

# Self-Assembly and Guest Binding Properties of Pyrene-Edged Fe<sub>4</sub>L<sub>6</sub> Tetrahedra

Tanya K. Ronson,<sup>1</sup> Aaron B. League,<sup>2</sup> Laura Gagliardi,<sup>2</sup> Christopher J. Cramer<sup>2</sup> and Jonathan R. Nitschke<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK. E-mail: tr352@cam.ac.uk

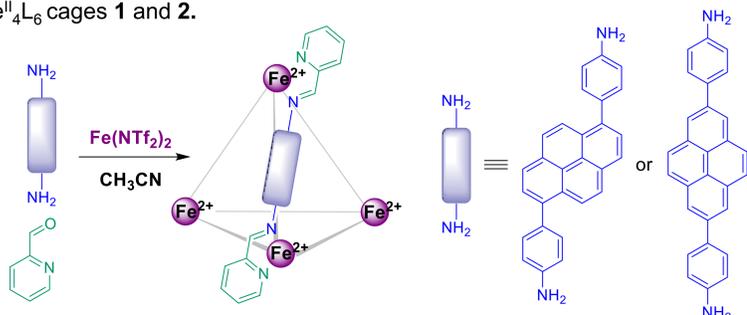
<sup>2</sup>Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455, U.S.A.

## INTRODUCTION

Self-assembled metal-organic cages have been a topic of great interest in recent years due to their applications in trapping unstable species, separation of gases and fullerenes, the discrimination of chiral guest species and as catalysts. We have reported the formation of a variety of metal-organic container molecules using *subcomponent self-assembly*, which relies upon metal template effects to generate complex structures from simple precursors through the formation of both dynamic-covalent (C=N) and coordinative (N→M) linkages in a single reaction step.<sup>[1]</sup> As well as generating a large increase in molecular complexity in a single reaction step, this approach allows the properties of the cages to be readily altered through variation of the subcomponents employed.<sup>[2]</sup> Here we demonstrate the preparation of two new Fe<sup>II</sup><sub>4</sub>L<sub>6</sub> cages from two isomeric pyrene-containing diamines. The two cages display contrasting host-guest properties depending on the arrangement of the pyrene panels around the surface of the cage.<sup>[3]</sup>

## IRON(II) TETRAHEDRAL CAGES

The reaction of diamines 1,6- or 2,7-bis(4-aminophenyl)pyrene (6 equiv.), 2-formylpyridine (12 equiv.) and Fe(NTf<sub>2</sub>)<sub>2</sub> (4 equiv.) gives rise to pyrene-edged Fe<sup>II</sup><sub>4</sub>L<sub>6</sub> cages 1 and 2.



Statistical mixture of *T* ( $\Delta\Delta\Delta\Delta/\Lambda\Lambda\Lambda\Lambda$ ), *C*<sub>3</sub> ( $\Delta\Delta\Delta\Lambda/\Lambda\Lambda\Delta\Lambda$ ), and *S*<sub>4</sub> ( $\Delta\Delta\Lambda\Lambda$ ) diastereomers

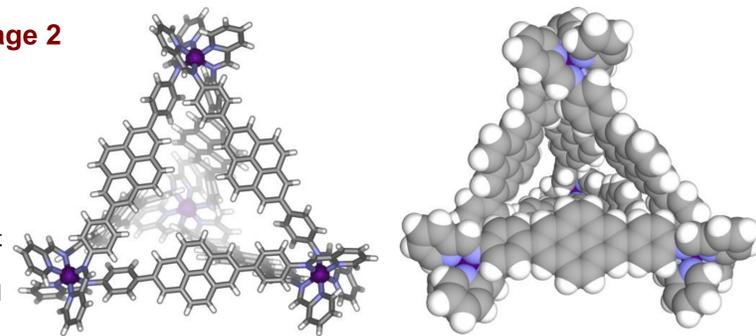
Cage 1

Cage 2

## X-ray Crystal Structure of Cage 2

Single crystals of cage 2 were isolated by diffusion of benzene vapour into an MeCN solution.

Cage 2 crystallised as the *C*<sub>3</sub> diastereomer with both  $\Lambda\Lambda\Delta$  and  $\Delta\Delta\Delta\Lambda$  enantiomers present in the unit cell. Three *syn* ligands bridge Fe<sup>II</sup> centres of opposing handedness, and three *anti* ligands link Fe<sup>II</sup> centres of the same handedness.



