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Side chain-directed assembly of triangular molecular panels into a tetrahedron *vs.* open cone†

Michito Yoshizawa,[a] Muneki Nagao,[a] Kazuhiko Umemoto,[a] Kumar Biradha,[a] Makoto Fujita,*[a] Shigeru Sakamoto[b] and Kentaro Yamaguchi[b]

[a] *Department of Applied Chemistry, School of Engineering, The University of Tokyo and CREST, Japan Science and Technology Corporation (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: mfujita@appchem.t.u-tokyo.ac.jp*

[b] *Chemical Analysis Center, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan*

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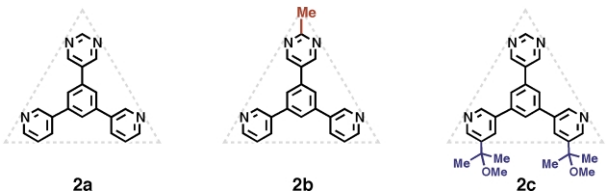
Despite their structural similarity, triangular tetradentate ligands 2b and 2c experience different assembly pathways on complexation with (en)Pd(NO_3)$_2$ to give M_8L_4 tetrahedral (3) and open cone (4) structures, respectively, due to steric restriction by side chains at the corner or on the edge of the ligands.

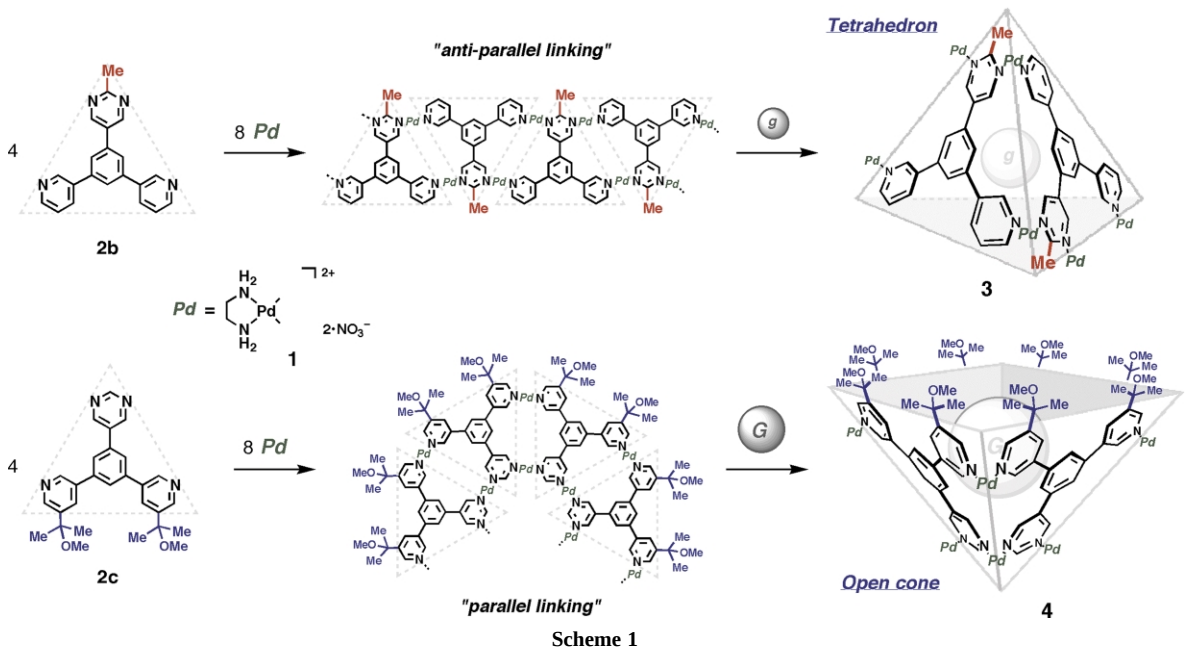
Self-assembly of coordination polyhedra from metal ions and panel-like ligands is referred to as *molecular paneling*.[1] Upon complexation, a family of planar *exo*-multidentate organic ligands (molecular panels) are assembled into different polyhedral structures according to the number and position of coordination sites on the ligands.[1,2] Regarding the metal component, a 90° coordination block, (en)Pd(NO_3)$_2$ (en = ethylenediamine) (**1**), has shown powerful potential for constructing a variety of coordination polyhedra from relatively simple triangular, square, or rectangular molecular panels.[1]

We have recently shown that triangular tetradentate panel **2a** can be linked in either antiparallel or parallel ways on complexation with **1**, giving rise to M_8L_4 tetrahedral or square-pyramidal open cone structures, respectively.[3] These two structures are in equilibrium, which cannot be controlled by the intrinsic nature of the ligand. Here we show that the tetrahedral and open cone structures can be efficiently controlled by attaching sterically demanding substituents (side chains) at the corner or on the edge of **2a**. Thus, we have designed two panels: panel **2b** having a bulky group at a corner and panel **2c** having two bulky groups on an edge. We show that the methyl group at the corner of **2b** allows only the antiparallel link of the ligands giving rise to the self-assembly of M_8L_4 tetrahedron **3** (Scheme 1). Similarly, alkyl substituents at the edge of **2c** strictly direct the self-assembly of M_8L_4 open cone **4** *via* parallel linking.



