

Side chain-directed complementary *cis*-coordination of two pyridines on Pd(II): Selective multicomponent assembly of square-, rectangular-, and trigonal prism-shaped molecules

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Abstract

This paper describes a new strategy to regulate multicomponent assembly from two kinds of pyridine-based ligands and *cis*-protected Pd(II) ions. The introduction of sterically hindered substituents to only one of the two ligands directs the complementary *cis*-coordination of the two ligands on the Pd(II) center, leading to the selective multicomponent assembly of two- and three-dimensional polynuclear Pd(II) complexes (e.g., square-, rectangular-, and trigonal prism-shaped molecules).

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1. Introduction

Complementary complexation of molecules by non-covalent interaction is widely utilized for the formation of highly organized three-dimensional structures in biological systems [1]. For example, DNA double helical structures are assembled from two different polynucleotide strands with complementary nucleobase pairs and heterotopic protein assemblies are formed through complementary interaction between amide acid residues. In artificial systems, the methodology is especially well incorporated into hydrogen-bonded structures [2]. Whereas metal–ligand coordination, which is also a useful tool for non-covalent bonding [3], is sometimes applied to complementary complexation, the increasing

number of metal-to-ligand components leads to a mixture of assemblies [4]. Actually, when two different ligands (L and L') are mixed with a metal (M), homotopic complexes (M_xL_y and $M_xL'_z$) and heterotopic complexes $M_xL_vL'_w$ will be generated randomly [5,6]. To our knowledge, there is no general way to control such multicomponent coordination assemblies [7].

Herein we describe a new strategy for the design of complementary complexation of two different pyridine-based ligands upon *cis*-protected Pd(II) ions into a unique multicomponent assembly. Among the two kinds of ligands, only one possesses sterically hindered substituents (= *side chain*) adjacent to the coordination site. This simple design allows selective formation of two or three-dimensional structures (e.g., square, rectangle, or trigonal prism) through complementary *cis*-coordination of the two different ligands on the Pd(II) center by steric control. The side-chain directed coordination discussed here is a prototype of a “complementary complexation” in sophisticated biological systems [1,8].

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2. Results and discussion

2.1. Strategy of side chain-directed complementary coordination

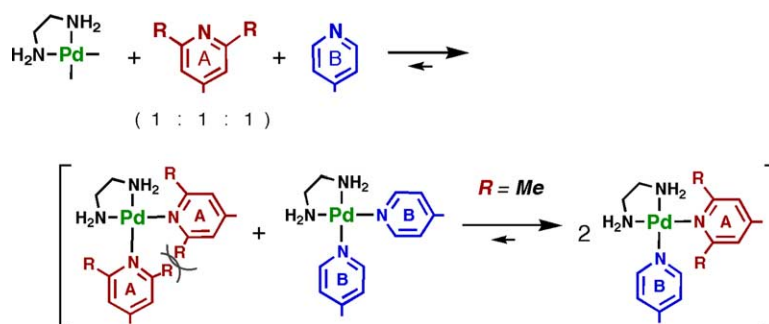
To design complementary complexation through metal–ligand coordination, pyridine-based ligands and a *cis*-protected Pd(II) ion were chosen. They have been widely used for constructing various architecture [9]. From the viewpoint of steric control on coordination, we first explored the complexation of two kinds of *p*-substituted pyridyl ligands (Py^A and Py^B) and (en)Pd(NO₃)₂ (**1**, en = ethylenediamine), as shown in Scheme 1. Upon complexation of Py^A (R = H) and Py^B with **1** in a 1:1:1 ratio, homo- and heterotopic complexes ((en)PdPy₂^A, (en)PdPy₂^B, and (en)PdPy^APy^B) should be formed in statistical distribution (ca. 1:1:2 ratio). In contrast, if sterically hindered methyl groups are introduced at the 2,6-position of Py^A, heterotopic complex (en)PdPy^APy^B is expected to be favored over the homotopic ones due to the steric repulsion between the methyl groups of (en)PdPy₂^A. Molecular modeling also suggested that minimized energy of two molecules of (en)PdPy^APy^B is lower than that of the sum of (en)PdPy₂^A and (en)PdPy₂^B ($\Delta E = 11.6$ kcal/mol) [10]. Accordingly, the equilibrium should be pushed toward the right, as illustrated in Scheme 1.

