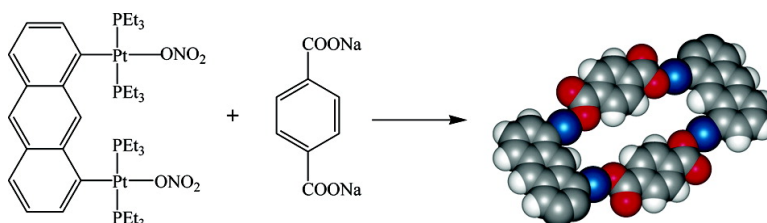


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Facile Self-Assembly of Predesigned Neutral 2D Pt-Macrocycles via a New Class of Rigid Oxygen Donor Linkers

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In the past decade many finite, nanoscopic supramolecular two-dimensional (2D) and three-dimensional (3D) structures with well-defined shapes have been prepared via the coordination-driven self-assembly of simple building blocks.¹ Much of this construction has been based on the coordination bonding motif between Pd(II)/Pt(II) acceptor units and nitrogen donor ligands.¹ In these cases the product assemblies are always ionic.¹ A few examples of neutral assemblies based on other metals such as Mo,² Rh,^{2b,3} Re,⁴ Zn,^{4e-f} and Fe^{4g} have been reported. Hence, it was of interest whether the self-assembly of anionic oxygen donors with the readily available, widely employed Pt(II) linkers would afford neutral supramolecules. Bonding of this type has not been utilized as a driving force in self-assembly.⁵ Complexes incorporating Pt(II)–O bonds were generally believed to be unstable due to the weak bond formed between a soft metal and a hard ligand.⁶ Herein, we report two stable, neutral, Pt(II)–O bond-containing macrocycles prepared via the self-assembly of rigid, dicarboxylate-based oxygen donors and platinum-containing **1** (Scheme 1).

The 1:1 stoichiometric combination of an acetone solution of **1** with an aqueous solution of the linear dicarboxylate **2a** rapidly produced a light-yellow precipitate (**3a**) in 98.3% isolated yield. ³¹P{¹H} NMR analysis of the product indicated the formation of a single highly symmetrical species (**3a**) by the appearance of a sharp singlet with concomitant ¹⁹⁵Pt satellites, shifted 1.40 ppm upfield ($-\Delta\delta$) relative to **1** ($\Delta^1J_{\text{Pt}} = -24.8$ Hz). The very small change in the position of the phosphorus resonance in comparison to the starting material (**1**) is due to the formation of a Pt–O coordinate bond replacing a similar Pt–O coordinate bond (Pt–OOC– vs Pt–ONO₂) in the starting “clip”. Likewise,⁸ reaction of **1** with the linear fumarate dianion ligand **2b** yields the analogous rectangle **3b** in 98.7% isolated yield. ³¹P{¹H} NMR analysis of this product also showed it to be a single, highly symmetrical species (**3b**) by the appearance of a sharp singlet with concomitant ¹⁹⁵Pt satellites, shifted 2.24 ppm upfield ($-\Delta\delta$) relative to **1** ($\Delta^1J_{\text{Pt}} = -21.8$ Hz).

