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Engineering Stacks of Aromatic Rings by the Interpenetration of Self-Assembled Coordination Cages

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When stacked in layers, aromatic molecules exhibit unique electroconductive and photophysical properties.¹ There are numerous examples of the infinite stacks of aromatic molecules in crystalline and liquid-crystalline states.² However, the examples of discrete aromatic stacking are mostly limited to those containing only a few, covalently fixed, aromatic rings.³ The discrete stacking of more than several aromatic molecules with the strict control of the number and the order has seldom been achieved because of the absence of efficient methods for constructing such structures.⁴ Hence their physical properties, particularly those in solution, have not been studied. Here we report the self-assembly of aromatic columns consisting of seven to nine discretely stacked aromatic rings. Our method utilizes the three-dimensional interpenetration of two identical box-shaped coordination cages. By interpenetration, a large void space is divided into three blocks, to each of which are intercalated large aromatic compounds, providing well-defined discrete aromatic stacking structures with the lengths of up to ca. 3 nm. All the processes take place via self-assembly, thereby forming such unique structures only by mixing seven to nine aromatic molecules with six pillar molecules and 12 metal hinges.

The key to the selective formation of the septet aromatic stacked motif is the precise adjustment of the pillar length. We carefully optimized the pillar length for the septet aromatic stacking and selected *trans*-1,2-bis(4-pyridyl)ethene (**1**) as the most suitable pillar (Figure 1a,b). Pillar **1** (28 μmol), tris(4-pyridyl)-2,4,6-triazine (**2**; 20 μmol), triphenylene (**3**; 60 μmol) as an aromatic plate, and (en)Pd(NO₃)₂ (**4**; 60 μmol) as a metal hinge were combined in D₂O (1.0 mL), and the resulting suspension was stirred at 100 °C for 3 h. After excess **3** was removed by filtration, the ¹H NMR spectrum of the solution showed distinct signals (Figure 1c). The single product was assigned as the septet aromatic stacking structure **5** by COSY and NOESY.⁵ Namely, the following observations are fully consistent with the structure **5**. (i) Triphenylene is placed in two different positions in a 2:1 ratio (see integral ratios of H_f : H_g : $H_{g'}$ = 2:1), where all the signals are considerably shifted upfield ($\Delta\delta$ = -1.3~-4.5 ppm) because of the shielding effect by plates **2**. (ii) The plate molecule **2** is located in two different positions in a 1:1 ratio (see integral ratios of H_d : $H_{d'}$ = H_c : $H_{c'}$ = 1:1). The signals of the inside plates ($H_{d'}$ and $H_{c'}$) are shielded upfield more largely than those of the outside plates because the inside plates are sandwiched by two triphenylene molecules. (iii) The (en)Pd²⁺ unit is also located in two different positions in a 1:1 ratio (see signals *en* and *en'*). (iv) The pillar molecule **1** is desymmetrized ($H_{a-c} \neq H_{a'-c'}$). (v) The stoichiometry of components **1**, **2**, **3**, and **4** is 6:4:3:12.

In addition to the satisfactory NMR observation, the structure of **5** in solution was also supported by CSI-MS.⁵ From a series of prominent peaks of $[\mathbf{5} - (\text{NO}_3^-)_m + (\text{DMF})_n]^{m+}$ (e.g., 1269.9 ($m = 5, n = 2$), 1084.6 ($m = 6, n = 5$), and 931.3 ($m = 7, n = 6$)),

