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Self-Assembly of Molecular Prisms via an Organometallic “Clip”

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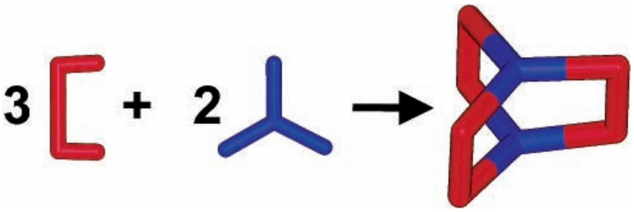
ABSTRACT



Under the appropriate conditions, the combination of two tritopic pyridyl ligands with three metal-containing molecular “clips” spontaneously generates supramolecular coordination cages with trigonal prismatic frameworks.

Self-assembly via metal coordination has led to a fascinating variety of novel two- and three-dimensional supramolecular constructs. The formation of such species is thermodynamically controlled by self-correction due to the reversible dative interactions between predesigned building units. This approach allows for the predictable preparation of complex, highly symmetrical nanoscopic architectures.[1]

Of the various types of structures reported to date, tetranuclear molecular squares have mostly dominated the literature. However, we recently described the self-assembly reactions of a molecular “clip” (**1**) as an efficient entry into the more synthetically challenging rectangular shape.[2] This design principle was based on the premise that lower symmetry structures are inherently desirable due to the potential development of receptors showing enhanced guest specificity. Since cage-like hosts are known to be superior to 2D systems, we sought an extension of this design principle into three dimensions.

Although M_3L_2 prismatic cages are among the simplest three-dimensional constructs, they remain relatively uncommon. Of those reported,[3] most usually either require the use of templates to assemble in solution or assemble only in the solid state. A possible reason for this limitation is that, in most cases, flexible ligands were necessary. This is because metal ions with labile coordination sites available in a *cis*

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(1) (a) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2022. (b) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (c) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (e) Caulder, D. L.; Brückner, C.; Powers, R. E.; König, S.; Parac, T. N.; Leary, J. A.; Raymond, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 8923. (f) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (g) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185. (h) Chambron, J.-C.; Dietrich-Buchecker, C.; Sauvage, J.-P. Transition Metals as Assembling and Templating Species. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair Ed.; Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Exec. Eds.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 2, p 43. (i) Baxter, P. N. W. Metal Ion Directed Assembly of Complex Molecular Architectures and Nanostructures. In *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Chair Ed.; Atwood, J. L., Davis, J. E. D., MacNicol, D. D., Vögtle, F., Exec. Eds.; Pergamon Press: Oxford, 1996; Vol. 9, Chapter 5, p 165. (g) Fujita, M. *Chem. Soc. Rev.* **1998**, *6*, 417. (j) Uller, E.; Demleitner, I.; Bernt, I.; Saalfrank, R. W. Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry. In *Structure and Bonding*; Fujita, M., Ed.; Springer: Berlin, 2000; Vol. 96, p 149. (k) Baxter, P. N. W.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1999**, *5*, 102.

(2) (a) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634. (b) Kuehl, C. J.; Mayne, C. L.; Arif, A. M.; Stang, P. J. *Org. Lett.* **2000**, *2*, 3729.

(3) For other related examples of self-assembled trigonal metallaprisms, see: (a) Fujita, M.; Nagao, S.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 1649. (b) Hiraoka, S.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 10239. (c) Hiraoka, S.; Kubota, Y.; Fujita, M. *Chem. Commun.* **2000**, 1509. (d) Ikeda, A.; Udzu, H.; Zhong, Z.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 3872. (e) Ikeda, A.; Yoshimura, M.; Udzu, H.; Fukuhara, C.; Shinkai, S. *J. Am. Chem. Soc.* **1999**, *121*, 4296. (f) Liu, H.-K.; Sun, W.-Y.; Ma, D.-J.; Yu, K.-B.; Tang, W.-X. *Chem. Commun.* **2000**, 591.

