

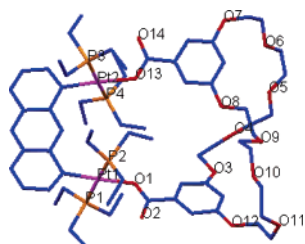
Incorporating a Flexible Crown Ether into Neutral Discrete Self-Assemblies Driven by Metal Coordination

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Driven by metal coordination, a flexible crown ether was self-assembled into neutral discrete complexes with two organoplatinum acceptors. Specifically, a [1 + 1]-assembled structure was separated from self-assemblies with different stoichiometries by vapor diffusion of acetone into their dichloromethane solution. The formation of these crown ether-incorporated self-assemblies was confirmed by NMR, elemental analysis, and X-ray single-crystal analysis.

In the past decade the preparation of finite two-dimensional (2D) and three-dimensional (3D) nanostructures by self-assembly of simple building blocks in solution has received considerable attention.¹ Coordination-driven self-assembly using metal systems is a growing area at the forefront of supramolecular chemistry.¹ Much of this construction has been based on the coordination motif between Pd(II)/Pt(II) acceptor species and neutral nitrogen donor units.^{1c,i,k-m} Therefore, usually ionic self-assemblies were obtained. Neutral assemblies are believed to be more suitable for encapsulation of neutral organic guests, so recently we utilized Pt–oxygen bonding to fabricate some neutral, discrete, nanoscopic assemblies.² First, we used rigid or flexible dicarboxylate-based nonfunctional building blocks (terephthalate, fumarate, isophthalate, muconate, etc.) to fabricate rectangles,^{2a,b} rhomboids,^{2b} and triangles.^{2b} Later, we prepared a neutral ferrocene-containing heterobimetallic rectangle and a rhomboid.^{2c} Due to their three-dimensional aromaticity, carboranes have many important applications in material

sciences.³ Therefore, we made a carborane-containing neutral rectangle and a rhomboid.^{2d} Recently we synthesized enantiopure chiral tartrate-based rectangles,^{2e} which exhibited induced circular dichroism.

Applications of crown ethers in supramolecular chemistry can be dated back to Pederson's discovery of the alkalai-metal-templated synthesis of crown ethers.⁴ They have been widely used as hosts of metal ions and small organic molecules.⁵ More recent studies focused on complexation between dibenzo crown ethers and organic guests.⁶

Previously we prepared three ionic, discrete assemblies by incorporation of a flexible pyridine-functionalized 18-membered diaza crown ether via coordination-driven self-assembly.⁷ Herein we report the successful preparation of two neutral, discrete assemblies from a flexible 32-membered dibenzo crown ether and two organoplatinum acceptors based on Pt–oxygen bonding (Scheme 1) and their characterization, including X-ray single-crystal analysis of one assembly.

The disodium salt **1** was prepared by neutralizing bis(5-carboxy-*m*-phenylene)-32-crown-10⁸ with NaHCO₃ in a 1:1 water/acetone solution. Dropwise addition of an aqueous solu-

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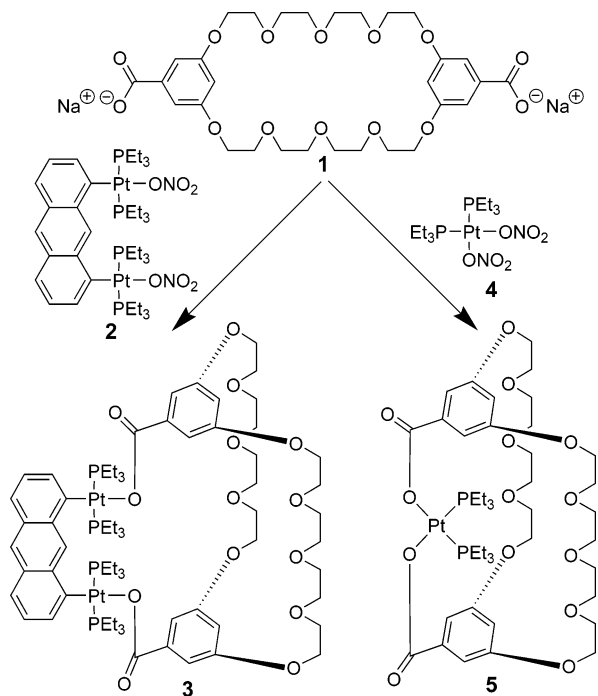
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SCHEME 1. Self-Assembly of **1** with Platinum Acceptor **2** and **4**

