An organic channel structure formed by the supramolecular assembly of trithiocyanuric acid and 4,4′-bipyridyl

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Trithiocyanuric acid (TCA) and 4,4′-bipyridyl (BP) form hydrogen-bonded co-crystals with aromatic compounds such as benzene, toluene, *p*-xylene and anthracene. The TCA–BP co-crystal is composed of cavities formed by the N–H⋯N hydrogen bonds between the two molecules, and the three-dimensional structure contains channels of approximately 10 Å where aromatic molecules are accommodated. The molar ratios of TCA, BP and the aromatic compound in the co-crystals are 2:1:1 or 2:1:0.5. Benzene, toluene and *p*-xylene are removed from the channels around 190, 183 and 170 °C respectively, and these aromatic guests can be reintroduced into the empty channels of the apo-hosts. The apo-hosts with empty channels have reasonable thermal stability and exhibit shape selectivity in that the empty channels accommodate *p*-xylene but not *m*- or *o*-xylene or mesitylene.

1 Introduction

A variety of inorganic microporous solids have been synthesized in recent years because of their use in catalysis and separation technology.[1–3] These structures are generally prepared by using structure-directing template molecules such as organic amines. Organic amines are also employed extensively to synthesize open-framework metal phosphates and carboxylates.[3] A few organic porous structures containing transition metal ions have been synthesized.[4,5] The supramolecular assembly formed by trimesic acid (benzene-1,3,5-tricarboxylic acid) with cobalt nitrate and pyridine reported by Yaghi *et al.*[4] is a good example of such a metal–organic microporous material. The recently reported nanoporous material formed between trimesic acid and cupric nitrate reported by Chui *et al.*[6] highlights the role of metal–organic interactions in supramolecular assemblies. There is also considerable interest in designing organic microporous solids by making use of supramolecular assemblies. Thus, hexagonal channel structures formed by trimesic acid and its anion have been described.[7] There are also other organic channel structures comprising large pores in three-dimensional structures reported in the literature.[8,9] The nanoporous molecular sandwiches formed by guanidium ions and disulfonate ions serve as representative examples.[8] It has been shown recently that the hexagonal rosette structure formed through hydrogen bonding between cyanuric acid and melamine gives rise to channels in the three-dimensional structure.[10] Self-assembly of three-dimensional networks with large chambers has been reported by using a pyridone as the tecton.[11] Inclusion compounds of urea and thiourea as well as the quinol clathrates also belong to this class of organic solids, but they are not engineered supramolecular designs. We have been exploring several possible designs of organic porous solids for some time and have found that the hydrogen bonded co-crystal between trithiocyanuric acid (TCA) and 4,4′-bipyridyl (BP) has channels in the three-dimensional structure that can accommodate benzene.[12] We have carried out detailed investigations to explore whether other aromatic compounds can be introduced in these channels and if so, whether there is shape selectivity. The study has shown that the supramolecular hydrogen-bonded structure formed by TCA and BP accommodates several aromatic molecules, with some shape selectivity and thermal stability.

TCA   **BP**
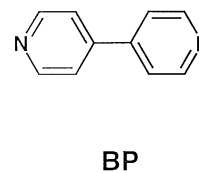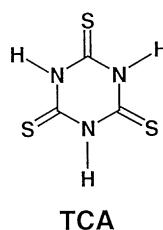
2 Experimental

The 2:1 co-crystal of TCA with BP was first prepared by the co-crystallization of the two compounds in methanol solution, but the crystals were not very stable, because of the loss of methanol. After the loss of methanol, the crystallinity was not sufficiently good to carry out a single crystal study. In the presence of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene or anthracene, however, the crystals of the 2:1 co-crystal of TCA and BP were stable. In a typical preparation, 106 mg of TCA and 47 mg of BP were taken up in 15 mL of methanol in the presence of an aromatic compound (5 mL). In the case of anthracene, the same quantities of TCA and BP as above were taken up in 15 mL of methanol along with 55 mg of anthracene. After slow evaporation, crystals containing the 2:1 co-crystal of TCA with BP, containing different proportions of the aromatic compounds were obtained. We designate the co-crystals containing benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and anthracene by **1**, **2**, **3**, **4**, **5** and **6** respectively. We could not prepare the 2:1 TCA–BP cocrystal with mesitylene. The crystals were generally needle-shaped and yellow in colour. The as-prepared crystals were dried at room temperature over a period of two days prior to the characterization studies.

