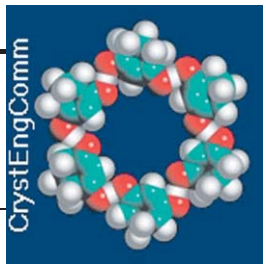
Host–guest and network structures of some tetraphenylmethane derivatives†



Paper

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Dinitro and tetracyano derivatives of tetraphenylmethane (TPM) are identified as new host materials that include THF, water and MeCN. The crystal structures of the host–guest complexes are reminiscent to those of the related host compound tetranitrotetraphenylmethane (TNTPM) studied by us previously. Guest loss has been measured quantitatively. The crystal structures are characterized by O–H···O, C–H···O, C–H···N and C–H···π interactions. It is interesting to note that while the unsubstituted TPM and some of its other derivatives form guest-free crystals, the nitro and cyano derivatives form more open structures.

Introduction

Crystal engineering has grown into a subject that attracts intense attention because the ability to control molecular organization in the solid state can lead to materials with novel structure and function.[1] A contemporary concern is the construction of rigid and porous three-dimensional network structures.[2] In this context, there have been major advances with organic–inorganic hybrid systems.[3] However, much interesting structural chemistry has also emerged from all-organic systems.[4] Typically, a tetrahedral molecule with "sticky sites" assembles into a diamondoid network that may interpenetrate and/or include guest molecules. The interactions of these sticky sites should be strong, specific and directional, so that they play a dominant role in determining how neighbouring molecules are oriented, despite competition from other interactions. The recent work of Wuest and co-workers on extremely porous solids is notable in this connection.[5]

Keeping within the theme of tetrahedral molecules, the crystal chemistry of the tetraphenylmethanes (TPM) has always offered opportunities for the study of packing preferences and solid-state properties.[6] We have previously discussed the structural chemistry of the inclusion compounds of tetrakis(4-nitrophenyl)methane, TNTPM.[7] This host forms diamondoid and rhombohedral networks. In the present study, we report the guest inclusion properties of related hosts bis(4-nitrophenyl)-diphenylmethane, DNTPM, and tetrakis(4-cyanophenyl)methane, TCTPM. DNTPM forms solvates with water and THF. TCTPM forms an acetonitrile solvate. The guest free form (apohost) of TCTPM forms a close packed structure.

† Electronic supplementary information (ESI) available: ORTEP diagrams of the compounds in this study; structure solution and refinement details for $(TCTPM)\cdot(MeCN)_{0.5}$. See http://www.rsc.org/suppdata/ce/b4/b403858b/

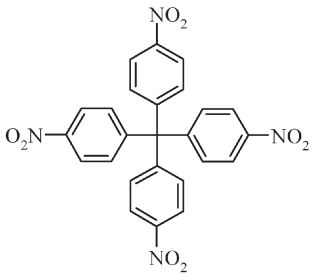
Experimental

1. Synthesis

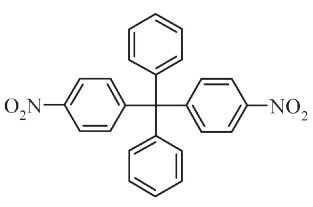
DNTPM was prepared from 4-nitrotriphenylmethanol and aniline according to the literature procedure.[8] The initial product, 4-nitro-4′-aminotetraphenylmethane was purified and recrystallized from 1:1 $MeOH/CH_2Cl_2$. Oxidation to the dinitro derivative was carried out with peroxytrifluoroacetic acid. The crude product was purified *via* column chromatography. mp 240 °C, ^{1}H NMR δ ($CDCl_3$) 8.15 (d, *J* 9, 4 H), 7.45 (d, *J* 9, 4 H), 7.41–7.16 (m, 10H). IR (KBr): 3090, 1514, 1344, 1107, 841 cm^{-1}. TCTPM was prepared by treatment of tetrakis(4-bromophenyl)methane with CuCN in dry DMF.[9] The crude product was purified by column chromatography. mp 312 °C, ^{1}H NMR δ ($CDCl_3$) 7.41 (d, *J* 9, 8 H), 7.03 (d, *J* 9, 8 H). IR (KBr): 3067, 2227, 1664, 1481, 1074 cm^{-1}.