tion of **1** to an acetone solution of the anthracene-based platinum acceptor **2** at room temperature resulted in gradual precipitation of some pale yellow solid, which was collected, washed with acetone and water, and dried under vacuum. The proton NMR spectrum (Figure 1b) of the crude product shows some peaks of impurities, indicating that it contains not only the [1 + 1] assembly, but also assemblies with other stoichiometries. Increasing the reaction temperature even to 80 °C did not change the product composition. This is interesting considering that only [1 + 1] ionic assembly was obtained when a pyridine-functionalized 18-membered diaza crown ether and clip **2** were used as building blocks.⁷ Vapor diffusion of acetone into the dichloromethane solution of the crude product afforded pure **3** as yellow crystals. Only a sharp singlet with concomitant ¹⁹⁵Pt satellites appeared in the ³¹P NMR spectrum of **3** (Figure 2b), indicating that its four P atoms have equivalent chemical

environments. The small downfield shift (Figure 2a,b), 1.09 ppm, of this peak relative to that of **2** is understandable considering that the four P atoms are in the deshielding field of the crown ether aromatic rings and formation of a Pt–O coordinate bond replacing a similar Pt–O coordinate bond (Pt–OOC– vs Pt–ONO₂) in the starting “clip”.

X-ray-quality single crystals of **3** were prepared by vapor diffusion of pentane into a dichloromethane solution of **3**. Crystallography unambiguously established the structure of **3**, a discrete neutral species (Figure 3). In this structure, the dibenzo crown ether part is folded and its two ethylene glycol chains have a gauche conformation. These are similar to conformations observed in complexes of analogues of **1**.⁹ The two aromatic rings of **3** are not parallel to each other, but are splayed at an angle of 35.5° with a centroid–centroid distance of 7.44 Å. This distance is close to the corresponding distance, 7.39 Å, in two complexes of analogues of **1**,^{9a,b} but larger than in some other analogous complexes.^{9c,f}

Dropwise addition of an aqueous solution of **1** to an acetone solution of 90° organoplatinum acceptor **4** afforded only [1 + 1] self-assembly **5**; proton and phosphorus NMR spectra of the product show only one set of peaks. The relatively large upfield shift (Figure 2c,d), 7.40 ppm, of the sharp peak in the ³¹P NMR spectrum of **5** relative to **4** is in contrast to the small downfield shift of the corresponding peak of **3** relative to **2**. This is possibly due to the inclusion of the two electron-poor P atoms in the electron-rich cavity of the crown ether unit of self-assembly **5**, which is not possible in self-assembly **3** because the anthracene moiety is too big. The shielding effect of two aromatic rings of the crown ether part and electron donation from the ethereal oxygen atoms make this upfield shift relatively large.

In summary, we successfully prepared two neutral discrete self-assemblies from a flexible crown ether and two organoplatinum acceptors based on Pt–oxygen bonding. Specifically, [1 + 1] self-assembly **3** was successfully separated from self-assemblies with different stoichiometries by vapor diffusion of acetone into their dichloromethane solution and its structure unambiguously established via X-ray crystallography.

Experimental Section

Methods and Materials. Organoplatinum compounds **2**¹⁰ and **4**¹¹ were prepared as reported.

