Supplementary Material (ESI) for Chemical Communications

Supporting Information for Tailoring Pores for Guest Entrapment in a Unimolecular Surface Self-Assembled Hydrogen Bonded Network

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Pore C_{60} Occupancy

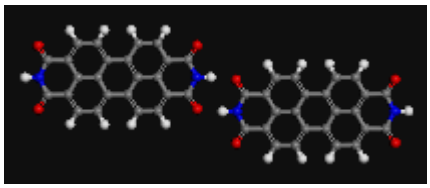
Analysis of two images with C60 encapsulated within the molecular cavities, avoiding areas with defects in the molecular arrangement, with no tip change, was used to find the level of occupancy. Results from the images indicated little variation in relative occupancy, see table.

	Total pores	Single C_{60} Occupancy	Double C_{60} Occupancy	Empty pores
Image 1	**192**	**86**	**10**	**93**
relative		0.448	0.052	0.484
Image 2	**126**	**52**	**14**	**57**
relative		0.413	0.111	0.452
Total	318	138	24	150
Relative error (1/sqrt(n))	0.05607722	0.08512565	0.204124145	0.081649658
Relative coverage (n/Total pores)		0.43396226	0.075471698	0.471698113
Error (RE1+RE2)*value		0.06127672	0.019637839	0.064965506
Occupancy		43 ± 6.1 %	7.5 ± 2.0 %	47.2 ± 6.5 %

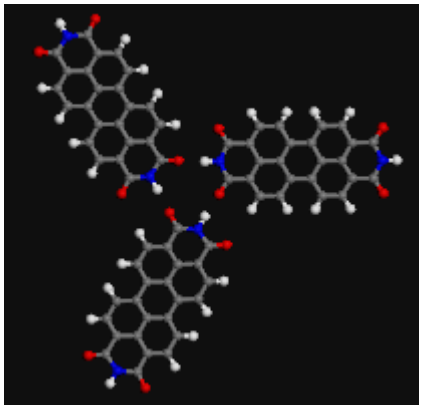
Density functional theory calculations

Geometry optimization calculations were performed on several molecular configurations in order to obtain stabilization energy values and geometries. The substrate was not included in the calculations. All calculations were performed using density functional theory (DFT) within the DMol^3 package,[S1,S2] provided with Accelerys Materials Studio 4.0. The general gradient approximation with Perdew-Burke-Ernzerhof gradient correction was used.[S3] Double numerical plus polarization basis set was used with no core treatment (all electron) and orbital cutoff set to fine (4 Å). Similar methodologies have been reported to provide consistent values for energy and reproduces well geometries found in experiments in structures stabilized by hydrogen bonding.[S4,S5]

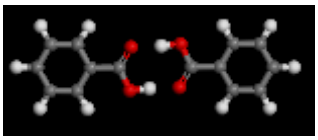
System	Total energy (cutoff fine)	Stabilisation energy (cutoff fine)	Configuration
PTCDI	-1330.0496707 Ha		
PTCDI-PTCDI	-2660.1169880 Ha	-0.4802 eV	**I**
PTCDI trimer	-3990.1778075 Ha	-0.7835627 eV	**II**
Benzoic acid	-420.4921763 Ha		
Benzoic acid – Benzoic acid (carboxylic-carboxylic)	-841.0138531 Ha	-0.80275 eV	**III**
Benzoic acid – 1,8-naphthalenedicarboxylic acid imide		-0.6085 eV	**IV**



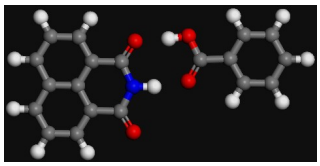
Configuration **I**



Configuration **II**



Configuration **III**



Configuration **IV**

Supporting Information References

S1. B. Delley, *J. Chem. Phys.* **1990**, *92*, 508.
S2. B. Delley, *J. Chem. Phys.* **2000**, *113*, 7756.
S3. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
S4. L. M. A. Perdigão, G. N. Fontes, B. L. Rogers, N. S. Oxtoby, G. Goretzki, N. R. Champness, P. H. Beton, *Phys. Rev. B*, **2007**, *76*, 245402.
S5. J. Ma, B. L. Rogers, M. J. Humphry, D. J. Ring, G. Goretzki, N. R. Champness, P. H. Beton, *J. Phys. Chem. B*, **2006**, *110*, 12207.