Crystals of **1–6** prepared as above were employed for the determination of molecular structure by single crystal X-ray diffraction. The relevant details of the crystal structures of the co-crystals are listed in Table 1.† The intensity data were collected on a SMART system, Siemens, equipped with a CCD area detector,[13] using Mo-Kα radiation. The structures were solved and refined using SHELXTL[14] software. The refinements were uncomplicated and converged to good *R*-factors as

†CCDC reference number 1145/171. See http://www.rsc.org/suppdata/jm/1999/2407 for crystallographic files in .cif format.

Table 1 Crystal data for the complexes, 1–6, formed between trithiocyanuric acid and 4,4′-bipyridyl along with various guest molecules

	1	2	3	4	5	6
Formulae	$2(C_3H_3N_3S_3)$: $C_{10}H_8N_2$:C_6H_6	$2(C_3H_3N_3S_3)$: $C_{10}H_8N_2$:C_7H_8	$2(C_3H_3N_3S_3)$: $C_{10}H_8N_2$:C_8H_{10}	$2(C_3H_3N_3S_3)$: $C_{10}H_8N_2$:C_8H_{10}	$2(C_3H_3N_3S_3)$: $(C_{10}H_8N_2)$: $0.5(C_8H_{10})$	$2(C_3H_3N_3S_3)$: $C_{10}H_8N_2$: $0.5(C_{14}H_{10})$
Mol. wt.	588.82	602.85	616.87	616.87	872.23	599.82
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.018(1)	7.112(1)	7.282(1)	10.324(1)	10.359(1)	10.472(1)
b/Å	10.344(1)	10.489(1)	10.621(1)	11.615(1)	11.467(1)	11.419(1)
c/Å	10.757(1)	10.681(1)	10.648(1)	12.319(1)	18.412(1)	12.932(1)
α/°	63.75(1)	65.40(1)	66.30(1)	102.16(1)	83.65(1)	100.46(1)
β/°	75.78(1)	76.58(1)	76.53(1)	93.46(1)	75.00(1)	107.69(2)
γ/°	73.82(1)	73.05(1)	70.42(1)	90.68(1)	67.94(1)	111.28(2)
Cell vol./Å^3	665.8(1)	687.4(1)	705.9(1)	1441.0(2)	1957.7(3)	1296.5(2)
Z	1	1	1	2	1	2
μ/mm^{-1}	0.54	0.53	0.52	0.51	0.55	0.56
T/K	293	293	293	293	293	293
Total reflectn.	2581	2887	2781	6134	7548	4996
Non-zero reflectn.	1838	1928	1970	4109	5489	3556
R	0.032	0.063	0.067	0.082	0.058	0.049
R_w	0.077	0.183	0.184	0.219	0.132	0.098

shown in Table 1. Except for the atoms of the guest molecules (toluene, o-xylene and m-xylene) in the complexes **2**, **3** and **4**, all the other atoms are oriented in well resolved positions. Non-hydrogen atoms in all the structures except guest molecules in **2**, **3** and **4** were refined anisotropically while the hydrogen atoms were refined isotropically, except in the structures where the hydrogen atoms were placed in the calculated positions using AFIX routines of SHELXTL. The guest molecules in **2** and **5** were refined isotropically only owing to the disorder. The crystal structures reveal that the ratio of TCA, BP and the aromatic molecules in the co-crystals **1–4** was 2:1:1. The ratio was 2:1:0.5 in **5** and **6**. We see from Table 1 that the unit cells of **1–3** are similar and the unit cells of **4–6** form another set. As an illustrative example, we list the structural parameters of **2** in Table 2. These data typify the structures of the TCA–BP co-crystals examined here. We have not given the data for the other co-crystals for the purpose of brevity. Intermolecular interactions were calculated using the PLATON[15] programme.

Thermogravimetric analysis (TGA) of the co-crystals was carried out over the temperature range 25 °C to 200 °C by employing a Mettler Toledo instrument. These curves showed mass loss due to the removal of the aromatic guest molecules. The apo-hosts thus obtained did not dissolve in benzene and other aromatic solvents. The apo-hosts were immersed in the respective aromatic liquid for several hours. The crystals were then taken out, and the TGA repeated. This procedure was repeated more than once to find out whether the inclusion of the guest molecule was reversible and also whether there was any change in the temperature of decomposition or the proportion of the aromatic compound in the co-crystal, with such cycling.

