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Pt(II)-Based Convex Trigonal Prismatic Cages via Coordination-Driven Self-Assembly and C₆₀ Encapsulation

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Abstract

The development of three dimensional supramolecular coordination complexes (SCCs) is of great interest from both fundamental and application points of view, because these materials are useful in molecular catalysis, separation and purification, sensing, etc. Herein, we describe the synthesis of two Klärner's molecular clip-based tetrapyrrolyl donors, which possess a C-shaped structure as shown by the X-ray analysis, and subsequently use them to prepare four convex trigonal prismatic cages via coordination-driven self-assembly with two 180° diplatinum(II) acceptors. The cages are fully characterized by multinuclear NMR (³¹P and ¹H) analysis, diffusion-ordered spectroscopy (DOSY), electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) and UV/Vis absorption spectroscopy. Moreover, the incorporation of molecular clip-based ligands provides these cages with free cavities to encapsulate fullerene C₆₀ via aromatic interactions, which may be useful for fullerene separation and purification. The studies described herein enlarge the scope of

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ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Syntheses and characterization data (NMR, ESI-TOF-MS, UV/Vis absorption spectra), including Figures S1–S39.

The authors declare no competing financial interest.

the Pt(II)-based directional bonding approach in the preparation of curved 3D metallacages and their host-guest chemistry.

Graphical abstract

INTRODUCTION

Nature has constructed numerous giant functional structures via the self-assembly of small molecular building blocks. Inspired by this, supramolecular coordination complexes (SCCs)¹ with well-defined shapes and geometries have been prepared via coordination-driven self-assembly. To date, various SCCs with different 2D² (triangles, rectangles, pentagons, hexagons, etc) and 3D geometries³ (tetrahedrons, cages, prisms, etc) have been constructed via the directional bonding approach.⁴ In this regard, Fujita *et al.* prepared a suite of M_nL_{2n} polyhedra via the self-assembly of Pd(II) ions and dipyridyl ligands and explored them as molecular flasks for chemical reactions.⁵ Using banana-shaped ligands, Clever and coworkers reported a series of Pd(II) coordination cages, tubular assemblies, and interlocked cages that allow light-controlled uptake and release of guest molecules.⁶ The group of Yoshizawa described the syntheses of polyaromatic encircled molecular capsules using anthracene appended donor systems. These systems result in highly emissive host-guest complexes upon the encapsulation of fluorescent dyes.⁷ Mukherjee and coworkers presented a self-templated method to prepare a molecular nanoball via the self-assembly of a Pd(II) ion and a 120° bidentate donor pyrimidine.⁸ Our group has devoted more than two decades to the preparation of well-defined SCCs ranging from 2D polygons and 3D polyhedral, including cuboctahedron and dodecahedron.⁹ Very recently, we introduced tetraphenylethene groups to construct emissive Pt(II) metallacycles and metallacages and demonstrated that these SCCs can be used as supramolecular theranostic agents combining both cancer diagnostic and therapeutic activity in a single entity.¹⁰ Nevertheless, the rational design of tetra-coordinated Pd(II)/Pt(II)-based SCCs are still challenging and sometimes interlocked structures as well as unexpected species are obtained.¹¹

Klärner *et al.* has developed a family of molecular clips having benzene or naphthalene groups surrounded by a belt of convergent aromatic rings¹² and used them as noncyclic receptors for a wide range of organic molecules. These recognitions depend upon multiple aromatic interactions that synergistically enhance the binding affinities. The calculated electrostatic surface potentials (ESPs) of these molecular clips are highly negative inside the cavity, making them suitable for guest molecules with positive ESPs. To the best of our knowledge, convex 3D SCCs are still rare in metallosupramolecular chemistry. We herein report on the synthesis and characterization of four convex trigonal prismatic cage structures derived from molecular clip-based tetrapyridyl donors (Figure 1) and 180° diplatinum(II) acceptors, as shown in Figure 2. Moreover, these trigonal prismatic cages possess cavities

suitable for the encapsulation of fullerenes, as confirmed by high-resolution mass spectrometry and ^1H NMR spectroscopy.¹³

RESULTS AND DISCUSSION

The key intermediate 2,3,11,12-tetrabromo-7,16-dimethoxy-(6a,8a,15a,17a)-6,8,15,17-tetrahydro-6,17:8,15-dimethanoheptacene (**1**) was synthesized according to a literature procedure.¹² Followed by a Suzuki or Sonogashira coupling reaction of **1** with pyridine-4-boronic acid or 4-ethynylpyridine (Scheme 1), tetrapyridyl ligands **2** and **3** were prepared in yields of 57% and 48%, respectively. The crystal structure of **2** (Figure 1) shows that it possesses a C-shaped structure, enabling ideal ligand preorganization for the further construction of convex trigonal prismatic cages via coordination-driven self-assembly.

