Bis(pseudopolyrotaxane)s Possessing Copper(II) Ions Formed by Different Polymer Chains and Bis(β-cyclodextrin)s Bridged with a 2,2′-Bipyridine-4,4′-Dicarboxy Tether

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ABSTRACT: Two novel nanoscale supramolecular assemblies have been synthesized from 2,2′-bipyridine-4,4′-dicarboxy-bridged bis(6-*O*-β-cyclodextrin)s possessing a coordinated copper(II) center threaded on different polymer chain (PPG and PDXL) respectively, and characterized by ^{1}H NMR, 2D NOESY, static light scattering, ESR, powder X-ray diffraction patterns, TG-DTA, STM, and TEM images, displaying two bis(pseudopolyrotaxane)s of length ca. 8−10 nm.

Introduction

Nanometer structural supramolecular assemblies created by synthetic receptors have attracted more and more attention in recent years because of their potential to serve as molecular devices and molecular machines, as well as nanostructured functional materials etc.[1] One system of current interest is the cyclodextrins and their derivatives, which exhibit selective binding of a wide variety of organic, inorganic, and biological guest molecules and form nanostructured supramolecular aggregates. Recently, Kaifer et al.[2] reported the formation of large network aggregates (∼300 nm) based on water-soluble gold nanoparticles (3.2 nm diameter) capped with thiolated γ-cyclodextrin hosts in the presence of C_{60} fullerene molecules. Harada et al.[3] reported a polyrotaxane described as a molecular necklace in which many cylcodextrins are threaded onto PEG. Shigekawa and co-workers[4] found that a cyclodextrin ring or two in such molecular necklace can be manipulated by using the tip of a scanning tunneling microscope like a molecular abacus. More recently, Willner et al.[5] reported a cyclodextrin-based light-driven molecular shuttle, which was organized on a gold electrode surface and can record optical information and transduce it by an electronic signal. Most of these investigations were with the native and simple modified α-, β-, and γ-cyclodextrins. However, reports of supramolecular aggregates based on bridged bis(cyclodextrin)s are still heretofore rare. In previous work, assemblies of bis(molecular tube)s of β-cyclodextrin derivatives containing selenium and platinum which might find potential application in drug delivery systems and the nanowires based on bridged bis(cyclodextrin)s and calix[4]arene derivatives have been reported.[6,7] Herein we wish to report our recent research in the preparation and characterization of two novel nanostructured supramolecular aggregates **3** and **4**.

Experimental Section

General Data. The NMR spectra were performed on a Varian Mercury VX300 spectrometer. A Brookhaven Instruments BI-200SM goniometer and a BI9000AT correlator were used in static light scattering experiment for vortially polarized $\lambda_0 = 514.5$ nm light (INNOVA 304), Ar$^+$ ion laser. Powder X-ray patterns were obtained using a Rigaku D/max-2500 diffractometer with Cu Kα radiation. The ESR spectra were conducted with a BRUKER EMX-6/1 spectrometer. The TG-DTA were recorded with a RIGAKU Standard type spectrometer. The 10^{-4} M aqueous solution of **3** dissolved in 0.1 N NaOH and the 10^{-4} M aqueous solution of **4** were dripped onto a freshly cleaned surface of pyrolytic graphite (HOPG) respectively, which were evaporated for at least 2 h under vacuum and then used for STM measurement (sample bias voltage +300 mV, tunneling current 2.10 nA, and a W tip).

The bridged bis(cyclodextrin)s **1** were prepared from β-CD and 2,2′-bipyridine-4,4′-dicarboxy according to our previous report.[8] Then its copper(II) complex (**2**) formed with a determined stoichiometry of 2:1 has also been reported recently.[9] When the PPG (average molecular weight 2000) was added to a saturated aqueous solution of the metallobridged bis(cyclodextrin)s **2**, it became turbid and with sonication for 30 min to enrich the precipitation. It was isolated by centrifugation and washed with water, then dried in vacuo to give **3** in 20% yield. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.03−1.05 (m, 3H × 68; CH_3 of PPG), δ 3.30−3.66 (m, 42H × 20; C_{2-6} H of **2**, 3H × 68; $-CH_2CHO-$ of PPG), δ 4.47 (s, 6H × 20; O-6 H of **2**), δ 4.82, 4.83 (d, 7H × 20; C-1 H of **2**), δ 5.68−5.76 (m, 14H × 20; O-2,3 H of **2**).