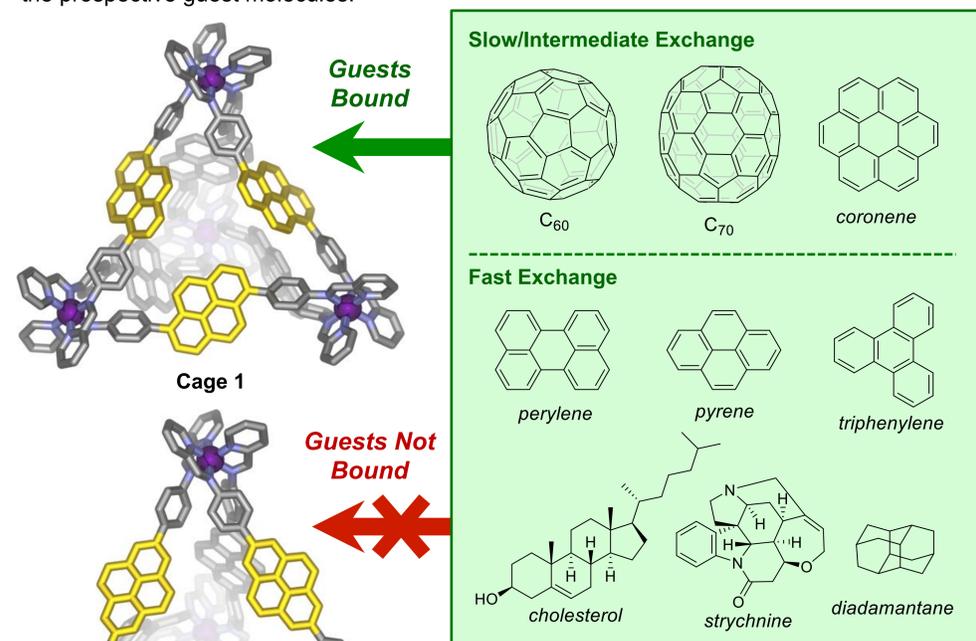
X-ray structure of 2. Volume = 620 Å<sup>3</sup>

Spacefilling view showing an open face.

The pyrene units of the *anti* ligands almost completely close the cage face that they define. The remaining three faces are more open, with large pores. The Fe-Fe separations are in the ranges 20.4-20.7 Å and 20.8-20.9 Å for the *syn* and *anti* ligands respectively.

## HOST-GUEST PROPERTIES

Cage 1 was observed to bind neutral, large hydrophobic guests while cage 2 showed no affinity for the prospective guest molecules.

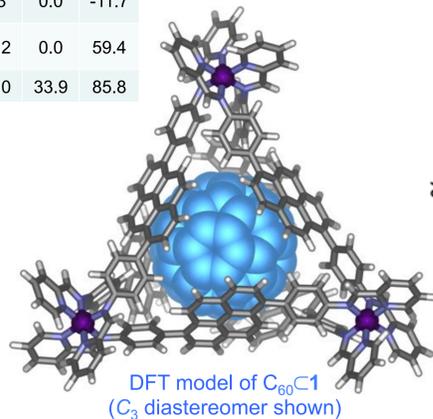


E (kJ mol <sup>-1</sup> )	1- <i>T</i>	1- <i>C</i> <sub>3</sub>	1- <i>S</i> <sub>4</sub>
1 E <sub>relative</sub>	6.3	0.0	-11.7
[C <sub>60</sub> ⊂ 1] E <sub>relative</sub>	22.2	0.0	59.4
ΔE <sub>deformation</sub>	41.0	33.9	85.8

## DFT Study

DFT energy-minimized structures of [C<sub>60</sub> ⊂ 1] predicted all six pyrene units to lie at a tangent to the edge of the cage, resulting in favourable π-π interactions with the encapsulated C<sub>60</sub> and a well-enclosed cavity.

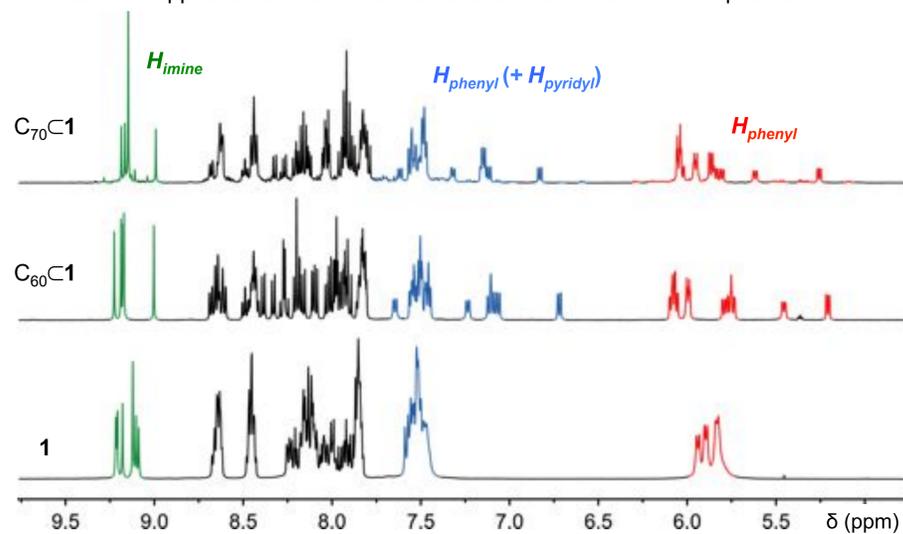
Calculations predict the 1-*S*<sub>4</sub> diastereomer to be favoured when empty. However the energetic cost of deforming it to accommodate the guest is significantly higher than predicted for the other two cage diastereomers, thereby disfavoured the formation of the [C<sub>60</sub> ⊂ 1-*S*<sub>4</sub>] host-guest complex.



