The Crystalline Sponge Method: A Systematic Study of the Reproducibility of Simple Aromatic Molecule Encapsulation and Guest – Host Interactions

Lilian M. Hayes, † Caroline E. Knapp,† Neil. J. Press,‡ Derek. A. Tocher† and Claire. J. Carmalt*†

†Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ

‡ Novartis Institutes for BioMedical Research, Basel, Switzerland

A systematic study detailing the uptake of a series of chemically related simple functionalised aromatic guest molecules into the pores of the crystalline sponge [{$(ZnI_2)_3$(tris(4-pyridyl)-1,3,5-triazine)$_2$.*x*(solvent)}$_n$] (**1**) has been performed. The reproducible positioning of the guest molecules within the unit cell has been documented through analysis of repeat encapsulation experiments. Analysis of guest-host and guest-guest interactions has shown the dominant role of π···π and CH···π interactions in the ability of the crystalline sponge to render the guest molecules regularly ordered. Further interactions specific to guest functionality, such as weak hydrogen bonds, are seen to contribute to the particular orientation of the guests, as shown in Fig. 1.

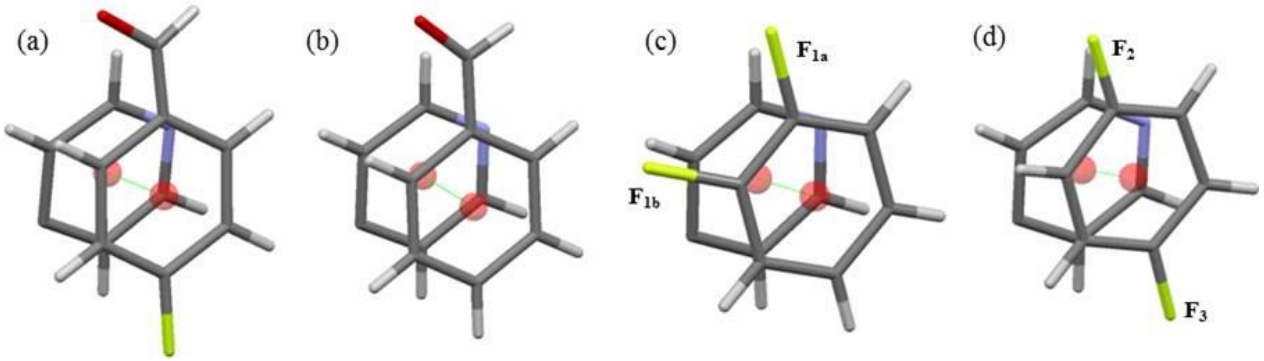

Figure 1 Face-to-face π···π interactions in the encapsulation complexes between the aromatic ring of encapsulated guest molecules and a pyridine ring in **1**, at a common site within the unit cell. (a) 4-fluorobenzaldehyde (b) benzaldehyde (c) fluorobenzene (rotational disorder shown, F_{1a} and F_{1b} occur with 50% occupancy) and (d) 1,4-difluorobenzene . Centroids shown as red spheres and intercentroid contacts in green.

* Corresponding Author

Prof Claire. J. Carmalt

Department of Chemistry,
20 Gordon Street
University College London,
WC1H 0AJ

c.j.carmalt@ucl.ac.uk

Tel: +44 (0)20 7679 7528
Fax: +44 (0)20 7679 7463

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†Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ. Email: c.j.carmalt@ucl.ac.uk

‡ Novartis Institutes for BioMedical Research, Basel, Switzerland

KEYWORDS crystalline sponge, π···π interactions , CH···π interactions, guest-host compounds,

ABSTRACT: A systematic study detailing the uptake of a series of chemically related simple functionalised aromatic guest molecules into the pores of the crystalline sponge $[\{(ZnI_2)_3(\text{tris(4-pyridyl)-1,3,5-triazine})_2.x(\text{solvent})\}_n]$ has been performed. The reproducible positioning of the guest molecules within the unit cell has been documented. Analysis of guest-host and guest-guest interactions has shown the dominant role of π···π and CH···π interactions in the ability of the crystalline sponge to render the guest molecules regularly ordered. Further interactions specific to guest functionality, such as weak hydrogen bonds, are seen to contribute to the particular orientation of the guests.

Introduction

In 2013 Fujita and co-workers published a ground-breaking paper introducing a technique that claimed to overcome the inherent limitations of single crystal X-ray diffraction (SCXRD).[1] As the premier method for unambiguously determining complete structural information, SCXRD can require significant investment of time and effort (*i.e.* single crystal growth and selection) and by definition is limited to single-crystals – meaning structures of liquid and amorphous solids are unobtainable by this method. The solution, 'crystal-free crystallography',[2] was a simple one; encapsulate your non-crystalline compound within a crystalline framework which, through the formation of strong guest-host interactions, may render it regularly ordered and thus capable of contributing to Bragg peaks and a diffraction pattern. It is not the idea of studying a guest enclatherated in a host framework that was novel (small guest molecules have been studied in clathrates[3,4,5] and latterly in porous organic material)[6,7] but the use of a specific host material - metal-organic frameworks (MOFs). The most successful MOF for this application has been $[\{(ZnI_2)_3(\text{tris(4-pyridyl)-1,3,5-triazine})_2{\cdot}x(\text{solvent})\}_n]$[8] suitable due to its heavy atom content for use in absolute structural determination *via* the Bijvoet method. Implementation of the technique has not been without difficulty[9] but its applicability has been tested and its value clearly demonstrated.[10–15]