The PDXL was prepared according to the literature.[10] FT-IR (KBr): 3500.7, 2938.8, 2881.1, 1453.9, 1414.2, 1114.2, and 1040.4 cm^{-1}. The average molecular weight was controlled to be not higher than 1912 by the proportion of reactants used.

Results and Discussion

Aggregate **3** was prepared by the metallobridged bis(cyclodextrin)s **2** and poly(propylene glycol) (PPG) in 20% yield. To compare the effects of metallobridged bis(cyclodextrin)s **2** threaded on different polymer chains, we also attempted to prepare the aggregate **4** composed of **2** and poly(1,3-dioxolane) (PDXL), but the solid-state product was not obtained as expected. It is of particular interest to examine the first evidence of the solid-state bis(pseudopolyrotaxane)s formed by metallobridged bis(cyclodextrin)s threaded on poly(propylene glycol), since such bis(pseudopolyrotaxane)s possess the potential to

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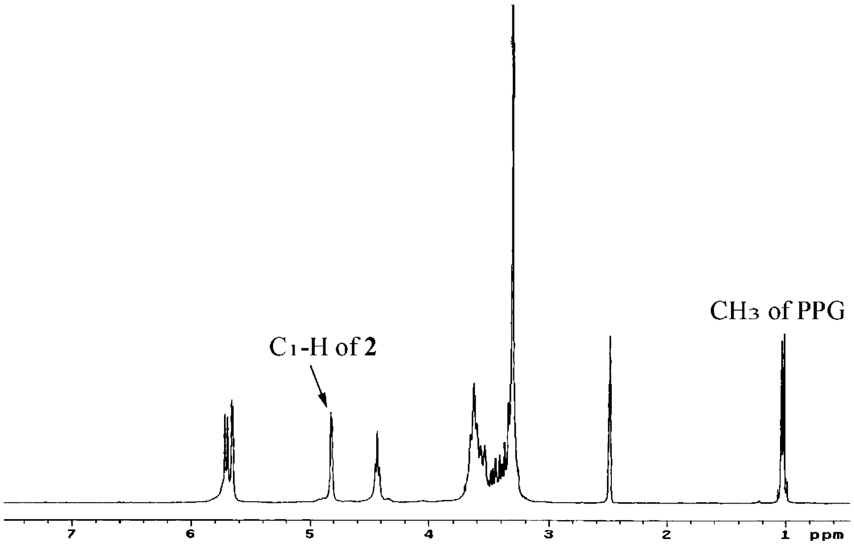
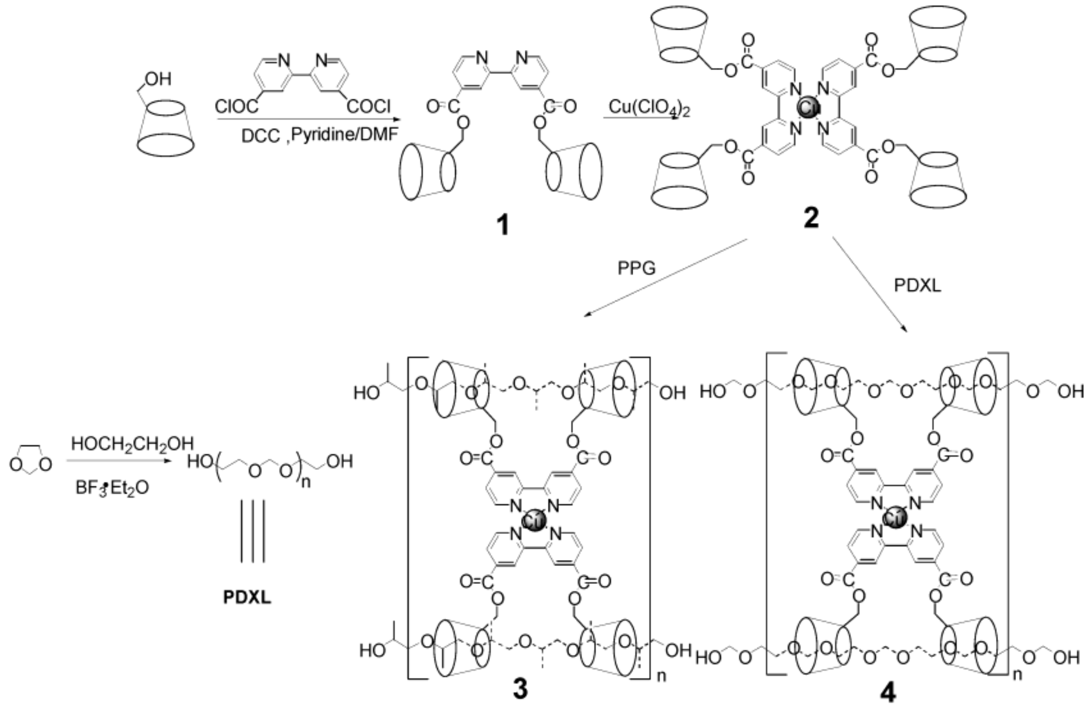