Tetrapyridyl ligand **2** or **3** and 180° diplatinum(II) acceptor **4** or **5** were mixed in a 2:1 molar ratio respectively in acetone/dichloromethane (1/1, *v/v*) and stirred at room temperature for 8 h. The reaction mixture was then poured into diethyl ether to give precipitates, which were collected by centrifugation to afford the corresponding cages **6**, **7**, **8** or **9** in yields of 92%–96%.

Multinuclear NMR (^{31}P and ^1H) analysis and electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) were obtained to confirm the formation of the metallacages. The $^{31}\text{P}\{^1\text{H}\}$ spectra (Figure 2, b–e) of these cages show sharp singlets (14.32 ppm for **6**, 13.61 ppm for **7**, 12.13 ppm for **8** and 11.81 ppm for **9**) with concomitant ^{195}Pt satellites corresponding to a single phosphorous environment, indicating the formation of a discrete, highly symmetric metallacages.¹⁴ In the ^1H NMR spectra (Figure 2, f–k), clear downfield shifts were observed for the α and the β pyridyl protons H_a and H_b for all the cages, which are consistent with previous reports and indicate the formation of Pt–N coordination bonds.¹⁵ For cages **6** and **8**, the downfield shifts were ca. 0.17 ppm for H_a and ca. 0.79 ppm for H_b . For cages **7** and **9**, these were ca. 0.18 ppm for H_a and ca. 0.34 ppm for H_b . Moreover, the aromatic protons H_c and H_d , and methine protons H_e and methyl protons H_f also shifted downfield in these cages as compared to the ligands.

ESI-TOF-MS provides further evidence for the correct stoichiometry of these cages. Prominent sets of peaks (Figure 3) with charge states from 5+ to 9+ were observed for all the cages due to the loss of counterions (OTf^-), and each peak closely matches the corresponding simulated isotopic pattern. Diffusion-ordered NMR spectroscopy (DOSY) further reveals the formation of a single assembly, as all the proton signals showed the same diffusion coefficient in the range of $8.00\sim 9.27 \times 10^{-11} \text{ m}^2/\text{s}$ (Figures S19–S23) in DMSO. This provides a hydro-dynamic radius of 1.18–1.36 nm for these cages as calculated via the Stokes–Einstein equation.

UV/Vis absorption spectra (Figures 4) of ligands **2–5** and cages **6–9** in 1,1,2,2-tetrachloroethane were collected. Ligand **2** exhibits one absorption band at 276 nm with $\epsilon = 3.11 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ while an absorption band at 306 nm with $\epsilon = 7.45 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ was observed for ligand **3**. Diplatinum(II) acceptors **4** and **5** show one broad absorption band centered at 342 nm with molar absorption coefficients (ϵ) of $3.35 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ and $3.72 \times$

$10^4 \text{ M}^{-1}\text{cm}^{-1}$, respectively. Upon formation of the cages, the absorptions increased due to the existence of multi ligands in a cage structure. We further compared the absorption spectra of these cages with the sum of their corresponding building blocks (Figure S25), suggesting that the metal-ligand interactions play a complex role in the photophysical properties of these cages. Cage **6** and **8** show one broad absorption peak centered at 324 nm and 336 nm with ϵ of $1.43 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$ and $1.01 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, respectively. Cage **7** exhibits one strong absorption peak at 335 nm and three shoulders at 282 nm, 326 nm and 348 nm with ϵ of 4.05×10^5 , 2.11×10^5 , 3.88×10^5 and $3.93 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, respectively. Cage **9** shows two strong absorption peaks at 328 nm and 344 nm and one shoulder at 288 nm with ϵ of 4.04×10^5 , 4.01×10^5 and $2.16 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$, respectively.