Control experiments, in the most simplified case, revealed that two molecules of 2,6-dimethylpyridines (Py^{Me₂}) can not bind to the (en)Pd unit, but both Py^{Me₂} and non-substituted pyridine (Py) can do simultaneously. Indeed, ¹H NMR study showed that a mixed D₂O solution of **1** and the two types of pyridines (1:1:1 ratio) gave the complementary pair (en)PdPy^{Me₂}Py in more than 80% yield. Accordingly, we first examined the complementary complexation of a square-shaped molecule from methyl-substituted bidentate ligands, non-substituted ones, and the (en)-Pd(II) ions.

2.2. Multicomponent assembly of molecular square and rectangle

As predicted, simple combination of 2,2',6,6'-tetramethyl-4,4'-bipyridine (**2**), 4,4'-bipyridine (**3**) and (en)-Pd(II) complex **1** gave an M₄L₂L'₂ square-shaped complex (**4**) as a sole product. Thus, upon addition of ligands **2** and **3** to a D₂O solution of **1** ([Pd] = 50 mM) in a 1:1:2 ratio at 100 °C for 1 h, ¹H NMR analysis of the clear solution showed the formation of **4** in almost quantitative yield (Fig. 1a). Three signals in the aromatic region (8.6, 7.8, and 7.6 ppm, same integration) were assigned to the protons of the framework of **4**. CSI-MS measurement clearly revealed the composition of **4** as a **1** + **2** + **3** (4:2:2) by intense peaks at *m/z* 388.5, 435.5, 504.4, and 620.3 corresponding to [4 – 6 · NO₃⁻ + 11 · DMF]⁶⁺, [4 – 5 · NO₃⁻ + 8 · DMF]⁵⁺, [4 – 4 · NO₃⁻ + 5 · DMF]⁴⁺, and [4 – 3 · NO₃⁻ + 2 · DMF]³⁺, respectively (Fig. 1b) [11]. Elemental analysis agreed as well with the formula of **4**. Moreover, reliable evidence of heterotopic coordination of **2** and **3** to the Pd(II) atom was shown by NOESY measurement: the methyl protons (H_a) of **2** (3.4 ppm) were strongly correlated to the terminal protons (H_c) of **3**. Therefore, the square structure of **4** certainly consists of two molecules of **2** and **3**, complementary *cis*-coordinating to the Pd(II) atoms. Undesirable heterotopic as well as homotopic assemblies such as **1**₄**2**₄ and **1**₄**3**₄ [9a] were hardly discernible in ¹H NMR and CSI-MS.

In a similar manner, the treatment of **1** with **2** and the elongated bidentate ligand (**5**) in a 2:1:1 ratio led to the clean formation of a rectangular molecule (**6**), whose ¹H NMR spectrum displayed five signals with identical integral ratio in the aromatic region (8.8–5.7 ppm) as shown in Fig. 2. A correlated cross peak between the terminal protons (H_c) of **5** and the methyl protons (H_a) of **2** was observed in the NOESY spectrum indicating the complementary complexation of **5** and **2** with **1**. Since the aromatic protons H_f in the middle of **5** were highly upfield shifted



Scheme 1. Side chain-directed complementary *cis*-coordination of *p*-substituted pyridine-based ligands (Py^A and Py^B) upon *cis*-protected Pd(II) ion **1** in a 1:1:1 ratio. The equilibrium should be pushed toward the right in the case of R = Me.