Figure 1. ^{1}H NMR spectrum of **3**.

Scheme 1



serve as a connector in the manufacturing of functional materials. The aggregates **3** and **4** were prepared as shown in Scheme 1.

From the ^{1}H NMR spectrum shown in Figure 1, the average number of metallobridged bis(cyclodextrin)s **2** in **3** can be calculated from the integral of the peak of **2** (C-1 H) and that of the methyl protons on PPG. It is ca. 5. That is to say, five metallobridged bis(cyclodextrin)s **2** units (20 cyclodextrin parts) are threaded on two polymer(PPG) chains.

To validate the polymeric number and molecular weight of **4**, which does not exist in the solid state, we performed a static light scattering experiment at 25 °C in aqueous solution by using toluene as the standard reference. Since the molecular weight of **4** is considered to be relatively low and its angular dependence is poor consequently, we made the Debye plots at 90° using a value of $(\partial n/\partial C) = 0.123$, giving the weight-average molecular weight of **4** as 3.08×10^4 g·mol^{-1}. This result indicates that two PDXL chains and five metallobridged bis(cyclodextrin)s **2** units form the molecular aggregate **4**.

To further confirm the threading of metallobridged bis(cyclodextrin)s **2**, a representative 2D NOESY NMR spectrum of **3** is shown in Figure 2. The NOESY spectrum shows a strong cross-peak between the methyl protons of the PPG and the H-3, H-5 protons of **2**, indicating the metallobridged bis(cyclodextrin)s **2** threaded onto the PPG.

The peak related to the bipyridine protons of metallobridged bis(cyclodextrin)s **2** was unable to be observed in the ^{1}H NMR spectrum because of paramagnetic disturbance caused by the ligated copper(II).[9] On the other hand, the paramagnetism of copper(II) can provide a powerful method to estimate the environment of copper(II) in metallobridged bis(cyclodextrin)s **2** by ESR spectroscopy. The ESR spectroscopy of **2** and **3** is shown in Figure 3.

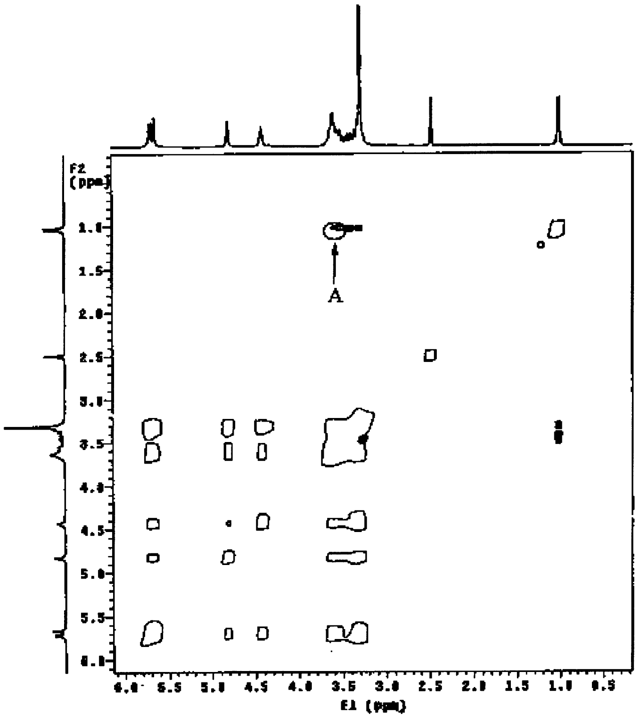


Figure 2. 2D NOESY NMR spectrum of **3**.