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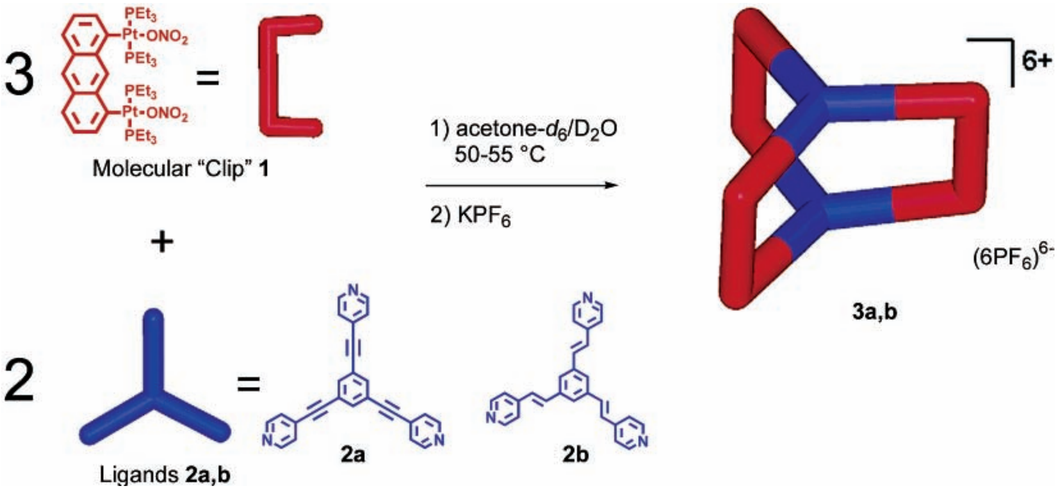

Figure 1. Self-assembly of molecular prisms **3a,b**.

arrangement ideally require tritopic ligands with mutual angles of 60°. By contrast, structures assembled from rigid, planar tritopic linkers and *cis*-metal ions are tetrahedral M_6L_4 cages.[1b]

Here we report the spontaneous self-assembly of molecular prisms from planar tritopic ligands, directed by a molecular “clip” as a preconstructed shape-defining unit. The structure of these macrobicyclic species was established with multinuclear NMR and electrospray ionization (ESI)-mass spectrometry.

The 3:2 stoichiometric combination of **1** with tritopic ethynylpyridyl ligand **2a**[4] in an acetone-d_6/D$_2$O mixture gives a suspension that slowly dissolves upon gentle heating to afford a clear yellow solution. $^{31}P\{^1H\}$ NMR analysis of the reaction solution showed the quantitative formation of a single, highly symmetrical species (**3a**) by the appearance of a sharp singlet with concomitant ^{195}Pt satellites, shifted 6.0 ppm upfield ($-\delta\Delta$) relative to **1** ($\Delta^1J_{PPt} = -231$ Hz). Likewise, reaction of component **1** with tritopic vinylpyridyl ligand **2b**[5] yielded the analogous molecular cage **3b**.

Examination of the ^{1}H NMR spectra of cages **3a,b** was also indicative of highly symmetrical structures and displayed significant spectroscopic differences from their monomeric subunits. Particularly diagnostic were the significant downfield shifts of the pyridyl signals ($\Delta\delta \approx 0.5$ ppm), associated with the loss in electron density on coordination by the electron lone pair to the platinum metal center. In accordance with previously reported[4b] molecular rectangles, the inner and outer pyridyl protons of **3a** were found to be inequivalent because of restricted rotation around the platinum−pyridine bond. The inner and outer pyridyl protons in **3b** were found to be essentially equivalent however, presumably as a result of the greater flexibility of ligand **2b** compared to that of **2a**. As an added point of note, this rotational barrier is also apparently related to the color of the assembled complexes. It was observed that for the previously reported[4] rectangular structures, where the unsaturated linker ligands naturally lie coplanar with the anthracene moieties, the self-assembly reactions were accompanied by a distinct color change from yellow to bright orange. However, the assembly of prisms **3a,b** imposes a ligand geometry where the pyridyls are forced to adopt an orientation perpendicular to the central benzene spacer. Thus, disrupted electronic conjugation was attributed to the fact that molecular prisms **3a,b** do not undergo significant color change upon formation.