2. Recrystallization

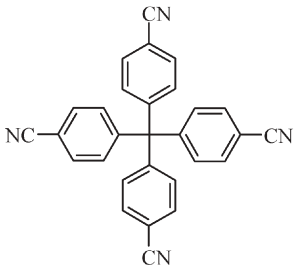
Diffraction quality crystals of DNTPM were obtained from benzene–Et_3N. When DNTPM was crystallized from *n*-hexane–EtOAc, crystals of $(DNTPM)_3\cdot(H_2O)_2$ were obtained. Crystals of (DNTPM)·(THF) were obtained from THF. Crystals of TCTPM and $(TCTPM)\cdot(MeCN)_{0.5}$ were obtained from MeCN.



TNTPM



DNTPM



TCTPM

 DOI: 10.1039/b403858b

Table 1 Crystallographic data for the compounds under study

Compound	DNTPM	$(DNTPM)_3\cdot(H_2O)_2$	(DNTPM)·(THF)	TCTPM	$(TCTPM)\cdot(MeCN)_{0.5}$
Empirical formula	$C_{25}H_{18}N_2O_4$	$C_{75}H_{58}N_6O_{14}$	$C_{78}H_{54}N_6O_{16}$	$C_{29}H_{16}N_4$	$C_{29}H_{16}N_4$
Solvent	C_6H_6–Et_3N	H_2O	THF	MeCN	MeCN
M_w	410.41	1267.27	1331.27	420.5	420.46
Crystal system	Monoclinic	Trigonal	Trigonal	Monoclinic	Orthorhombic
Space group	$P2_1/n$	R–3	R–3	$P2_1/n$	$Pbca$
T/K	293(2)	293(2)	293(3)	293(2)	123(2)
Diffractometer	Nonius FAST	Rigaku AFC7R	Nonius FAST	Enraf-Nonius MACH-3	SMART CCD
a/Å	7.5520(15)	20.909(2)	20.916(3)	9.782(1)	15.413(3)
b/Å	16.296(3)	20.909(2)	20.916(3)	11.907(2)	17.607(3)
c/Å	16.174(3)	25.247(4)	25.122(5)	20.242(3)	18.504(3)
α/°	90	90	90	90	90
β/°	98.71(3)	90	90	98.13(1)	90
γ /°	90	120	120	90	90
Z	4	6	6	4	8
V/Å^3	1967.5(7)	9559(2)	9517(3)	2334.0(3)	5021.5(15)
D_{calc}/g cm^{-3}	1.3856(5)	1.3209(3)	1.3937(4)	1.1944(2)	1.1666(3)
F [000]	856	3972	3591	872	1744
μ/mm^{-1}	0.095	0.092	0.079	0.072	0.067
θ Range/°	2.81–28.68	1.38–24.03	2.39–23.24	2.46–27.28	2.07–22.50
Reflections collected	4771	16506	3012	5432	25749
Unique reflections	4771	3353	3012	5254	3278
Reflections with $I > 2\sigma(I)$	3053	2195	2029	1759 $>6\sigma$(F)	1993
Solution and refinement	SHELX-97	SHELX-97	SHELX-97	SHELX-97	SHELX-97 & SQUEEZE
R_1	0.0642	0.0673	0.0573	0.0664	0.0687
wR_2	0.1530	0.2173	0.1294	0.0857	0.1550

3. X-Ray crystallography

For data collection procedures, see Table 1 which also gives the details of structure solution and refinement.[10a] Atom-labelling schemes of the compounds in this study are provided in the supplementary information.† For $(TCTPM)\cdot(MeCN)_{0.5}$, the disordered MeCN molecules were incorporated in the model using PLATON/SQUEEZE program (see supplementary information).[10b]

CCDC reference numbers 233657–233661.

