Stacking Interactions

Discrete Stacking of Large Aromatic Molecules within Organic-Pillared Coordination Cages**

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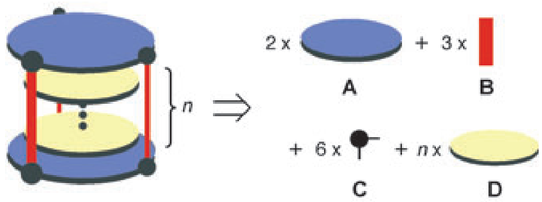
Aromatic stacking of π-conjugated planar molecules leads to the exhibition of unique chemical and physical properties. Discotic liquid crystals are, for example, a columnar assembly of aromatic compounds that contain long alkyl chains,[1] and organic electroconductive materials involve alternate charge-transfer stacking of electron-donating and -accepting π-conjugated compounds.[2] Whereas such infinite assemblies have been thoroughly studied, precisely controlled discrete assemblies composed of more than two π-conjugated molecules have been explored much less frequently.[3–6] As discrete assemblies of a limited number of π-stacked molecules are expected to show new properties different from those of isolated or infinitely stacked π-systems, a general method for constructing such structures has to be developed. Here, we report the self-assembly of a metal-hinged, organic-pillared cage with a large cavity that can accommodate two or more large π-conjugated molecules. The cage consists of two large organic panels (**A**), three rodlike pillars (**B**), and six metal hinges (**C**; Scheme 1). The large, box-shaped cavity accom-



Scheme 1. Schematic representation of the organic-pillared cage accommodating two or more π-conjugated guests. The ensemble self-assembles from components **A**–**D** (**A**: aromatic panel; **B**: rodlike pillar; **C**: metal hinge; **D**: aromatic guest).

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modates a limited number of π-conjugated molecules (**D**); this number is strictly controlled by the length of the pillar molecules.

To realize such a multistacked aromatic host–guest system, we have designed the self-assembly of prismlike cage $\mathbf{1}^{12+}$ from tridentate panel-like ligand **2**, bidentate pillar ligand **3**, and end-capped Pd^{II} complex $\mathbf{4}^{2+}$ (Figure 1 a). The resulting cage, as estimated by molecular modeling, can accommodate two large aromatic compounds. The space between the "floor" and the "roof" of the prism cage (≈7.5 Å) is approximately twice the thickness of planar aromatic compounds.[7] In fact, in the presence of coronene (**5**), we observed the quantitative self-assembly of a quadruple-stacking structure $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$. Four components, **2**, **3**, $\mathbf{4}^{2+}$, and **5**, were combined in a 2:3:6:2 ratio in D_2O ($[Pd^{II}]$ = 60 mM).[8] After stirring at 100 °C for 2 h the suspension became clear and the color changed from pale yellow to deep red. ^{1}H NMR analysis of the solution indicated the formation of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ as a single product (Figure 1 b). The NMR spectrum agreed with the D_{3h} symmetry of $\mathbf{1}^{12+}$ and with the stoichiometry of the components. The signal of **5** (H_e) is shifted strongly upfield due to encapsulation in the cavity of $\mathbf{1}^{12+}$. Remarkably, the $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ structure is stable even under CSI-MS conditions.[9] After anion exchange with PF_6^-, the CSI mass spectrum shows a series of peaks for $[\mathbf{1}\supset(\mathbf{5})_2+(12-m)PF_6+n\mathrm{DMF}]^{m+}$ (e.g., m/z = 767.7 (m = 6, n = 12), 906.2 (m = 5, n = 9), and 1023.3 (m = 4, n = 1)), Figure 1 b. Guest-free $\mathbf{1}^{12+}$ was hardly detected, which suggests strong π–π interactions between the host and the guest.

