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Hexagonal Host Framework of *sym*-Aryloxytriazines Stabilised by Weak Intermolecular Interactions

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2,4,6-Tris(4-halophenoxy)-1,3,5-triazine 1 is a convenient C₃ starting material for the self-assembly of hexagonal open frameworks mediated via the halogen...halogen trimer synthon and the π -stacked Piedfort Unit (PU). We examine in this paper crystal structures of 2,4,6-tris(2-iodo-3-pyridyloxy)-1,3,5-triazine 2, 2,4,6-tris(3-iodophenoxy)-1,3,5-triazine 3, 2,4,6-tris(6-methyl-3-pyridyloxy)-1,3,5-triazine 4, and 2,4,6-tris[4-(4'-bromophenyl)phenoxy]-1,3,5-triazine 5. Triazine 2 forms isostructural 2:1 host-guest adducts (guest = mesitylene, collidine) in the rhombohedral space group $R\bar{3}$ such that the host architecture is stabilised by the C_{3i}-PU and a helix of C–H...N interactions. The crystal structure of 3 is different from its chloro/bromo derivatives signifying the importance of the more polarisable I atom compared to Cl, Br. Pairs of C–H...O and C–H...N hydrogen bonds and C_{3i}-PU sustain the columnar structure of 3 (space group $R\bar{3}$). The PU has pseudo trigonal symmetry in picolinoxy triazine 4 (space group $P2_1/n$). In contrast to the phenyl derivatives, the extended aryl arms in biphenyl 5 do not adopt a trigonal

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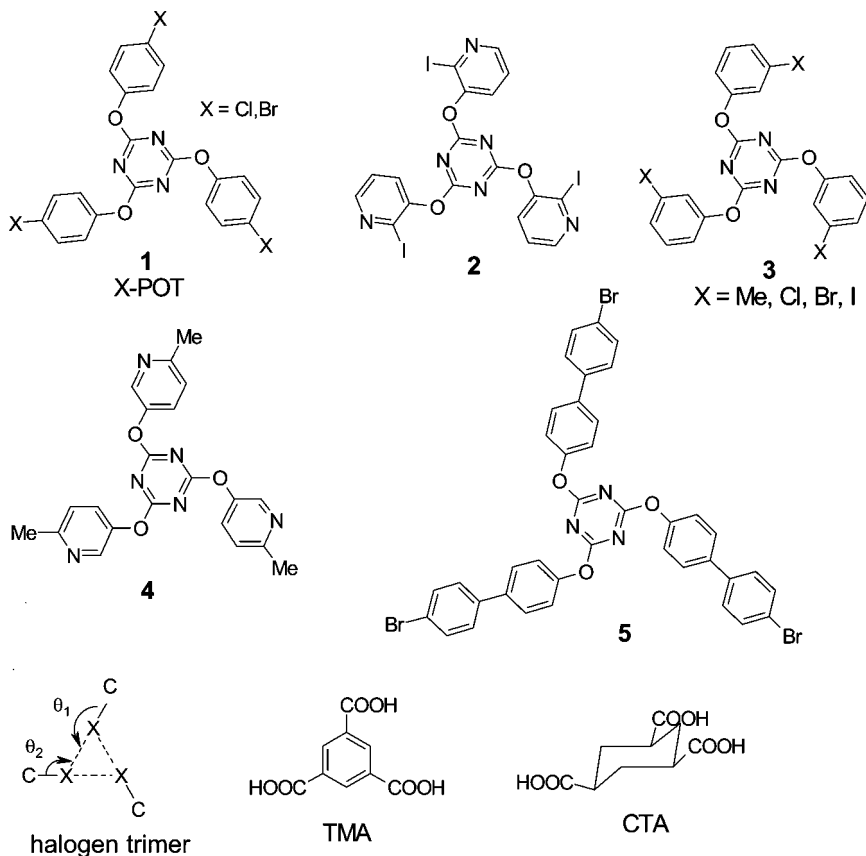
conformation: two biphenyl groups are oriented parallel that participate in $\text{Br} \cdots \text{Br}$ and $\text{Br} \cdots \pi$ interactions. We note that **1** and **2** readily form hexagonal host lattices for guest inclusion, while **3**, **4**, and **5** crystallise in solvent-free form. Thermal measurements (TGA, DSC) indicate that guest release occurs at a higher temperature in the cage type host-guest clathrates compared to the channel inclusion compounds for the same solvent. Statistics from the Cambridge Structural Database using CSD Symmetry show that the phenoxytriazine scaffold is unique among the trigonal molecules for the carry-over of symmetry relation from molecule to crystal. The ease of predicting crystal packing and space group in this family of compounds (**1**, **2**) makes them good candidates for the crystal engineering of host frameworks.

Keywords: DSC; halogen...halogen trimer; hexagonal crystal structures; Piedfort units; sym-aryloxytriazines; TGA