After the reactions were judged to be complete by NMR, each product was isolated as its hexafluorphosphate salt by precipitation with excess KPF$_6$.[6] The ESI-mass spectrum of

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(4) Olenyuk, B. O.; Whiteford, J. A.; Fechtenkötter, A.; Stang, P. J. *Nature* **1999**, *398*, 796.

(5) Amoroso, A. J.; Cargill Thompson, A. M. W.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828.

(6) **General Procedure for the Preparation of 3a,b.** In a 2-dram vial equipped with a magnetic stir bar were placed 20.0 mg (0.0172 mmol) of solid 1,8-bis(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))anthracene (**1**) with a 0.67 molar ratio of either **2a** or **2b**. Next, 1 mL of an acetone-d_6/D$_2$O mixture (1:2) was added to the vial, which was then sealed with Teflon tape and heated overnight in an oil bath at 50−55 °C, with stirring. The clear yellow solution was then transferred to an NMR tube for analysis. The product was precipitated with KPF$_6$, collected on a frit, washed with excess water, and dried in vacuo. **Bicyclo[tris[1,8-bis(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))anthracene]bis[1,3,5-tris(4-ethynylpyridyl)benzene]] (3a).** ^{1}H NMR (acetone-d_6/D$_2$O, 300 MHz): δ 9.41 (s, 3H, H$_9$), 9.02 (d, 6H, $^3J_{HH} = 5.4$ Hz, $H_{\alpha-Py}$), 8.90 (d, 6H, $^3J_{HH} = 5.4$ Hz, $H_{\alpha-Py}$), 8.35 (s, 3H, H$_{10}$), 8.00 (d, 6H, $^3J_{HH} = 5.1$ Hz, $H_{\beta-Py}$), 7.92 (d, 6H, $^3J_{HH} = 5.1$ Hz, $H_{\beta-Py}$), 7.85 (s, 6H, $H_{benzene}$), 7.70 (d, 6H, $^3J_{HH} = 8.1$ Hz, $H_{4,5}$), 7.61 (d, 6H, $^3J_{HH} = 6.0$ Hz, $H_{2,7}$), 7.15 (m, 6H, $H_{3,6}$), 1.42 (m, 72H, $PC\mathit{H}_2CH_3$), 0.81 (m, 108H, $PCH_2C\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (acetone-d_6/D$_2$O, 121.4 MHz): δ 8.9 (s, $^1J_{PPt} = 2624$ Hz). ESI-MS: 2228.2 (calcd for $(M - 2PF_6)^{2+}$ 2228.6), 1437.4 (calcd for $(M - 3PF_6)^{3+}$ 1437.4), 1041.9 (calcd for $(M - 4PF_6)^{4+}$ 1041.8). Yield: 97%. Anal. Calcd for $C_{168}H_{234}F_{36}N_6P_{18}Pt_6$: C, 42.48; H, 4.97; N, 1.77. Found: C, 42.48; H, 5.10; N, 2.02. **Bicyclo[tris[1,8-bis(*trans*-Pt(PEt$_3$)$_2$(NO$_3$))anthracene]bis[1,3,5-tris(*trans*-4-vinylpyridyl)benzene]] (3b).** ^{1}H NMR (acetone-d_6/D$_2$O, 300 MHz): δ 9.78 (s, 3H, H$_9$), 9.0 (d, 12H, $^3J_{HH} = 5.7$ Hz, $H_{\alpha-Py}$), 8.36 (s, 3H, H$_{10}$), 7.88 (m, 12H, $H_{\beta-Py}$), 7.72 (d, 6H, $^3J_{HH} = 8.4$ Hz, $H_{4,\,5}$), 7.64 (s, 6H, $H_{benzene}$), 7.60 (m, 12H, $H_{vinyl,2,7}$), 7.36 (d, 6H, $^3J_{HH} = 16.2$ Hz, H_{vinyl}), 7.16 (m, 6H, $H_{3,6}$), 1.52 (m, 72H, $PC\mathit{H}_2CH_3$), 0.83 (m, 108H, $PCH_2C\mathit{H}_3$). $^{31}P\{^1H\}$ NMR (acetone-d_6/D$_2$O, 121.4 MHz): δ 8.1 (s, $^1J_{PPt} = 2669$ Hz). ESI-MS: 2234.4 (calcd for $(M - 2PF_6)^{2+}$ 2234.6), 1441.4 (calcd for $(M - 3PF_6)^{3+}$ 1441.5), 1044.7 (calcd for $(M - 4PF_6)^{4+}$ 1044.9). Yield: 94%. Anal. Calcd for $C_{168}H_{246}F_{36}N_6P_{18}Pt_6$: C, 42.38; H, 5.21; N, 1.76. Found: C, 41.95; H, 5.27; N, 1.79.