See http://www.rsc.org/suppdata/ce/b4/b403858b/ for crystallographic data in CIF format.

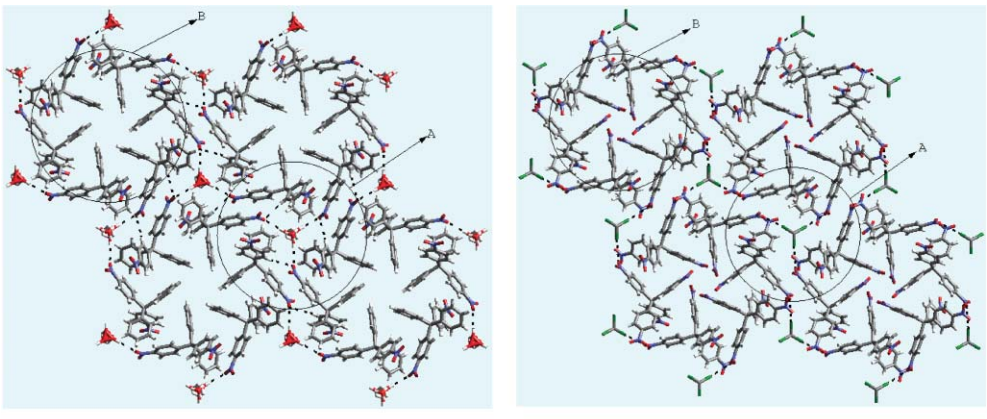
4. Thermal analysis

Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 822e module and thermogravimetry (TG) was performed on a Mettler Toledo TGA/SDTA 851e module. Crystals taken from the mother liquor were blotted dry on filter paper and placed in open alumina pans for the TG experiment and in crimped but vented aluminium sample pans for the DSC experiment. The sample size in each case was 5–7 mg. The temperature range was typically 30–300 °C at a heating rate of 10 °C min^{-1}. A stream of N_2 flowing at 150 mL min^{-1} for the DSC runs and 50 mL min^{-1} for the TG runs purged the samples.

Results and discussion

$(DNTPM)_3\cdot(H_2O)_2$

The rhombohedral crystal structure of this hydrate is reminiscent to the $CHCl_3$ solvate of TNTPM in that the layers may be dissected into trigonal motifs A and B, as shown in Fig. 1. The structure is based on a strong and distinctive pattern of interactions around the guest water molecules (Table 2).[11] That the water is held well by the host framework is shown by the fact that it is not lost upon heating till 168 °C. In motif A, the water molecule is disordered and has a 1/3 site occupancy on the special position forming O–H···O interactions (2.108 Å, 179.6°) with the nitro groups of the host framework (Fig. 2a). The half water molecule lies on the 3-fold axis forming O–H···O interactions with the full water molecule. The three other host molecules in Fig. 2b dovetail such that a phenyl ring is placed in the V-shaped cleft of the neighbour forming C–H···O interactions.[12] In motif B, the host molecules are stabilized by C–H···π interactions. The *meta* C–H group of



a b

Fig. 1 Hexagonal arrangement in (a) DNTPM, (b) TNTPM molecules showing, respectively, the H_2O and $CHCl_3$ molecules. The two motifs A and B are indicated.