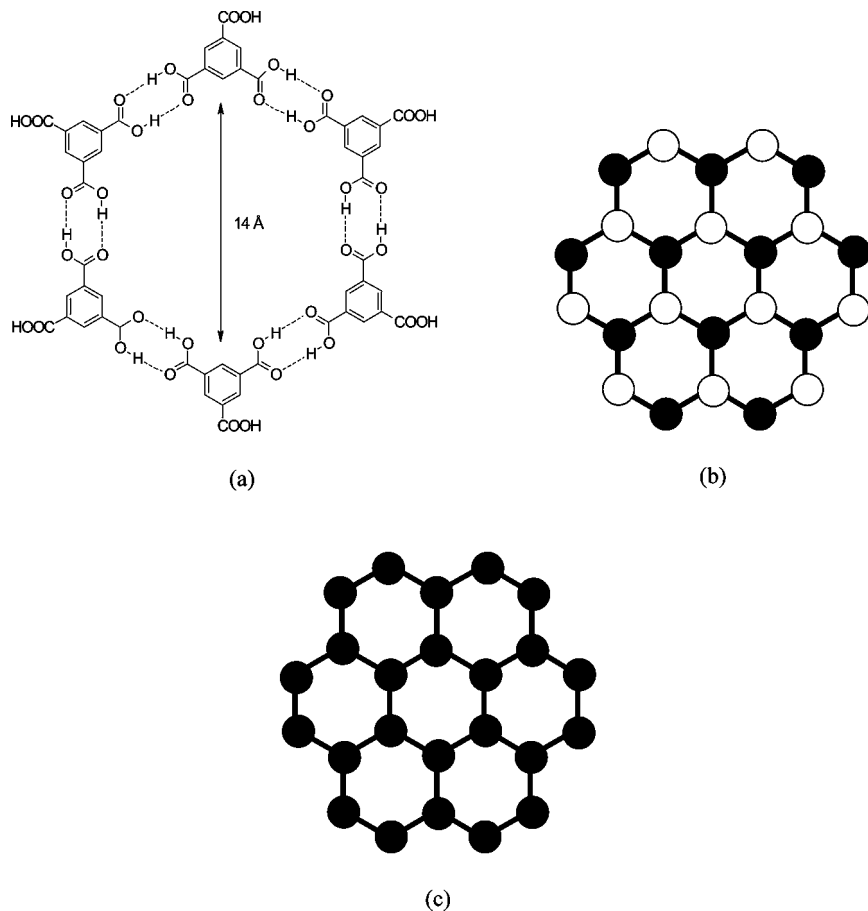
INTRODUCTION

The design and self-assembly of host-guest inclusion compounds [1–3] and interpenetrated network structures [4] is a contemporary theme in the crystal engineering of organic, inorganic and metal-organic solids. These studies are of fundamental importance because they lead to rational strategies for the construction of open frameworks and porous architectures. The empty void space (Nature abhors a vacuum!) is filled in one of two possible ways: guest inclusion or interpenetration. These two modes of space filling in crystals are not mutually exclusive because examples are known in which they occur in the same structure [5,6]. Host-guest crystals and interpenetrated networks find applications in supramolecular materials for NLO and magnetism, gas storage devices, chiral catalysts, topochemical reactions, and drug delivery systems [1–4].

A number of strategies are being developed for the crystal engineering of one dimensional (1D) helices [7], chains and ladders [8], 2D layers, hexagons, parquet grids and square patterns [9], and 3D architectures based on the adamantane network [10]. Our recent studies focus on understanding the tecton [11] → synthon [12] → crystal self-assembly model for the design of target honeycomb structures and the synthesis of functional solids. Thus, starting from suitably functionalised building blocks with appropriate symmetry, recognition is mediated *via* robust, high-probability supramolecular synthons that in turn lead to the desired crystal architecture. In this paradigm, C_3 molecules lead to hexagonal or honeycomb networks and T_d tectons produce diamondoid solids. We discuss in this paper the transformation of some C_3 molecules to hexagonal open frameworks, exemplified in Scheme 1 with the archetypal trimesic acid (TMA). In 2,4,6-*tris*



(4-halophenoxy)-1,3,5-triazine **1** (X-POT), self-assembly is mediated *via* the recurring halogen trimer synthon to a hexagonal framework with an internal diameter of *ca.* 12 Å [13]. These hexagons stack without offset to give channel type host architectures that include a variety of aromatic guest species [14]. Cage type lattice inclusion host [13,14] and polar host-guest assembly [15] have been obtained depending on the nature of weak halogen...halogen and C-H...X (X = halogen, oxygen, nitrogen) interactions. Modification of the 4-halophenoxy group in **1** with different aromatic and heteroaromatic groups (**2**, **3**, **4**, **5**) and its influence on intermolecular interaction synthons and crystal packing are discussed in this paper. Using the recently released software CSD Symmetry by the Cambridge Crystallographic Data Centre [16], we show that C_3 triazine molecules reproducibly form high-symmetry hexagonal host lattices, a unique feature of the X-POT series not



SCHEME 1 (a) Archetypal honeycomb network in trimesic acid (TMA). (b) Triazine and halogen trimer synthons alternate at the nodes, e.g. as in **1**. (c) The nodes are occupied by triazine molecule **2** or TMA.

shared by other trigonal molecules. Thermal analysis (TGA, DSC) of some clathrates of halophenoxytriazine **1** reported earlier [13,14] and iodopyridyloxytriazine **2** are also presented.

RESULTS AND DISCUSSION

Open frameworks may be constructed in inorganic systems (e.g., zeolites), with metal atom bonded to organic ligand (coordination polymers, hybrid structures), and with purely organic molecules.

There are several advantages in designing porous frameworks built from an organic core [3]. (1) Structural diversity can be grafted on the molecule by functional group addition and/or manipulation using synthetic reactions and reagents. (2) Supramolecular synthons (recurring hydrogen bond motifs) permit the design and engineering of diverse host lattices and porous architectures from functionalised molecules. (3) The nature, size and shape of pores and cavities may be systematically altered with hydrogen bonding and hydrophobic interactions. (4) The guest molecule may be used as a template to induce crystallisation of the adduct.

2,4,6-*Tris*(4-halophenoxy)-1,3,5-triazine

We have recently shown that a combination of molecular symmetry and intermolecular interaction geometry may be exploited for the design of crystal structures in high-symmetry space groups [3,13–15,17]. Crystallisation of 2,4,6-*tris*(4-halophenoxy)-1,3,5-triazine **1** (halo = chloro, bromo; Cl-POT, Br-POT) from a variety of solvents and guest molecules (e.g., benzene, mesitylene, collidine, trinitrobenzene, hexamethylbenzene, hexachlorobenzene, hexamethylphosphoramide, etc.) afforded diffraction-quality crystals in the hexagonal space group $P6_3/m$. A slice of the honeycomb layer consists of alternating triazine molecule and halogen trimer synthon at the nodes of the hexagon. Such layers may stack without offset to give a continuous channel structure ($P6_3/m$, $P6_3$) or a finite cavity such that triazine and halogen trimers surround the guest ($R\bar{3}$). The diameter of the hexagonal cavity in **1** is 12–13 Å with a cross-sectional area of 100–110 Å². A stereoview of the hexagonal layer in ClPOT·TNB (2:1, TNB = 1,3,5-trinitrobenzene) is shown in Figure 1. The halogen trimer is a cooperative array of C–X...X–C interactions having polarisation-induced type II geometry (Cl...Cl 3.42 Å, θ_1 170.6°, θ_2 110.6°) [18], the difference between the two angles being *ca.* 60° because of crystallographic symmetry. In idealised type I approach $\theta_1 = \theta_2 \approx 150^\circ$ (halogen atoms related across an inversion centre) and in type II geometry $\theta_1 \approx 180^\circ$, $\theta_2 \approx 90^\circ$ (halogen atoms related by a screw axis or a glide plane). The fully ordered structure is ascribed to the numerous heteroatom interactions between the nitro O atom of the guest and the O/Cl atoms on the host (O...O 3.16 Å, O...Cl 3.53 Å). Figure 1 shows the stacking of TNB guest molecules in the 1D channel of Cl-POT at a distance of 3.5 Å ($= c/2$), a unique motif of π -stacked electron-deficient aromatic rings at van der Waals separation in the Cambridge Structural Database [19], an archive of over quarter of a million crystal structures. In contrast to the channel structure of Cl-POT·TNB and Cl-POT·HCB