The linker utilised for this 'crystalline sponge' is the large panel-like tris(4-pyridyl)-1,3,5-triazine (TPT), a well-established component used in container-compounds,[16,17] 3D networks[18] and supramolecular chemistry (where the electron-poor heteroaromatic moiety is implicated in key supramolecular interactions (*i.e.* hydrogen bonds or π interactions). TPT's high aromaticity and electron deficiency imparts an ability to form π-π, CH-π and charge-transfer interactions with electron rich molecules. By incorporation into a MOF structure, most commonly combined with ZnI_2,[19] these properties are exploited and enhanced through the creation of 'sticky' hydrophobic pores which absorb guest molecules *via* thermodynamic solvent-guest exchange allowing equilibration of their positions through the porous framework.

In order to expand the application of this technique a range of MOFs are required to allow for the study of a diverse range of natural products and biologically active molecules, of varying size and functionality. Achieving a greater understanding of guest-host interactions will aid in the judicious selection of inorganic and organic moieties potentially allowing MOF hybrid architecture to be tailored to fulfil the demands of specific guest encapsulation, for example allowing encapsulation of hydrophilic guests of varying steric requirements.

Therefore we present here a crystallographic study detailing the uptake and specific locations of a series of chemically related simple functionalised aromatic guest molecules within the crystalline sponge together with analysis of possible guest-host interactions, something which has only been touched upon previously.[20] As no systematic study has been reported before we hope to develop an understanding of the currently used crystalline sponge, its scope and why it displays such unique properties.

Results and Discussion

Crystal Growth

Before full publication of the preparative method for the crystalline MOF and guest-uptake protocol outlined by Fujita *et al.* used in their ~~in the~~ original Nature paper,[20,21] a procedure was developed in-house involving the use of a nitrobenzene/1,2-dichlorobenzene solvent mixture for the dissolution of TPT. This resulted in the successful production of the desired $[\{(ZnI_2)_3(TPT)_2{\cdot}(\text{solvent})\}_n]$ (**1**) crystalline sponge. Latterly, use of the simplified synthesis developed by Ramandhar *et al.* yielded good quality single crystals with greater rapidity and reliability, and with the more labile $CHCl_3$ solvent in the pores negating the need for solvent exchange before guest encapsulation.[10] As a result, all crystals used in this study were synthesised by this method. However, a second crystalline Zn-TPT MOF has been observed to form alongside the desired phase with formula $[\{(ZnI_2)_3(TPT)_2{\cdot}CHCl_3\}_n]$(**2**) (Fig. 1) and significantly smaller pore size (Table. 1). Its fortuitously distinct crystal morphology (Fig. 2) allows it to be easily identified and discarded before guest encapsulation. More recently, the formation of a third form was identified, having a morphology indistinguishable from the desired crystal but consistently giving a distinct set of unit cell parameters (Table 1). Although such crystals have not been obtained of sufficient

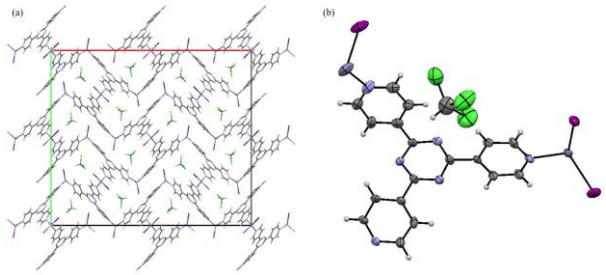

Figure 1 The extended structure viewed down the *c*-axis (a) and asymmetric unit cell (b) of 2 obtained alongside the desired phase. TPT acts as an exo-tridentate ligand as in the original structure (1). Thermal ellipsoids shown at 50% occupancy.

our range of guests within the host structure. Ease of identification of the guest within the refined host framework varied according to the extent of disorder, all display significant thermal motion and in some cases additional static and/or dynamic disorder. Solvent accessible voids (SAVs) are present in the majority of structures but solvent masking techniques were not used so as to maintain accurate chemical representation of the systems. The level A *check*CIF alerts relating to the presence of SAVs are tolerable[10] and are not thought to interfere with the analysis performed here. However, the SQUEEZE routine in *PLATON*[22] was employed to analyse the content of the voids (see Section S4).

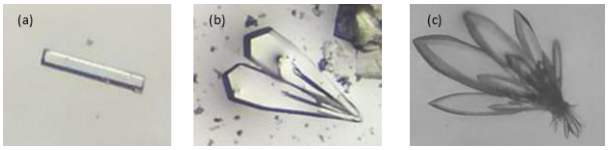

Figure 2 Micrographs of a standard rod shaped crystal of desired Zn-TPT phase 1 (a) compared to novel polymorph 2 (b) and (c) showing two distinct characteristic morphologies.

	Space group	a / Å	b /Å	c /Å	β/°	V/ Å^3
Form 2	*F*dd2	3 9.7112(4)	34.5319(4)	8.26132(8)	90	11328.8(2)
Form 3	*P*nma	13.2732(14)	29.356(3)	12.8023(14)	90	4988.4(9)

Table 1 Cell parameters of undesired Zn-TPT forms alongside the desired form **1**.

quality to run full data analysis it is further evidence for the sensitivity of the experimental method and the challenge in its application. It is thought these second and third forms arise from minor changes in temperature, humidity and variations in initial mixing during the layering process of crystal synthesis.