3 Results and discussion

Co-crystallization of TCA with BP from methanol solution gives a 2:1 hydrogen bonded co-crystal containing the solvent of crystallization. The crystal structure of the co-crystal reveals the presence of intermolecular N–H⋯N hydrogen bonds between TCA and BP as shown in Fig. 1. This hydrogen bonded structure has a cavity of 10 Å (calculated using CERIUS, version 3.0), occupied by methanol molecules. These crystals were unstable under ambient conditions because of the evaporation of methanol. However the 2:1:1 co-crystals of TCA with BP incorporating benzene, **1**, or toluene, **2**, were highly stable. These crystals gave the same two-dimensional hydrogen bonded structure with a cavity as in Fig. 1. Besides

Table 2 Bond lengths and angles of **2**

Distances/Å		Angles/°	
S(23)–C(23)	1.654(6)	C(21)–N(23)–C(23)	123.3(5)
S(22)–C(22)	1.651(6)	C(16)–C(11)–C(12)	116.5(6)
S(21)–C(21)	1.662(6)	N(14)–C(15)–C(16)	122.4(7)
N(23)–C(21)	1.357(8)	C(22)–N(22)–C(23)	125.4(5)
N(23)–C(23)	1.369(8)	C(13)–C(12)–C(11)	119.6(6)
C(11)–C(16)	1.387(9)	N(23)–C(23)–N(22)	115.8(5)
C(11)–C(12)	1.393(9)	N(23)–C(23)–S(23)	123.4(4)
C(15)–N(14)	1.339(8)	N(22)–C(23)–S(23)	120.9(5)
C(15)–C(16)	1.393(9)	C(11)–C(16)–C(15)	120.5(6)
N(22)–C(22)	1.363(7)	C(22)–N(21)–C(21)	126.1(5)
N(22)–C(23)	1.378(7)	N(21)–C(22)–N(22)	113.4(5)
C(12)–C(13)	1.392(9)	N(21)–C(22)–S(22)	122.8(5)
N(21)–C(22)	1.361(8)	N(22)–C(22)–S(22)	123.7(5)
N(21)–C(21)	1.369(7)	C(13)–N(14)–C(15)	117.5(6)
N(14)–C(13)	1.327(9)	N(23)–C(21)–N(21)	115.9(6)
C(4)–C(7)	1.26(3)	N(14)–C(13)–C(12)	123.5(7)
C(4)–C(5)	1.47(3)	C(7)–C(4)–C(5)	71(2)
C(4)–C(6)	1.78(3)	C(7)–C(4)–C(6)	115(2)
C(3)–C(5)	1.35(4)	C(5)–C(3)–C(6)	50(2)
C(3)–C(6)	1.53(4)	C(5)–C(3)–C(2)	88(3)
C(3)–C(2)	1.97(5)	C(6)–C(3)–C(2)	38(2)
C(5)–C(6)	1.23(3)	C(6)–C(5)–C(3)	72(3)
C(5)–C(7)	1.60(3)	C(6)–C(5)–C(4)	82(2)
C(2)–C(6)	1.20(3)	C(3)–C(5)–C(4)	154(4)
		C(6)–C(5)–C(7)	130(3)
		C(3)–C(5)–C(7)	158(4)
		C(6)–C(2)–C(3)	51(2)
		C(2)–C(6)–C(5)	148(3)
		C(2)–C(6)–C(3)	91(3)
		C(5)–C(6)–C(3)	57(2)
		C(2)–C(6)–C(4)	157(3)
		C(5)–C(6)–C(4)	55(2)
		C(3)–C(6)–C(4)	112(3)
		C(4)–C(7)–C(5)	61(2)