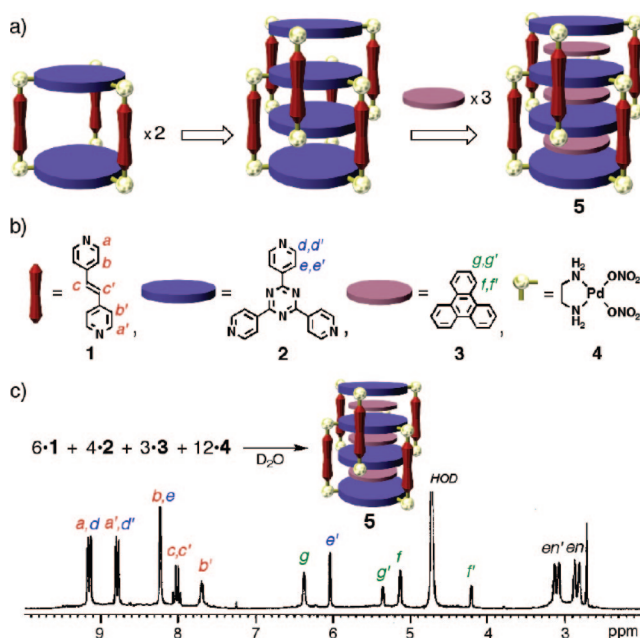


Figure 1. Design and synthesis of septet stacking of aromatic molecules **5**. (a) Hypothetical scheme of the formation of septet aromatic stacking **5**. (b) Chemical structures of the components for **5**. (c) ¹H NMR spectrum (500 MHz, room temperature) of **5** in D₂O.

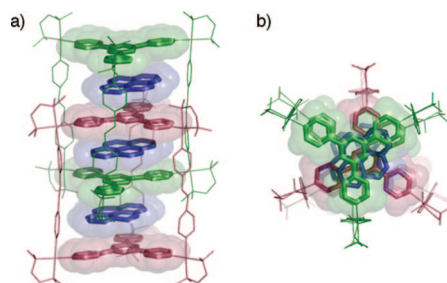


Figure 2. X-ray crystal structure of **5'**: (a) side view and (b) top view.

the molecular weight was determined to be 6513.7 Da, which agrees with the $\mathbf{1}_6\mathbf{2}_4\mathbf{3}_3\mathbf{4}_{12}$ stoichiometry of **5**.

The unique septet aromatic stacking structure of **5** was unambiguously confirmed by X-ray crystallographic analysis.⁵ Single crystals suitable for X-ray analysis were grown by the slow evaporation of water over 2 weeks from the aqueous solution of **5'** (which is an analogue of **5**, where the en end-cap group and the guest **3** are replaced by *N,N,N',N'*-tetramethylethylenediamine and pyrene (**6**), respectively). As shown in Figure 2, two identical box-shaped coordination cages (green and red frameworks) interpenetrate each other and three aromatic guests (blue) are intercalated in the void of the frameworks. As a result, the seven aromatic rings are efficiently layered with maximum overlap and with 3.3 Å

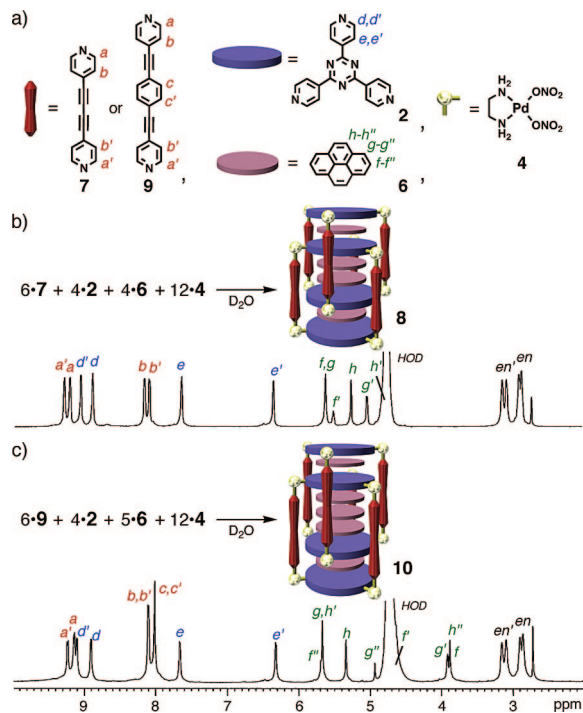


Figure 3. Schematic representation of quantitative formation of octet and nonameric aromatic stackings (**8** and **10**, respectively) and their ^1H NMR spectra (500 MHz, room temperature) in D_2O .

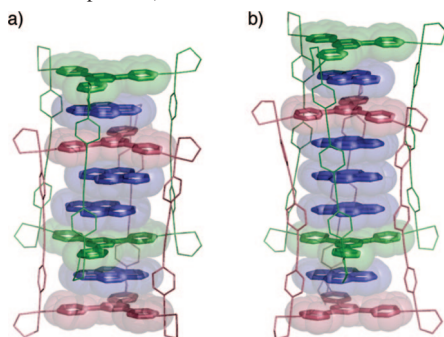


Figure 4. (a) X-ray structure of **8** and (b) optimized structure of **10**.

interplane distance between the adjacent rings, giving rise to an aromatic column with the length of 2.1 nm.

