



Coordination-driven self-assembly of dibenzo-18-crown-6 functionalized Pt(II) metallacycles

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ABSTRACT

Coordination-driven self-assembly was used to construct two metallacycles of a dicarboxylate-functionalized dibenzo-18-crown-6 in combination with either a 0° anthracene-based clip-type acceptor or a 60° phenanthrene-based acceptor. The angularities of these moieties make them suitable for the formation of a [2+2] rectangle and a [3+3] triangle, respectively. The synthesis, characterization and host-guest chemistry of two metallacycles were described and supported by ³¹P{¹H}, ¹H NMR spectra and electrospray mass spectrometry.

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Supramolecular self-assemblies have attracted great attention not only because of their methodological importance, but also due to their successful applications in sensors [1–6], catalysis [7–13], medical reagents [14–18] and smart materials [19–26]. Coordination-driven transition-metal mediated self-assembly is one of the highly efficient approaches for the construction of discrete or consecutive metal organic cycles/cages (COCs) with programmed shapes and geometries [26–31]. By incorporating functional macrocycles, such as porphyrin [32–36], calixarene [37–39], cavitand [40–42], and pillararene [43–46] into the discrete assemblies, artificial functional nanoscale devices with precisely controlled geometries can be fabricated. Because of their interesting host-guest properties with metal and organic cations, crown ethers have attracted much attention and have been widely used in cation transport and separation, chemosensors, molecular machines and supramolecular polymers [47–54]. Previous works have demonstrated that crown ethers can also be used as flexible building blocks in the construction of discrete complexes [55–58]. As the earliest and most prominent class of crown ethers, 18-crown-6 (18C6) is well known for its strong binding affinity to various metal and ammonium cations, which promote their applications in many

fields [59–65], including phase transfer catalysis, superconductors, crystal engineering and mass spectrometry.

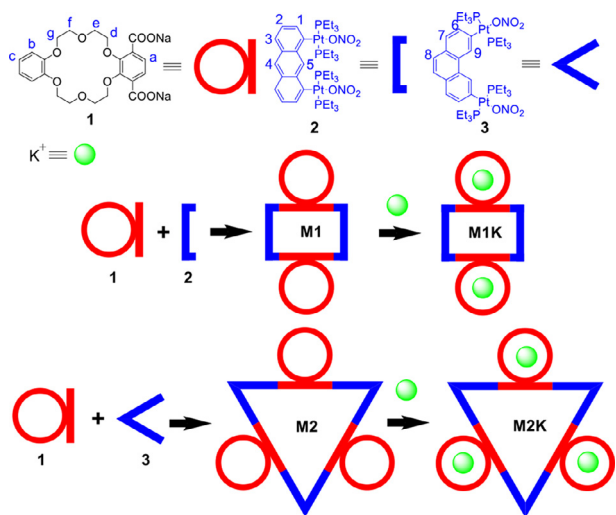
In the present work, we combined a dicarboxylate-functionalized dibenzo crown ether **1** with the well-established platinum(II)-oxygen coordination driven self-assembly to report the syntheses, spectroscopic characterization and host-guest chemistry of an A₂D₂ (A=acceptor and D=donor) rectangle metallacycle **M1** and an A₃D₃ triangle metallacycle **M2** based on 18-crown-6, respectively (Scheme 1, Schemes S2 and S3 in Supporting information).

The dicarboxylate-functionalized dibenzo 18C6 donor **1** was easily synthesized in four steps from commercially available reagents (Scheme S1 in Supporting information). As shown in Scheme 1, the neutral rectangle **M1** and triangle **M2** were then prepared via two component coordination-driven self-assembly by stirring **1** with either the anthracene-based clip **2** or the 60° phenanthrene-based acceptor **3** respectively, in a 1:1 ratio H₂O/CH₂Cl₂ solution. As the reaction proceeded, the metallacycles were extracted into the organic phase, while the inorganic byproduct remained in the aqueous solution. After washing with water to remove the residual inorganic salts, pure metallacycles were furnished in almost quantitative yields. As far as we know, this is the first report to perform coordination-driven self-assembly in a biphasic system.

The ³¹P{¹H} spectroscopy supported the formation of single, discrete 2D metallacycles with highly symmetric structures (Fig.