Guest encapsulation

The manner in which guest molecules interact through their aromatic rings and functional groups is analysed and the question asked as to the extent to which the guests' functionalisation (rather than simply size) determine their interaction with the host framework and consequential ordering. The simple organic aromatic guests encapsulated here were benzene (**i**), 4-fluorobenzaldehyde (**ii**), 1,3-dichlorobenzene (**iii**), benzonitrile (**iv**), benzaldehyde (**v**), fluorobenzene (**vi**) and 1,4-difluorobenzene (**vii**) (Fig. 3). All are liquid at room temperature and miscible with chloroform, ensuring a high concentration gradient during encapsulation experiments and consequent high occupancy of the pores. All 11 guest–host complexes reported here are novel, although guest-host complexes of benzene and benzonitrile in an interpenetrated $[\{(ZnI_2)_3(TPT)_2{\cdot}x(guest)\}_n]$ framework have been reported previously.[8] (*N.B* when solvent molecules are present from synthesis they are not referred to as guests – this title is reserved only for those molecules purposefully encapsulated.)

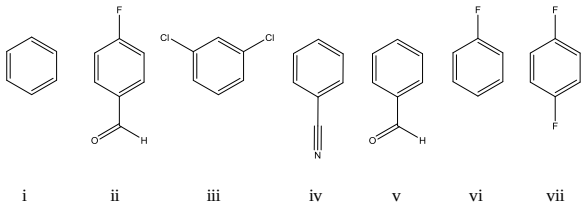

Figure 3 Molecules chosen for encapsulation into **1**: benzene (**i**) 4-fluorobenzaldehyde (**ii**), 1,3-dichlorobenzene (**iii**), benzonitrile (**iv**), benzaldehyde (**v**), fluorobenzene (**vi**).1,4-difluorobenzene (**vii**).

All guest–host complexes were found to crystallise in the centrosymmetric space group *C*2/c, showing a slight expansion in cell dimensions from the as prepared crystalline sponge **1**, as expected from specific interactions and steric demands of

Reproducibility

In order to reliably assess the interactions present in these guest-host complexes we first set out to confirm that guests consistently take up specific sites in the unit cell, before seeking to determine the nature of guest-host interactions governing this positional specificity. Encapsulation experiments with intended guests **i**, **ii**, **iii** and **iv** were performed in duplicate yielding encapsulation complexes with benzene (**1i** and **1i'**) 4-fluorobenzaldehyde (**1ii** and **1ii'**), 1,3-dichlorobenzene (**1iii** and **1iii'**) and benzonitrile (**1iv** and **1iv'**). Evaluating the crystallographic data by viewing the crystal structures down the *b*-axis allows clear visualisation of the different sites taken up by the guests within the infinite networks of solvent-accessible channels. It is clear guests consistently take up favourable positions and orientations, specific (but not exclusive) to their type (Figures 4a – e). Guest molecules have been coloured according to symmetry equivalence to allow facile comparison of crystal structures.

Benzene (1i and 1i')

The number and position of benzene molecules occupying the crystalline sponge shows complete reproducibility (Fig. 4a and b), with five guest molecules (green, orange, blue, purple and pink) taking up identical specific sites in each structure, along with one residual $CHCl_3$ solvent molecule.

4-fluorobenzaldehyde (1ii and 1ii')

Similarly, the number and position of 4-fluorobenzaldehyde molecules occupying the crystalline sponge shows complete reproducibility (Fig. 4c and d). Three guest molecules (red, blue and green) take up identical specific sites in each structure.

1,3-dichlorobenzene (1iii and 1iii')

In the case of 1,3-dichlorobenzene, the two independent encapsulation experiments yielded comparable results with 5 equivalent guest molecules present in both (Fig. 4e and f). The only distinguishing feature was rotational disorder of the 'blue' guest molecule in **1iii'** (visualised as light and dark blue in Fig. 4f), leading to 50:50 occupancy of the site.

Benzonitrile (1iv and 1iv')

In the final comparison, the encapsulation of benzonitrile, the crystal structures show distinct similarities and some variation in guest position evident by the comparison of Fig. 4g and h. Each structure has 6 distinct guest sites (with some residual $CHCl_3$ solvent in **1iv**) the majority of these are common to both structures; molecules positioned in such sites are coloured blue, green, pink, red, and yellow. Within this subset two instances of minor rotational disorder of the aromatic rings were observed, where both parts share approximately the same positions but variable orientation of the nitrile group (Fig. 5a). One instance is consistent between structures (light and dark green in Fig. 4g and h) whilst the second is seen only in **1iv** (red and burgundy, see Fig. 5a).

However, most significant for this study were the variations between structures **1iv** and **1iv'** that relate to occupation of unique sites; (i) the molecule coloured purple in **1iv'** (Fig. 4h, sitting on inversion centre) is unique to that structure. However, its occupancy is low (freely refined to 25%), in fact lowest of all guest occupancies in this study. (ii) Uptake of unique sites but with certain overlap observed in two cases, one being consistent between the two structures (light green and yellow , see Fig. 5a) and one being confined to **1iv** (pink and light blue, see Fig. 5b). In this latter example, the two molecules in each pair share the terminal nitrogen atom of their nitrile group. The significant disorder between the two components suggests relatively weak π-π interactions.

