Self-Assembly

A Palladium(II)-Clipped Aromatic Sandwich**

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Enclathration of large π-conjugated molecules by a synthetic receptor is an interesting task because the properties of these molecules, such as stability, reactivity, solubility, and photo- and electroresponse, can be controlled.[1] To enclathrate large π-conjugated molecules, however, a synthetic receptor with a cavity is required, whose dimensions should be larger than that of the π-conjugated guests. While there are many examples of three-dimensional receptors,[2] large two-dimensional receptors have been less explored.[3] Herein we describe the self-assembly of a π-stacked host–guest system in which large aromatic guests are sandwiched by metal-clipped π-conjugated ligands. The ligand **1** is a roughly 2-nm-sized hexagonal planar molecule that consists of ten aromatic rings with six pyridyl donor sites at the periphery. Upon complexation with $[(\mathrm{en})\mathrm{Pd}(\mathrm{NO}_3)_2]$ (en = 1,2-ethanediamine) this ligand is assembled to give large two-dimensional receptors. In the presence of D_{3h}-symmetric guests (**2**), sandwich complexes $[\mathbf{2}\subset\mathbf{3}]^{12+}$, where $\mathbf{3}^{12+}$ has a composition of $[\{(\mathrm{en})\mathrm{Pd}\}_6(\mathbf{1})_2]^{12+}$, are quantitatively assembled. The guest molecule is wrapped by two ligands whose pyridyl donor sites

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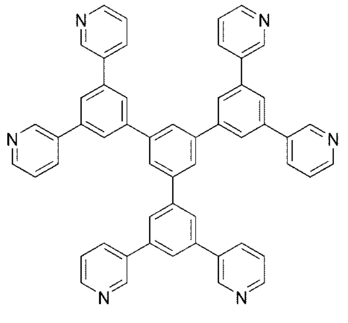

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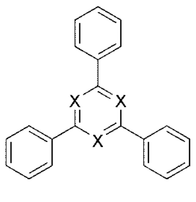
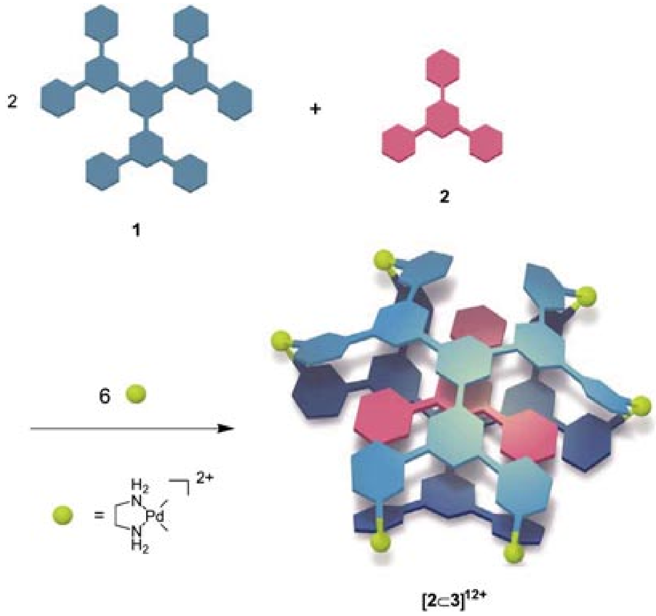


2a: X = N

2b: X = CH

are fully clipped by six $\{(en)Pd\}^{2+}$ units at the rim of the structure (Scheme 1).



Scheme 1. The self-assembly of $[\mathbf{2}\subset\mathbf{3}]^{12+}$ complex.