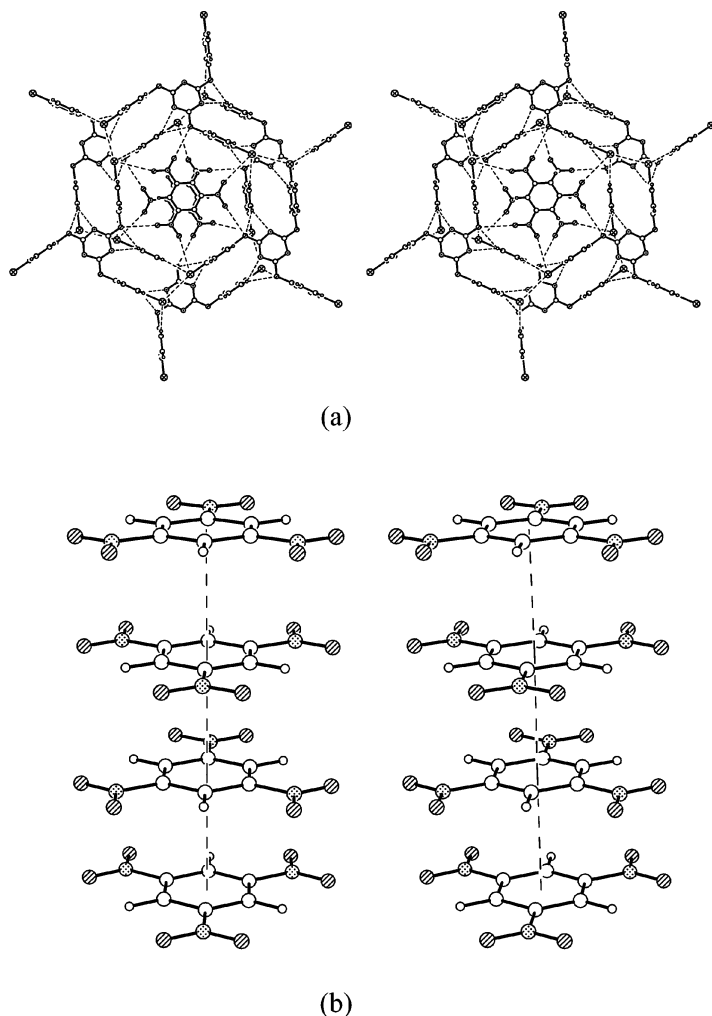


FIGURE 1 (a) Stereoview of the hexagonal network formed by alternating triazine **1** and halogen trimer synthons at the nodes in ClPOT·TNB (2:1). Note the O···Cl and O···O host···guest interactions. This type of honeycomb network is depicted in Scheme 1(b). (b) Planar conformation of 1,3,5-trinitrobenzene (phenyl ring and nitro oxygen atoms occupy the same plane) in the 1D channel of Cl-POT. The centroid-to-centroid distance of adjacent phenyl rings is 3.5 Å (= $c/2$).

(HCB = hexachlorobenzene), the crystal structure of Br-POT·HCB (space group $R\bar{3}$) is layered because the host molecules are stacked with offset in adjacent layers. Similar to the TNB guest, the

host-guest structure is fully ordered because of numerous weak heteroatom interactions ($\text{O}\cdots\text{Cl}$ 3.53 Å). The hexagonal channels of the Br-POT host lattice can accommodate fullerene guests (C_{60} , C_{70}), albeit in a disordered arrangement [20].

O-Aromatic/Heteroaromatic Groups on Triazine

Upon observing the structural robustness of the hexagonal framework in the supramolecular architecture of Cl-POT and Br-POT mediated by the halogen trimer synthon, we replaced the phenyl ring with the pyridyl group, as in **2**, for two reasons: (1) to find out if these molecules retain the hexagonal symmetry in their crystal structures; (2) to profitably use the pyridyl group for making $\text{C}-\text{H}\cdots\text{N}$ interactions [21] along the channel walls. In preliminary crystallisation experiments we obtained single crystals with mesitylene and collidine solvents. X-ray diffraction showed the structures, **2**· C_9H_{12} and **2**· $\text{C}_8\text{H}_{11}\text{N}$, to be isomorphous solvent inclusion adducts in the rhombohedral space group $R\bar{3}$ (2:1 H·G, Table 1). Triazine **2** self-assembles *via* the C_{3i} -PU (3.30 Å, 3.28 Å) [22] in the *ab*-plane together with a helix of $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds (2.42 Å, 139.5°; 2.39 Å, 137.8°, Table 2) along the *c*-axis to generate a hexagonal host framework (Fig. 2). The disordered guest molecules are sandwiched in the hexagonal cavity with a diameter of 11 Å (excluding van der Waals thickness of the phenyl ring) between the C_{3i} -PU of host molecules. In contrast to Cl/Br-POT structures **1** with halogen trimer synthon, crystal structure **2** is stabilised by van der Waals stacking in the PU. Attempts to model guest disorder from the diffuse electron density map did not give a better *R*-factor.

The inclusion of solvent/guest molecule in channel/cavity is the norm in this family of crystal structures studied thus far (Scheme 2). The following three examples illustrate packing in guest-free crystal structures.

The crystal structure of *meta*-chloro/bromo/methyl-phenoxytriazine **3** was determined previously [23]. These compounds are isostructural (space group $P\bar{3}c1$) and contain both C_{3i} -PU and D_3 -PU motifs. On the other hand, *meta*-iodophenoxytriazine **3I**, upon crystallisation from THF/mesitylene mixture, afforded crystals in $R\bar{3}$ space group. The polarisation-induced $\text{I}\cdots\text{I}$ interaction (type II, 3.85 Å, 169.9°, 83.0°) aggregates the molecules in a helical motif parallel to the *c*-axis (Fig. 3). A combination of C_{3i} -PU and three pairs of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds [23] control the self-assembly of the columnar structure. The more polarisable iodine atom compared to chlorine and bromine is