the strong N–H⋯N bonds (H⋯N, 1.82 Å) responsible for the formation of the cavity, there are weak C–H⋯S bonds (H⋯S, 2.91, 2.93 Å) between the TCA and BP molecules. In addition, there are N–H⋯S hydrogen bonds between TCA molecules (H⋯S, 2.5 Å). The three-dimensional structure of **2** is shown in Fig. 2. The structure clearly reveals the presence of channels formed by the stacking of the layers with cavities. The channels accommodate aromatic molecules as can be seen in Fig. 2(a). Fig. 2(b) shows another projection of **2** where we see layers of TCA·BP with toluene molecules residing in the regions of the
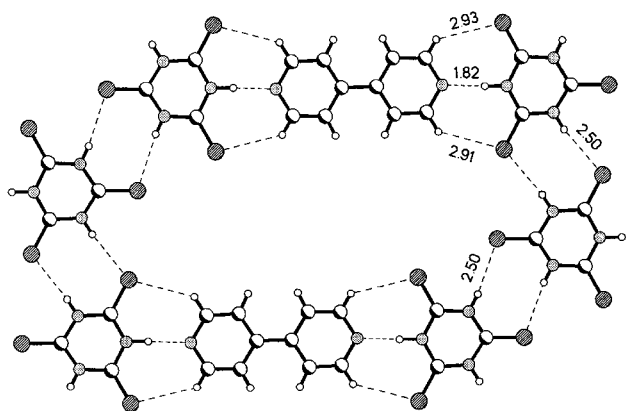
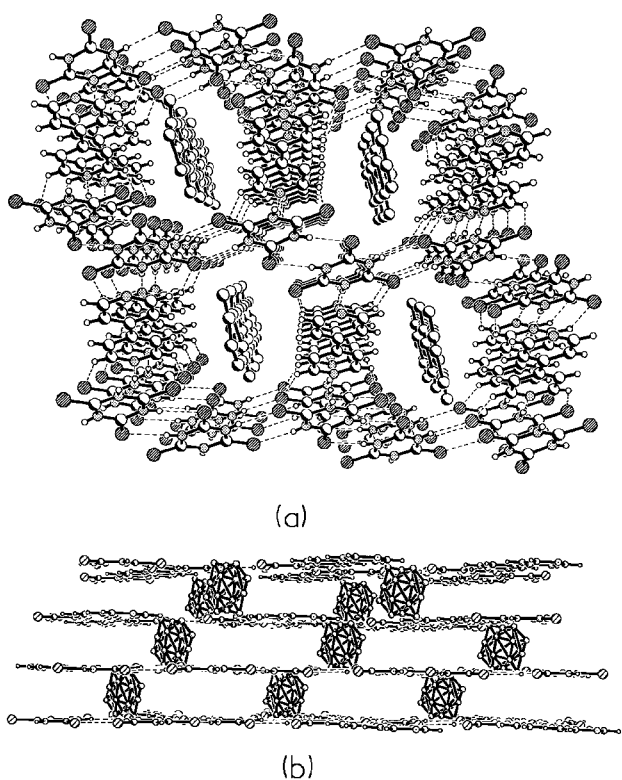Fig. 1 Self assembly of TCA and BP forming a layered network with a cavity.

(a)

(b)

Fig. 2 (a) Three-dimensional structure of the 2:1 TCA–BP co-crystal containing toluene, 2, in the channels. (b) Stacking arrangement of molecular sheets perpendicular to the channels.

cavity. The crystals were stable and heating them up to 180 °C or slightly higher, did not destroy them.

The hydrogen-bonding pattern observed in **1** is interesting in terms of the multi-point recognition.[16] The hydrogen-bonding pattern with one N–H⋯N and two C–H⋯S bonds corresponds to the highly robust three-point recognition pattern. Different possible three-point recognition patterns of the type are shown below. While the patterns represented in (a) and (b) correspond to the motifs comprising strong hydrogen bonds, pattern (c) is a result of weak C–H⋯O hydrogen bonds.[17] A search of the Cambridge Structural Database[18] (CSD) suggests that the pattern present in **1** corresponding to (d) is indeed unique. No other such system appears to be reported in the literature.