Due to the large curved aromatic surfaces of these cages, their binding towards fullerene was investigated. For example, after heating **7** with an excess of C_{60} for 12 h (Figure 5a), ESI-TOF-MS was obtained that showed peaks at m/z (Da) = 1571.1957, 1691.2314, 1914.6212 and 2058.5686, corresponding to $[\mathbf{7} - 6\text{OTf}]^{6+}$, $[\text{C}_{60}@\mathbf{7} - 6\text{OTf}]^{6+}$, $[\mathbf{7} - 5\text{OTf}]^{5+}$, $[\text{C}_{60}@\mathbf{7} - 5\text{OTf}]^{5+}$, respectively (Figure 5c). ^1H NMR (Figures 5d and 5e) provides further information about the formation of the $\text{C}_{60}@\mathbf{7}$ complex.¹⁶ As shown in Figure 5e, both complexed (ca. 30%) and uncomplexed protons were seen in the spectrum, indicating a slow-exchange of the host-guest complex. Moreover, the spectrum (Figure 5f) recorded for the one-pot self-assembly of **3**, **4** and C_{60} is roughly the same as that of $\text{C}_{60}@\mathbf{7}$ (Figure 5e). Therefore, the pre-assembly of the metallocages are not required to obtain these host-guest complexes. DOSY study was also performed, the diffusion coefficients of a fullerene encapsulated cage and the corresponding free cage are similar, suggesting that the encapsulation doesn't alter the size of the whole system in a large extent. (Figure S24). The encapsulation of C_{60} by other cages was also studied as showed in the SI (Figures S26–S39).

CONCLUSION

In summary, we have prepared four convex trigonal prismatic cages **6–9** via the coordination-driven self-assembly of Klärner's molecular clip-based tetrapyrrolyl donors and 180° diplatinum acceptors. Due to the use of curved aromatic pyridyl ligands, these cages encapsulate fullerenes through aromatic-aromatic interactions, as demonstrated by ESI-TOF-MS and ^1H NMR analysis. This study not only enriches the family of SCCs with convex structures but also opens up their host-guest chemistry towards fullerenes.

EXPERIMENTAL SECTION

Materials and Methods

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds **1**,^{12b} **4**,¹⁷ and **5**¹⁷ were prepared according to the published procedures. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The UV-vis experiments were conducted on a Hitachi U-4100 absorption spectrophotometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray

ionization with a MassLynx software suite. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

Synthesis of 2

To a mixture of compound **1** (100 mg, 0.128 mmol), pyridine-4-boronic acid (126 mg, 1.02 mmol), potassium carbonate (282 mg, 2.04 mmol) and tetrakis(triphenylphosphine)palladium (14.8 mg, 0.0128 mmol, 10 mol%) under argon was added degassed DMF (20 ml) and water (6 ml). After being stirred at 120 °C for 12 h, the mixture was cooled and filtered. The solvent was removed under reduced pressure to give a crude product which was purified by flash column chromatography (SiO₂: CHCl₃/MeOH, 25:1, *v/v*) to afford compound **2** (56.5 mg, 57%) as a white solid. m.p. > 300 °C. ¹H NMR (400 MHz, CD₂Cl₂, 295 K): 8.41 (d, *J* = 6.0 Hz, 8H), 7.68 (s, 4H), 7.64 (s, 4H), 7.01 (d, *J* = 6.0 Hz, 8H), 4.63 (s, 4H), 3.89 (s, 6H), 2.60 (d, *J* = 8.2 Hz, 2H), 2.52 (d, *J* = 8.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, 295 K): 149.1, 148.3, 145.3, 139.4, 134.7, 131.6, 129.5, 124.4, 119.2, 63.5, 61.2, 47.6. HRMS: calcd for [**2** + H]⁺: 775.30675 Found: 775.30793.

Synthesis of 3

To a mixture of compound **1** (100 mg, 0.128 mmol), 4-ethynylpyridine (105 mg, 1.02 mmol), potassium carbonate (282 mg, 2.04 mmol) and tetrakis(triphenylphosphine)palladium (14.8 mg, 0.0128 mmol, 10 mol%) under argon was added degassed DMF (20 ml) and water (6 ml). After being stirred at 120 °C for 12 h, the mixture was cooled and filtered. The solvent was removed under reduced pressure to give a crude product which was purified by flash column chromatography (SiO₂: CHCl₃/MeOH, 25:1, *v/v*) to afford compound **3** (53.5 mg, 48%) as a yellow solid. m.p. > 300 °C. ¹H NMR (400 MHz, CD₂Cl₂, 295 K): 8.57 (d, *J* = 6.0 Hz, 8H), 7.91 (s, 4H), 7.59 (s, 4H), 7.36 (d, *J* = 6.0 Hz, 8H), 4.63 (s, 4H), 3.89 (s, 6H), 2.59 (d, *J* = 8.4 Hz, 2H), 2.49 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, 295 K): 149.5, 145.5, 139.0, 132.1, 131.4, 131.1, 125.1, 120.4, 119.1, 92.6, 90.0, 64.2, 61.4, 47.7. HRMS: calcd for [**3** + K]⁺: 909.26263. Found: 909.25753.