TABLE 1 Crystallographic Data on Triazines and their Inclusion Compounds

Complex	2-collidine	2-mesitylene	3	4	5
Structural formula	2(C ₁₈ H ₉ N ₆ O ₃ I ₃)·C ₈ H ₁₁ N	2 (C ₁₈ H ₉ N ₆ O ₃ I ₃)·C ₉ H ₁₂	C ₂₁ H ₁₂ I ₃ N ₃ O ₃	C ₂₁ H ₁₈ N ₆ O ₃	C ₃₉ H ₂₄ Br ₃ N ₃ O ₃
Chemical formula	C ₄₄ H ₂₉ I ₆ N ₁₃ O ₆	C ₄₅ H ₃₀ I ₆ N ₁₂ O ₆	C ₂₁ H ₁₂ I ₃ N ₃ O ₃	C ₂₁ H ₁₈ N ₆ O ₃	C ₃₉ H ₂₄ Br ₃ N ₃ O ₃
Formula weight	1597.20	1596.21	735.04	402.41	822.34
Crystal system	hexagonal	hexagonal	hexagonal	monoclinic	triclinic
Space group	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$	<i>P</i> ₂₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>T</i> , K	123(2)	183(2)	223(2)	293(2)	183(2)
<i>a</i> , Å	16.655(2)	16.750(2)	23.421(3)	9.569(2)	9.567(2)
<i>b</i> , Å	16.655(2)	16.750(2)	23.421(3)	18.851(4)	10.099(2)
<i>c</i> , Å	16.601(3)	16.800(3)	7.301(2)	11.255(2)	19.349(3)
α , deg	90	90	90	90	86.198(4)
β , deg	90	90	90	93.496(4)	77.005(3)
γ , deg	120	120	120	90	67.205(3)
<i>V</i> , Å ³	3988(1)	4082(1)	3468(1)	2026.3(8)	1678.7(5)
<i>Z</i>	3	3	6	4	2
ρ_{calc} , g cm ⁻³	1.995	1.948	2.112	1.319	1.627
μ , mm ⁻¹	3.562	3.480	4.082	0.092	3.648
<i>R</i>	0.0504, 0.0831	0.0574, 0.1073	0.0576, 0.0698	0.0566, 0.0809	0.0563, 0.0912
<i>R</i> _w	0.1206, 0.1465	0.1191, 0.1433	0.1554, 0.1655	0.1592, 0.1774	0.1286, 0.1478
<i>C</i> _k	0.65	0.64	0.65	0.65	0.67

TABLE 2 Geometry of Hydrogen Bonds and Intermolecular Interactions

Complex	Interaction	<i>d</i> , Å	<i>D</i> , Å	<i>θ</i> , deg
2 •collidine	C–H...O	2.588(3)	3.494(7)	140.7(4)
	C–H...N	2.394(6)	3.278(9)	137.8(4)
		2.742(5)	3.580(8)	134.0(4)
	C–H...I	3.301(1)	4.171(6)	138.2(4)
	I... π		3.88(2)	167.5(4)
2 •mesitylene	π ... π		3.28	
	C–H...O	2.598(4)	3.516(9)	142.1(4)
	C–H...N	2.423(6)	3.322(9)	139.5(4)
		2.782(5)	3.628(10)	134.9(4)
	C–H...I	3.335(1)	4.205(8)	138.2(4)
3	I... π		3.95(1)	168.2(3)
	π ... π		3.30	
	C–H...N	2.688(5)	3.563(8)	137.6(4)
	C...O	2.576(5)	3.497(6)	142.4(2)
	C–H...I	3.053(8)	4.021(6)	149.0(3)
4	I...I		3.852(1)	169.9, 82.9
	C–H...N	2.674(2)	3.422(3)	125.9(2)
		2.549(2)	3.484(4)	144.1(2)
		2.679(2)	3.645(3)	148.3(2)
		2.661(2)	3.577(4)	142.0(2)
5	C–H...O	2.700(2)	3.533(3)	133.5(2)
		2.669(2)	3.505(3)	133.6(2)
	C–H...N	2.707(4)	3.647(6)	144.9(2)
	C–H...O	2.833(3)	3.720(6)	139.0(2)
		2.857(4)	3.818(6)	148.0(2)
		2.924(3)	3.923(6)	153.4(2)
	C–H...Br	2.833(1)	3.648(6)	132.1(3)
		2.884(1)	3.792(5)	141.4(2)
		3.080(1)	3.891(4)	132.2(2)
	C–H... π	2.75	3.72	149.3
		2.87	3.91	160.1
		2.80	3.76	148.2
		2.73	3.80	172.2
		2.70	3.54	133.8
	Br...Br		3.513(1)	164.9(2), 108.8(1)
	Br... π		3.503(4)	149.4(1)
			3.543(4)	163.5(1)

responsible for this halogen-directed crystal structure. Triazine rings are separated by 3.42 and 3.87 Å in the PU and connected *via* C–H...O and C–H...N interactions in a columnar array through the *ortho*-H donors of the phenyl ring (2.57 Å, 142.4°; 2.68 Å, 137.7°). The *meta*-H atoms participate in C–H...I interactions (3.05 Å, 149.0°).

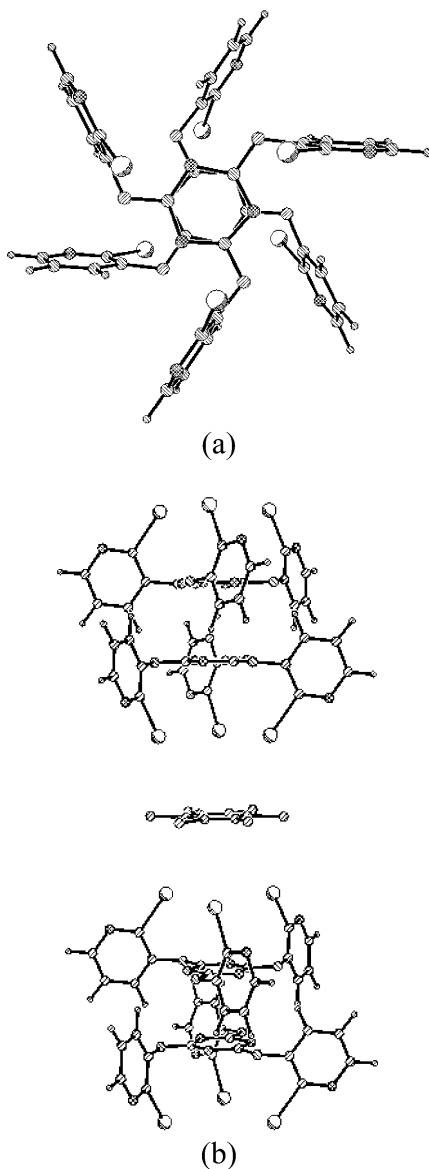
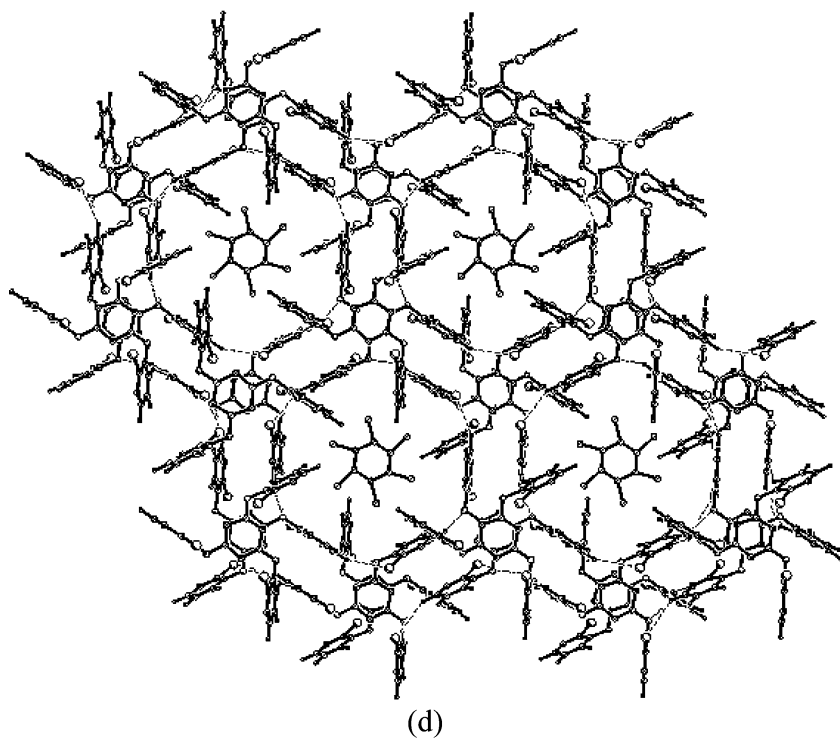
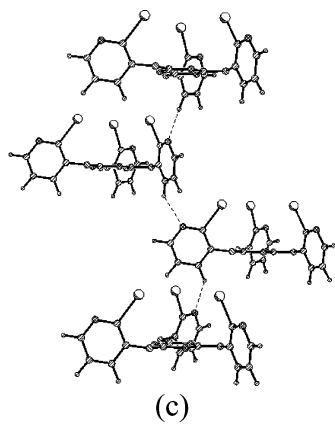
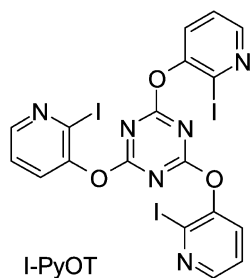
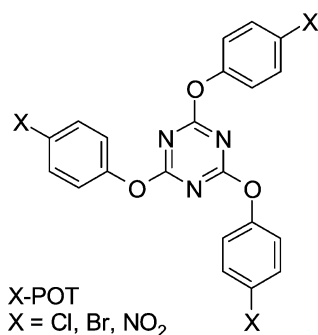