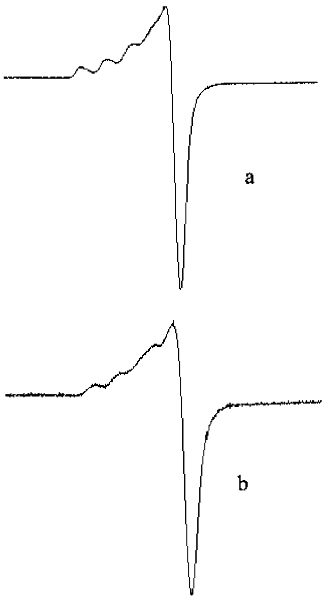


Figure 3. ESR spectroscopy of **3** (a) and **2** (b).

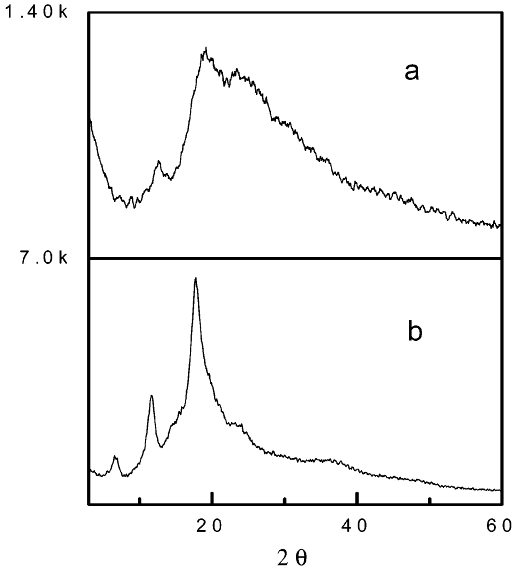


Figure 4. X-ray powder diffraction patterns of **2** (a) and **3** (b).

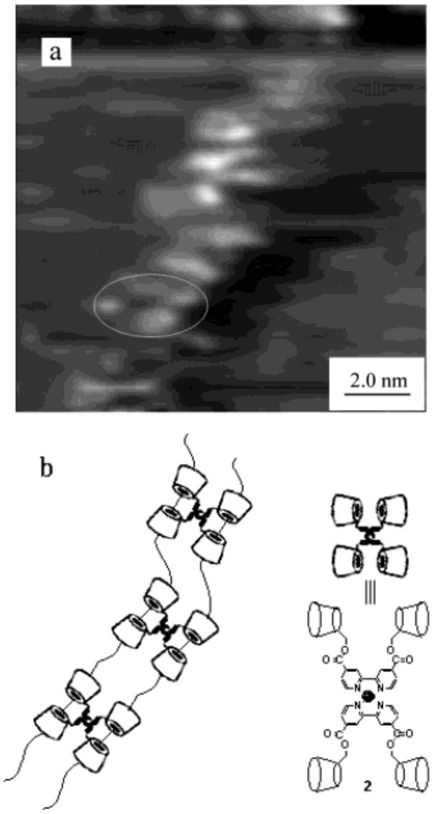


Figure 5. STM image of **3** (a) and its chemical structure (b).

It is easy to recognize from the electron spin resonance (ESR) spectra that the copper(II) in metallobridged bis(cyclodextrin)s **2** possesses the octahedral configuration with tetragonal elongation since a larger parallel Cu hyperfine coupling can be seen. In the low-field region, all four of the lines corresponding to the parallel hyperfine coupling from Cu ($I = {}^3/_2$) exhibit some distinction for Figure 3, parts a and b. In Figure 3a, the four lines are resolved due to a complete averaging effect of coordinated pyridine sections. However, they give slight changes in Figure 3b. This illuminates that the averaging effect was disturbed by the polymer chain penetrating into the cavities of **2**. Since the cyclodextrin unit is large enough to separate the copper(II) center from the ambient environment, the polymer chain can come close enough to affect the copper(II) center only by being included in the cavities of cyclodextrins. This result also indicated the formation of **3**.