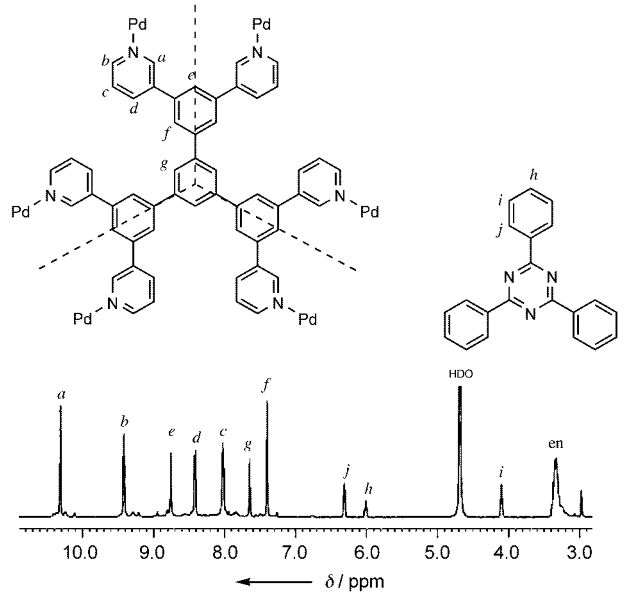


Figure 1. ^1H NMR spectrum of $[\mathbf{2a}\subset\mathbf{3}]^{12+}$. Assignments of H_a–H_j are given.

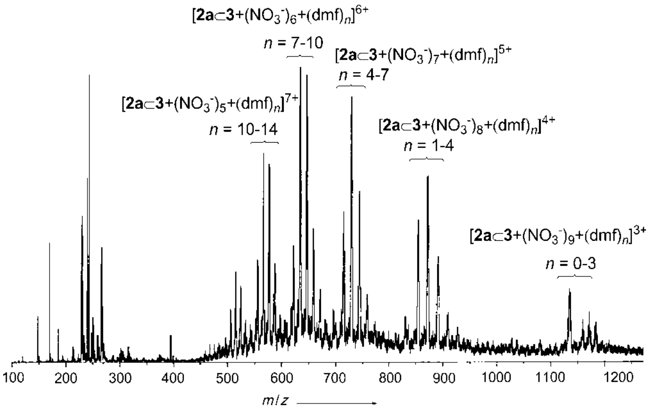


Figure 2. CSI-MS spectrum of $[\mathbf{2a}\subset\mathbf{3}]^{12+}$ (H_2O:CH_3CN:DMF = 12:6:1, RT).

An excess of **2a** (suspension) was treated with **1** (3.5 μmol) and $[(en)Pd(NO_3)_2]$ (15 μmol) in D_2O:CD_3CN (2:1; 0.7 mL) for 2 h at 60 °C. After filtration of non-enclathrated **2a**, a simple ^1H NMR spectrum was obtained from the clear solution, which indicated the formation of a single product (Figure 1). The seven signals observed in the aromatic region (H_{a-g}) agree with the D_{3h} structure of $\mathbf{3}^{12+}$. Highly upfield-shifted signals (H_{h-j}), showing a typical phenyl splitting pattern, were assigned to guest **2a** accommodated within the cavity of $\mathbf{3}^{12+}$. The $[\mathbf{2a}\subset\mathbf{3}]^{12+}$ structure was strongly supported by NOESY experiment, which showed correlation between H_f of $\mathbf{3}^{12+}$ and H_j of **2a**.[4]

Cold spray ionization mass spectroscopy (CSI-MS) clearly suggested the formation of $[\mathbf{2a}\subset\mathbf{3}]^{12+}$, it showed a series of prominent peaks corresponding to $[\mathbf{2a}\subset\mathbf{3}+(NO_3^-)_m+(dmf)_n]^{12-m+}$ ($m = 5$–9, $n = 0$–14). For example, in 4^+ and 5^+ regions, two intense peaks at m/z 872.3 and 729.4 were assigned to $[\mathbf{2a}\subset\mathbf{3}+(NO_3^-)_8+(dmf)_2]^{4+}$ and $[\mathbf{2a}\subset\mathbf{3}+(NO_3^-)_7+(dmf)_5]^{5+}$, respectively (Figure 2).[5] Note that, under CSI-MS conditions, there was little indication for the presence of either guest-free species or fragmented species, which shows the remarkable stability of the $[\mathbf{2a}\subset\mathbf{3}]^{12+}$ complex in solution.