FIGURE 2 Crystal structure of iodo-pyridinoxy triazine **2**. (a) C_{3i} -PU at $\pi \cdots \pi$ distance of 3.3 Å. (b) Disordered mesitylene guest sandwiched between the C_{3i} -PUs. The *ortho*-iodine atoms project into the cavity. (c) The helix of C–H \cdots N interactions stabilizes the structure along the *c*-axis. (d) A view of the *ab*-layer to show the hexagonal cavity of **2** and the included guest (mesitylene) molecules. This type of honeycomb network is depicted in Scheme 1(c).

**FIGURE 2** Continued.



BrPOT.hexamethylbenzene (HMB), (2:1)
 BrPOT.1,3,5-trinitromesitylene (TNM), (2:1)
 BrPOT.2,4,6-collidine (CLN), (1:1)
 BrPOT.1-methylnaphthalene (MNP), (1:1)
 BrPOT.mesitylene (MES), (1:1)
 BrPOT.hexachlorobenzene (HCB), (2:1)
 BrPOT.hexabromobenzene (HBB), (2:1)
 BrPOT.hexamethylphosphoramide (HMPA)
 .cyanuric acid (CA), (2:4:1)
 BrPOT.1,3,5-tribromobenzene (TBB), (1:1)
 BrPOT.1,3,5-triiodobenzene (TIB), (1:1)
 ClPOT.hexachlorobenzene (HCB), (2:1)
 ClPOT.hexamethylbenzene (HMB), (2:1)
 ClPOT.1,3,5-trinitrobenzene (TNB), (2:1)
 ClPOT.hexamethylphosphoramide (HMPA), (2:1)
 ClPOT.1,3,5-tribromobenzene (TBB), (1:1)
 ClPOT.1,3,5-triiodobenzene (TIB), (1:1)
 NO₂POT.chloroform (1:3)
 NO₂POT.1,3,5-tribromobenzene (TBB), (1:1)
 NO₂POT.hexachlorobenzene (HCB), (2:1)
 NO₂POT.benzene (2:1)
 NO₂POT.hexamethylbenzene (HMB), (3:1)

I-PyOT.mesitylene (MES)
 I-PyOT.collidine (CLN)

SCHEME 2 *sym*-Aryloxytriazines and their guest inclusion adducts.

The picolinoxy triazine **4** crystallises from EtOAc in $P2_1/n$ space group. Inversion related molecules are stacked with slight offset (0.36 Å) as PU motif with pseudo trigonal symmetry in the crystal structure. With the loss of C_3 symmetry, two pyridyl rings are oriented above the triazine plane while the third pyridyl group is twisted down with respect to the N atom (Fig. 4). These PUs are connected by C—H...O and C—H...N interactions (2.70 Å, 133.5°; 2.68 Å, 148.3°) involving the activated methyl group. The molecules form 2D pseudo-hexagonal layer motifs, with layers being separated by 3.38 Å within the PU and by 3.68 Å between PUs.

The effect of extending the aryl group is examined next. In bromo-biphenyloxy triazine **5**, crystallised from CHCl₃ with a few drops of *meta*-xylene added, the crystal structure is layered ($P\bar{1}$) without