Figure 4 shows the powder X-ray diffraction patterns of **3** and metallobridged bis(cyclodextrin)s **2**. Since reports about the X-ray powder pattern of bridged bis(cyclodextrin)s are unavailable, not like that of native cyclodextrins and their complexes with guest molecules, it is difficult to compare and deduce the structure of compounds **2** and **3**. But it is easy to observe that the diffractogram of **3** is much different from that of metallobridged bis(cyclodextrin)s **2**. The increasingly diffraction peaks in Figure 4b indicate that **3** is more

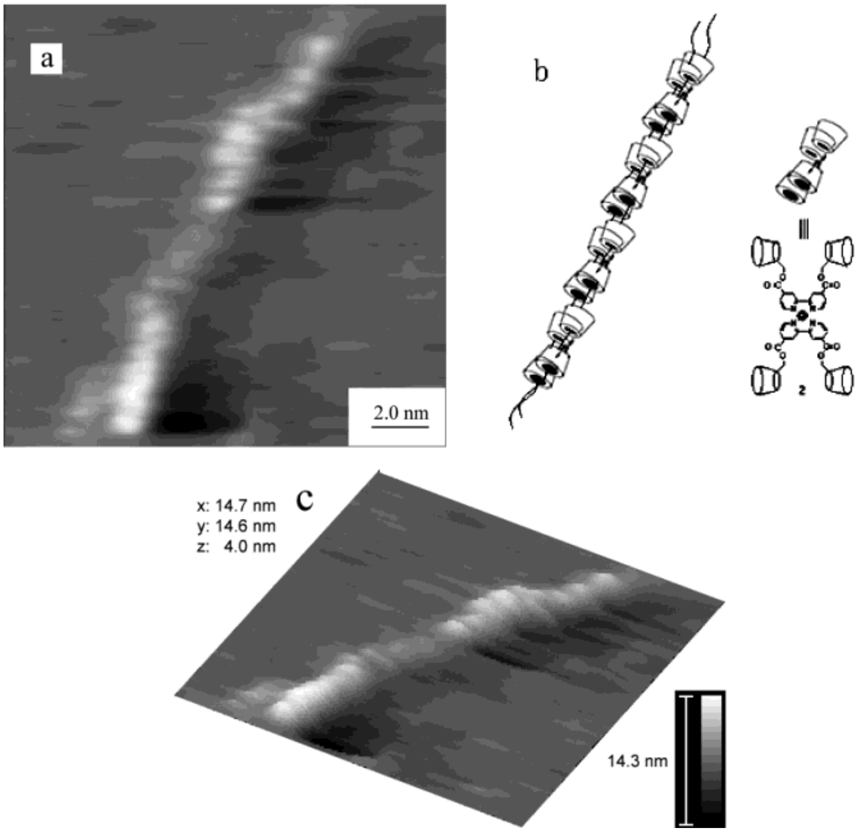


Figure 6. STM image of **4** (a, c) and its chemical structure (b).

like a crystalline than metallobridged bis(cyclodextrin)s **2**. On the other hand, few diffraction peaks observed for the metallobridged bis(cyclodextrin)s **2** in Figure 4a suggest that its structure is on the border between crystalline and noncrystalline. These results show that the threading of the polymer chain somewhat ordered the structure of metallobridged bis(cyclodextrin)s **2**.

To compare the thermal stabilities of **2** and **3**, the thermogravimetric (TG) and differential thermal analysis (DTA) were performed. TG shows that the decomposition point of compound **3** is higher than that of metallobridged bis(cyclodextrin)s **2**. The decomposing temperatures of **3** and **2** are 236 and 192 °C, respectively, which may be attributed to the cleavage of the ester bonds in **2** and **3**. Simultaneously, DTA shows exothermic peaks at 317 °C for **2** and at 344 °C for **3**. Considering that the native β-cyclodextrin decomposes above 300 °C, these temperatures may refer to the decomposition of cyclodextrin in **2** and **3**. It is clearly indicated that PPG plays a stabilizing role for **2**.