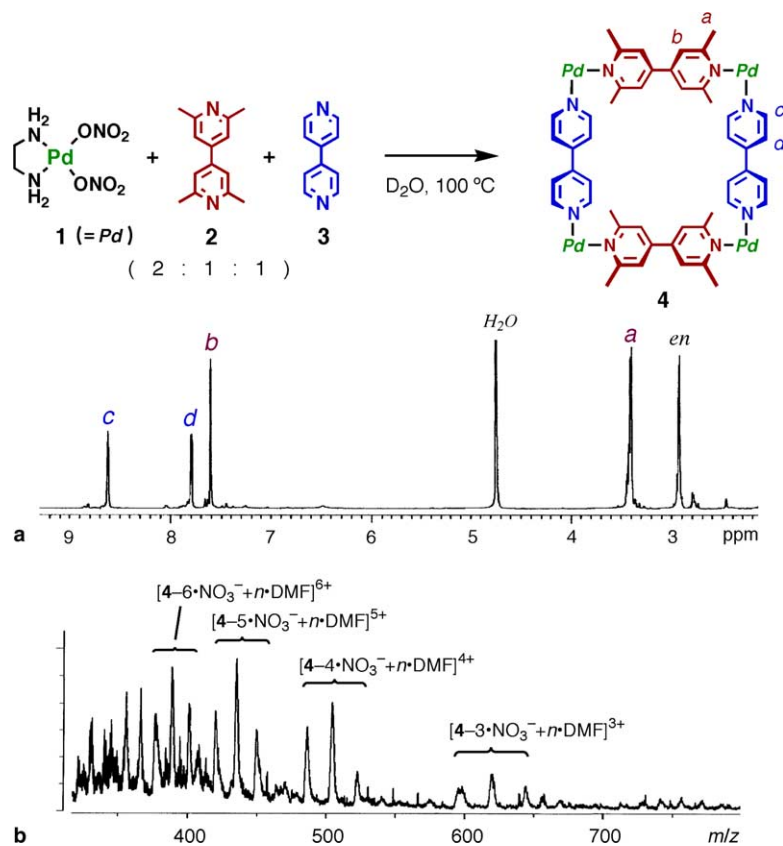


Fig. 1. Schematic representation of multicomponent assembly of molecular square 4 from 1, 2, and 3 in a 2:1:1 ratio. (a) ¹H NMR (500 MHz, D₂O, r.t.) and (b) CSI-MS (H₂O:DMF = 98:2) spectra of 4 (*en* = ethylenediamine).

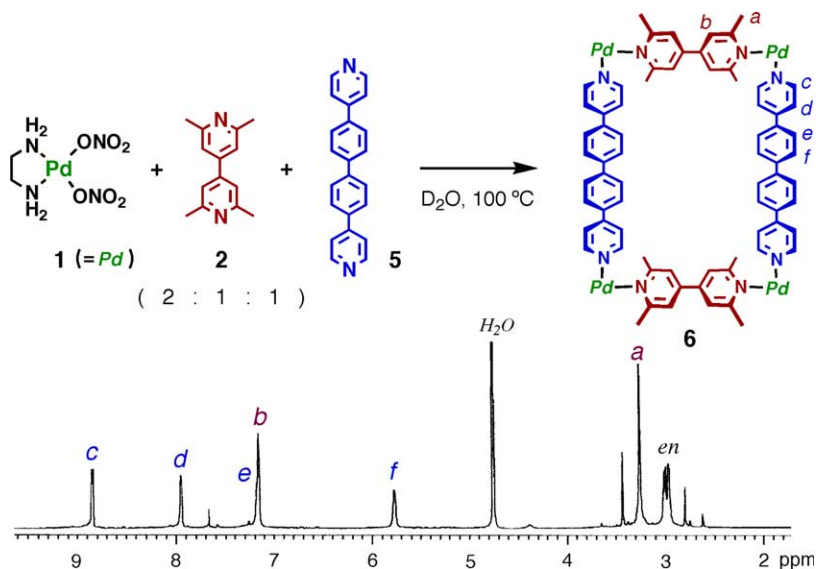


Fig. 2. Schematic representation of multicomponent assembly of molecular rectangle 6 from 1, 2, and 5 in a 2:1:1 ratio and ¹H NMR (500 MHz, D₂O, r.t.) spectrum of 6.

($\Delta\delta = -2.0$ ppm) due to the shielding effect of the aromatic rings, the framework of 6 should be twisted into a figure of eight. Regarding the CSI-MS measurement of 6, the spectrum showed a series of multiply charged

molecular ions of 6 with solvated DMF molecules (e.g., m/z 466.5 [$6 - 5 \cdot \text{NO}_3^- + 6 \cdot \text{DMF}$]⁵⁺, 562.2 [$6 - 4 \cdot \text{NO}_3^- + 4 \cdot \text{DMF}$]⁴⁺, and 698.6 [$6 - 3 \cdot \text{NO}_3^- + \text{DMF}$]³⁺).

