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Pairwise Selective Formation of Aromatic Stacks in a Coordination Cage

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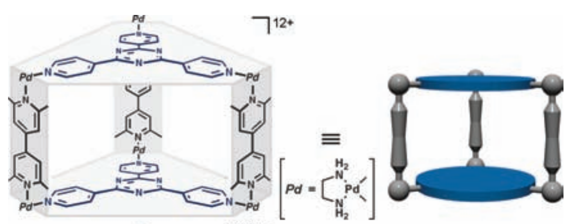
Electrostatic interactions between electron-rich (donor, **D**) and electron-poor (acceptor, **A**) aromatics are an important driving force in the self-assembly of stacked aromatics.[1,2] Previously, we have shown that electrostatic and hydrophobic interactions are essential in the formation of discrete stacks within the box-shaped cavities of organic pillared coordination cages, such as complex **1** and derivatives.[3] The stacking number *n* is uniquely determined by simply adjusting the length of the organic pillar sets. When *n* is odd, alternating donor−acceptor (**D**−**A**) arrays such as **A**−**D**−**A**−**D**−**A** are obtained with the electron-poor triazine panels as bookend acceptors. But when *n* is even, idealized alternating arrays cannot form due to the triazine panel acceptors on both ends. For example, if cage **1** hosts two donor molecules, the **A**−**D**−**D**−**A** stack ($n = 4$) includes two **D**−**A** interactions and one unfavorable **D**−**D** interaction (Scheme 1a). If cage **1** contains one donor and one acceptor aromatic, the resulting **A**−**D**−**A**−**A** exhibits two nondegenerate **D**−**A** interactions and one **A**−**A** interaction (Scheme 1b).



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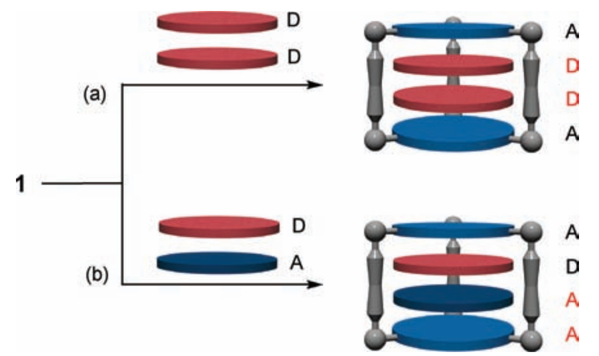
In this report, we examined the destabilization of one **D**−**D** and one **A**−**A** interaction within discrete quadruple stacks (Scheme 1) and found that **A**−**A** interactions are better tolerated.[4] As a result, cage **1** can be used to selectively bind donor and acceptor guest aromatics in a pairwise fashion. Importantly, the resultant hetero **D**−**A** host−guest complexes are dissymmetrized and enable the study of guest dynamics.

The **A**−**D**−**A**−**A** inclusion complex **1**•(**3**•**4**) selectively formed from a 1:1 mixture of donor **3** and acceptor **4** (Figure 1). Triazine panel **2** (6.3 mg, 0.020 mmol), triphenylene (**3**; 4.6 mg, 0.020 mmol), naphthalenediimide[5] **4** (5.9 mg, 0.020 mmol), pillar ligand **5** (6.4 mg, 0.030 mmol), and (en)Pd(NO_3)$_2$ (**6**; 17 mg, 0.060 mmol) were suspended in D_2O (1.0 mL) and heated at 100 °C. After 2 h, the solution was yellow and excess guests (**3** and **4**) were removed by filtration. ^{1}H NMR spectroscopy revealed the formation of a single dissymmetrical product consistent with complex **1**•(**3**•**4**) (Figure 1b−d). CSI-MS confirmed the stable solution structure of complex **1**•(**3**•**4**) with a molecular weight of 4439.8 Da. Finally, the structure of complex **1**•(**3**•**4**) was unambiguously determined by the X-ray crystallographic analysis of the analogous complex **1′**•(**3**•**4**) (Figure 2).[6]

The exclusive formation of **1**•(**3**•**4**) under equilibrium conditions emphasizes the greater stability of the hetero **A**−**D**−**A**−**A** complex

Scheme 1. Schematic Image of Quadruple Aromatic Stacks Using Cage **1**: (a) **A**−**D**−**D**−**A** and (b) **A**−**D**−**A**−**A**



over either homo complexes, **1**•(**3**)$_2$ or **1**•(**4**)$_2$. Independently, by treating the cage components with only donor **3**, the **A**−**D**−**D**−**A** complex **1**•(**3**)$_2$ was successfully prepared, but when treated with **4**, one molecule of **3** was displaced to give the hetero **1**•(**3**•**4**) complex (Scheme 2). The efficient homo **A**−**A**−**A**−**A** stacking was