From these three studies it is clear that there is reproducibility in the uptake of guests to specific sites within the unit cell of **1**. The small variations that have been observed between repeat encapsulation experiments are thought to be a result of marginal differences in external conditions. These may be experimental (*e.g.* variable interfacial mixing during synthesis of **1**), environmental (*e.g.* humidity and ambient temperature) and/or as a result of refinement challenges (*e.g.* slight variations in crystal quality and size). Although care was taken to ensure conditions remained constant minor variation must be expected unless impractical automation was used, such is the delicacy of the method. However, overall we can be confident that guest molecules preferentially take up specific sites and hence, multiple repetitions of the encapsulation procedure is not required in every case.

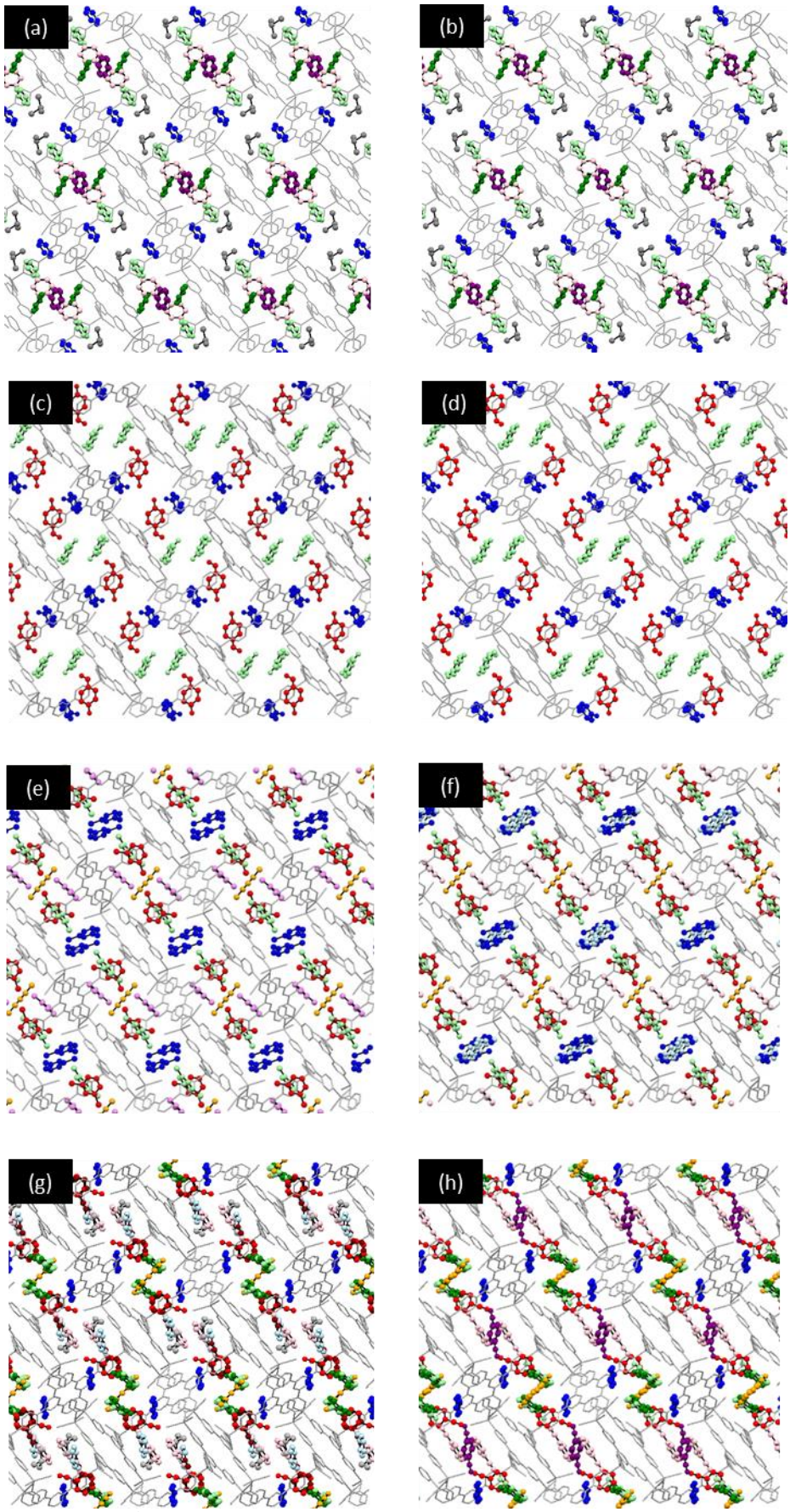

Figure 4 Plot of X-ray crystal structures of encapsulation complexes analysed in reproducibility study viewed down the *b*-axis: benzene (a) **1i** and (b) **1i'**, 4-fluorobenzaldehyde (c) **1ii** and (d) **1ii'**; 1,2-dichlorobenzene (e) **1iii** and (f) **1iii'**; benzonitrile (g) **1iv** and (h) **1iv'**. Guest molecules shown as ball and stick models with colours corresponding to equivalent sites, framework shown as grey wire frame. Hydrogen atoms omitted for clarity.