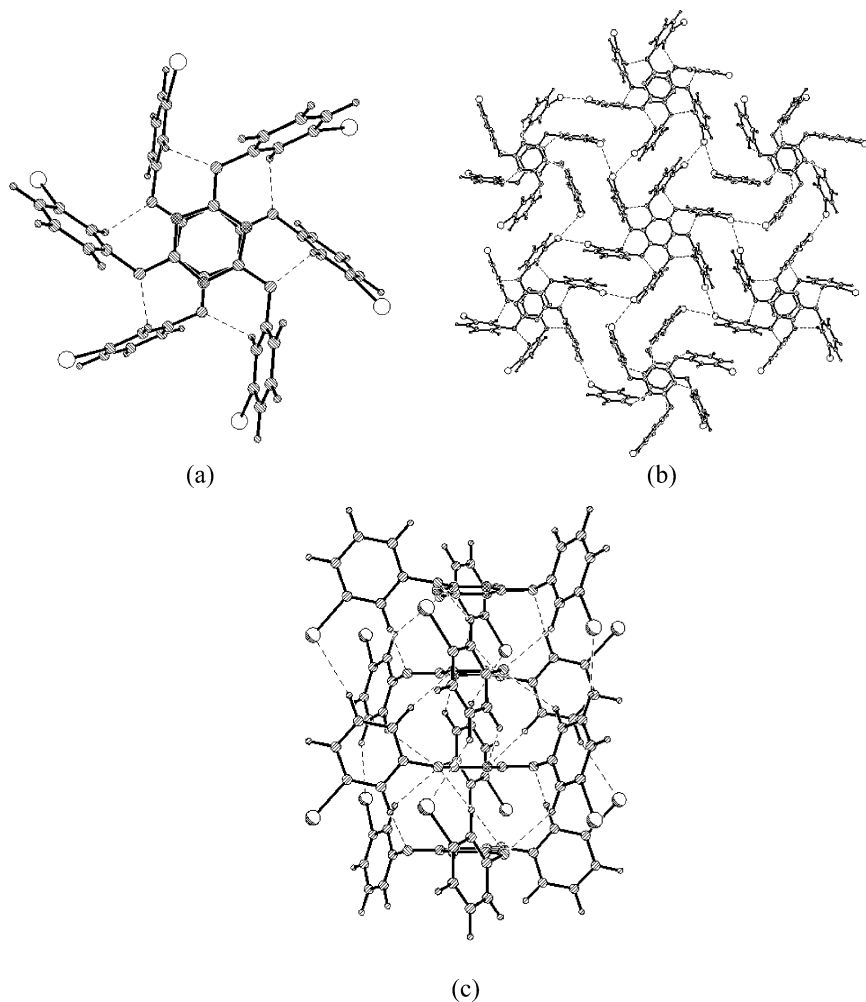
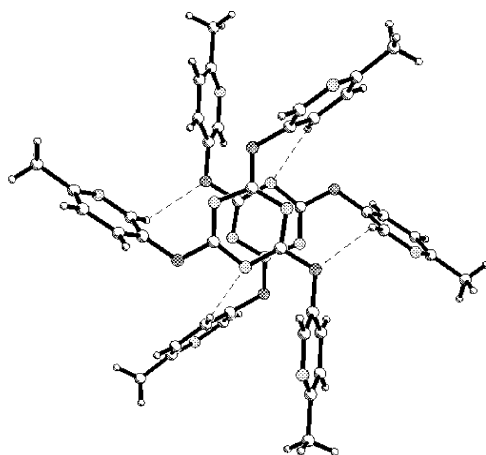
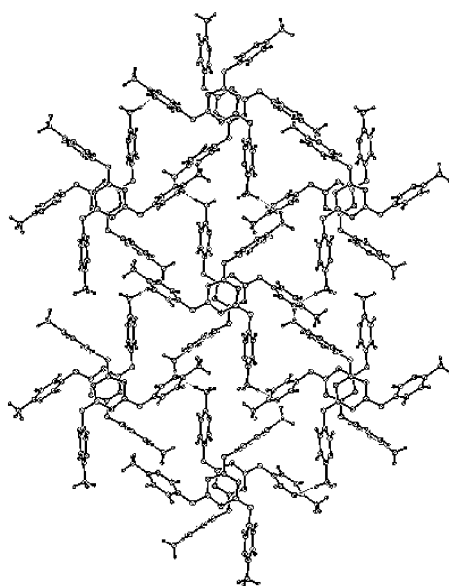


FIGURE 3 Crystal structure of *meta*-iodo triazine **3**. (a) C_{3i} -PU and C-H...O interactions. (b) Helical iodo trimer motif. (c) Columnar structure along the c -axis stabilised by C-H...O/N/I interactions.

included solvent. In contrast to previous structures in which the trigonal molecule adopts a C_3 (or pseudo C_3) conformation in the crystal, the two aryloxy groups in **5** are oriented parallel and the third group points in a different direction [24], in effect making a tuning fork-like molecular conformation (Fig. 5). Two bromine atoms are involved in type II Br...Br interaction (3.51 Å, 164.9°, 108.7°) and the third



(a)



(b)

FIGURE 4 (a) $\pi \cdots \pi$ stacking and C-H \cdots O/N hydrogen bonds in the PU of picolinoxyl triazine **4**. The molecule has pseudo C_3 symmetry. Note that N atom of two pyridyl rings is oriented above the triazine plane while the third points below. (b) The PUs are connected through C-H \cdots N bonds. The PU in this structure has pseudo C_3 symmetry.

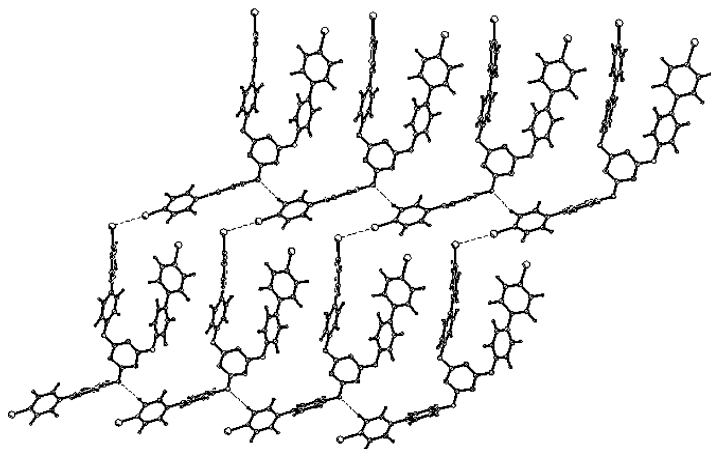


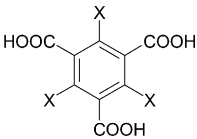
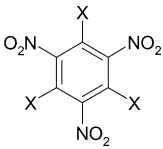
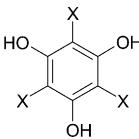
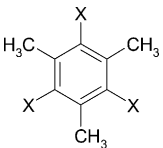
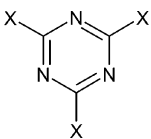
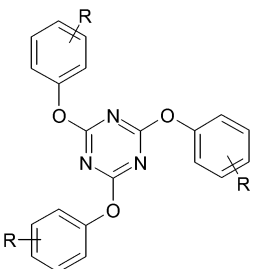
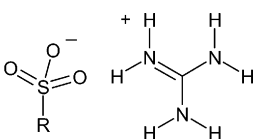
FIGURE 5 Crystal structure of bromo-biphenyloxy triazine **5**. Note the absence of C_3 symmetry and the tuning fork shape molecular conformation. Type II $\text{Br} \cdots \text{Br}$ and $\text{C}-\text{H} \cdots \text{O}$ interactions are shown.

bromine engages in $\text{Br} \cdots \pi$ interaction (3.50 \AA , 149.4°). Miscellaneous $\text{C}-\text{H} \cdots \text{X}$ ($\text{X} = \text{O}, \text{N}, \pi$) interactions are present in the layered structure with inter-layer separation of 3.35 and 4.10 \AA .