Self-assembly of 6

In a 2:1 molar ratio, **2** (0.77 mg, 1.00 μmol) and **4** (2.57 mg, 2.00 μmol) were dissolved in CH₂Cl₂/CH₃COCH₃ (1/1, *v/v*, 1.0 mL) in a 5 mL dram vial. The whole mixture was heated at 50 °C for 8 h and cooled. Then ethyl ether (5.0 mL) was added to give a precipitate, which was collected by centrifugation to give **6** (3.17 mg, 95%) as a white powder. The sample was dissolved in DMSO-*d*₆ for further characterization. ¹H NMR (400 MHz, DMSO-*d*₆, 295 K): 8.40–8.70 (m, 24H), 7.94–8.02 (m, 12H), 7.81–7.87 (m, 12H), 7.36–7.48 (m, 24H), 7.07–7.15 (br, 24H), 4.68 (s, 12H), 3.78–3.95 (m, 18H), 3.33–3.39 (m, 12H), 1.65–1.85 (m, 144H), 0.96–1.17 (m, 216H). ³¹P{¹H} NMR (DMSO-*d*₆, 295 K, 121.4 MHz) δ (ppm): 14.32 ppm (s, ¹⁹⁵Pt satellites, ¹*J*_{Pt-P} = 2306.4 Hz). ESI-TOF-MS: *m/z* 965.89 [**6** – 9OTf]⁹⁺, 1105.23 [**6** – 8OTf]⁸⁺, 1284.20 [**6** – 7OTf]⁷⁺, 1523.09 [**6** – 6OTf]⁶⁺, 1857.37 [**6** – 5OTf]⁵⁺.

Self-assembly of **7**

In a 2:1 molar ratio, **3** (0.87 mg, 1.00 μmol) and **4** (2.57 mg, 2.00 μmol) were dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (1/1, *v/v*, 1.0 mL) in a 5 mL dram vial. The whole mixture was heated at 50 °C for 8 h and cooled. Then ethyl ether (5.0 mL) was added to give a precipitate, which was collected by centrifugation to give **7** (3.16 mg, 92%) as a yellow powder. The sample was dissolved in $\text{DMSO}-d_6$ for further characterization. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 295 K): 8.74–8.81 (m, 24H), 8.19–8.23 (m, 12H), 7.76–7.87 (m, 24H), 7.36–7.48 (m, 24H), 7.09–7.15 (br, 24H), 4.67 (s, 12H), 3.86 (s, 18H), 1.65–1.85 (m, 144H), 0.96–1.15 (m, 216H). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 295 K, 121.4 MHz) δ (ppm): 13.61 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2309.0$ Hz). ESI-TOF-MS: m/z 883.37 [**7** – 10OTf] $^{10+}$, 997.96 [**7** – 9OTf] $^{9+}$, 1141.28 [**7** – 8OTf] $^{8+}$, 1325.39 [**7** – 7OTf] $^{7+}$, 1571.14 [**7** – 6OTf] $^{6+}$, 1914.77 [**7** – 5OTf] $^{5+}$.

Self-assembly of **8**

In a 2:1 molar ratio, **2** (0.77 mg, 1.00 μmol) and **5** (2.72 mg, 2.00 μmol) were dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (1/1, *v/v*, 1.0 mL) in a 5 mL dram vial. The whole mixture was heated at 50 °C for 8 h and cooled. Then ethyl ether (5.0 mL) was added to give a precipitate, which was collected by centrifugation to give **8** (3.35 mg, 96%) as a white powder. The sample was dissolved in $\text{DMSO}-d_6$ for further characterization. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 295 K): 8.50–8.61 (m, 24H), 7.96–8.02 (m, 12H), 7.82–7.87 (m, 12H), 7.52–7.58 (m, 24H), 7.39 (br, 24H), 7.21–7.31 (m, 24H), 4.68 (s, 12H), 3.78–3.94 (m, 18H), 1.65–1.90 (m, 144H), 0.96–1.20 (m, 216H). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 295 K, 121.4 MHz) δ (ppm): 12.13 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2301.0$ Hz). ESI-TOF-MS: m/z 1016.67 [**8** – 9OTf] $^{9+}$, 1162.20 [**8** – 8OTf] $^{8+}$, 1349.58 [**8** – 7OTf] $^{7+}$, 1599.18 [**8** – 6OTf] $^{6+}$, 1947.17 [**8** – 5OTf] $^{5+}$.