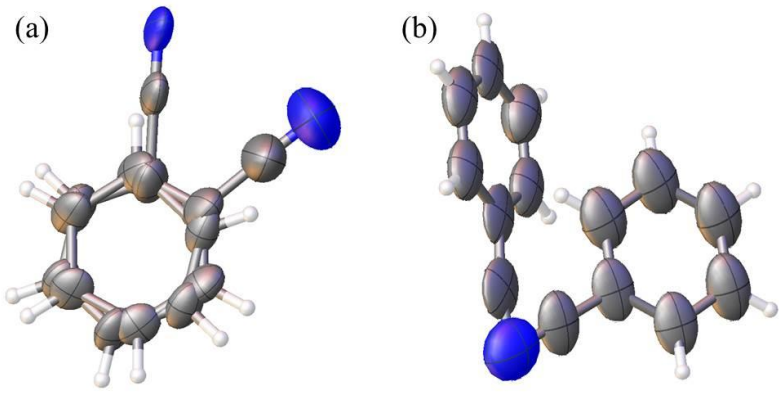

Figure 5 Two types of benzonitrile disorder observed in the unit cell of encapsulation compound **1iv**. (a) Rotational disorder within a specific site resulting in variable orientation of the nitrile group (b) Significant displacement between two disordered about the nitrile nitrogen atom. Atoms are show as thermal ellipsoids at 50% probability.

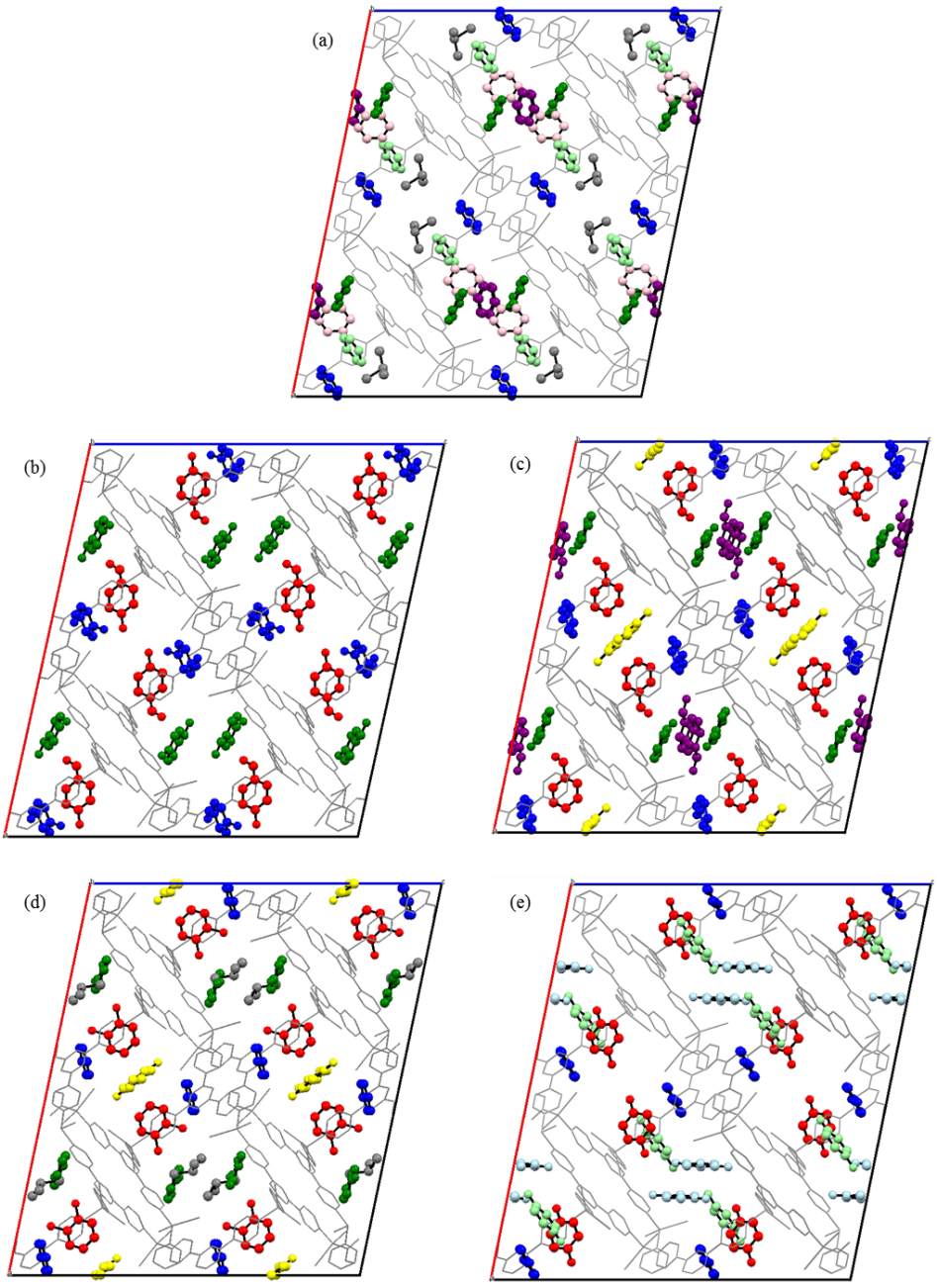

Figure 6 Unit cells of X-ray crystal structures of encapsulation complexes (a) **1i** (benzene), (b) **1ii** (4-fluorobenzaldehyde), (c) **1v** (benzaldehyde)**,** (d) **1vi (**fluorobenzene) and (e) **1vii** (1,4-difluorobenzene) viewed down the *b*-axis. The colouring of guest molecules indicates positional equivalence *both* within each structure *and* between the five structures.