Scheme 1. Self-Assembly of Molecular Rectangles **3a,b**

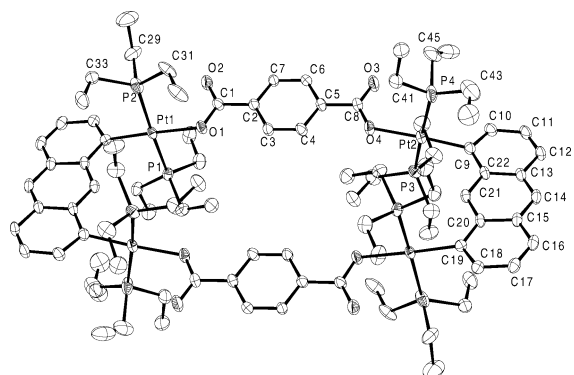
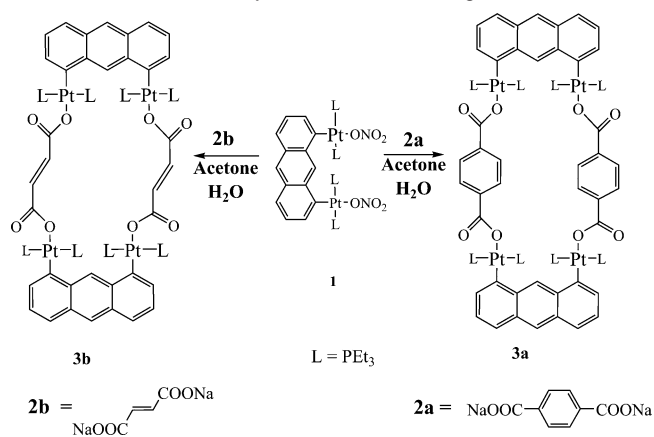


Figure 1. ORTEP diagram of **3a**. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability.

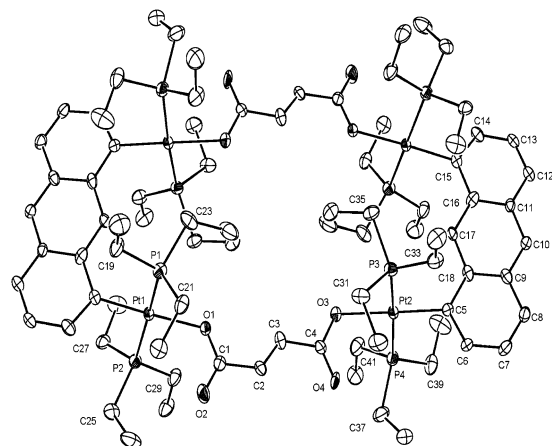


Figure 2. ORTEP diagram of **3b**. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn to 30% probability.

Examination of the ¹H NMR spectrum⁹ of each rectangle **3** showed that the dicarboxylates **2** had indeed been incorporated into the product. A sharp singlet at 8.15 ppm was assigned to the protons on the benzene ring of the terephthalate in **3a**. Similarly, a singlet at 6.76 ppm in the ¹H NMR spectrum of **3b** indicated the incorporation of **2b**.

Diffraction quality single crystals of **3a** and **3b** were grown overnight by vapor diffusion of acetone into a chloroform/dichloromethane solution of each individual complex. X-ray structure analysis¹⁰ revealed the existence of disordered solvent molecules in each case although the crystals were solvent independent. Figures 1 and 2 show the ORTEP representations of rectangles **3a** and **3b** respectively. The structure of **3a** is very slightly bowed in the middle, due to the steric repulsion of the triethylphosphines that to a small extent push the platinum atoms apart.

Likewise, the crystal structure of **3b** shows a similar type of rectangle with an inversion center located at the midpoint of the two ethylenic C=C moieties. The O(1)–Pt(1)–Pt(1) and O(1)–Pt(1)–Pt(2) angles in **3b** of 89.9(4)° and 92.2(4)° respectively, are consistent with other square planar Pt(II) complexes.¹¹ The overall dimensions of the rectangles, as defined by the metal corners are 5.5 Å × 11.2 Å for **3a** and 5.5 Å × 9.1 Å for **3b**. The dimension of **3a** is almost identical to the related ionic macrocycle obtained using the nitrogen donor linker 4,4'-dipyridine. However, these neutral self-assemblies are smaller in length in comparison to the other ionic rectangles of **1** with larger N-donor linkers.^{11b}

The distance between the centroids of the benzene ring of the bridging terephthalate in **3a** is 8.04 Å, while the distance between the center of each ethylenic C=C moiety of the two bridging fumarates is 8.03 Å. An important point to note is that in most of the reported 2D ionic self-assemblies,¹ the cationic macrocycles stack on top of each other to form cavities while in the present cases, the packing diagrams do not reveal this type of stacking. Moreover, in most of the metal fumarate complexes, fumarate acts as a bis-unidentate bridging ligand in an *anti-anti* fashion,¹² but in **3b** the fumarate bridges two Pt atoms in a less common *syn* fashion¹³ through O(1) and O(3) instead of O(1) and O(4).