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Scheme 1. Self-assembly of dibenzo-18-crown-6-functionalized metallacycles **M1** and **M2** and their complexation with K^+ .

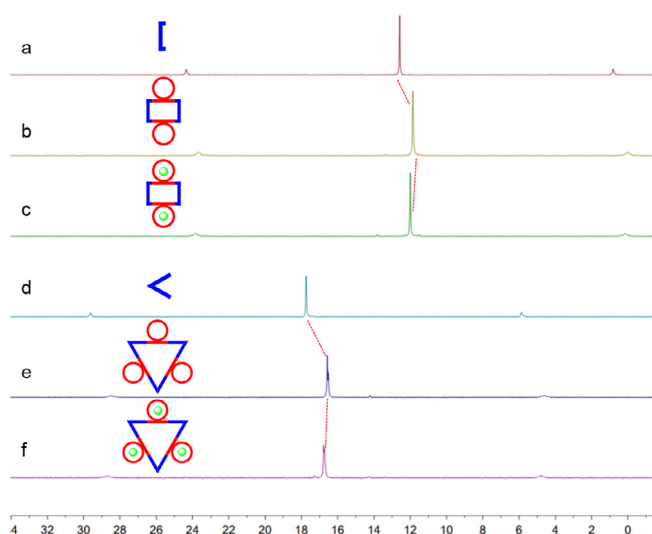


Fig. 1. $^{31}P\{^1H\}$ NMR (121.4 MHz, $CD_2Cl_2/CD_3COCD_3 = 2:1$, 22 °C) spectra: (a) **2**; (b) **M1**; (c) **M1** + 2 equiv. KPF_6 ; (d) **3**; (e) **M2**; (f) **M2** + 3 equiv. KPF_6 .

1). For example, the $^{31}P\{^1H\}$ NMR spectra for **M1** and **M2** showed a sharp singlet at δ 11.85 (Fig. 1b) and 16.55 ppm (Fig. 1e), respectively, suggesting a single phosphorus environment as expected. The peaks of **M1** and **M2** shifted upfield from the starting platinum acceptors **2** (δ 12.59 ppm, Fig. 1a) and **3** (δ 17.73 ppm, Fig. 1d). Since 18-crown-6 is an excellent host for selective complexation of potassium cation, we investigated the host-guest behavior of these two neutral metallacycles. After the addition of corresponding KPF_6 respectively, the ^{31}P NMR spectra still showed sharp singlets, but they shifted downfield slightly (δ 11.99 ppm for **M1K** and δ 16.79 ppm for **M2K**) (Figs. 1c and f). These results indicated that the binding of the K^+ slightly changed the chemical environment of the phosphorus atoms.

The 1H NMR spectra of **M1** and **M2** (Figs. 2b and f) also confirmed the highly symmetric discrete structures and displayed significant spectroscopic differences from the precursor building blocks **2** and **3** respectively (Fig. 2). The upfield shifts of H_a , H_b and H_c after the dicarboxylic acid **1-A** (Fig. 2) was incorporated into the rectangle **M1** or the triangle **M2** could be attributed to the formation of new Pt-O coordinate bonds (Pt-OOC- instead of Pt-ONO₂). The upfield shifts of H_{d-g} indicated the metal-coordination could

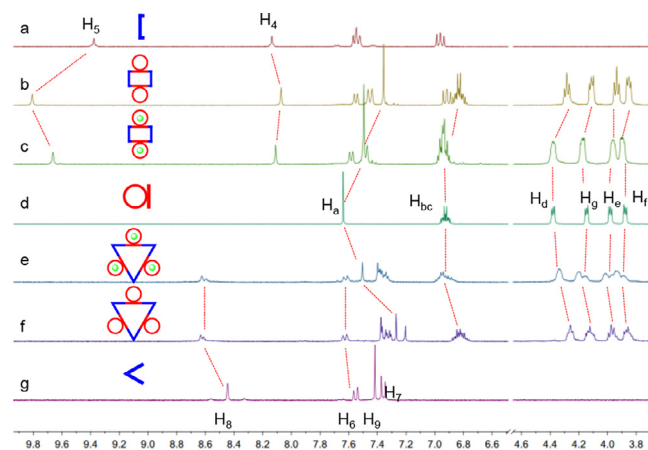


Fig. 2. Partial 1H NMR (400 MHz, $CD_2Cl_2/CD_3COCD_3 = 2:1$, 22 °C) spectra: (a) **2**; (b) **M1**; (c) **M1** + 2 equiv. KPF_6 ; (d) dicarboxylic acid **1-A**; (e) **M2** + 3 equiv. KPF_6 ; (f) **M2**; (g) **3**.