When guest **2a** was replaced by 1,3,5-triphenylbenzene (**2b**), single crystals suitable for X-ray analysis were obtained by slow diffusion of THF into an aqueous solution of the complex.[6] The X-ray analysis revealed the expected structure where two molecules of **1** are clipped by six $\{(en)Pd\}^{2+}$ units allowing the complete wrapping of the large planar guest (Figure 3). The conformation of **1** is not planar but slightly concave. The pyridine ring centers are situated above the face of the core benzene ring at an average separation of 1.2 Å. The 3-pyridyl groups are tilted by 31–42° with respect to adjacent phenyl groups so that they coordinate to Pd^{II} centers with ideal bite angles (89–91°). Thus, host distortion exists not around the Pd^{II} centers but along the large framework of **1**, which suggests that close host–guest packing generates a

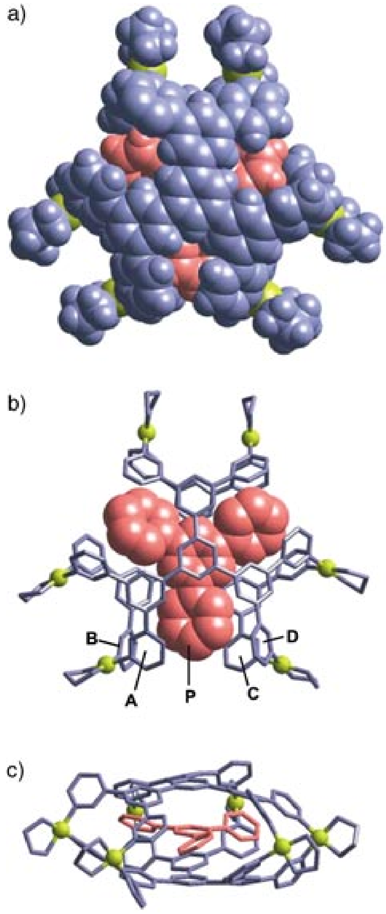
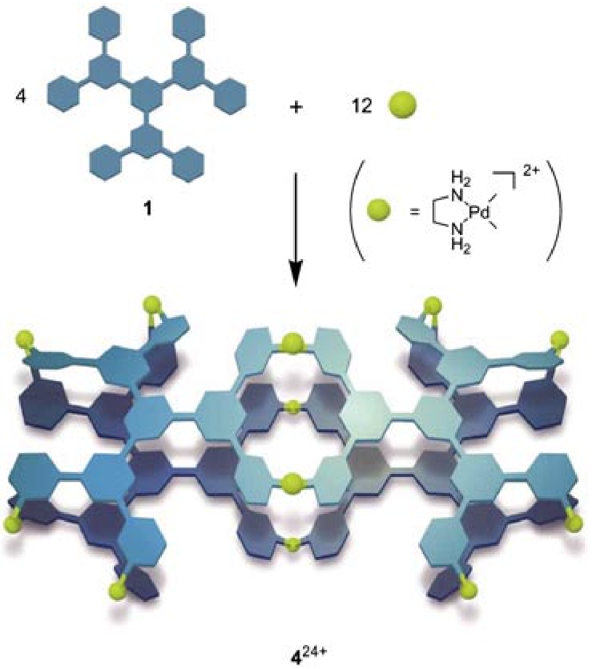


Figure 3. X-ray crystallographic structure of $[\mathbf{2b}\subset\mathbf{3}]^{12+}$. a) Space-filling representation (top view), b) top view showing the D_3 orientation of guest **2b**. Around the phenyl group **P**, π–π stacking with pyridine rings **A** and **C**, and CH–π contact with pyridine rings **B** and **D** are observed; c) A side view.

greater distortion. The core benzene ring of **2b** is tightly stacked with the two ligands (3.5 Å van der Waals contact). In the crystal, D_3 symmetry is observed (not D_{3h}), each phenyl group of the guest being tilted by 30–36° allowing efficient π–π and CH–π interactions with four surrounding pyridine rings (Figure 3b). As a result, **2b** is fully wrapped by $\mathbf{3}^{12+}$.