Table 2 Selected intermolecular interactions for the compounds in this study

Structure	Interactions	D/Å	d/Å[a]	θ /°
DNTPM	C2–H2···O2	3.235	2.565	119.2
	C8–H8···O4	3.629	2.572	164.8
	C3–H3···O4	3.530	2.501	158.3
$(DNTPM)_3{\cdot}(H_2O)_2$	O2W–H3WB···O1	3.091	2.108	179.6
	O2W–H2WA···O1W	2.863	2.066	124.4
	O1W–H1W···O2W	2.863	2.458	104.2
	C21–H21A···O1	3.702	2.627	171.8
	C9–H9A···O3	3.469	2.564	140.4
	C11–H11A···O3	3.411	2.716	121.6
	C4–H4A···O4	3.442	2.669	126.1
	C9–H9A···O3	3.469	2.564	140.4
	C12–H12A···O2	3.336	2.487	134.3
	C10–H10A···π	3.682	2.837	151.7
(DNTPM)·(THF)	C3–H3A···O3	3.512	2.632	137.9
	C3–H3A···O4	3.677	2.606	170.1
	C4–H4A···O6A	3.544	2.798	126.0
	C1–H1A···O3	3.280	2.461	131.5
	C17–H17A···O1	3.396	2.476	142.0
	C25–H25A···O2	3.345	2.598	125.5
	C24–H24A···O2	3.781	2.706	171.8
	C2–H2A···π	3.653	2.668	150.8
(TCTPM)	C17–H17A···N2	3.641	2.567	170.7
	C10–H10A···N3	3.296	2.526	127.2
	C7–H7A···N4	3.613	2.575	160.1
	C14–H14A···N4	3.638	2.654	150.7
	C28–H28A···N2	3.842	2.765	173.1
$(TCTPM){\cdot}(MeCN)_{0.5}$	C20–H20···N4[b]	3.326	2.290	159.4
	C13–H13···N5	3.305	2.319	150.4
	C24–H24···N2	3.389	2.633	126.3
	C17–H17···N1	3.318	2.641	120.1
	C4–H4···N2	3.584	2.534	163.2

[a] All the C–H and O–H distances are neutron normalized to 1.083 and 0.983 Å. [b] The parameters correspond to the final refinements prior to the SQUEEZE procedure (and including acetonitrile solvent).

one of the phenyl rings interacts with the π-cloud of an adjacent phenyl ring (Fig. 3).[13] The overall arrangement of the motifs down the 3-fold axis is ···ABA ABA ABA··· In this and all other solvates in this study, the host:guest ratio is not strictly stoichiometric and the nearest integral or convenient fractional values are given. In all cases, the solvent is disordered and it is not possible to obtain the exact amount. However, the crystallographic refinement procedure and the TGA experiments lead to nearly the same host:guest ratio in each case.

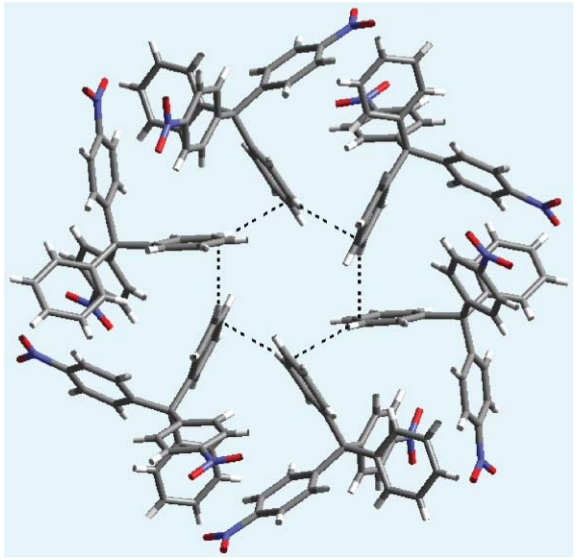


Fig. 3 Motif B in $(DNTPM)_3.(H_2O)_2$ stabilized by C–H···π interactions. Click here to access a 3D view of Fig. 3.