CSD Symmetry

Crystallographers are used to seeing symmetrical molecules crystallise in space groups with lower symmetry. The only molecular symmetry element that carries over routinely into the crystal structure is the inversion centre [25]. We note the high occurrence of space groups with hexagonal/rhombohedral symmetry in C_3 symmetry triazine structures. This is not so common. The well-known trigonal molecule trimesic acid produces a honeycomb chicken wire pattern but in monoclinic crystal system $C2/c$. Although matching of molecular and supramolecular symmetry has been examined in a limited number of crystal structures [26], the triazine scaffold is the first example of a family of trigonal molecules that crystallises in the hexagonal crystal system with high probability. CSD Symmetry [16] was used to search for the carry-over of molecular symmetry to the crystal for some common trigonal scaffolds used in crystal engineering: trimesic acid, trinitrobenzene, phloroglucinol, mesitylene, guanidine, triazine, phenoxytriazine (Table 3). If a trigonal molecule occupies the Wyckoff position in a high symmetry space group, e.g., $P6_3/m$, $P\bar{3}c1$, $R\bar{3}$, $P\bar{3}$,

TABLE 3 CSD Symmetry Statistics on Molecular and Crystal Relation in Some Trigonal Molecules

Compound type	Structures in high symmetry space group	Structures in low symmetry space group
	1	19
	6	62
	2	11
	9	58
	6	38
	35	7
	0	94

etc. then Z' will be 0.33, 0.17 or 0.08 depending on whether 1/3, 1/6 or 1/12 molecule is present in the asymmetric unit. An automated search of Z' values for the sub-set of trigonal molecules in the CSD was carried out and the frequencies tabulated. Perusal of Table 3 shows that, in general, trigonal molecules do not crystallise in higher crystallographic symmetry. For trimesic acid and phloroglucinol, the frequency for adopting one of the hexagonal symmetry space groups is 1/20 and 2/13, respectively. In the 100 or so guanidinium–sulfonate host–guest structures [27], there is no occurrence of high-symmetry space groups. On the other hand, the phenoxytriazine core shows a dramatic increase in the preference for trigonal molecular symmetry being related to the hexagonal crystal system: 35/42 hits (= 83%). This kind of success rate is the highest among molecular symmetry elements, save the inversion centre. The global average for C_3 molecules occupying the 3-fold rotation Wyckoff position in crystal structures is 66% [28]. Two specific cases of symmetry transformation deserve mention. Tetraarylmethanes XPh_4 and molecules with XPh_3 fragment crystallise in unit cells with tetragonal and rhombohedral symmetry. Brock [29] and Dance [30], in independent studies, ascribe this to the occurrence of a herringbone motif that fills the voids through pairs of diphenyl groups, and due to the stabilisation gained from bimolecular hexaphenyl embraces, respectively, as the reason for these molecules adopting high symmetry space groups. We believe that the carry over of molecular symmetry to the crystal in phenoxytriazine is because of the stabilisation from the C_3/D_3 -Piedfort Unit supra-molecular aggregate and the polarisation-induced cooperative halogen trimer synthon [31].

DSC/TGA Measurements

In addition to crystallographic characterisation of host–guest structures, thermochemical analysis provides valuable information about the strength of guest to host interactions. The difference between the onset temperature for guest release from the host lattice compared to the normal boiling point of that solvent, $T_{on} - T_{bp}$, is a measure of how strongly the guest molecule is enclosed in the host (cage) architecture [32]. Examination of the host framework suggests that the guest molecule can escape from the channel type structure ($P6_3/m$) with relative ease because there are no strong host–guest interactions. On the other hand, when the guest molecule is sandwiched between the aromatic groups of the cage architecture ($R\bar{3}$), evolution of the guest will require severe fragmentation of the framework and so guest release should occur at a higher temperature or at the melting stage.

TABLE 4 Thermal Analysis (TGA/DSC) on Inclusion Compounds of Triazines

Inclusion compound ^a	Observed weight loss from TGA (%)	Calculated weight loss (%)	Guest release $T_{\text{on}}/^{\circ}\text{C}$	B.p. of Guest $T_b/^{\circ}\text{C}$	ΔH (J g ⁻¹) calibrated
BrPOT·MES	16.6	20.2	139	162–164	99.37
BrPOT·CLN	17.3	20.4	145	171–172	84.08
BrPOT·MNP	1st step 8.4	23.9	127	240–243	14.16
	2nd step 10.3		187		51.56
IPyOT·MES	7.6	8.1	200	162–164	70.81
IPyOT·CLN	7.4	8.2	197	171–172	75.69

^aSee Scheme 2 for abbreviated names of host and guest.

TGA/DSC confirms this to be the case. Although the host···host and host···guest intermolecular interactions are weak in both channel and cage type hosts, guest release occurs at a higher temperature from the latter framework in TGA measurements (Table 4, Fig. 6). Mesitylene and collidine escape from the channel structure of Br-POT **1** at about their boiling point and the observed weight loss is in good agreement with that calculated from the host:guest stoichiometry determined from the X-ray crystal structure. While collidine and mesitylene are lost in a single endothermic step over a narrow range of *ca.* 20°C, 1-methylnaphthalene evolution occurs in two slow steps, 120–150°C and 150–200°C. Since the MNP guest molecules are disordered in the host channel, the stepwise TGA behaviour is difficult to explain. DSC of channel inclusion adducts shows two endotherms, first the release of solvent/guest and then melting of the host compound. In contrast to the channel structures, release of collidine and mesitylene guest from the cage lattice of iodo-pyridyloxy triazine **2** occurs at 50–70°C higher temperatures. This shows that the host architecture is quite strong and thermally stable even though it is assembled with weak C–H···O/N and van der Waals interactions. Some of the highest recorded values of $T_{\text{on}} - T_{\text{bp}}$ are 320°C and 370°C for the release of CH₄ and CF₄ from the interstitial void of calix[4]arene host lattice [33]. In the case of solid guest (e.g., 1,3,5-tribromobenzene), the compound decomposes in a single step at the melting point of the adduct crystal.

CONCLUSIONS AND FUTURE OUTLOOK

We are currently working on two different *C*₃ symmetry molecules for the construction of hexagonal and honeycomb layer architectures.