In conclusion, the above results demonstrate that Pt-based neutral self-assemblies can be constructed utilizing Pt–oxygen bonding interactions instead of the much more widely used Pt–nitrogen linkage that generally produces ionic assemblies. The use of carboxylate-containing linkers in conjunction with Pt-acceptor units and formation of neutral ensembles has the potential to considerably expand the range of the directional bonding paradigm in self-assembly. Studies are under way to establish the full scope of this new methodology.

Acknowledgment. Financial support by NSF (CHE-0306720) is gratefully acknowledged.

Supporting Information Available: ³¹P and ¹H NMR spectra of **3a** and **3b** (four figures) (PDF). X-ray crystallographic files (in CIF format) of **3a** and **3b**. This material is available free of charge via the Internet at <http://pubs.acs.org>

References

- (1) (a) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (b) Swiegers, G. F.; Malefsete, T. J. *Coord. Chem. Rev.* **2002**, *225*, 91. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *41*, 2022. (d) Dinolfo, P. H.; Hupp, J. T. *Chem. Mater.* **2001**, *13*, 3113. (e) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (f) Cotton, F. A.; Lin, C.; Murillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (g) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (h) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (i) Caulder, D. L.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185.
- (2) (a) Cotton, F. A.; Donahue, J. P.; Murillo, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 5436. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 478. (c) Cotton, F. A.; Lin, C.; Murillo, C. A. *Inorg. Chem.* **2001**, *40*, 6413. (d) Cheng, H.; Chun-Ying, D.; Chen-jie, F.; Yong-jiang, L.; Qing-jin, M. *J. Chem. Soc., Dalton Trans.* **2000**, 1207. (e) Cotton, F. A.; Daniels, L. M.; Lin, C.; Murillo, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 4538.
- (3) Cotton, F. A.; Lin, C.; Daniels, M. L.; Murillo, C. A.; Yu, S.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 502.
- (4) (a) Bala, M.; Thanasekaran, P.; Rajendran, T.; Liao, R. T.; Liu, Y. H.; Lee, G. H.; Peng, S. M.; Rajagopal, S.; Lu, K. L. *Inorg. Chem.* **2003**, *42*, 4795. (b) Rajendran, T.; Manimaran, B.; Liao, R. T.; Lin, R. J.; Thanasekaran, P.; Lee, G. H.; Peng, S. M.; Liu, Y. H.; Cheng, I. J.; Rajagopal, S.; Lu, K. L. *Inorg. Chem.* **2003**, *42*, 6388. (c) Manimaran, B.; Rajendran, T.; Lu, Y. L.; Lee, G. H.; Peng, S. M.; Lu, K. L. *Eur. J. Inorg. Chem.* **2001**, *3*, 633. (d) Slone, R. V.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Inorg. Chem.* **1996**, *36*, 4096. (e) Saalfrank, R. W.; Reimann, U.; Goritz, M.; Hampel, E.; Scheurer, A.; Heinemann, F. W.; Busches, M.; Daub, J.; Schunemann, V.; Trautwein, A. X. *Chem. Eur. J.* **2002**, *8*, 3614. (f) Saalfrank, R. W.; Trummer, S.; Reimann, U.; Chowdhry, M. M.; Hampel, F.; Waldmann, O. *Angew. Chem., Int. Ed.* **2000**, *39*, 3492. (g) Saalfrank, R. W.; Horst, G.; Bernhard, D.; Hampel, Volker, S.; Chwdhuri, M. M.; Trautwein, A. X.; Vaughen, G. B. M.; Robert, Y.; Davis, A. V.; Raymond, K. N. *Chem. Eur. J.* **2002**, *8*, 893.