Guest series

Packing diagrams showing the units cells of the encapsulation complexes with guests benzene (**1i**), 4-fluorobenzaldehyde (**1ii**), benzaldehyde (**1v**), fluorobenzene (**1vi**) and 1,4-difluorobenzene (**1vii**) as viewed down the *b*-axis are displayed in Fig. 6. Guest molecules are coloured by their symmetry equivalence within their own encapsulation complex and also positional equivalence to guests in the other four structures. It is immediately apparent that certain positions within the unit cell are particularly favourable. A detailed examination of the packing diagrams and short contacts as defined in Mercury[23] gives a clear indication of the dominant interactions. These are; (i) electrostatic aromatic interactions (both CH···π and π···π), (ii) hydrogen bonding between the aldehyde group and fluorine atom donors, and (iii) weaker, longer range van der Waals interactions.

Looking across the series it is evident that the positions guest molecules take up within the pores of **1** do vary with the variation in functionality, but not in every case**.** One specific position has been identified as common to all five guest species, observable in Fig. 6 by the blue coloured guest molecules. In this instance the molecules generally adopt a perpendicular y–shaped arrangement with the pyridine ring of the framework. The length of the CH···π interaction varies (see Table 2) as expected from the subtle variation in orientation observed in the crystal structures. Whilst guest molecules in **1i**, **1ii**, **1v** and **1vi** sit at broadly similar distances and orientations to the framework, interacting with only one pyridine ring, 1,4-difluorobenzene molecules in **1vii** are sufficiently displaced to interact with two. This difference is visualised in Fig. 7 showing the contrasting positions of 4-fluorobenzaldehyde and 1,4-difluorobenzene in relation the section of the framework with which they interact. Furthermore, the guests appear to be stabilised by several interactions between both hydrogen and non-hydrogen ring substituents and the triazide or pyridine rings of the host.

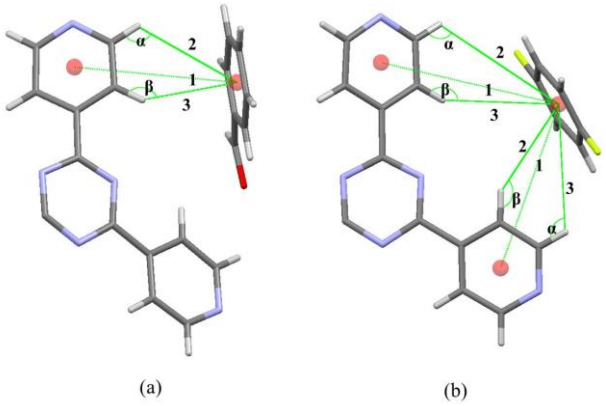

Figure 7 (a) Perpendicular y–shaped interaction of benzaldehyde and the host framework in **1v**, also representative of interactions in **1ii** and **1vi** (b) Offset y–shaped interaction of 1,4-difluorobenzene in **1vii**.

		Length* /Å			Angle* /°	
		1	2	3	α	β
Benzene	**1i**	4.83	3.28	3.16	119.69	123.91
4-fluorobenzaldehyde	**1ii**	5.46	3.86	3.56	125.18	137.91
benzaldehyde	**1v**	4.91	3.41	3.01	118.64	135.76
fluorobenzene	**1vi**	5.14	3.75	3.17	116.04	141.69
1,4-difluorobenzene	**1vii**	5.57	4.36	3.54	111.28	146.97
1,4-difluorobenzene	**1vii**	5.43	4.20	3.46	110.99	140.80

Table 2 Parameters used to describe CH···π interactions in structures **1i**, **1ii 1v**, **1vi** and **1vii** between the centroid of the 'blue' guest molecules and hydrogen substituents of the framework in closest proximity. *Lengths and angles defined in Fig. 8(a).

Two sites in the unit cell have been identified as common to four of the five guest species irrespective of functionalisation, identified in Fig. 6 by red (found in structures **1ii**, **1v**, **1vi** and **1vii**) and dark green (in **1i**, **1ii**, **1v** and **1vi)** coloured guest molecules. In both cases whilst the positon and inclination of the aromatic ring is broadly the same, the orientation of the functional group varies.

The interactions governing the positioning of guests coloured dark green is broadly similar to those discussed above in the 'blue' site – a y-shaped CH···π interactions between the guest and a framework pyridine ring. Analysis of the contact distances shows fluorobenzene and benzene in **1i** and **1vi** are positioned almost identically, as are fluorobenzaldehyde and benzaldehyde in **1ii** and **1v** (see Table S1). Contact measurements reveal the presence of C(H)=O···$HC_{pyridine}$ interactions in the latter pair (2.64 and 2.89 Å for **1ii** and **1v** respectively), thought to be the cause of their relatively offset orientation.