The selective formation of **4** and **6** from eight components is attributed to the steric control imposed by the methyl groups of the pyridyl ligands. They facilitate the complementary *cis*-coordination of two kinds of ligands on the Pd(II) center. In fact, without the methyl groups on **2**, homotopic molecular square (composed of **1** and **3**) and gel-like precipitate were predominantly found in the combination of **1**, **3**, and **5**. Assemblies **4** and **6** are the thermodynamically favored products as no rearrangement of the framework was observed in solution.

2.3. Multicomponent assembly of a trigonal prism

To further verify this methodology, we undertook the assembly of a three-dimensional structure from multiple components. Herein we designed a trigonal prism (**8**) in which a complementary pair of three linear bidentate li-

gands **2** and two planar exo-tridentate ligands **7** are held together with six *cis*-protected Pd(II) ions **1** (Fig. 3). The structure is expected to possess a large enough cavity to accommodate two large molecules of aromatic guests. Considering such assembly, the side chains on ligand **2** should be crucial, because, without the methyl protection, homotopic M_4L_4 square **9** composed of **1** and **3** as well as $M_6L'_4$ cage **10** composed of **1** and **7** will be preferably formed [9a,12].

Along the lines of the design, we explored the complexation of **2** and **7** with Pd(II) ions in the presence of guest molecules, which revealed the formation of trigonal prism **8** without any other complexes. When **1**, **2**, and **7** in a 6:3:2 ratio were mixed in D_2O together with excess amounts of pyrene (**11**) at 100 °C for 1 h, the color of the solution dramatically changed from pale yellow to deep red. The 1H NMR spectrum exhibited a simple pattern of signals indicating the formation of **8**

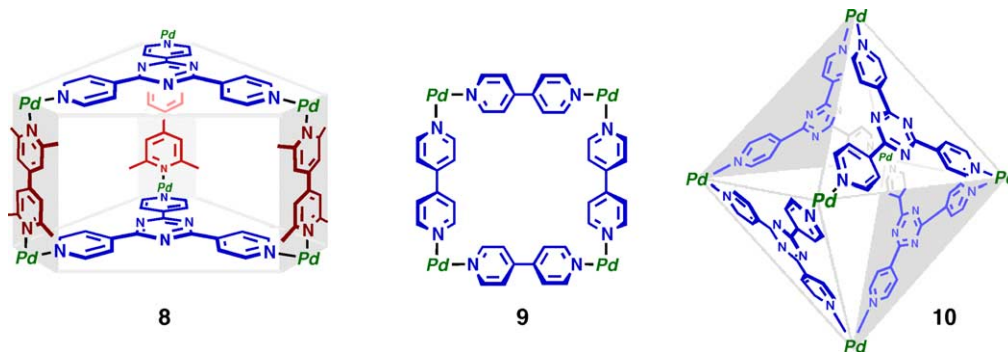


Fig. 3. Chemical structures of trigonal prism **8**, M_4L_4 square **9**, and $M_6L'_4$ cage **10** ($Pd = (en)Pd(NO_3)_2$).