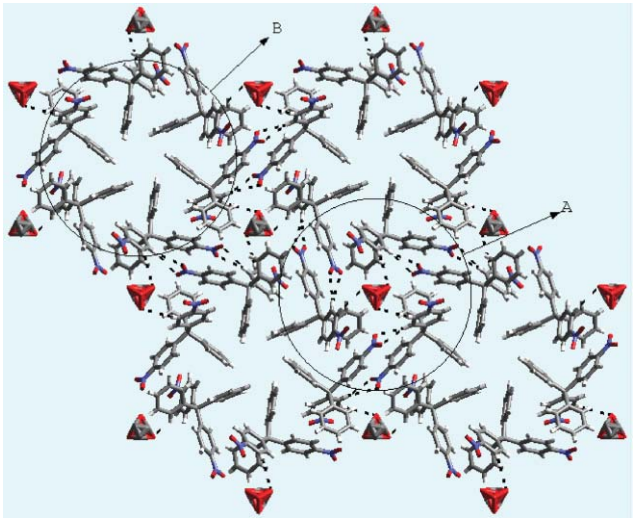
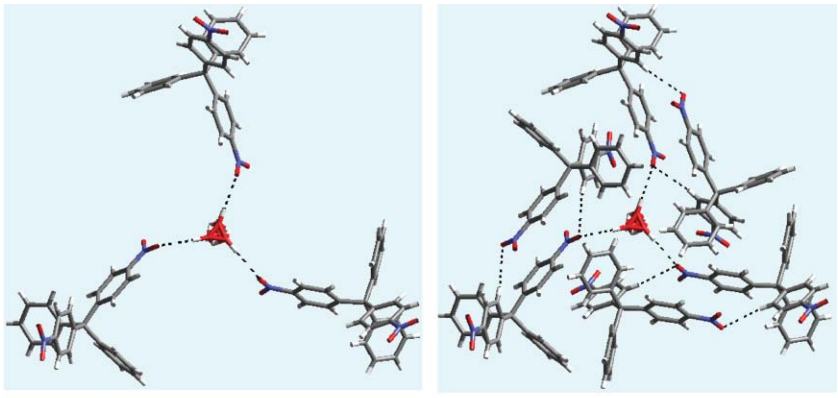


Fig. 4 Hexagonal arrangement of host molecules in (DNTPM)·(THF). Notice motifs A and B.

(DNTPM)·(THF)

The structure of (DNTPM)·(THF) is similar to that of $(DNTPM)_3{\cdot}(H_2O)_2$. In this case, also the layers may be dissected into trigonal motifs A and B as shown in Fig. 4. In the place of water molecules in $(DNTPM)_3{\cdot}(H_2O)_2$, the disordered THF molecule lies in the channels of the host framework forming very weak C–H···O interactions (2.798 Å, 126°) with the host molecules. In motif A, the host framework is stabilized by C–H···O interactions. The *meta* C–H group of the



a **b**

Fig. 2 (a) Motif A in $(DNTPM)_3{\cdot}(H_2O)_2$. The disordered H_2O molecule is connected to three molecules of DNTPM by O–H···O_2N interactions. (b) The three other host molecules are connected to each other by C–H···O interactions.

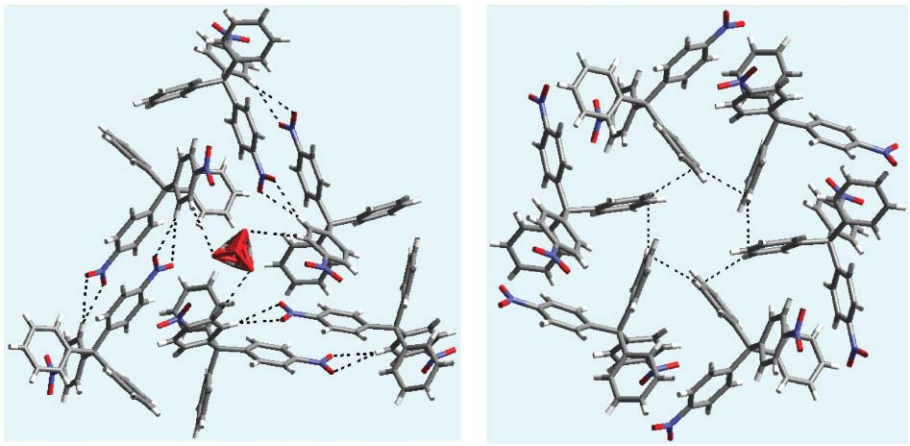


Fig. 5 (a) Disordered THF molecule lying in the channels of host framework in motif A of (DNTPM)·(THF). (b) Motif B is stabilized by C–H···π interactions.