Self-assembly of **9**

In a 2:1 molar ratio, **3** (0.87 mg, 1.00 μmol) and **5** (2.72 mg, 2.00 μmol) were dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$ (1/1, *v/v*, 1.0 mL) in a 5 mL dram vial. The whole mixture was heated at 50 °C for 8 h and cooled. Then ethyl ether (5.0 mL) was added to give a precipitate, which was collected by centrifugation to give **9** (3.37 mg, 94%) as a yellow powder. The sample was dissolved in $\text{DMSO}-d_6$ for further characterization. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, 295 K): 8.76–8.82 (m, 24H), 8.12–8.27 (m, 12H), 7.71–7.89 (m, 24H), 7.48–7.59 (m, 24H), 7.24–7.31 (m, 24H), 4.67 (s, 12H), 3.83–3.88 (m, 18H), 1.67–1.88 (m, 144H), 0.95–1.20 (m, 216H). $^{31}\text{P}\{^1\text{H}\}$ NMR ($\text{DMSO}-d_6$, 295 K, 121.4 MHz) δ (ppm): 11.81 ppm (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2311.8$ Hz). ESI-TOF-MS: m/z 1048.87 [**9** – 9OTf] $^{9+}$, 1196.33 [**9** – 8OTf] $^{8+}$, 1390.68 [**9** – 7OTf] $^{7+}$, 1647.12 [**9** – 6OTf] $^{6+}$, 2005.27 [**9** – 5OTf] $^{5+}$.

Supplementary Material

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Acknowledgments

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16. We also tried to perform ¹³C NMR to study the host-guest complexations between the cages and C₆₀. However, no good ¹³C NMR spectra were obtained even by scanning for 24 hours, which is probably due to their poor solubility in DMSO.
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Synopsis

A new type of convex trigonal prismatic cages was prepared via the coordination-driven self-assembly of molecular clip-based tetrapyrindyl donors and 180° diplatinum acceptors. Due to the use of curved aromatic pyridyl ligands, these cages show the ability to encapsulate C₆₀ through aromatic-aromatic interactions.

Figure 1.

Crystal structure of compound **2**. The hydrogen atoms were omitted for clarity. Oxygen atoms are red, nitrogen atoms are blue and carbon atoms are black.

Figure 2.

(a) Synthetic routes and representations of trigonal prismatic cages **6–9**. $^3\text{P}\{^1\text{H}\}$ (b–e) and partial ^1H NMR (f–k) spectra (121.4 MHz or 400 MHz, $\text{DMSO}-d_6$, 298 K) of **2** (g), **3** (j), **6** (b and f), **7** (c and i), **8** (d and h) and **9** (e and k).

Figure 3. ESI-TOF-MS spectra of **6** (a), **7** (b), **8** (c) and **9** (d). Inset: Experimental (red) and calculated (blue) ESI-TOF-MS spectra of $[M - 9OTf]^9+$.

Figure 4. Absorption spectra of ligands **2–5** and cages **6–9** in $\text{CHCl}_2\text{CHCl}_2$ ($c = 10 \mu\text{M}$).

Figure 5.

(a) Representation of the formation of host-guest complex by stepwise self-assembly. (b) Representation of the formation of host-guest complex by one-pot self-assembly. (c) ESI-TOF-MS spectrum of $C_{60}@7$. ^1H NMR (400 MHz, DMSO- d_6 , 298 K) spectra of (d) **7**, (e) $C_{60}@7$ by stepwise self-assembly and (f) $C_{60}@7$ by one-pot self-assembly of **3**, **4** and C_{60} . The complexed peaks are showed in green.

Scheme 1.
Synthesis of molecular clip-based tetrapyridyl ligands **2** and **3**.