

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

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Introduction

Aromatic stacking of π -conjugated planar molecules leads to the exhibition of unique chemical and physical properties. Discotic liquid crystals are, for example, columnar assembly of aromatic compounds with long alkyl chains. Organic electroconductive materials involve alternative charge-transfer stacking of electron-donating and -accepting π -conjugated compounds. Whereas such infinite assemblies have been thoroughly studied, precisely controlled discrete assemblies composed of more than two π -conjugated molecules are much less explored. Here we report the self-assembly of a metal-hinged organic-pillared cage **1** with a large cavity which can accommodate two large π -conjugated molecules. The cage consists of two large organic panels **2**, three rod-like pillars **3**, and six metal-hinges 4^{2+} (Figure 1a). The large box-shaped cavity accommodates π -conjugated molecules in limited numbers.^[1]

Results

In the presence of coronene (**5**), we observed the quantitative self-assembly of a quadruple-stacking structure $[1\supset(5)_2]^{12+}$. Four components **2**, **3**, 4^{2+} , and **5** were combined in a 2:3:6:2 ratio in D₂O ([Pd^{II}] = 60 mM). After being stirred at 100 °C for 2 h, the suspension became clear and turned from pale yellow to deep red. ¹H NMR analysis of the solution indicated the formation of $[1\supset(5)_2]^{12+}$ as a single product (Figure 1b). The spectrum agreed with the D_{3h} -symmetry of 1^{12+} and with the stoichiometry of the components. The signal of **5** (H_c) was highly up-field shifted due to the encapsulation in the cavity of 1^{12+} . Remarkably, the $[1\supset(5)_2]^{12+}$ structure was stable even under CSI-MS conditions.^[9] After anion exchange with PF₆⁻, CSI-MS showed a series of peaks for $[1\supset(5)_2]^{12+} + (12-m)PF_6^- + nDMF^{m+}$. Guest-free 1^{12+} was hardly detected suggesting strong π - π interactions between the host and the guest.

X-ray crystallographic analysis provided a reliable evidence for the quadruple-stacking structure of $[1\supset(5)_2]^{12+}$. When pyrene (**6**) was used as a large planar guest, a dark-reddish single crystal of $[1\supset(6)_2]^{12+}$ was obtained over a few weeks at room temperature by the slow diffusion of ethanol vapor into an aqueous solution containing $[1\supset(6)_2]^{12+}$. Diffraction data were collected by synchrotron X-ray radiation at -184 °C. Despite severe solvents and counter ions disorder, the prism-like

structure of 1^{12+} accommodating two molecules of **6** in the cavity was successfully solved (Figure 2). The cage is twisted by 36° resulting in the efficient quadruple aromatic stacking. The inter-plane distances $2\cdots 6$ and $6\cdots 6$ are 3.4 and 3.3 Å, respectively.

In summary, we have achieved the quadruple stacking of large π -conjugated molecules by self-assembly.

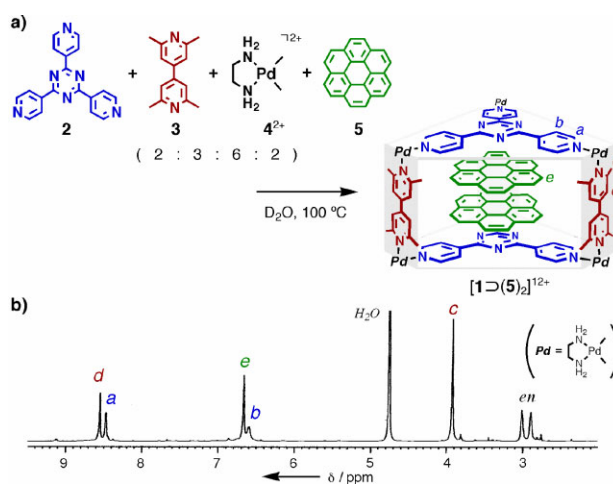


Figure 1. a) Schematic representation of the self-assembly of $[1\supset(5)_2]^{12+}$ and b) ¹H NMR (500 MHz, D₂O, RT) spectrum after the combination of **2**, **3**, 4^{2+} , and **5** in a 2:3:6:2 ratio at 100 °C for 2 h (en = ethylenediamine).

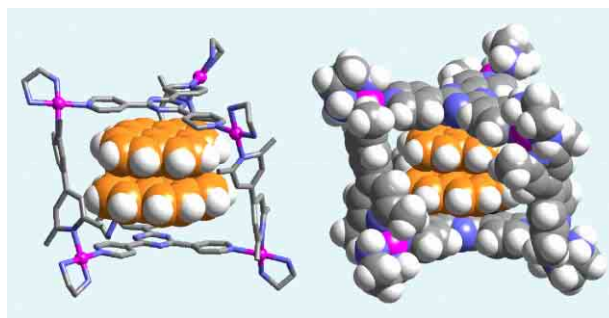


Figure 2. X-ray crystal structure of $[1\supset(6)_2]^{12+}$ (**6**: pyrene).

References

[1] M. Yoshizawa et al, *Angew. Chem., Int. Ed.*, 44, 1810 (2005).

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