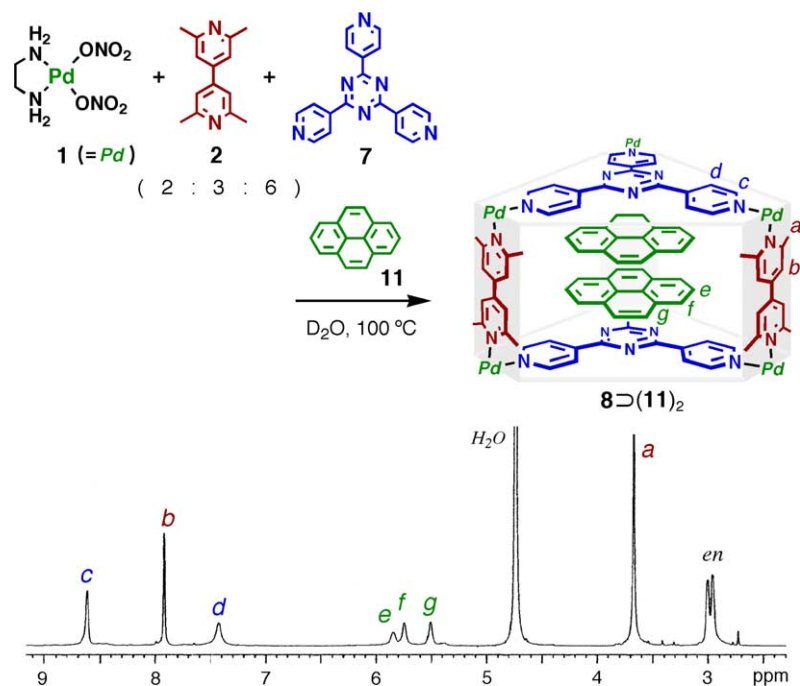


Fig. 4. Schematic representation of multicomponent assembly of trigonal prism **8** with $(11)_2$ from **1**, **2**, and **7** in a 6:3:2 ratio in the presence of pyrene (**11**) and 1H NMR spectrum (500 MHz, D_2O , r.t.) of **8** with $(11)_2$.

with two equivalents of guests **11** (Fig. 4). This was strongly supported by elemental analysis and by CSI-MS experiments using a different guest (coronene). In the ^1H NMR spectrum of the aromatic region, three signals ($\text{H}_{\text{b-d}}$) derived from **8** agreed with the $D_{3\text{h}}$ -symmetry of **8** and with the proposed stoichiometry ($1:2:7 = 6:3:2$). Again, NOESY spectrum showed a correlated signal between protons H_{a} and H_{c} derived from ligands **2** and **7**, respectively. The coordination fashion was finally confirmed by X-ray crystallographic analysis as previously reported [13]. The signals of the two molecules of **11** (5.8–5.5 ppm) are strongly shifted upfield due to their enclathration in **8**.

The presence of both the planar aromatic guest (**11**) and the methyl groups on **2** is essential for the selective formation of prism **8** from 11 components. Thus, the guest acts as a template for the assembly [7c] and the methyl groups regulate the way of the coordination of two types of ligand. In control experiments, the reaction of **1**, **3** (without methyl groups), and **7** provided a trigonal prism in only 60% yield even with the template, whereas no prism was formed without the template. The molecular modeling of $\mathbf{8} \supset (\mathbf{11})_2$ suggested that two aromatic guests are accommodated in the cavity in a parallel fashion where effective π - π interaction between host and guests can be predicted. Indeed, UV-vis spectrum of $\mathbf{8} \supset (\mathbf{11})_2$ in H_2O (deep red solution) showed new absorption bands at 326 and 344 nm attributed to charge transfer interaction between π -stacked **8** and **11**.

3. Summary

We have developed a new strategy for the selective formation of multicomponent assembly from two kinds of pyridine-based ligands and *cis*-protected Pd(II) ions, which gave rise to $\text{M}_4\text{L}_2\text{L}'_2$ square and rectangle, and $\text{M}_6\text{L}_3\text{L}'_2$ trigonal prism structures. The key to success in generating such assemblies is the complementary complexation of the two different ligands with the Pd(II) atom by steric control from the methyl groups (= side chain) incorporated to the ligand. We expect that our strategy referred to as *side chain-directed complementary coordination* will become a general method for selective synthesis of multicomponent assemblies, especially for molecules which have two kinds of functional groups (e.g., electron donor/acceptor or molecular recognition/transformation) within the framework.

4. Experimental

4.1. Materials and instrumentations

NMR spectral data were recorded on a Bruker DRX-500 (500 MHz) spectrometer. TMS (CDCl_3 solution) in

a capillary served as external standard ($\delta = 0$ ppm). CSI-MS (coldspray ionization mass spectroscopy) data were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source [10]. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. UV-visible spectral data were recorded on a SHIMADZU UV-3150. Melting points were determined on a Yanaco MF-500 V melting point apparatus. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemicals Industries Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without further purification. Deuterated solvents were acquired from Cambridge Isotope Laboratories, Inc. and used as supplied for the complexation reactions and NMR measurements. Ligand **2** was prepared from 4-bromo-2,6-lutidine via homo-coupling by Ni catalyst [J.A. Berson, T. Cohen, J. Org. Chem. 20 (1955) 1461].