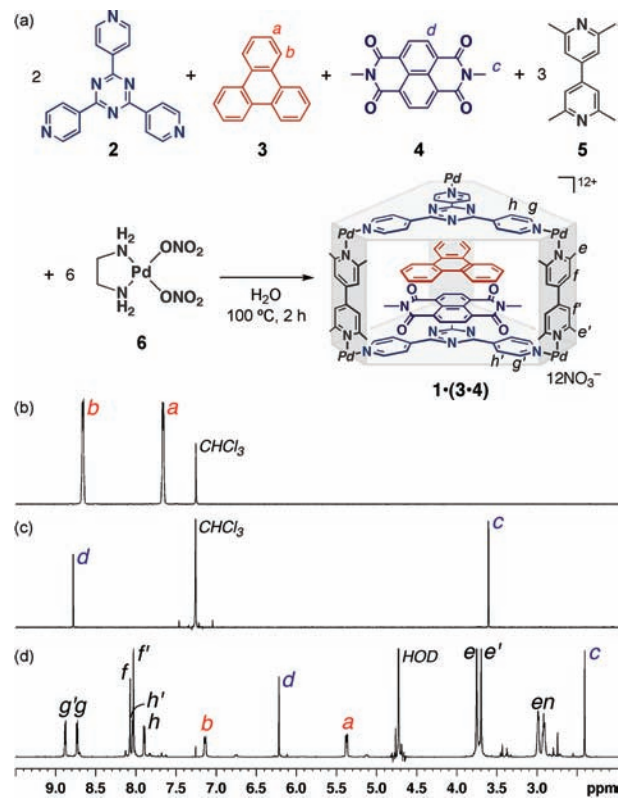


Figure 1. (a) Self-assembly of inclusion complex **1**•(**3**•**4**). (b−d) ^{1}H NMR spectra (500 MHz, 300 K) of (b) donor **3** (in $CDCl_3$), (c) acceptor **4** (in $CDCl_3$), and (d) inclusion complex **1**•(**3**•**4**) (in D_2O).

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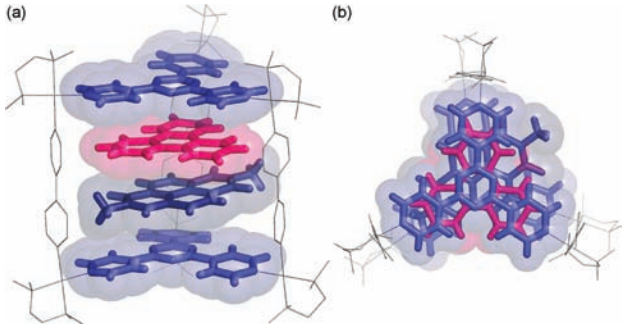
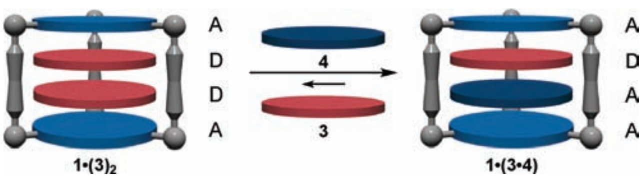


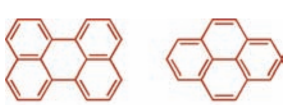
Figure 2. X-ray crystal structure of **1′**•(**3**•**4**): (a) side view and (b) top view. A space-filling depiction of the stacked aromatics is shown in the background.

not obtained. These results indicate that simple electrostatic models,[7] which predict the order of stability to be **A**−**A** > **D**−**A** > **D**−**D**, are insufficient to describe the multiple forces governing these self-assembling systems and that quadrupole interactions (charge transfer) most likely determine the final arrangement.

Scheme 2. Guest Exchange between Complexes **1**•(**3**)$_2$ and **1**•(**3**•**4**)

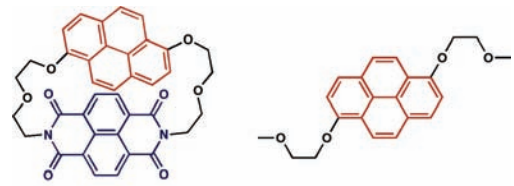


The unsymmetrical **D**−**A** pair (**3**•**4**) breaks the symmetry of the cage **1**, and host−guest dynamics can be now examined using variable-temperature (VT) ^{1}H NMR measurements. Upon heating, cage signals *g* and *g′* coalesced at 360 K, indicating the rapid site-exchange between **3** and **4** (see Supporting Information).[8] Similar dynamic behavior was observed for donor aromatics **7** and **8**. From the line-shape analysis of the ^{1}H NMR spectra, the energy barriers of exchange process, $\Delta G^{\ddagger}_{ex}$, were estimated to be 73.7, 68.7, and 62.1 kJ·mol^{-1} for **3**, **7**, and **8**, respectively. Given that triphenylene **3** has the highest oxidation potential of the three donor molecules,[9] the stronger binding probably stems from more efficient **D**−**A** (quadrupole) interactions between **3** and triazine panel **2** due to similar symmetry (D_{3h}).[10]



7 **8**

The site-exchange process most likely involves the initial dissociation of the weaker bound acceptor **4**. When the donor and acceptor moieties are covalently linked, **D**−**A** pair **9**, the coalescence temperature (T_c) increased relative to the similar but nonlinked **10** and **4** (ΔT_c = 10 K).



9 **10**

In summary, we employed the box-shaped framework of **1** to engineer unusual symmetrical **A**−**D**−**D**−**A** and dissymmetrical **A**−**D**−**A**−**A** quadruple stacks. Pillared cages thus enable the precise control of not only the stacking number but also the stacking order, providing opportunities to study the hitherto unexplored properties of discrete stacks of aromatic compounds.

Supporting Information Available: Experimental procedures, physical properties, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) In the formation of complex **1′**•(**3**•**4**), 4,4′-bipyridine (**5′**) and (tmeda)Pd-$(NO_3)_2$ (**6′**) are employed instead of **5** and **6**, respectively. A single crystal suitable for X-ray crystallographic analysis was obtained by the slow evaporation of water from an aqueous solution of **1′**•(**3**•**4**) over 2 weeks. The crystallographic data are available from the Cambridge Crystallographic Data Centre (CCDC 766964).

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