unsubstituted phenyl ring interacts with the neighbouring NO_2 group of the phenyl ring of another DNTPM molecule. Further stabilization is obtained from bifurcated C–H···O hydrogen bonds involving the *meta* C–H groups of the nitro-substituted phenyl rings (Fig. 5a). In motif B, the host framework is stabilized by C–H···π interactions (Fig. 5b). The *meta* C–H of a phenyl ring interacts with the π-ring of an adjacent molecule. Again, the overall projection of motifs down the unique axis is ···ABA ABA ABA···

bis(4-Nitrophenyl)diphenylmethane, DNTPM

The unsolvated form of DNTPM forms a 2-fold interpenetrated network structure. The molecules of DNTPM form a helical chain along the *b*-axis involving C–H···O (2.565 Å, 119.2°) hydrogen bonds. These chains are further connected through other C–H···O bonds (2.572 Å, 164.8°) by another helical chain generating a network in the *ab*-plane. Close packing is achieved by 2-fold parallel interpenetration (Fig. 6). The network extends into three dimensions with other C–H···O interactions.

tetrakis(4-Cyanophenyl)methane, TCTPM

Crystallization of TCTPM from MeCN afforded both the 1:1 solvate and the unsolvated form concomitantly. The latter gives a close packed structure with C–H···N interactions (Fig. 7) forming zigzag tapes along the *b*-axis. These tapes are further connected to inversion related tapes by bifurcated C–H···N interactions. These are extended into three dimensions resulting in a closely packed structure.

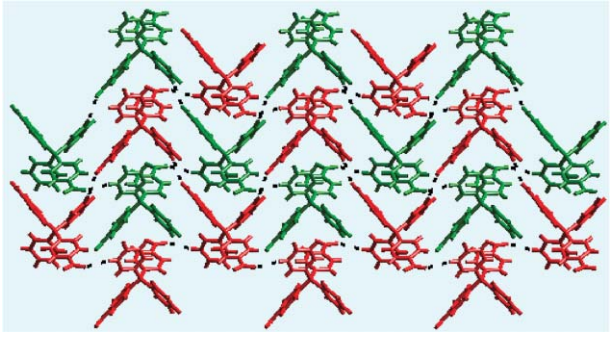


Fig. 6 2D interpenetrated network structure in unsolvated DNTPM. Click here to access a 3D view of Fig. 6.

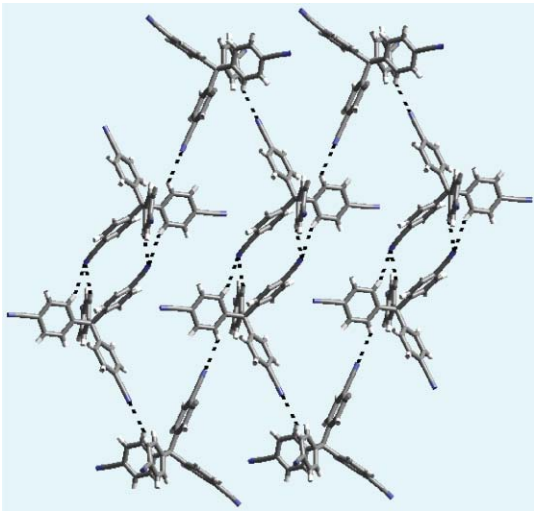


Fig. 7 Zigzag tapes of TCTPM molecules with C–H···N and bifurcated C–H···N interactions form a close packed structure. Click here to access a 3D view of Fig. 7.