4.2. Preparations and physical data

Assembly of square-shaped molecule 4. A mixture of $(\text{en})\text{Pd}(\text{NO}_3)_2$ (**1**) 14.5 mg (50.0 μmol), ligand **2** 5.3 mg (25.0 μmol), and 4,4'-bipyridine (**3**) 3.9 mg (25.0 μmol) was stirred in a D_2O solution (1.0 mL) at 100 °C for 1 h. ^1H NMR revealed the formation of a square-shaped structure in quantitative yield. After filtration, the structure was isolated as a white precipitate (21.6 mg; 11.4 μmol) by addition of ethanol in 91% yield. Physical data: ^1H NMR (500.13 MHz, D_2O , 27 °C, TMS as external standard): δ 8.63 (d, $J = 6.0$ Hz, 8H), 7.80 (d, $J = 6.0$ Hz, 8H), 7.61 (s, 8H), 3.41 (s, 24H), 2.91 (s, 16H); ^{13}C NMR (125.77 MHz, D_2O , 27 °C, TMS as external standard): δ 160.7 (C_{q}), 152.1 (CH), 147.1 (C_{q}), 146.8 (C_{q}), 124.9 (CH), 122.3 (CH), 47.5 (CH_2), 46.5 (CH_2), 25.7 (CH_3); IR (KBr, cm^{-1}): 3428, 3073, 1616, 1356, 1226, 1062, 833, 685; m.p.: ~ 235 °C (decomposed); CSI-MS ($\text{H}_2\text{O}:\text{DMF} = 98:2$): m/z 376.7 $[\mathbf{4} - 6 \cdot \text{NO}_3^- + 10 \cdot \text{DMF}]^{6+}$, 388.5 $[\mathbf{4} - 6 \cdot \text{NO}_3^- + 11 \cdot \text{DMF}]^{6+}$, 400.6 $[\mathbf{4} - 6 \cdot \text{NO}_3^- + 12 \cdot \text{DMF}]^{6+}$, 420.0 $[\mathbf{4} - 5 \cdot \text{NO}_3^- + 7 \cdot \text{DMF}]^{5+}$, 435.5 $[\mathbf{4} - 5 \cdot \text{NO}_3^- + 8 \cdot \text{DMF}]^{5+}$, 449.3 $[\mathbf{4} - 5 \cdot \text{NO}_3^- + 9 \cdot \text{DMF}]^{5+}$, 486.1 $[\mathbf{4} - 4 \cdot \text{NO}_3^- + 4 \cdot \text{DMF}]^{4+}$, 504.4 $[\mathbf{4} - 4 \cdot \text{NO}_3^- + 5 \cdot \text{DMF}]^{4+}$, 522.1 $[\mathbf{4} - 4 \cdot \text{NO}_3^- + 6 \cdot \text{DMF}]^{4+}$, 620.3 $[\mathbf{4} - 3 \cdot \text{NO}_3^- + 2 \cdot \text{DMF}]^{3+}$, 644.3 $[\mathbf{4} - 3 \cdot \text{NO}_3^- + 3 \cdot \text{DMF}]^{3+}$; E.A. Calc. for $\text{C}_{56}\text{H}_{80}\text{N}_{42}\text{O}_{36}\text{Pd}_6 \cdot (\text{H}_2\text{O})_4$: C, 34.12; H, 4.50; N, 17.05. Found: C, 34.30; H, 4.64; N, 17.12.

Assembly of rectangular-shaped molecule 6. To an aqueous solution (0.8 mL) of $(\text{en})\text{Pd}(\text{NO}_3)_2$ (**1**; 11.6 mg; 40.0 μmol), **2** (4.2 mg; 20.0 μmol) and **5** (6.2 mg; 20.0 μmol) was added and stirred for 12 h at 100 °C. The resulting solution gave a complex **6** in quantitative yield, which was isolated as a white precipitate (15.8 mg; 7.2 μmol) by addition of ethanol in 72% yield. Physical data: ^1H NMR (500.13 MHz, D_2O , 27 °C, TMS as external standard): δ 8.85 (d, $J = 5.4$ Hz, 8H),