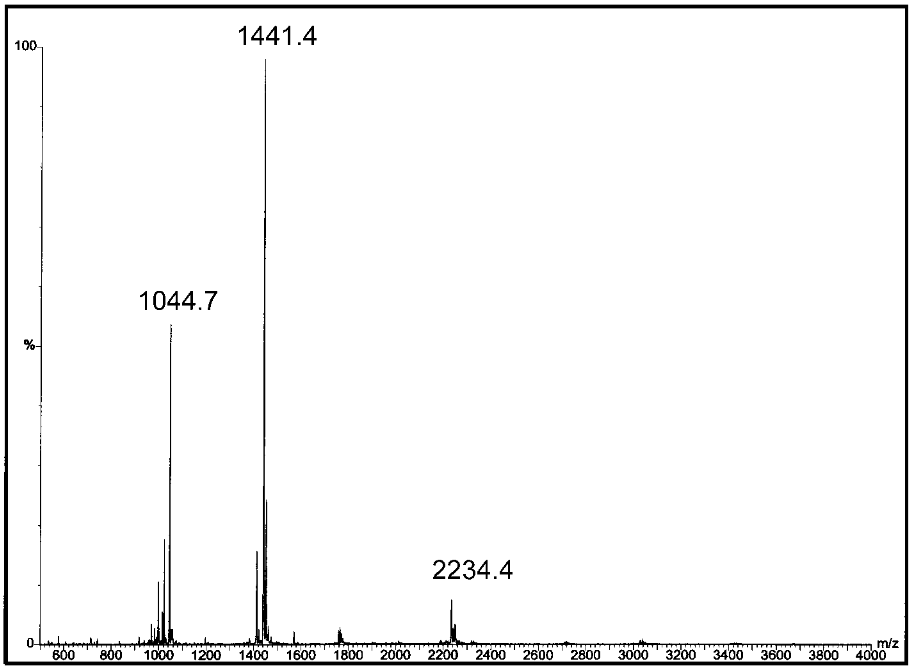

Figure 2. ESI-mass spectrum of molecular prism **3b**.

3a and **3b** showed prominent peaks (isotopically unresolved) attributable to the consecutive loss of PF_6^- counterions, M $-$ $2PF_6$, M $-$ $3PF_6$, and M $-$ $4PF_6$ peaks, lending further evidence to their structural similarity. The ESI-mass spectrum for **3b** is presented in Figure 2. For **3b**, $[M - 2PF_6]^{2+}$$\{m/z = 2234.4$ (calcd 2234.6)$\}$, $[M - 3PF_6]^{3+}$$\{m/z = 1441.4$ (calcd 1441.5)$\}$, and $[M - 4PF_6]^{4+}$$\{m/z = 1044.7$ (calcd 1044.9)$\}$, where M represents the intact prismatic cage, were detected.

In conclusion, molecular “clip” **1** was successfully employed as a rigid directing subunit in the design and synthesis of metallabicyclic supramolecular cages **3a,b**.

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