Crystal structures of **3–6** show that the cavities in these co-crystals are similar to those in **2**, a minor exception being **4** containing *m*-xylene, where the size and shape of the cavity are somewhat different. In Fig. 3, we show the two-dimensional

(a)   (b)   (c)   (d)
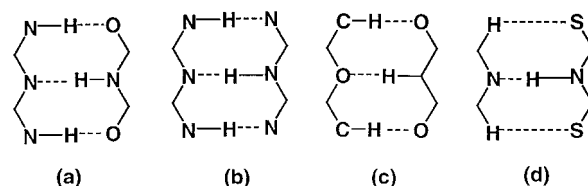
structure of the TCA–BP in **4** to illustrate the small differences between the cavities in this co-crystal and **1**. Here, the intermolecular N–H⋯N as well as the C–H⋯S bonds are slightly longer but the N–H⋯S bonds between the TCA molecules are similar to those in **2** (Fig. 1). A noticeable difference is the slight asymmetry in the cavity arising from the different intermolecular hydrogen bond distances on the two sides. In Fig. 4a, we show the three-dimensional structure of **6** where the guest molecule is anthracene. In Fig. 4b, we show another projection of **6** showing TCA·BP layers wherein anthracene molecules protrude through the cavity. Fig. 2 and 4 serve to demonstrate the similarity of the three-dimensional channels in the various co-crystals.

In Fig. 5, we show the TGA curve of the benzene co-crystal **1**, recorded at a heating rate of 2 °C min⁻¹. All the benzene is removed (mass loss, 13.9%) around 190 °C which is well above the boiling point of benzene (see curve 1). After the removal of benzene, the apo-host crystals were soaked in benzene for 36 hours and again subjected to TGA. (These crystals are insoluble in benzene as evidenced by the retention of the crystal morphology and absence of the relevant spots on the TLC plates.) The crystals showed the loss of benzene at a slightly lower temperature (158 °C), but the quantity of benzene in the channels is less by about 4% (see curve 2 in Fig. 5), compared to the as-prepared co-crystal. A repetition of this procedure showed that the removal of benzene continued to occur around 158 °C with the same mass loss (curve 3 in Fig. 5). It appears that after the benzene in the channels of the initial co-crystal is removed, there are some definitive changes in the channel structure, with the empty channels accommodating benzene to a smaller extent. The lower temperature at which benzene is removed also suggests that the guest molecules do not interact as strongly with the host channels. One difference that we notice is that the weak C–H⋯S interactions present in the as-formed co-crystal is absent after the removal of the guest molecules. The crystal structure of the TCA–BP co-crystal **1** heated to 200 °C (to remove all the benzene) gave a single crystal X-ray diffraction pattern, but the data were not sufficiently good to obtain the structure. We could not determine the structure after reintroducing benzene. Powder
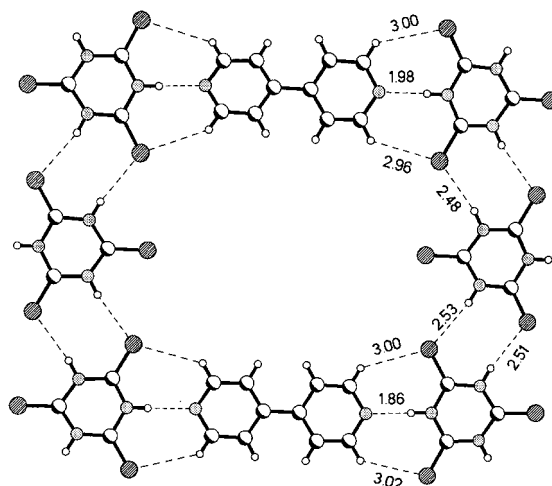

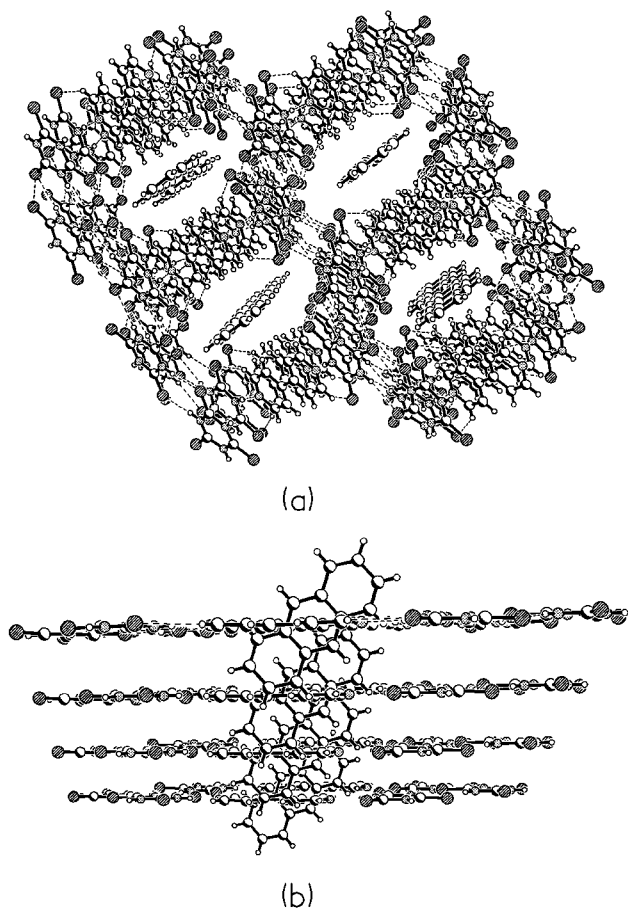Fig. 3 The two-dimensional layered network in the TCA–BP co-crystal containing *m*-xylene, **4**.