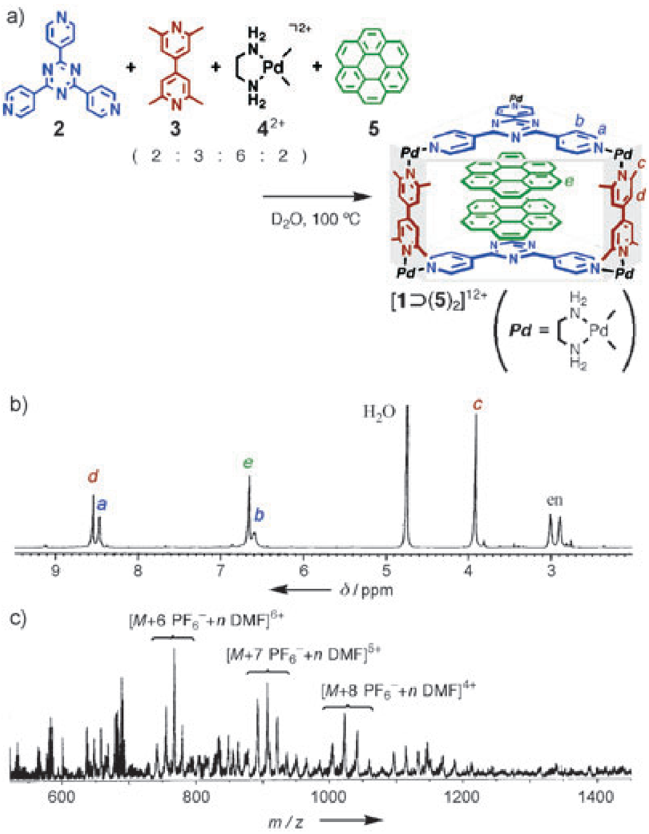


Figure 1. a) Schematic representation of the self-assembly of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$; b) ^{1}H NMR (500 MHz, D_2O, RT) spectrum after the combination of **2**, **3**, $\mathbf{4}^{2+}$, and **5** in a 2:3:6:2 ratio at 100 °C for 2 h (en = ethylenediamine); c) CSI mass spectrum of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ after anion exchange with PF_6^-.

The selective formation of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ from thirteen components ($2\times\mathbf{2}+3\times\mathbf{3}+6\times\mathbf{4}^{2+}+2\times\mathbf{5}$) is due to two dominant factors: the template effect of the aromatic guests and ligand steric hindrance. Without the guests **5**, the assembly of cage $\mathbf{1}^{12+}$ occurs with considerable amounts of a homotopic M_6L_4 cage[10] (composed of **2** and $\mathbf{4}^{2+}$) and some oligomeric products (composed of **3** and $\mathbf{4}^{2+}$). The α-methyl groups on the pyridyl pillars **3** provide a steric bulk that prevents the coordination of two pillar ligands to the same Pd^{II} center.[11,12]

X-ray crystallographic analysis provided concrete evidence for the quadruple-stacking structure of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$. When pyrene (**6**) was used as a large planar guest,[13] a dark-reddish single crystal of $[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$ was obtained after a few weeks at room temperature by the slow diffusion of ethanol vapor into an aqueous solution containing $[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$. The diffraction data were collected by synchrotron X-ray radiation (KEK, PF-AR beamline NW2) at −184 °C.[14] Despite severe disorder of the solvents and counterions, the prismlike structure of $\mathbf{1}^{12+}$ accommodating two molecules of **6** in the cavity was successfully solved (Figure 2). The cage is twisted by 36°, which results in efficient quadruple aromatic stacking. The interplane distances **2**⋯**6** and **6**⋯**6** are 3.4 and 3.3 Å, respectively.

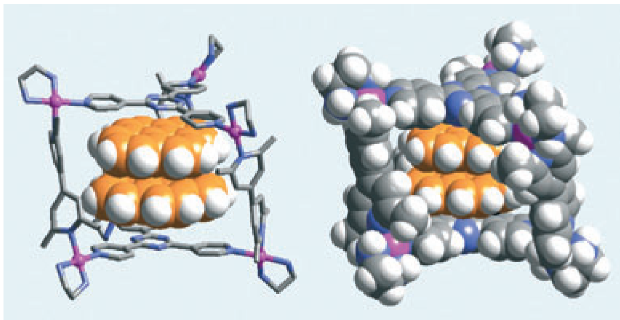


Figure 2. X-ray crystal structure of $[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$ (**6**: pyrene).