$(TCTPM)\cdot(MeCN)_{0.5}$

Six molecules of TCTPM are connected by two disordered MeCN molecules *via* C–H···N hydrogen bonds involving the *meta* C–H groups of the phenyl rings and the MeCN molecules, generating hexagonal networks in the *ab*-plane. The hexagonal networks close pack with inclined 3-fold interpenetration (Fig. 8).[14] The networks are held together by C–H···N (2.633 Å, 126.3°) *internetwork interactions* involving the *meta* C–H groups of the phenyl rings and the MeCN molecules. A schematic representation of the hexagonal network and the 3-fold interpenetration is shown in Fig. 9.

Thermal analysis

To study the thermal behavior of the inclusion compounds under study, TGA/DSC were performed on $(DNTPM)_3\cdot(H_2O)_2$ and (DNTPM)·(THF). These results are shown in Fig. 10. For $(DNTPM)_3\cdot(H_2O)_2$, guest loss takes place in a single step. The inclusion compound is stable up to 168 °C, because of the hydrogen bonds and the aromatic nature of the host that binds the guest molecules tightly. The DSC trace shows a broad endotherm with an onset temperature of 168 °C, corresponding to guest loss. A sharp endotherm at 240 °C corresponds to the melting of the host. In (DNTPM)·(THF), the guest loss

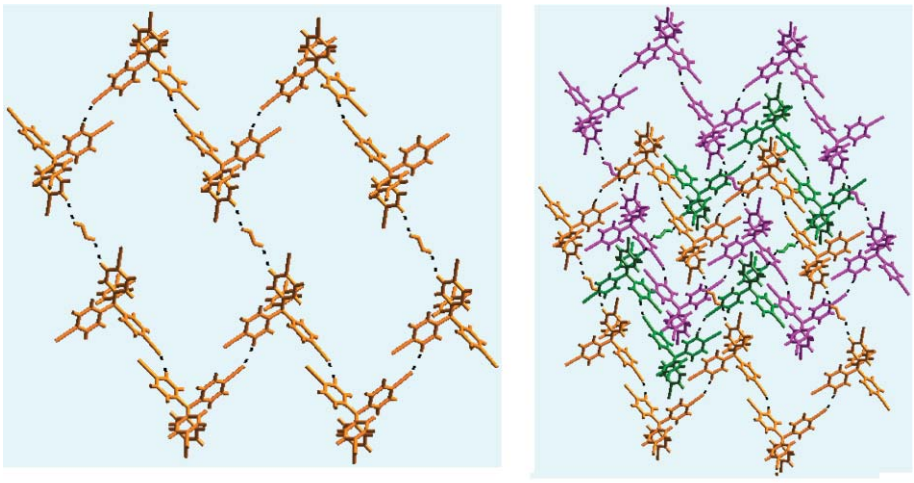


Fig. 8 (a) Hexagonal network in (TCTPM)·$(MeCN)_{0.5}$. (b) 3-fold Interpenetration of hexagonal networks. The methyl groups of the disordered MeCN molecules are removed for clarity (these figures are generated from the model before using the SQUEEZE program).