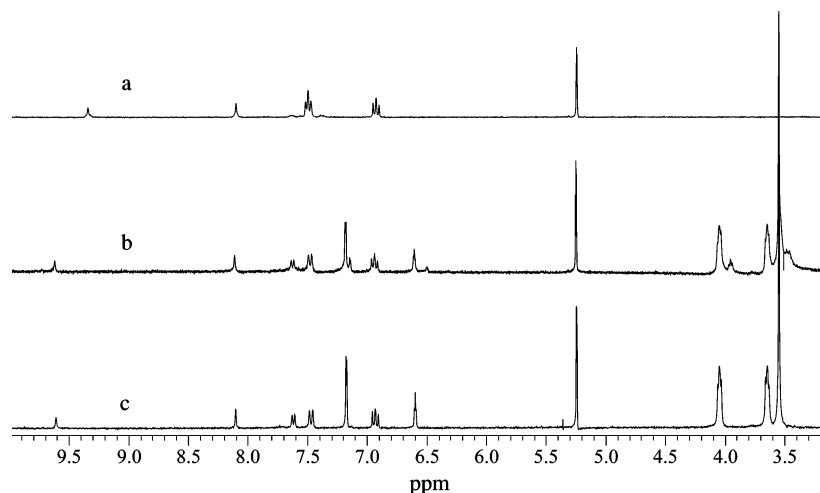


FIGURE 1. Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 22 °C) of (a) clip **2**, (b) crude product from the preparation of self-assembly **3**, and (c) self-assembly **3**.

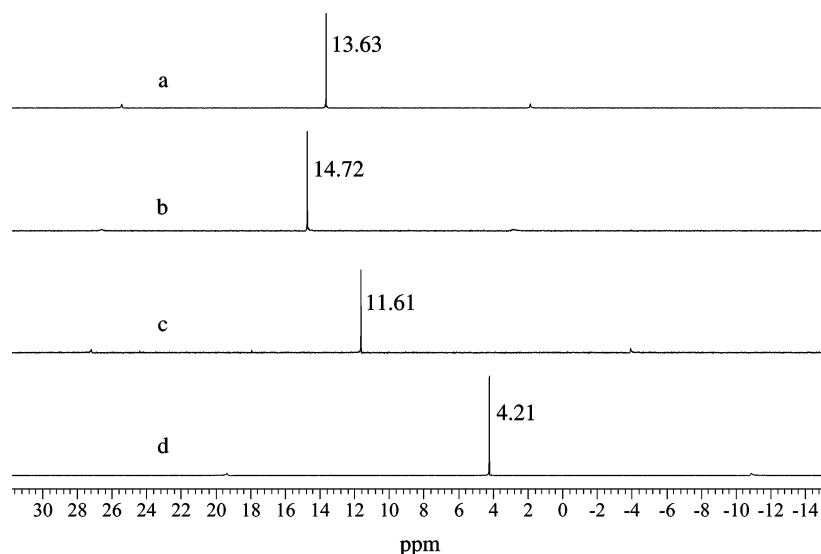


FIGURE 2. ^{31}P NMR spectra (121.4 MHz, CD_2Cl_2 , 22 °C) of (a) clip **2**, (b) self-assembly **3**, (c) 90° organoplatinum acceptor **4**, and (d) self-assembly **5**.

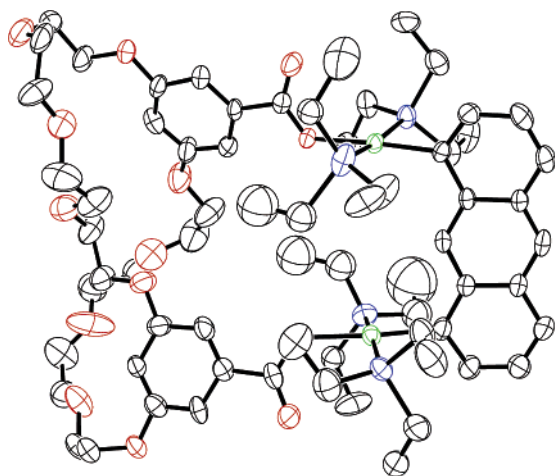


FIGURE 3. X-ray structure of **3** (30% thermal ellipsoids). Oxygen atoms are red, carbon atoms are black, platinum atoms are green, and phosphorus atoms are blue. Hydrogen atoms and solvent molecules have been omitted for clarity.