The selective formation of tetrahedron **3** was in fact accomplished with the aid of the stabilizing effect of a small guest such as CBr_4 (**5**); a complex mixture was formed in the absence of the guest, suggesting that the host–guest interaction is essential to the self-assembly of **3**. We note, however, that ligand **2b** undergoes only the antiparallel link due to its own intrinsic nature because none of the guests we examined directed the formation of open cone **4**. Thus, when coordination block **1** and ligand **2b** were combined in D_2O in the presence of **5** (excess amount) for 24 h at ambient temperature, the quantitative formation of a single product was observed by ^{1}H NMR (Fig. 1a).‡ This product was deduced as encapsulation complex **3**·**5** by the observation of a CBr_4 signal in the ^{13}C NMR (δ = −25.5) and CH_3-Py*H* NOESY correlation that suggests the antiparallel link of the ligands.

† Electronic supplementary information (ESI) available: physical properties of open cone **4** with mesitylene and CBr_4. See http://www.rsc.org/suppdata/cc/b3/b305129c/



Scheme 1

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Reliable evidence for the tetrahedral structure of **3·5** follows from X-ray crystallographic analysis.‡ The structure clearly showed that the four panels of **2b** were linked with **1** in an antiparallel fashion to form a distorted tetrahedron (Fig. 2). Methyl groups (red) are exposed outside at every corner of the tetrahedron minimizing the steric repulsion with neighboring ligands. The tetrahedral guest **5** was almost fully insulated within the framework of **3**.

For ligand **2c**, sterically demanding (MeO)Me_2C- groups on the edge allow only the parallel link of the ligands giving rise to open cone structure **4** (Scheme 1). Again, guest molecules assisted the efficient assembly. With a large guest, PhCOCOPh (**6**), the quantitative formation of **4·6** complex was observed by ^{1}H NMR spectrum (Fig. 1b) that displayed ten singlet signals derived from panel **2c** with its inherent symmetry (C_{2v}).§ Highly upfield-shifted guest signals agree with the accommodation of **6** in the large cavity of the open cone. CSI-MS[4] spectrum also evidenced the formation of **4·6** with a series of prominent peaks of $[\mathbf{4·6}–(NO_3^-)_n·(DMF)_m]^{n+}$: (*e.g.*, for n = 4, m/z 1026.1 (m = 0), 1044.4 (m = 1), and 1062.7 (m = 2)). It is noteworthy that this inclusion complex does not dissociate under the CSI-MS conditions despite the open cavity structure. Probably, bulky substituents that hung over at the rim of the cone prevent the facile escape of the included guest.

Due to the presence of side chains (two (MeO)Me_2C- substituents) on the edge, ligand **2c** is permitted to assemble into only open cone **4** regardless of the size and shape of organic guests. Large guest **6** could be smoothly exchanged by medium to small size molecules without the transformation of the host framework. Thus, the addition of mesitylene to an aqueous solution of **4·6** resulted in the formation of a fully guest-exchanged mesitylene-complex, which was, furthermore, converted to the inclusion complex of 1,2-dibromoethane and CBr_4 (**4·5**, Fig. 1c).† These results sharply contrast with the behavior of the host from non-substituted ligand **2a** where guest exchange by CBr_4 caused the smooth reorganization of the host framework from open cone into tetrahedron.[3]

In summary, we have shown that the self-assembly pathways of triangular ligands can be controlled by attaching sterically demanding substituent(s) at appropriate positions of the ligand. The principle demonstrated here potentially makes possible the design and self-assembly of highly ordered, less symmetrical architectures through specific orientation of component ligands.

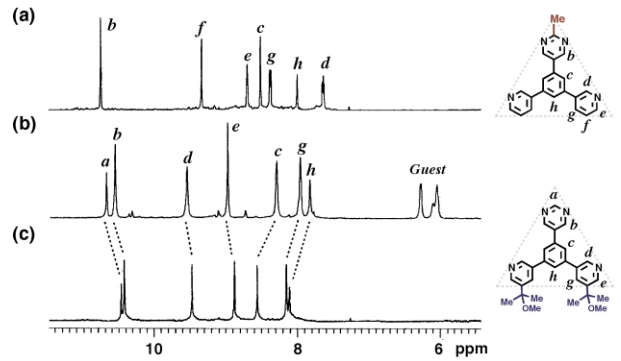

Fig. 1 ^{1}H NMR spectra (500 MHz, 27 °C, D_2O, TMS as an external standard) of (a) **3·5**, (b) **4·6**, and (c) **4·5**.