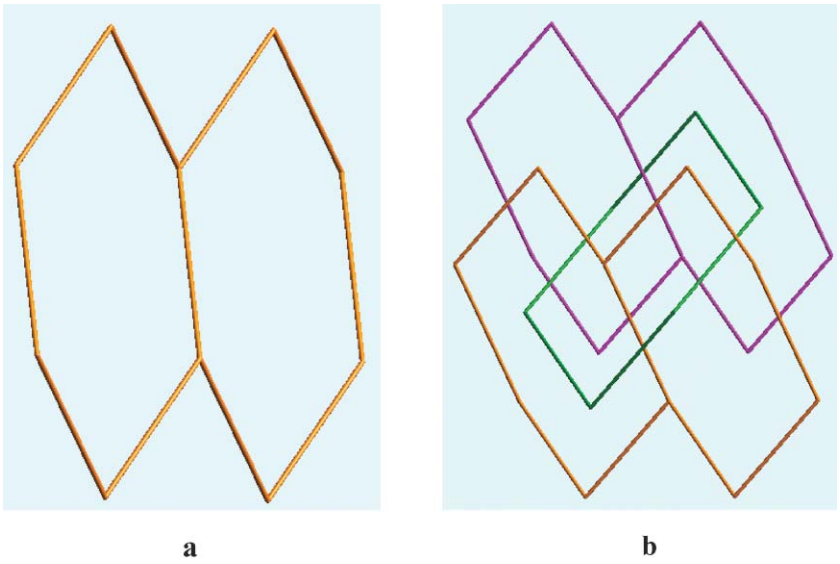


Fig. 9 Schematic representation of (a) hexagonal network, (b) 3-fold inclined interpenetration.

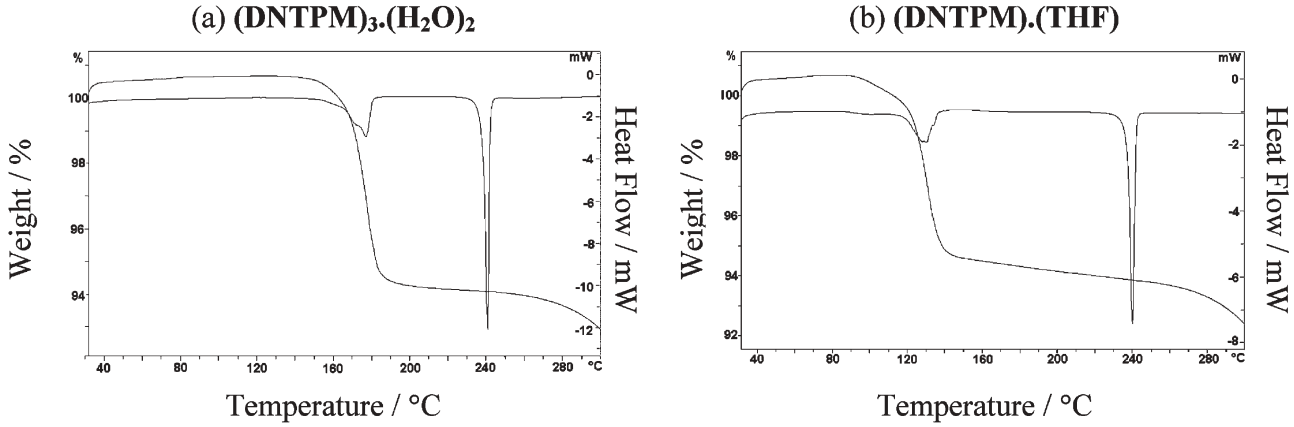


Fig. 10 TGA/DSC traces for the inclusion compounds (a) $(DNTPM)_3·(H_2O)_2$ and (b) (DNTPM)·(THF).

reaction also takes place in a single step and the inclusion compound is stable up to 119 °C. The DSC trace shows a broad endotherm with an onset temperature of 119 °C, corresponding to guest loss and a sharp endotherm at 240 °C, corresponding to the melting of the host.[15]

Conclusions

Although a smaller number of nitro groups are present in DNTPM when compared with TNTPM, guest inclusion properties are retained in contrast to the unsubstituted TPM which

forms guest-free crystals. The device of nitro-substitution on a TPM framework therefore appears to be a promising strategy to generate new host materials. Rigidity of the host molecule seems to be the key to promoting guest inclusion properties. With regard to TCTPM, more work needs to be done before any generalisation may be made with respect to guest inclusion. However, our initial experiment suggests that TCTPM is different from tetrabromo-TPM which forms only guest-free crystals.[16] Further studies with other guest molecules are in progress.

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