Synthesis of 3. To a 2 mL acetone solution containing 5.81 mg (0.00500 mmol) of **2** in an 8 mL vial was added an aqueous solution (2 mL) of disalt **1** (3.34 mg, 0.00500 mmol) drop by drop with continuous stirring (15 min). After the addition, the vial was sealed with Teflon tape, and the reaction mixture was stirred overnight. The yellow products, which precipitated, were filtered and washed with acetone and water, collected, and dried under vacuum. The

crude product was dissolved in 1.5 mL of dichloromethane. Vapor diffusion of acetone into this solution afforded pure **3** as yellow crystals (4.24 mg, 51%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 22 °C): δ (ppm) 14.72 (s, $^1J_{\text{PPt}} = 2874$ Hz). ^1H NMR (400 MHz, CD_2Cl_2 , 22 °C): δ (ppm) 9.69 (1H, s), 8.18 (1H, s), 7.69 (2H, d, $^3J_{\text{HH}} = 8.8$ Hz), 7.55 (2H, d, $^3J_{\text{HH}} = 10.8$ Hz), 7.25 (4H, d, $^3J_{\text{HH}} = 2.8$ Hz), 7.01 (2H, t, $^3J_{\text{HH}} = 10.0$ Hz), 6.67 (2H, t, $^3J_{\text{HH}} = 2.8$ Hz), 4.12 (8H, t, $^3J_{\text{HH}} = 5.6$ Hz), 3.72 (8H, t, $^3J_{\text{HH}} = 5.6$ Hz), 3.62 (16H, m), 1.57 (24H, m), and 1.04 (36H, m). Anal. Calcd for $\text{C}_{68}\text{H}_{106}\text{O}_{14}\text{Pt}_4\text{-Pt}_2\cdot\text{H}_2\text{O}$: C, 48.61; H, 6.48. Found: C, 48.38; H, 6.58.

Synthesis of 5. To a 2 mL acetone solution containing 3.65 mg (0.00500 mmol) of **4** in an 8 mL vial was added an aqueous solution (2 mL) of disalt **1** (3.34 mg, 0.00500 mmol) drop by drop with continuous stirring (15 min). After the addition, the vial was sealed with Teflon tape, and the reaction mixture was stirred overnight. Solvents were evaporated to afford a gel, which was dissolved in dichloromethane and washed with water three times. The organic layer was separated, evaporated, and dried under vacuum to provide **5** as a colorless gel (5.00 mg, 95%). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, CD_2Cl_2 , 22 °C): δ (ppm) 4.21 (s, $^1J_{\text{PPt}} = 3670$ Hz). ^1H NMR (400 MHz, CD_2Cl_2 , 22 °C): δ (ppm) 6.88 (4H, d, $^3J_{\text{HH}} = 2.8$ Hz), 6.37 (2H, t, $^3J_{\text{HH}} = 2.8$ Hz), 3.89 (8H, m), 3.80–3.51 (24H, m), 1.92 (12H, m), and 1.26 (18H, m). Anal. Calcd for $\text{C}_{42}\text{H}_{68}\text{O}_{14}\text{Pt}_4\text{-H}_2\text{O}$: C, 47.04; H, 6.58. Found: C, 47.30; H, 6.73.

X-ray Crystal Data for Self-Assembly 3. Crystallographic data: plate, yellow, $0.30 \times 0.23 \times 0.05$ mm 3 , $\text{C}_{68}\text{H}_{106}\text{O}_{14}\text{Pt}_4\text{-Pt}_2\cdot(\text{C}_5\text{H}_{12})_{0.5}$, FW 1697.66, triclinic, space group $P\bar{1}$, $a = 12.4457(6)$ Å, $b = 15.6835(9)$ Å, $c = 20.4400(10)$ Å, $\alpha = 106.507(3)^\circ$, $\beta = 96.998(4)^\circ$, $\gamma = 102.985(3)^\circ$, $V = 3653.1(3)$ Å 3 , $Z = 2$, $D_c = 1.543$ g cm $^{-3}$, $T = 150(1)$ K, $\mu = 3.973$ mm $^{-1}$, 19805 measured reflections, 12289 independent reflections, 772 parameters, 5 restraints, $F(000) = 1726$, $R_1 = 0.1041$, $wR_2 = 0.2116$ (all data), $R_1 = 0.0718$, $wR_2 = 0.1813$ [$I > 2\sigma(I)$], maximum residual density 0.96 e $^{-\text{Å}^{-3}}$, maximum/minimum transmission 0.8261/0.3819, and goodness-of-fit (F^2) 1.038.

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Supporting Information Available: NMR spectral data for self-assemblies **3** and **5** and X-ray crystallographic data of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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