The use of elongated pillar ligand **7** increased the size of the cavity (Figure 3 a). Indeed, the expanded prismlike cage $\mathbf{8}^{12+}$ was successfully assembled when the components **2**, **7**, and $\mathbf{4}^{2+}$ were combined in the presence of guest **5**. Surprisingly, cage $\mathbf{8}^{12+}$ binds two molecules of **5** and one molecule of ligand **2** within the cavity. The uncoordinated **2** is sandwiched by two coronene guests such that an $[\mathbf{8}\supset(\mathbf{5}{\cdot}\mathbf{2}{\cdot}\mathbf{5})]^{12+}$ structure is formed. The yield of this assembly was optimal when **2**, **7**, and $\mathbf{4}^{2+}$ were combined in a 3:3:6 ratio in the presence of an excess amount of **5** (Figure 3 a).[8]

The unique structure involving quintuple stacking (**2**⋯**5**⋯**2**⋯**5**⋯**2**) was strongly supported by NMR spectroscopy and CSI mass spectrometry. Simple ^{1}H NMR spectroscopy (Figure 3 b) showed that the two Pd^{II}-coordinated panel

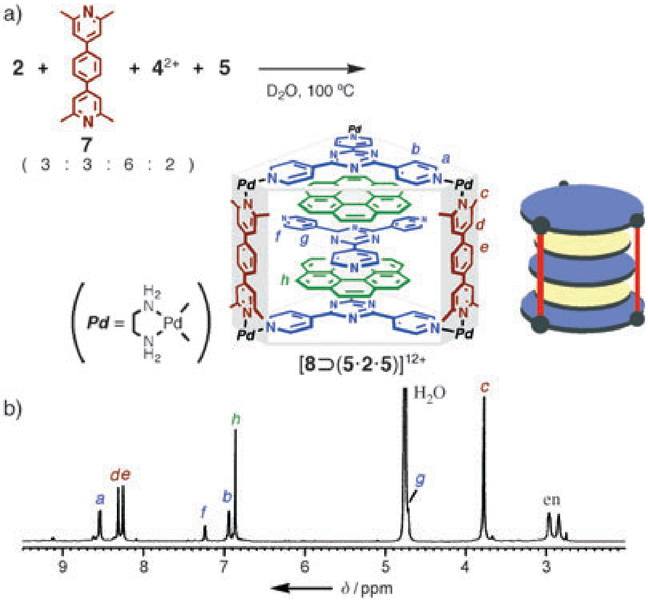


Figure 3. a) Quintuple-stacked, prismlike structure of $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$ which self-assembles from **2**, **7**, $\mathbf{4}^{2+}$, and **5** in a 3:3:6:2 ratio; b) ^{1}H NMR (500 MHz, D_2O, RT) spectrum of $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$.

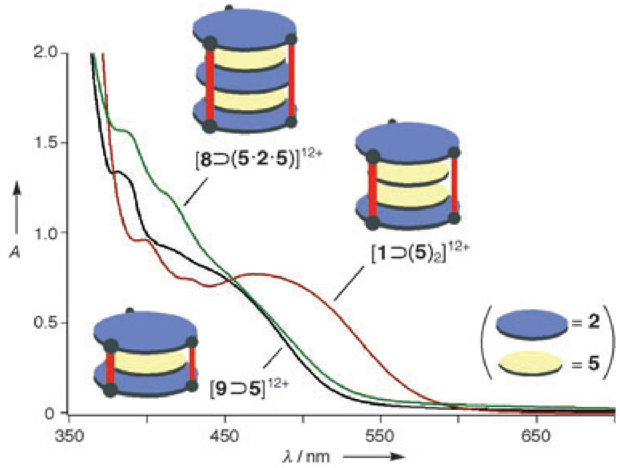
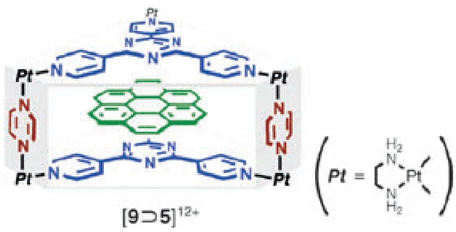


Figure 4. UV/Vis spectra (H_2O, RT) of the multistacked aromatic assemblies $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$, $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$, and $[\mathbf{9}\supset\mathbf{5}]^{12+}$.