For the quantitative formation of **5**, the presence of aromatic guest **3** is essential. In the absence of **3**, only homolytic assemblies, $2_4\cdot 4_6$ (an octahedral cage) and $1_4\cdot 4_4$ (a square box), were formed.⁶ Thus, the aromatic guest acts as a template for the assembly of **5**. Besides **3**, many aromatic guests (e.g., perylene, fluoranthene, and coronene) could be used as the template.⁵

Once we had established the design principles of the septet assembly via the interpenetration of two cages, we then set about extending this for the construction of an octet aromatic stacking motif. The ideal Pd–Pd distance is ca. 3.3 Å (π – π stacking distance) $\times 5 =$ ca. 16.5 Å. This distance corresponds to the length of bis(4-pyridyl)diacetylene (**7**, 12.3 Å) plus double the Pd–N distance (2.1 Å $\times 2$). We therefore prepared the diacetylene ligand **7** according to our design brief.

As expected, the octet aromatic stacking structure **8** was assembled when pillar **7**, plate **2**, metal hinge **4** (in a 6:4:12 ratio), and an excess amount of pyrene (**6**, suspended) were combined in D_2O at 60 °C for 3 h (Figure 3a,b). The structure of **8** was clearly revealed by detailed NMR studies (see Supporting Information).

X-ray crystallographic analysis confirmed the octet aromatic stacking structure (Figure 4a).⁵ The aromatic rings are layered in

the fixed order of **2-6-2-6-6-2-6-2**. The height of the whole is 2.4 nm. The crystal packing exhibits infinite columnar structure of **8** via intermolecular π -stacking interactions. The columns are aggregated, and the butadiyne part of the pillar is bent inward to some extent due to the packing.

The triazine plate **2** and the guest **6** show electron acceptor (A) and donor (D) properties, respectively. Therefore, **5** includes A-D-A-D-A-D-A alignment, whereas the order in **8** is A-D-A-D-D-A-D-A. We have previously observed the absorption of A-D-A and A-D-D-A systems around 440 and 460 nm, respectively.^{4d} The UV–visible absorption of **5** at $\lambda_{\text{max}} = 449$ nm is ascribed to the charge transfer of the A-D-A portions. Meanwhile, **8**, involving both the A-D-A and the A-D-D-A systems, showed considerably broadened absorption around 450 nm because of the overlap of the two absorptions around 440 and 460 nm.⁵

Our next challenge was the construction of a nonameric aromatic stacking motif by the further elongation of the pillar component. To achieve this goal, we designed the pillar 1,4-bis(4-pyridylethynyl)benzene (**9**) with a length of 16.5 Å (Figure 3a). The targeted columnar compound (**10**) with nonameric aromatic stacking includes the components **9**, **2**, **4**, and **6** in a 6:4:12:5 stoichiometry. Thus, in the presence of excess aromatic guest (**6**), the pillar **9** was combined with the triazine plate (**2**) and the metal hinge (**4**) in a 6:4:12 ratio in D_2O . After 3 h at 60 °C, we observed the formation of a single product which can be assigned as the expected compound **10** (Figure 3c). The assignment of ^1H NMR signals of **10** shown in Figure 3c was fully supported by COSY and NOESY analyses (see Supporting Information). Optimized structure of **10** by a force-field calculation showed the discrete columnar structure of large aromatic molecules with the length of 2.7 nm (Figure 4b).⁷

In summary, we have constructed aromatic towers consisting of seven to nine discretely stacked motifs with large aromatic molecules via the precisely controlled noncovalent interactions. These structures provide vertical (not coplanar) π -conjugations and are of great interest since they will have interesting physical properties and are potential elements for nanofabrication systems for unique electroconductive and photophysical devices that lie between the well-known dimers and infinite arrangements.

Supporting Information Available: Experimental details and spectroscopic data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) See the Supporting Information. Crystallographic data for **5'** and **8** were deposited at the Cambridge Crystallographic Data Centre (CCDC 646901 and 646911, respectively). Symmetry operation must be applied to generate the actual interlocked stack structures. Since this class of large molecules contains a considerable amount of disordered solvents and counterions, their structural analysis is not routine but rather challenging.
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