Synthesis of **3.** **1** (126.9 mg), β -cyclodextrin (170.2 mg), and CH₃COOH (0.5 mL) were dissolved in 20 mL of DMF. Then, a DMF solution (30 mL) of **2** (64.5 mg) was added dropwise, and the resultant mixture was stirred in dark for 48 h at room temperature under nitrogen. After removing the solvent in vacuo, the residue was washed repeatedly with chloroform and water to remove the unreacted materials and possible byproducts. The crude product was dried in vacuo to give **3** (yield 36%). ¹H NMR (600 MHz, DMSO-*d*₆, TMS): δ -2.83 (s, 2H, N–H), 3.29–3.67 (m, 42H, C–H), 4.49 (m, 7H, O–H), 4.82 (d, 7H, C–H), 5.68–5.74 (m, 14H, O–H), 7.01 (d, 4H), 7.84 (m, 6H), 7.94 (d, 4H), 8.11 (d, 4H), 8.29 (d, 4H), 8.77 (s, 2H, CH=N), 8.94 (m, 8H, β -pyrrole). FT-IR (KBr, cm⁻¹): ν 3315, 2922, 2731, 1733, 1699, 1652, 1622, 1603, 1558, 1540, 1494, 1471, 1349, 1301, 1201, 1078, 1031, 966, 850, 729, 703, 666. Anal. Calcd for (C₁₈₈H₂₁₂O₇₀N₁₂·6H₂O)_n: C, 58.38; H, 5.84; N, 4.35. Found: C, 58.59; H, 5.42; N, 4.37.

Synthesis of **4.** To a solution of **3** (18.8 mg) in 20 mL of DMF was added C₆₀ (72 mg), and the mixture was stirred in dark for 24 h at room temperature under nitrogen. Then, the unreacted C₆₀ was removed by centrifugation. After removing the solvent in vacuo, the residue was dried in vacuo to give **4** in a yield of 42%. ¹H NMR (600 MHz, DMSO-*d*₆, TMS): δ -2.83

(s, 2H, N–H), 3.29–3.67 (m, 42H, C–H), 4.45 (m, 7H, O–H), 4.83 (d, 7H, C–H), 5.66–5.72 (m, 14H, O–H), 7.00 (d, 4H), 7.85 (m, 6H), 7.95 (d, 4H), 8.12 (d, 4H), 8.32 (d, 4H), 8.81 (s, 2H, CH=N), 8.93 (m, 8H, β -pyrrole). FT-IR (KBr, cm⁻¹): ν 3317, 2922, 2735, 1732, 1699, 1652, 1622, 1600, 1557, 1540, 1494, 1471, 1435, 1260, 1155, 1078, 1030, 946, 799, 706, 667, 576, 526. Anal. Calcd for (C₄₃₆H₄₂₄O₁₄₀N₂₄·9H₂O)_n: C, 62.32; H, 5.30; N, 4.00. Found: C, 62.21; H, 5.45; N, 4.29.

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Supporting Information Available: GPC and fluorescence titration spectra, TG curve of **4**, and STM image of the end of **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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