ligands (**2**, signals H_a and H_b) and two coronene guests (**5**, signal H_h) are equivalent. These results are in good agreement with the expected D_{3h} symmetry of the system. The middle panel **2** is shifted significantly upfield (signals H_f and H_g at $\delta =$ 7.23 and 4.71 ppm, respectively) due to intercalation between two molecules of **5**. After counteranion exchange, the CSI mass spectrum showed clear peaks for $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5}) + (12-m)PF_6^- + n\mathrm{DMF}]^{m+}$. Note that the noncovalently associated $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$ structure is still stable under the CSI-MS conditions.[8]

The efficient π-stacking in the $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$ structure is ascribed to donor–acceptor charge-transfer (CT) interactions throughout the aromatic components. The Pd^{II}-coordinated ligand **2** is highly electron deficient due to metal coordination at the three pyridyl sites. Even the guest molecule of **2** possesses an electron-deficient triazine core because of the electron-withdrawing effect of the pyridyl groups. Therefore, electron-rich coronenes are apt to form a CT complex with both coordinated and free molecules of **2** such that the $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$ structure is stabilized by A–D–A–D–A aromatic stacking (A: acceptor; D: donor).

The even–odd-number effect of the stacking aromatic rings was clearly demonstrated by UV/Vis absorption spectroscopy (Figure 4). The pyrazine-pillared prismlike cage $\mathbf{9}^{12+}$ was found to bind coronene (**5**) to form an A–D–A stack with a $[\mathbf{9}\supset\mathbf{5}]^{12+}$ structure.[4] A weak CT band (shoulder) was observed for the A–D–A stack at around 450 nm. In contrast, a stronger CT absorption at around 475 nm ($\varepsilon = 3500\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) was observed for $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$, which involves A–D–D–A stacking. As the HOMO level of the stacked $(\mathbf{5})_2$ dimer is higher than that of **5**, the charge transfer band is red-shifted. For $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$, the absorption moves back to around 450 nm because of A–D–A-type stacking similar to that of $[\mathbf{9}\supset\mathbf{5}]^{12+}$.



In summary, we have achieved quadruple and quintuple stacking of large π-conjugated molecules by self-assembly. Our strategy can, in principle, be extended to multiply stacking π-systems. Such discrete stacking should produce unique photochemical and electrochemical properties that are uncommon for isolated or infinitely stacked π-systems. Further investigations in these areas are now in progress.

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[8] Physical data of $[\mathbf{1}\supset(\mathbf{5})_2]^{12+}$ and $[\mathbf{8}\supset(\mathbf{5}\cdot\mathbf{2}\cdot\mathbf{5})]^{12+}$ are given in the Supporting Information.

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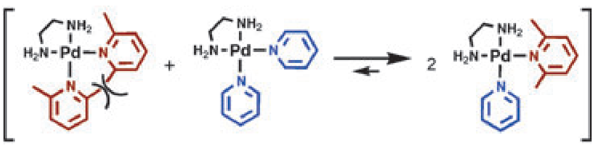

[13] Other large π-aromatic guests (e.g., pyrene and perylene) were also efficiently incorporated within $\mathbf{1}^{12+}$ to afford the corresponding quadruple-stacking structures. See also the Supporting Information.

[14] X-ray crystallographic data of $[\mathbf{1}\supset(\mathbf{6})_2]^{12+}$: $C_{244}H_{272}N_{66}O_{80}Pd_{12}$, $M = 6602.02$, crystal dimensions $0.48\times0.04\times0.04$ mm^3, orthorhombic space group $C222_1$, $a = 20.4596(14)$ Å, $b = 35.453(3)$ Å, $c = 53.544(6)$ Å, $V = 38839(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.129$ g cm^{-3}, $F(000) = 13392$, λ(synchrotron radiation) = 0.6890 Å, $T = 89(2)$ K, reflections collected/unique 56652/25550 ($R_{int} = 0.1703$). The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-squares methods on F^2 with 1376 parameters. $R_1 = 0.1579$ ($I > 2\sigma(I)$), $wR_2 = 0.3822$, GOF 1.122; max/min. residual density 0.621/ −0.549 e Å^{-3}. The counterions and water molecules were severely disordered. CCDC-251181 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