- (5) Carboxylates have been used in the formation of some porous solids but not with Pt. See, for example: (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.
- (6) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984.
- (7) (a) Kuehl, C. J.; Yamamoto, T.; Seidel, S. R.; Stang, P. J.; *Org. Lett.* **2002**, *4*, 913. (b) Kuehl, C. J.; Kryshchenko, Y. K.; Radhakrishnan, U.; Seidel, S. R.; Huang, S. D.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4933.
- (8) **General Procedure for the Preparation of 3a, b.** To a 3-mL acetone solution containing 11.62 mg (0.010 mmol) of 1,8-bis(*trans*-Pt(PeT₃)₂(NO₃))anthracene (**1**), an aqueous solution (3 mL) of either **2a** or **2b** (0.010 mmol) was added drop-by-drop with continuous stirring (15 min). The light-yellow products, which precipitated, were filtered and washed. **3a**: ³¹P{¹H} NMR (CDCl₃, 121.4 MHz): δ 13.2 (s, ¹J_{PPt} = 2879.8 Hz). Yield: 98.3%. Anal. Calcd for C, 45.92; H, 6.03% Found: C, 45.83; H, 6.08. **3b**: ³¹P{¹H} NMR (CDCl₃, 121.4 MHz): δ 12.36 (s, ¹J_{PPt} = 2876.8 Hz). Yield: 98.7%. Anal. Calcd for C, 43.75; H, 6.12. Found: C, 43.67; H, 6.18.
- (9) See Supporting Information.
- (10) Compound **3a** (C₉₆H₁₅₂Cl₈O₈P₈Pt₄); (*M_r* = 2745.90) crystallized in the triclinic space group *P1* with *a* = 11.872(2) Å, *b* = 12.835(3) Å, *c* = 20.981(4) Å; α = 79.834(10)°, β = 74.165(11)°, γ = 73.595(12)°; *V* = 2933.55(10) Å³; *Z* = 1; *R*₁ = 0.046 (*I* > 2σ(*I*)); *wR*₂ = −0.119; *T* = 150 K; *GOF* = 1.041. Compound **3b** (C₈₆H₁₄₂Cl₆O₈P₈Pt₄); (*M_r* = 2544.82) crystallized in the monoclinic space group *P2₁/c* with *a* = 16.536(3) Å, *b* = 14.578(3) Å, *c* = 22.375(3) Å; β = 110.644(11)°; *V* = 5047.99(15) Å³; *Z* = 2; *R*₁ = 0.094 (*I* > 2σ(*I*)); *wR*₂ = 0.268 0.; *T* = 150 K; *GOF* = 1.124.
- (11) (a) Kuehl, C. J.; Mayne, C. L.; Arif, A. M.; Stang, P. J. *Org. Lett.* **2000**, *2*, 3227. (b) Kuehl, C. J.; Huang, S. D.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9634.
- (12) (a) Mukherjee, P. S.; Dalai, S.; Mostafa, G.; Zangrando, E.; Mallah, T.; Lu, T. H.; Chaudhuri, N. R. *Chem. Commun.* **2001**, 1346. (b) Frosch, W.; Back, S.; Rheinwald, G.; Kohler, K.; Zsolnai, L.; Huttner, G.; Lang, H. *Organometallics* **2000**, *19*, 5769. (c) Gupta, M. P.; Sinha, S. K. *Ind. J. Phys., A* **1978**, *52*, 363.
- (13) Zhang, S. L.; Tong, M. L.; Fu, R. W.; Chen, X. M.; Ng, S. W. *Inorg. Chem.* **2001**, *40*, 3562.

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