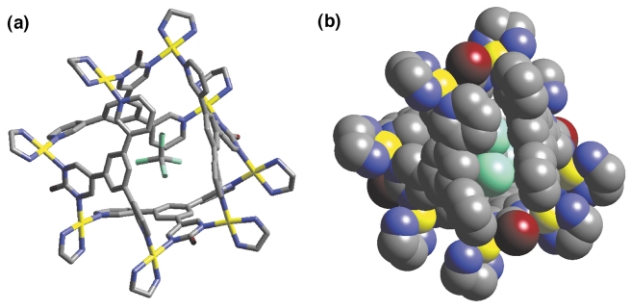

Fig. 2 The crystal structure of **3·5** represented by (a) cylinder and (b) ball models (Me = red, C = grey, N = blue, Pd = yellow, Br = cyan).

Notes and references

‡ *Typical procedure*: To an aqueous suspension (1.0 mL) of (en-)$Pd(NO_3)_2$ (**1**, 6.2 mg; 21.3 μmol) and ligand **2b** (2.8 mg; 7.9 μmol), excess (*ca.* 27 μmol) CBr_4 (**5**) was added and the mixture was stirred for 24 h at ambient temperature. After filtration, the resulting clear solution was concentrated to precipitate included complex **3·5** in 77% isolated yield. Complex **3·5**: ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ = 10.48 (s, 4H), 10.44 (s, 8H), 9.48 (s, 8H), 8.89 (s, 8H), 8.57 (s, 8H), 8.15 (s, 8H), 8.11 (s, 4H), 3.12 (m, 32H), 3.00 (s, 24H), 1.57 (s, 24H), 1.56 (s, 24H); ^{13}C NMR (125.77 MHz, D_2O, 27 °C, TMS as external standard): δ= 161.1 (*C*H), 158.8 (*C*H), 149.4 (*C*H), 148.0 (*C*H), 145.3 (C_q), 138.2 (C_q), 137.5 (C_q), 136.2 (*C*H), 135.2 (C_q), 131.8 (C_q), 128.6 (*C*H), 126.2 (*C*H), 76.5 (C_q), 50.4 (CH_3), 47.7 (CH_2), 47.0 (CH_2), 26.6 (CH_3), −25.5 (C_q, **5**).

Crystal data for **3·5**: $C_{101}H_{174}N_{48}O_{73}Br_4Pd_8$, M = 4399.72, monoclinic, space group $C2/c$, a = 31.439(4), b = 44.137(6), c = 27.987(4) Å, β = 107.253(3)°, V = 37088 Å^3, T = 173(2) K, Z = 8, D_c = 1.576 g cm^{-3}, λ = 0.71073 Å, 44275 reflections measured, 32651 unique (R_{int} = 0.4402) which were used in all calculations. R_1 = 0.1073 and wR_2 = 0.2412. CCDC reference number 210396. See http://www.rsc.org/suppdata/cc/b3/b305129c/ for electronic files in .cif format.

§ Complex **4·6**: ^{1}H NMR (500.13 MHz, D_2O, 27 °C, TMS as external standard): δ = 10.70 (s, 4H), 10.58 (s, 8H), 9.54 (s, 8H), 8.99 (s, 8H), 8.30 (s, 8H), 7.97 (s, 8H), 7.83 (s, 4H), 6.27 (s, 4H, **6**), 6.07 (m, 6H, **6**), 3.14 (m, 32H), 2.96 (s, 24H), 1.49 (s, 24H); ^{13}C NMR (125.77 MHz, D_2O, 27 °C, TMS as external standard): δ = 193.7 (C_q, **6**), 160.6 (*C*H), 159.2 (*C*H), 148.9 (*C*H), 148.3 (*C*H), 145.2 (C_q), 137.2 (C_q), 136.9 (C_q), 135.7 (C_q), 135.5 (*C*H), 133.9 (*C*H, **6**), 131.3 (C_q), 130.9 (C_q, **6**), 128.1 (*C*H), 128.0 (*C*H, **6**), 127.6 (*C*H, **6**), 126.0 (*C*H), 76.4 (C_q), 50.3 (CH_3), 47.8 (CH_2), 46.9 (CH_2), 26.6 (CH_3), 26.1 (CH_3); Elemental Analysis Calcd. for $C_{142}H_{162}N_{32}O_{10}Pd_8P_{16}F_{96}·(H_2O)_{17}$ (counter ions of **4·6** was replaced by PF_6^-): C, 28.56; H, 3.34; N, 7.51. Found: C, 28.75; H, 3.73; N, 7.26.

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