While $[\mathbf{2}\subset\mathbf{3}]^{12+}$ complexes are stabilized by sufficient host–guest interactions, the host framework itself is considerably distorted. In the absence of a guest, therefore, less distorted structure $\mathbf{4}^{24+}$ is formed (Scheme 2). Compound $\mathbf{4}^{24+}$ is a dimer of $\mathbf{3}^{12+}$ generated through the breaking of two Pd–N bonds. The high-yield formation of $\mathbf{4}^{24+}$ was confirmed by NMR spectroscopy and CSI-MS spectrometry. When **1** and $[(en)Pd(NO_3)_2]$ were mixed in a 1:3 ratio without guest molecules, 19 resonance signals, corresponding to half the framework of **1**, appeared in the aromatic region indicating the reduction, after complexation, of the inherent D_{3h} symmetry of **1** into D_{2h} symmetry (Figure 4a). CSI-MS measurement showed the molecular weight of 6562 Da, which is exactly twice as much as $\mathbf{3}^{12+}[NO_3^-]_{12}$, supporting the proposed $M_{12}L_4$ dimeric structure $\mathbf{4}^{24+}$.



Scheme 2. Self-assembly of the dimeric structure, $\mathbf{4}^{24+}$.

A smaller aromatic guest, triphenylene (**5**), is included in the cavity of $\mathbf{4}^{24+}$ (which is expanded compared to that of $\mathbf{3}^{12+}$) in a 1:2 ratio upon treating it with a solution of $\mathbf{4}^{24+}$ for 2 h at 60 °C. The formation of the $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ complex was revealed by NMR spectroscopy with the highly upfield-shifted signals of **5** ($\delta = 6.9$ and 6.0 ppm) and the slightly shifted 19 signals in the aromatic region of the host (Figure 4b). Some minor signals in Figure 4b may be assigned to other host–guest complexes, such as 1:1 complex $[\mathbf{5}\subset\mathbf{4}]^{24+}$ or monomer complex $[\mathbf{5}\subset\mathbf{3}]^{12+}$. CSI-MS also indicated the required stoichiometry for the $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ complex (see Supporting Information).

When guest **2a** was suspended in the solution of the $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ complex, guest exchange took place at 60 °C within 24 h concomitant with host monomerization.[7] That is, $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ was converted into $[\mathbf{2a}\subset\mathbf{3}]^{12+}$, as shown by NMR spectroscopy (Figure 4b–e). Clearly, the self-assembly of hosts $\mathbf{3}^{12+}$ and $\mathbf{4}^{24+}$ is dynamic owing to the labile nature of the Pd–N bond. The host–guest stabilization in $[\mathbf{2a}\subset\mathbf{3}]^{12+}$ dominates over the distortion of the host framework, whereas less distorted $\mathbf{4}^{24+}$ is favored when a guest is absent or less efficiently trapped by the host.

In summary we have constructed a large π-conjugated, expanded two-dimensional receptor by self-assembly. Extension of this study could ease the handling of very large π-molecules, such as molecular graphites, which are in general tedious to treat in solution because of their very poor solubility. The chemical and physical properties of such large π-molecules may be restricted within large two-dimensional cavities.

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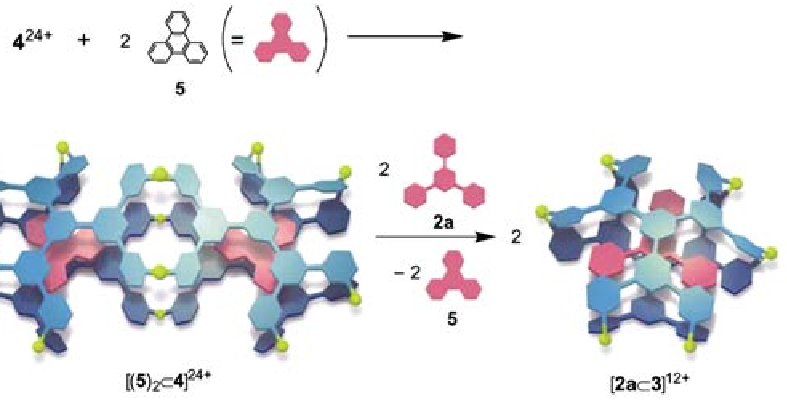