Guests indicated by red coloration in structures **1ii**, **1v**, **1vi** and **1vii** (Fig. 6) engage in face-to-face π···π interactions with the pyridine ring that separates the two distinct chambers in the crystalline sponge. Given benzene is not seen to take up this position, evidence suggests the formation of this π···π interaction is facilitated by the presence of the substituent groups. This can be rationalised by considering that the electron withdrawing nature of functional groups –C(O)H and -F (relative to –H in benzene) favours a face-to-face π···π arrangement with the electron deficient framework. Interestingly however, the identity of the guests' substituent groups does not obviously affect the magnitude of this π···π interaction as determined by the intermolecular centroid-centroid distances of 3.72, 3.69, 3.79 and 3.78 Å for **1ii**, **1v**, **1vi** and **1vii** respectively, with all dihedral angles between mean planes of the guest and host rings <13°.

However, guest functionality does affect the orientation of the molecules as a result of different weak interactions with surrounding framework. Fig. 8 shows the guests in this position, highlighting their common face-to-face interaction with the pyridine ring of the framework but varied orientation. Substituents involved in this guest-host interaction are orientated towards the pyridine and triazide rings of TPT, rather than into the empty void space of the pores. The orientations of benzaldehyde and 4-fluorobenzaldehyde are determined through (O=)CH···$N_{triazide}$ hydrogen bonds (short contacts 2.84 and 2.54 Å respectively), with the fluorine atom present in the latter yielding no significant short contact interactions with the framework. This is unsurprising as C-F group compete unfavourably with aldehyde groups with regard to hydrogen bond formation. There is however suggestion of weak F_{red}···F_{red} interactions (3.14 Å) between symmetrically equivalent guests.

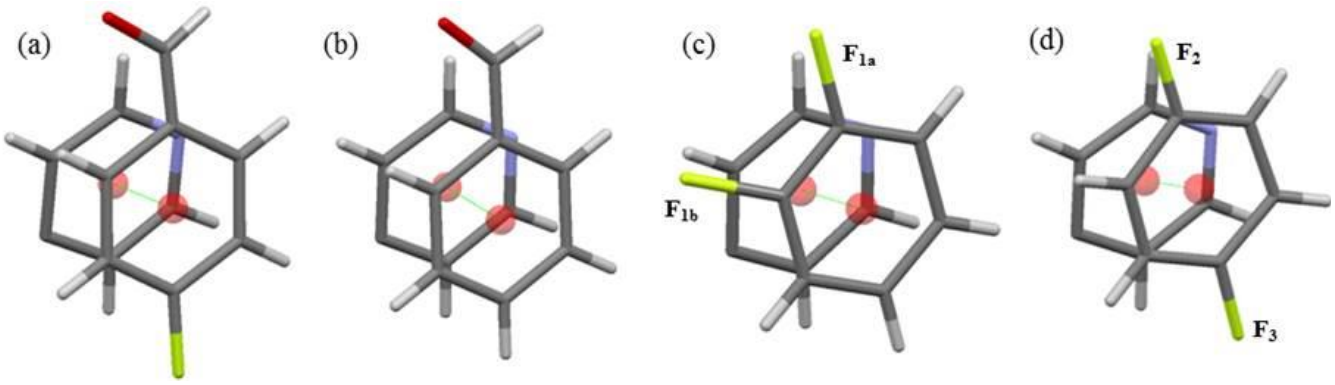

Figure 8 Face-to-face π···π interactions in the encapsulation complexes between the aromatic ring of guest molecules and a pyridine ring, at a common site within the unit cell. (a) 4-fluorobenzaldehyde **1ii** (b) benzaldehyde **1v** (c) fluorobenzene **1vi** (rotational disorder shown, F_{1a} and F_{1b} occur with 50% occupancy) and (d) 1,4-difluorobenzene **1vii** (fluorine atoms labelled to distinguish). Centroids shown as red spheres and intercentroid contacts in green.

In the case of fluorobenzene (**1vi**, Fig. 8c) the fluorine atom takes up a similar position to the absent aldehyde group, interacting with the equivalent part of the framework albeit with longer contact distance (F_{1a}···$N_{triazide}$, 3.11 Å). There is also a comparable interaction with a carbon atom in the same triazide ring (F_{1a}···$C_{triazide}$, 3.13 Å). Similarly the closest contacts of the fluorine substituent on the equivalent 1,4-fluorobenzene guest in **1vii** are F_2···$C_{triazide}$ (3.16 Å) and F_2···$N_{triazide}$ (3.26 Å). Analysis of the fluorine atom (F_3) para to this yielded no significant short contact measurements with the framework, but as in **1ii** there is suggestion of guest – guest F_{red}···F_{red} interactions (3.39 Å). It is important to note that the interaction of fluorine is sufficiently weak in fluorobenzene (**1vi**) for disorder to occur with 50:50 occupancy of two positions (Fig. ~~7~~8c). The interaction determining this second orientation appears to be F_{1b}···$HC_{pyridine}$ with an intermolecular distance of 2.78 Å. This distance is greater than the sum or the van der Waals radii of fluorine and hydrogen and in the range of a weak hydrogen bond.