7.95 (d, $J = 5.4$ Hz, 8H), 7.18 (s, 8H), 7.16 (s, 8H), 5.76 (d, $J = 5.4$ Hz, 8H), 3.25 (s, 24H), 2.99–2.96 (m, 16H); ^{13}C NMR (125.77 MHz, D_2O , 27 °C, TMS as external standard): δ 160.6 (C_q), 152.3 (CH), 149.9 (C_q), 146.6 (C_q), 140.3 (C_q), 134.1 (C_q), 126.9 (CH), 126.3 (CH), 123.7 (CH), 121.8 (CH), 47.6 (CH_2), 46.6 (CH_2), 25.6 (CH_3); IR (KBr, cm^{-1}): 3421, 3197, 1616, 1381, 1225, 1036, 812, 668; m.p.: ~ 222 °C (decomposed); CSI-MS ($\text{H}_2\text{O}:\text{CH}_3\text{CN}:\text{DMF} = 30:50:2$): m/z 452.2 $[\text{6} - 5 \cdot \text{NO}_3^- + 5 \cdot \text{DMF}]^{5+}$, 466.5 $[\text{6} - 5 \cdot \text{NO}_3^- + 6 \cdot \text{DMF}]^{5+}$, 481.7 $[\text{6} - 5 \cdot \text{NO}_3^- + 7 \cdot \text{DMF}]^{5+}$, 562.2 $[\text{6} - 4 \cdot \text{NO}_3^- + 4 \cdot \text{DMF}]^{4+}$, 581.2 $[\text{6} - 4 \cdot \text{NO}_3^- + 5 \cdot \text{DMF}]^{4+}$, 676.3 $[\text{6} - 3 \cdot \text{NO}_3^-]^{3+}$, 698.6 $[\text{6} - 3 \cdot \text{NO}_3^- + \text{DMF}]^{3+}$, 721.9 $[\text{6} - 3 \cdot \text{NO}_3^- + 2 \cdot \text{DMF}]^{3+}$.

Assembly of trigonal prism-shaped molecule 8 ($\mathbf{11}$)₂. 2.64 mg (30.0 μmol), 2,4,6-tris(4'-pyridyl)-1,3,5-triazine (**7**) 6.2 mg (20.0 μmol), and pyrene (**11**) 18.0 mg (60.0 μmol) were added to an aqueous solution (0.6 mL) of (en)Pd(NO₃)₂ (**1**) 17.4 mg (60.0 μmol), and then, the suspended mixture was stirred at 100 °C for 1 h. After the obtained deep red solution was filtrated and evaporated to dryness, the residue was recrystallized from small amount of water. A deep red solid of $\mathbf{8} \supset (\mathbf{11})_2$ (35.8 mg (8.2 μmol)) was obtained in 82% yield. Physical data: ^1H NMR (500.13 MHz, D_2O , 27 °C): δ 8.62 (s, 12H), 7.92 (s, 12H), 7.43 (s, 12H), 5.84 (s, 4H, **11**), 5.75 (s, 8H, **11**), 5.51 (s, 8H, **11**), 3.67 (s, 36H), 3.00 (s, 12H), 2.96 (s, 12H); ^{13}C NMR (125.77 MHz, D_2O , 27 °C): δ 166.8 (C_q), 161.2 (C_q), 151.9 (CH), 148.6 (C_q), 144.1 (C_q), 128.3 (C_q , **11**), 125.5 (CH, **11**), 125.2 (CH, **11**), 124.9 (CH), 124.1 (C_q , **11**), 123.2 (CH, **11**), 123.0 (CH), 46.5 (CH_2), 26.0 (CH_3); IR (KBr, cm^{-1}): 3407, 3067, 1520, 1375, 1059, 951, 804, 674; m.p.: ~ 250 °C (decomposed); CSI-MS ($\text{H}_2\text{O}:\text{DMF} = 20:1$, guest: coronene (**12**)): m/z 636.3 $[\mathbf{8} \supset (\mathbf{12})_2 - 6 \cdot \text{NO}_3^- + 8 \cdot \text{DMF}]^{6+}$, 732.1 $[\mathbf{8} \supset (\mathbf{12})_2 - 7 \cdot \text{NO}_3^- + 5 \cdot \text{DMF}]^{5+}$, 857.4 $[\mathbf{8} \supset (\mathbf{12})_2 - 8 \cdot \text{NO}_3^- + \text{DMF}]^{4+}$, 1140.2 $[\mathbf{8} \supset (\mathbf{12})_2 - 9 \cdot \text{NO}_3^-]^{3+}$; E.A. Calc. for $\text{C}_{126}\text{H}_{144}\text{N}_{42}\text{O}_{36}\text{Pd}_6 \cdot (\text{H}_2\text{O})_{17.3}$: C, 40.11; H, 4.77; N, 15.59. Found: C, 39.71; H, 5.01; N, 15.99.

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