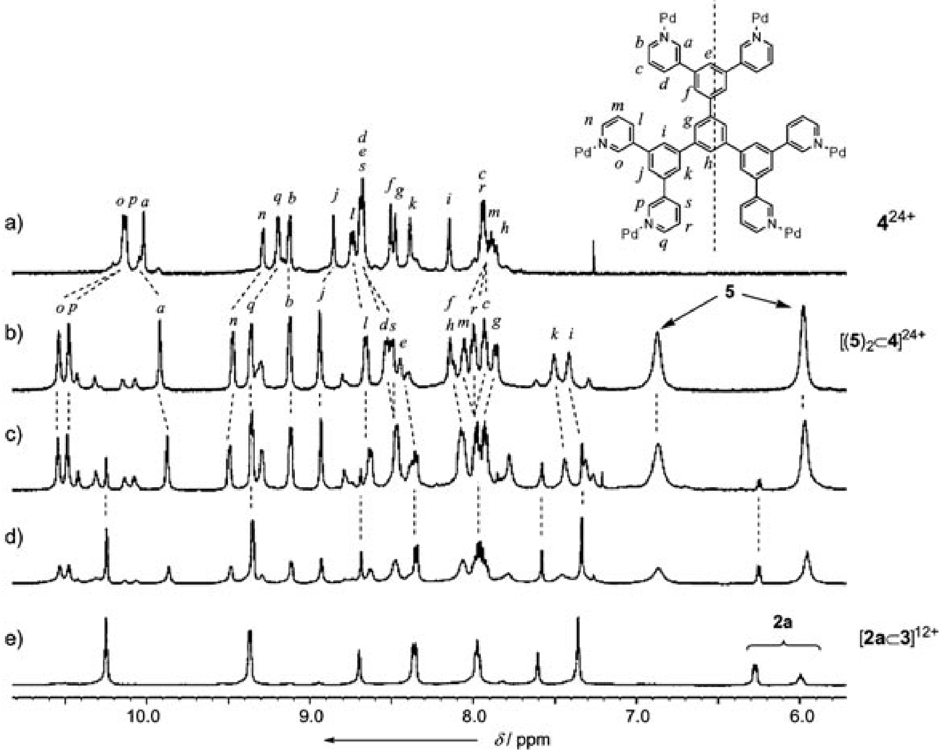

Figure 4. ^{1}H NMR spectroscopic monitoring of the conversion of $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ into $[\mathbf{2a}\subset\mathbf{3}]^{12+}$. The spectrum of a) dimeric host $\mathbf{4}^{24+}$, b) $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$, c) the spectra upon the addition of **2** (1 equiv) to the $[(\mathbf{5})_2\subset\mathbf{4}]^{24+}$ solution after 1 h, d) after 24 h, e) The spectrum after filtration, further addition of **2** (1 equiv) to the solution, and stirring the mixture for an additional 2 h.

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[4] In the NOESY spectrum, not only host–guest correlation but also the orientation of the ligand **1** (between H_a and H_e) were assigned, see the Supporting Information.

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[6] Crystal data for $[\mathbf{2b}\subset\mathbf{3}]^{12+}$: $C_{144}H_{138}N_{36}O_{57}Pd_6$, $M_r = 3927.85$, crystal dimensions $0.40\times0.20\times0.20$ mm^3, monoclinic, $P2(1)/n$, $a = 20.5995(11)$, $b = 26.3842(15)$, $c = 30.3963(16)$ Å, $V = 16340.8(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.597$ g cm^{-3}, $F(000) = 7951$,

$\lambda(\text{Mo}_{K\alpha}) = 0.71073$ Å, $T = 173(2)$ K, 104788 reflections collected, 37340 independent reflections observed; 2079 number of parameters; $R_1 = 0.0556$; $wR_2 = 0.1403$. CCDC-238928 (**2b**$\subset$**3**$^{12+}$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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