There are other positions within the unit cell that are taken up by more than one of the guests in the series, *i.e.* sites indicated by yellow coloured guests in **1v** and **1vi** (Fig. 6c and 6d respectively) and purple in **1i** and **1v** (Fig.6 a and 6c respectively). Yet there are instances where guest molecules take up positions either favoured by a minority or novel to their species alone. This latter variation can be found in structure **1vii** with two positions identified as novel to this encapsulation complex, shown in Fig. 6e as occupied by light blue and light green 1,4-difluorobenzene molecules. Interestingly, those guests coloured light green would appear to be stabilised by interactions with multiple framework pyridine rings through *both* π···π interactions (intercentroid distance of 3.93 Å and dihedral angle 10.24°) and CH···π interactions (CH···$centroid_{pyridine}$ 3.43 Å, dihedral angle 74.21°). Those molecules coloured light blue are stabilised by π···CH interactions with one pyridine ring (centroid···$HC_{pyridine}$ 3.48 Å, dihedral angle 56.54°) and F···H interactions with a second (CF···$HC_{pyridine}$ 2.69 Å). The question still remains however as to why only 1,4-difluorobenzene molecules take up these positions, and the answer may be down to guest–guest interactions. There is evidence for the formation of two H_{green}···F_{pink} interaction (3.13 and 3.18 Å) and $F_{light\ green}$··· $F_{light\ green}$ (3.78 Å) which may aid in the stabilisation and ordering of 1,4-difluorobenzene in these positions. Additionally, a $F_{light\ green}$···H_{red} interaction at 2.50 Å is evidence for fluorine – hydrogen bonds between guest molecules.

Conclusions

Through the encapsulation of simple organic aromatic guests into the crystalline sponge we were able to show guest molecules take up specific sites within the unit cell consistently albeit with minor variations in orientation and disorder. Measurement of guest – host and guest – guest interactions confirm π - π and CH - π interactions persist throughout the structure and we can be confident of their dominant role in the ability of the crystalline sponge to render the guest molecules regularly ordered. Nevertheless certain guests have unique interactions according to their functionality, such as hydrogen bonds which contribute to both the position and specific orientation of the molecules.

Experimental

Crystalline sponge synthesis and guest encapsulation

$[\{(ZnI_2)_3(\text{tris(4-pyridyl)-1,3,5-triazine})_2 \cdot x(CHCl_3)\}_n]$ was prepared following procedure reported in the literature.[10] For guest encapsulation, the mother liquor was reduced to the minimum volume whilst still covering the crystals and the guest liquid (~1 cm^3) pipetted in. After a specific number of days (5–7, see Table S2) incubating at ~22°C, suitable rod or block shaped crystals were selected and subjected to SCXRD. Crystals used for repeat experiments came from different batches.

Crystallographic procedures

Crystals were placed in Fomblin and single crystals selected and mounted onto nylon loops. X-ray diffraction data were recorded on an Agilent Super Nova Dual Diffractometer (Agilent Technologies Inc, Santa Clara CA) with Cu-Kα radiation (λ = 1.5418 Å) at 150K. Unit cell determination, data reduction and absorption corrections were carried out using CrysAlisPro.[24] The structures were solved with the Sir2004[25] structure solution program by direct methods or Superflip[26] and

refined by full matrix least squares on the basis of F^2 using SHELX 2013[27] within the OLEX2[28] GUI. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Details of the treatment of individual guest molecules are found in the supplementary material.

Supporting Information Available

This information is available free of charge via the Internet at http://pubs.acs.org/.

- Crystal data and refinement details; encapsulation conditions; additional contact distance measurements (PDF)

Accession Codes

CCDC 1463754–1463765 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK, by emailing data_request@ccdc.cam.ac.uk, or by fax: +44 1223 336033.

Author Information

* Corresponding Author
Email: c.j.carmalt@ucl.ac.uk
Tel: +44 (0)20 7679 7528
Fax: +44 (0)20 7679 7463

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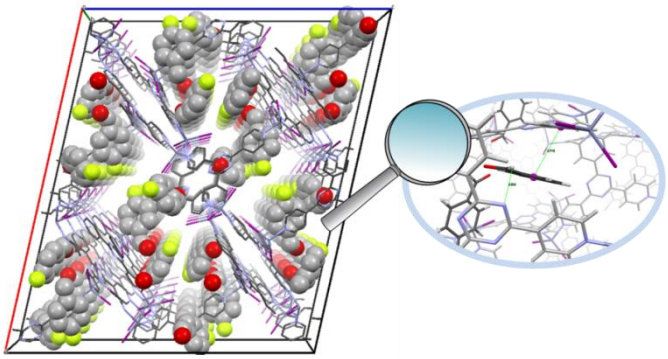
For Table of Contents Use Only:

The Crystalline Sponge Method: A Systematic Study of the Reproducibility of Simple Aromatic Molecule Encapsulation and Guest – Host Interactions

Lilian M. Hayes, † Caroline E. Knapp,† Neil. J. Press,‡ Derek. A. Tocher† and Claire. J. Carmalt*†
†Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ
‡ Novartis Institutes for BioMedical Research, Basel, Switzerland

Table of Contents Graphic and Synopsis



A systematic study detailing the uptake of a series of chemically related simple functionalised aromatic guest molecules into the pores of the crystalline sponge $[\{(ZnI_2)_3(\text{tris(4-pyridyl)-1,3,5-triazine})_2.x(\text{solvent})\}_n]$ is reported. The reproducible positioning of the guest molecules within the unit cell has been shown along with the role of π···π , CH···π interactions and weak hydrogen bonds in rendering guests regularly ordered.