

A comparative study of crystal structures and inclusion properties of fluorinated triazines

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Abstract

Three perfluorinated host compounds of the triazine type, namely 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine (**1**), 2,4,6-tris(pentafluorothiophenoxy)-1,3,5-triazine (**2**) and 2,4,6-tris(pentafluorophenamin)-1,3,5-triazine (**3**), were synthesized differing only in the linking heteroatom (O, S and NH) between the triazine core and the pentafluorophenyl groups. The crystal structures involving compounds **1**, **2** and their inclusion compounds are dominated by a variety of fluorine interactions (phenyl-perfluorophenyl, C–H...F, F...F, C–F...π_F). However, in the structure of **3**, possessing additional hydrogen atoms of the linkage NH-groups, the formation of hydrogen bonds is favoured, whereas fluorine contacts are less apparent. Investigations by powder X-ray diffraction and thermogravimetric analysis revealed substantial differences in the host–guest interactions of the inclusion compounds.

Keywords: Fluorine compounds; Triazines; Inclusions; Host–guest compounds; Fluorine interactions

1. Introduction

Over the last few years fluorine has become more and more important in crystal engineering [1]. Up to now a number of fluorinated compounds were synthesised to investigate phenyl-perfluorophenyl [2], H...F [3], F...F [4] and C–F...π_F [5] interactions to study their influence on crystal structures [6,7].

However, unexpected behaviour of fluorine is seen in the case of hydrogen bonds: as fluorine has the highest electronegativity, it is predestined to form strong hydrogen interactions. In fact, F[−] is one of the best hydrogen acceptors, but the so called “organic fluorine ... hardly ever accepts hydrogen bonds” forming only weak interactions [3]. Except the phenyl-perfluorophenyl stacking, showing a stabilizing energy of about 30 kJ mol^{−1} [8,9], fluorine interactions are mostly weak.

There are only a few examples of fluorine containing compounds that deal with fluorinated inclusion compounds involving the influence of fluoro substituents on host–guest

interaction. One example stems from coordination chemistry, where the fluorination of ligands prevents an interpenetration of molecules allowing the formation of flexible networks [10].

Recently, we reported on a series of phenoxy-substituted 1,3,5-triazines providing evidence for a supramolecular control of fluorine. Here, the highly fluorinated compound 2,4,6-tris(pentafluorophenoxy)-1,3,5-triazine **1** forms channel-type inclusions with *p*-xylene and *p*-chlorotoluene [11]. Consequently, it is of interest to know, how inclusion properties change by replacing the linkage atom between the triazine core and the pentafluorophenyl groups (S or NH). Therefore, we synthesized the compounds 2,4,6-tris(pentafluorothiophenoxy)-1,3,5-triazine **2** and 2,4,6-tris(pentafluorophenamin)-1,3,5-triazine **3**. The present article is highlighting a comparison of five crystal structures involving the free host and respective inclusion compounds with mesitylene and 1,4-dioxane.

2. Results and discussion

A comparison of compounds **1–3** (Fig. 1) revealed substantial differences in the crystal structures and inclusion

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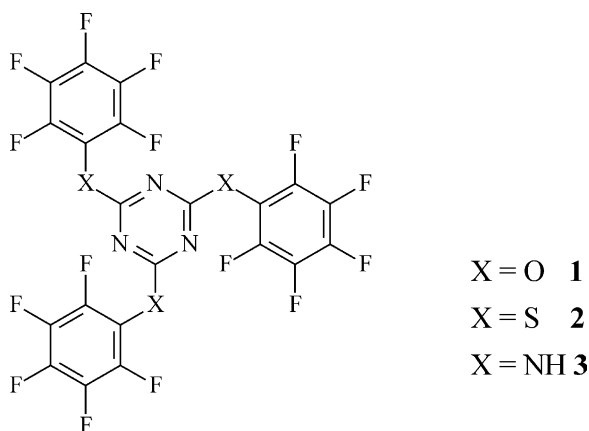


Fig. 1. Molecular structures of perfluorinated triazines.

properties caused by the replacement of the linkage atom oxygen by sulfur or NH-group. All three compounds yielded inclusions with typical guest molecules summarized in Table 1. Inclusions of **1** crystallized all in the same structure, whereas **2** showed channel inclusions exhibiting various crystal packings depending on the guest molecule. In the case of **3**, major differences between crystal structures of inclusions were observed, which seems to be caused by the hydrogen atoms of the NH-group. Consequently, the crystal structures and inclusions of **1** and **2**, on one hand, and that of **3** will be discussed separately.