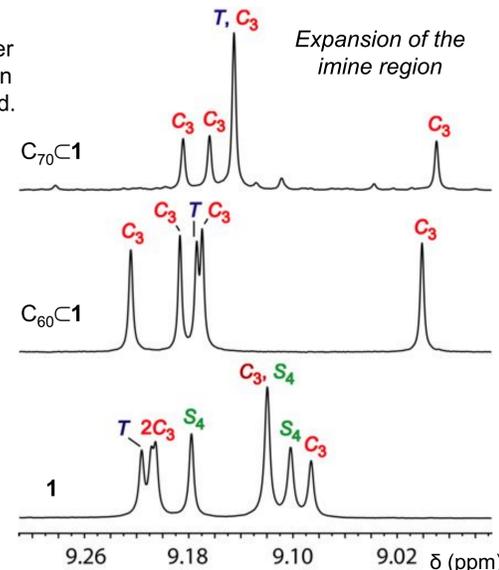
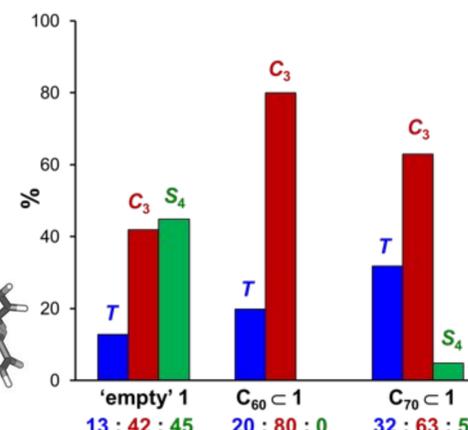
DFT model of C<sub>60</sub>⊂1 (*C*<sub>3</sub> diastereomer shown)

## Guest Binding Induces Diastereomeric Reconfiguration of Cage 1

Both C<sub>60</sub> and C<sub>70</sub> were observed to form 1:1 host-guest complexes with cage 1 in CD<sub>3</sub>CN by ESI-MS. Encapsulation of C<sub>60</sub> was confirmed by an intense signal at 140.1 ppm in the <sup>13</sup>C NMR spectrum and the appearance of a new set of resonances in the <sup>1</sup>H NMR spectrum.



Fullerene binding resulted in re-equilibration among the different cage diastereomers in order to maximize the binding affinity of the system. In each case the *S*<sub>4</sub> diastereomer was disfavoured.



## CONCLUSION

The two isomeric pyrene-edged cages show very different host-guest properties depending on the arrangement of the pyrene groups around the surface of the tetrahedron. Cage 2, based on a 2,7-pyrene scaffold with an open cavity, was not observed to bind neutral guests. In contrast, isomeric cage 1, based on a 1,6-pyrene scaffold, is able to provide a well-enclosed cavity and is a good host for large aromatic and hydrophobic guests, demonstrating the importance of cavity enclosure for strong host-guest interactions. This cage was shown to adapt when binding fullerenes, amplifying the diastereomers best able to bind the guest in order to maximize binding affinity. Cage 1 also displayed binding affinity for steroid derivatives, allowing these asymmetric guests to be bound without the need to design an asymmetric host.

**Acknowledgements:** We thank the UK Engineering and Physical Sciences Research Council (EPSRC) and the US National Science Foundation (NSF CHE-1124244) for financial support, the EPSRC Mass Spectrometry Service at Swansea for carrying out high resolution mass spectrometry and Diamond Light Source (UK) for synchrotron beamtime on I19.

**References:** [1] T. K. Ronson, S. Zarra, S. P. Black and J. R. Nitschke, *Chem. Commun.*, 2013, 49, 2476. [2] R. A. Bilbeisi, J. K. Clegg, N. Elgrishi, X. de Hatten, M. Devillard, B. Breiner, P. Mal and J. R. Nitschke, *J. Am. Chem. Soc.*, 2012, 134, 5110-5119. [3] T. K. Ronson, A. B. League, L. Gagliardi, C. J. Cramer and J. R. Nitschke, *J. Am. Chem. Soc.*, 2014, 136, 15615.