Fig. 4 (a) Three-dimensional structure of the 2:1 TCA–BP co-crystal containing anthracene, **6**. (b) Stacking arrangement of planar molecular sheets perpendicular to the channels.

XRD patterns were identical after two cycles of guest removal, but the patterns of the apo-host were generally poorer in quality.

TGA of the toluene co-crystal **2** showed a mass loss of 14.8% at 183 °C. The host crystals with the empty channels were soaked in toluene for 36 hours and then subjected to TGA. These crystals showed a mass loss of 9.2% at 166 °C, a behaviour similar to that of the benzene co-crystal, **1**. TGA of the *p*-xylene cocrystal, **5**, showed a mass loss (12.2%) due to the removal of the aromatic guest around 167 °C. After reintroduction of *p*-xylene in the channels, the mass loss occurred around 139 °C, but the magnitude of mass loss was smaller
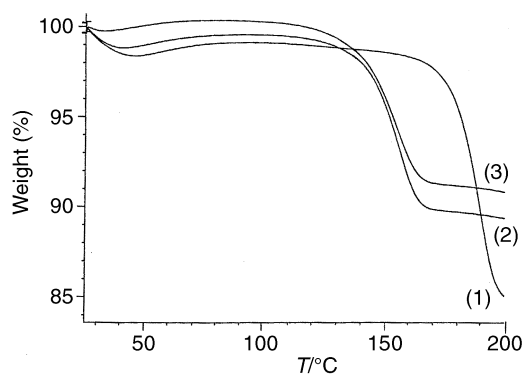

Fig. 5 Thermogravimetic analysis (heating rate 2 °C min⁻¹) of the 2:1 TCA–BP co-crystal containing benzene. Curve 1 is that of the as-prepared sample. Curve 2 was obtained with a sample obtained by immersing the host crystal with empty channels in the aromatic liquid for several hours. Curve 3 was obtained after repeating this procedure for a second time.

(8%). The temperature of decomposition and the mass loss did not change appreciably after further cycling in these cases as well. The co-crystals of *o*-, *m*-xylene, **3** and **4**, however, behaved entirely differently. Once the guest molecules were removed, they could not be reintroduced in the channels even after soaking the host crystals with empty channels for long periods. This observation suggests that there is some selectivity in the channels of the TCA–BP co-crystal. This can be understood from the differences in the shapes of *p*-, *o*- and *m*-xylenes. In *p*-xylene, the two methyl groups are symmetrically positioned and favor the ready re-incorporation into the channels of the host crystal. This is not the case in the other two isomers. Accordingly, the empty channel of the TCA–BP co-crystal only takes in *p*-xylene from a mixture of the three xylene isomers. It should be recalled that the channel does not accommodate mesitylene as well. In the apo-host obtained by removing benzene from co-crystal **1**, toluene could be introduced readily, but not *p*-xylene. We have attempted to understand the selectivity of the apo-host channels by carrying out powder XRD measurements before and after the removal of the guest molecules. Although the apo-hosts are still crystalline, we have not yet been able to come to any meaningful conclusions from the XRD patterns since the data are not entirely sufficient.

4 Conclusions

The stable organic solid containing channels formed by the supramolecular hydrogen-bonded assembly of trithiocyanuric acid and 4,4′-bipyridyl can accommodate aromatic molecules such as benzene, toluene and *p*-xylene. The apo-host is thermally stable up to 200 °C and exhibits shape selectivity with respect to the xylene isomers. The channels do not accommodate mesitylene. It would be interesting to carry out chemical reactions in these channels.

5 References

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