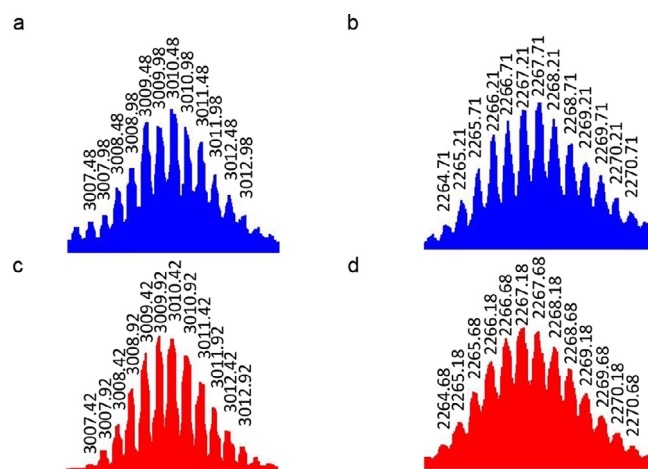


Fig. 3. ESI mass spectra of (a) $[M1 + K]^+$ and (b) $[M2 + 2K]^{2+}$ and their simulated spectra (c and d, respectively).

also affect the ethyleneoxy protons on **1** by decreasing the electron density of the crown ether. After the addition of KPF_6 , except for H_5 , the protons of **M1** and **M2** on the clip acceptor **2** shifted downfield somehow (Figs. 2c and e), especially for protons on **1**. This is consistent with the complex-induced slight downfield shifts observed in $^{31}P\{^1H\}$ NMR spectra, and the formation of **M1K** and **M2K** with the electron-deficient potassium cations.

Further evidence for the formation of the desired self-assembled metallacycles was obtained by electrospray ionization mass spectrometry (ESI-MS) studies. For **M1**, peaks were observed corresponding to $[M1 + H]^+$ (m/z 2971.51), $[M1 + K]^+$ (m/z 3010.48), $[M1 + H + K]^{2+}$ (m/z 1505.75) and $[M1 + 2K]^{2+}$ (m/z 1524.23). These were all isotopically resolved and in excellent agreement with their theoretical distributions (Figs. 3a and c, Fig. S4 in Supporting information). For **M2**, peaks were also found in excellent agreement with their theoretical isotopical distributions: $[M2 + K]^+$ (m/z 4495.14), $[M2 + 2H]^{2+}$ (m/z 2229.63), $[M2 + H + K]^{2+}$ (m/z 2248.64), $[M2 + Na + K]^{2+}$ (m/z 2259.62) and $[M2 + 2K]^{2+}$ (m/z 2267.71), as shown in Figs. 3b and d, Figs. S5 and S6 (Supporting information). We also found that no matter if univalent or bivalent components in their mass spectra, compared with other complexes, the highest peak is the one with K^+ . For instance, $[M1 + K]^+$ (m/z 3010.48) in Fig. S4 and $[M2 + 2K]^{2+}$ (m/z 2267.71) in Fig. S6. This further indicated the selective host-guest complexation of the neutral rectangle **M1** and triangle **M2** with K^+ .

In summary, a new dibenzo 18-crown-6 ether dicarboxylate donor **1** with 180° coordination angle was designed and synthesized. By employing this new unit, a discrete A₂D₂ rectangle **M1** and an A₃D₃ triangle **M2** were synthesized via coordination-driven self-assembly and characterized by ³¹P{¹H} NMR, ¹H NMR and electrospray ionization mass spectrometry. The complexation of the two metallacycles with K⁺ was further studied to present that the host-guest recognition of crown ethers did not interfere with the coordination-driven self-assembly. The convenient preparation and simple purification of these metallacycles make it possible to prepare crown ether functionalized self-assemblies for catalysis, molecular devices or chemical sensors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.05.035.

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