The most direct evidence for the formation of bis(pseudopolyrotaxane)s **3** is given in Figure 5 by scanning tunneling microscope (STM), which has been recognized as one of the most powerful tool for detecting the microstructures of certain substances. As can be seen from Figure 5a, a typical STM image of **3** on a graphite substrate indicated that the bis(pseudopolyrotaxane)s have been fabricated via the metallobridged bis(cyclodextrin)s **2** threaded on two poly(propylene glycol) chains. According to the size, one bright dot in Figure 5a corresponds to a β-cyclodextrin unit, which lies with its longitudinal axis parallel to the surface, and four bright dots compose a block as metallobridged bis(cyclodextrin)s **2**. Although there is some overlapping, we notice that there exist more than three of such blocks in a regular alignment. The average distances between two adjacent cyclodextrins units are 1.8 and 2.2 nm in two directions. The former is closely related to the two cyclodextrins linked by 2,2′-bipyridine-4,4′-dicarboxy tether, and the latter refers to the two cyclodextrins threaded on two polymer chains, respectively. On the other hand, the STM investigation of **4** is consistent with the results obtained in 2D NOESY (see Supporting Information). As can be seen from Figure 6, the STM images of **4** clearly show the bis(pseudopolyrotaxane)s composed of perpendicular metallobridged bis(cyclodextrin)s **2** and PDXL. We can see two bis(pseudopolyrotaxane)s indicated by about eight bright dots, which means that there are four metallobridged bis(cyclodextrin)s **2** threaded on PDXL.

To further confirm the formation mode of the aggregates **3** and **4**, a control experiment has been performed in the same condition to obtain the STM image of bis(cyclodextrin)s **1** and PDXL (see Supporting Information). The wirelike array obtained suggests that the polymer chain should thread through two cavities of **1** in turn rather than in random fashion. Therefore, this control experiment ensures that the formation mode we deduced in Figure 5b and Figure 6b is in fact the dominant recognition event between **2** and polymer chains.

The transmission electron microscopy (TEM) image provides further insight into the size and shape of **3** (Figure 7). For the TEM image, aqueous solution of **3** was brought onto a carbon-coated copper grid, and then was shaded with chromium to thicken and make the image clearer. Therefore, the TEM image prepared in this way could not be used to measure the width of the assembly, but only to calculate its length. From Figure 7, we can note clearly some chain-shape structures in the length scales of about 10−300 nm that correspond to the single assembly **3** and the aggregates of many

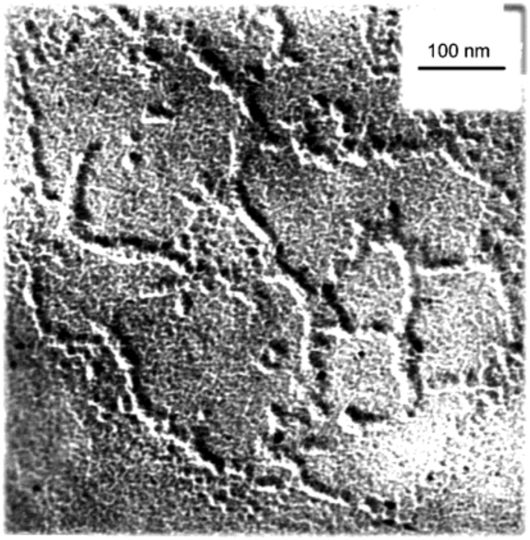


Figure 7. TEM image of **3**.

assemblies **3**, respectively, which are identical with the results obtained in the STM image (Figure 5).

In conclusion, we have synthesized two novel bis(pseudopolyrotaxane)s composed of metallobridged bis(cyclodextrin)s possessing the ligated copper(II) center and polymer chains. Though the bis(pseudopolyrotaxane)s **4** formed by PDXL and **2** were not directly observed in the solid state, the STM image and 2D NOESY spectrum show the formation of this assembly. It is important that the solid-state bis(pseudopolyrotaxane)s **3** formed by PPG and **2** were observed directly because of the formative precipitation of assembly in solution. The present study reveals that the two different polymer chains both form assemblies with **2,** which can be used as nanoconnectors for designing novel functional materials and possess the potential to serve as molecular devices and molecular machines. As a consequence, further investigation is in progress.

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Supporting Information Available: Figures showing the 2D NOESY spectrum of **4** and the STM image of the **1**-PDXL complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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