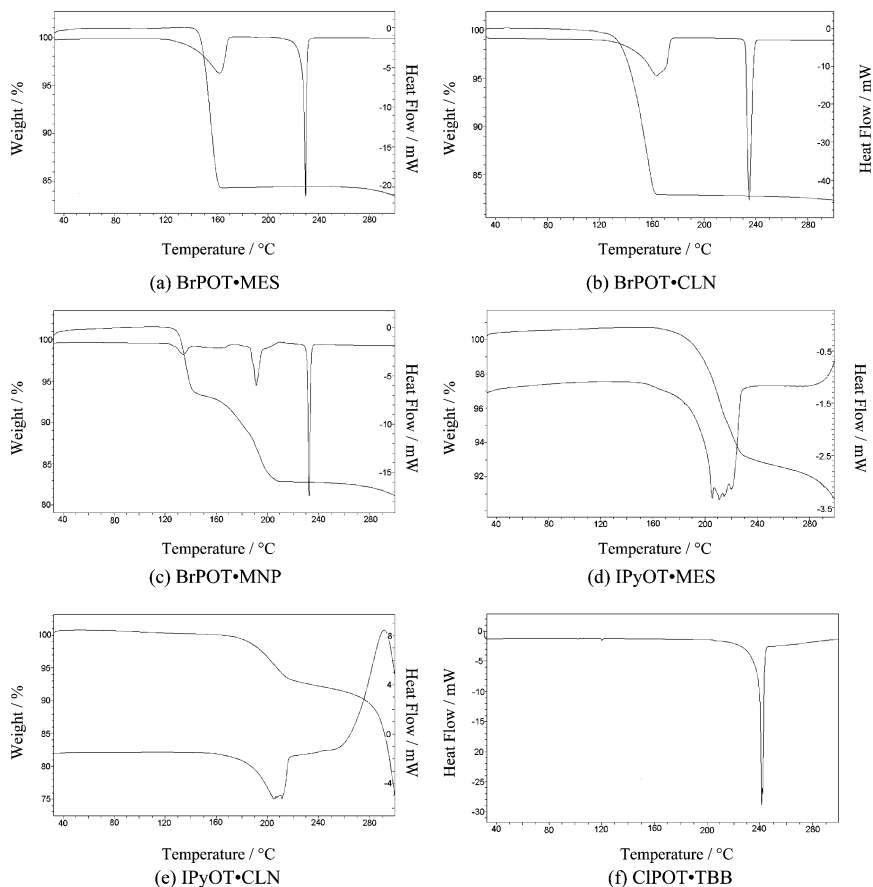


FIGURE 6 TGA and DSC trace of inclusion adducts of Cl-POT/Br-POT = 1 and I-PyOT = 2. See scheme 2 for guest abbreviation. The weight loss of guest in TGA matches with the endotherm in DSC (a-e). There is no release of solid guest in thermogram (f) and decomposition of the host occurs at its melting point.

Some recent advances on the triazine scaffold are discussed in this paper. Results with cocrystals of 1,3-*cis*,5-*cis*-cyclohexane tricarboxylic acid (CTA) are published elsewhere [34]. Our studies with these two C_3 molecules for building hexagonal network structures prompt several related questions. (1) Why do triazine molecules adopt hexagonal crystal symmetry whereas TMA/CTA crystallise in monoclinic/triclinic systems? (2) Why do triazines prefer guest inclusion whilst the tricarboxylic acid adducts fill the porous network through

interpenetration? (3) Is it possible to induce a guest-inclusion system towards interpenetration, and vice versa? (4) What covalent and non-covalent spacers should be used to modularly tune the pore diameter? We hope to address some of these issues in our ongoing studies on the crystal engineering of host-guest adducts and interpenetrated network structures.

EXPERIMENTAL

Synthesis

Equimolar quantities of ArOH and KOH (4 mmol) were dissolved in THF and stirred for 30 min at room temperature. The reaction mixture was cooled to 0°C and then slowly 1 mmol of cyanuric chloride was added and stirred for 1 h at 0°C. After continued stirring at room temperature for 48 hours, the reaction mixture was poured into crushed ice. The heavy white precipitate was filtered by vacuum suction and washed with methanol, dried and purified by column chromatography. All compounds showed satisfactory NMR and IR spectra.

2,4,6-*Tris*(2-iodo-3-pyridyloxy)-1,3,5-triazine **2**: $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ 8.27 (m, 3H), 7.38 (m, 3H), 7.28 (m, 3H). $^{13}\text{C-NMR}$ δ 173, 149, 148, 130, 124, 115. 2-Iodo-3-pyridinol was prepared by the iodination of 3-hydroxypyridine with NaOCl/NaI [35]. Instead of the reported 6-iodo-3-pyridinol isomer, 2-iodo-3-pyridinol was obtained by oxidation at the most activated C atom between the OH group and N atom.

2,4,6-*Tris*(3-iodophenoxy)-1,3,5-triazine **3**: $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ 7.59 (m, 3H), 7.48 (s, 3H), 7.12 (m, 6H). $^{13}\text{C-NMR}$ δ 173, 151, 135, 131, 130, 121, 93.

2,4,6-*Tris*(6-methyl-3-pyridyloxy)-1,3,5-triazine **4**: $^1\text{H-NMR}$ (CD_3OD , 200 MHz) δ 8.33 (s, 3H), 7.57 (d, $J = 8$ Hz, 3H), 7.30 (d, $J = 8$ Hz, 3H), 2.50 (s, 9H). $^{13}\text{C-NMR}$ δ 173, 155, 146, 142, 129, 123, 23.

2,4,6-*Tris*[4-(4'-bromophenyl)phenoxy]-1,3,5-triazine **5**: $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ 7.52 (d, $J = 8$ Hz, 6H), 7.51 (d, $J = 8$ Hz, 6H), 7.35 (d, $J = 8$ Hz, 6H), 7.20 (d, $J = 8$ Hz, 6H). $^{13}\text{C-NMR}$ δ 168, 146, 134, 133, 127, 123, 122, 116.

Crystallography

Reflections were collected for the single crystal of **2**·collidine, **2**·mesitylene, **3** and **5** on a Siemens SMART CCD area detector system at 123(2) K, 183(2) K, 223(2) K and 183(2) K, respectively (Mo- $K\alpha$ radiation, $\lambda = 0.71073$ Å). Data for **4** were collected on a Bruker SMART CCD 1 K area detector at 293(2) K (Mo- $K\alpha$ radiation). Empirical

absorption corrections using SADABS [36–38] were applied for **2**, **3** and **5**. Structure solution and refinement were performed with SHELXS-97 and SHELXL-97 packages [39,40]. Hydrogen atoms were generated with idealised geometries and isotropically refined using the riding model. The guest molecules were refined isotropically. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms was carried out by the full-matrix least-squares method. The final R indices and other crystallographic parameters are listed in Table 1. All C–H distances are neutron normalised to 1.083 Å for the intermolecular contacts in Table 2.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822e instrument and thermogravimetry (TGA) on a Mettler Toledo TGA/SDTA 851e, and data manipulated in the STAR software module. Crystals taken from the mother liquor were blotted dry on a filter paper and placed in open alumina pans for TGA measurements and in crimped aluminium but vented sample pans for DSC measurements. Sample size in each case was 5–7 mg. The temperature range was 30–300°C at a heating rate of 10°C/min. The samples were purged with a stream of dry nitrogen at a flow rate of 150 ml/min for DSC and 50 ml/min for TGA.

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