2.1. Crystal structures of the solvent free compounds and inclusions of **1** and **2**

A previous paper [11] dealt with the crystal structure of the host compound **1**, showing that triazine molecules are arranged in layers, which are stacked congruently along the *a*-axis. Compound **2** features similar properties. Here, triazines build up two different layers that are stacked alternating along the *a*-axis. Neither compound **1** nor **2** show specific interactions. Molecules are closed packed featuring $F \cdots F$ distances in the range of 2.6–2.8 Å.

Compound **1** is known to form channel-type inclusions with guest molecules such as *p*-xylene, *p*-chlorotoluene and *p*-methylbenzotrifluoride showing a host:guest ratio of 2:1. All these inclusions crystallize in the same structure with the triclinic space group $P\bar{1}$. Triazines are stacked congruently along the *a*-axis featuring a distance of about 6 Å. Guest

Table 1
Host:guest ratios for inclusions of **1–3** with various guest molecules

	1	2	3
Xylene	2:1	1:2	1:1
Toluene	–	1:2	1:1
Mesitylene	–	1:1	1:1
Benzene	–	–	1:1
4-Methylbenzotrifluoride	2:1	1:2	
Dioxane	–	–	1:2.5

In the case of **1** and **2**, the ratios were determined by thermogravimetric analysis while the inclusions of **3** were analysed by NMR.

Table 2
Phenyl-pentafluorophenyl contacts in crystal structures of inclusion compounds of **1–3**

	Atoms phenyl(A) ··· pentafluorophenyl(B)	Centroid– centroid distance (Å)	Angle (°)
1 <i>p</i> -Xylene	C31···C4	4.17	30.8
2 Mesitylene	C56···C35	3.59	12.4
	C47···C23	3.70	15.7
	C47···C29	3.66	16.0
3 Mesitylene	C56···C3	3.75	20.7
	C93···C24	3.67	20.6

Phenyl and pentafluorophenyl groups are given by one carbon atom A and B of each group. The centroid is calculated based on six atoms and the angles are determined between the centroid–centroid line and the normal of the phenyl plane.

molecules are accommodated in channels showing a van der Waals cross section of $7.6 \times 3 \text{ \AA}^2$. The channel wall is mainly made up by stacked pentafluorophenyl groups. Short host–guest interactions formed by CH_3 -groups involve weak $\text{C–H} \cdots \text{O}$ (2.9 Å, 117.8°) [12] as well as $\text{C–H} \cdots \pi_{\text{F}}$ hydrogen bond type interactions investigated by solid-state NMR [11]. Measured phenyl-pentafluorophenyl contacts do not show typical values of phenyl-perfluorophenyl stacking (Table 2). Therefore, this feature seems to be caused by the hydrogen interactions of the CH_3 -groups.

Compound **2** formed channel-type inclusions with *p*-xylene, *p*-chlorotoluene, *p*-methylbenzotrifluoride (host:guest ratio: 1:2) and mesitylene (host:guest ratio: 1:1) featuring a larger size.

The crystal structure of **2**-mesitylene (space group $P2_1/n$) is built up by layers, which are formed by host and guest molecules, where one guest is surrounded by four triazines (Fig. 2). These layers are stacked congruently along the *b*-axis with a distance of about 7.9 Å, generating channels with van der Waals cross section of $3.1 \times 5.5 \text{ \AA}^2$ which are smaller compared with the inclusions of **1** (see above). Moreover, unlike $\mathbf{1} \cdot (\textit{p}\text{-xylene})_{0.5}$, where the guest molecules are located around a centre of symmetry, the channels of **2**-mesitylene are unsymmetrical, where one side of the channel wall is built up by fluorine atoms. Thus, in contrast to **1**, the channel wall of the present structure shows a higher density of fluorine atoms giving rise to a higher number of short $\text{F} \cdots \text{H}$ contacts (2.4–2.8 Å) between host and guest molecules (Table 3). **2**-Mesitylene shows phenyl-perfluorophenyl stacking with a centroid–centroid distance of 3.6–3.7 Å and angles of 12–16° (Table 2), which is within the limit of reported values [2].

2.2. Crystal structures and inclusion properties of **3**

Unsolvated single crystals of **3** (obtained by sublimation) crystallized in the space group $P2_1/n$. The structure features a congruent stacking of triazines along the *a*-axis with a distance of 7.8 Å. Similar to the host compounds mentioned above, compound **3** does not show a three-fold symmetry. An essential

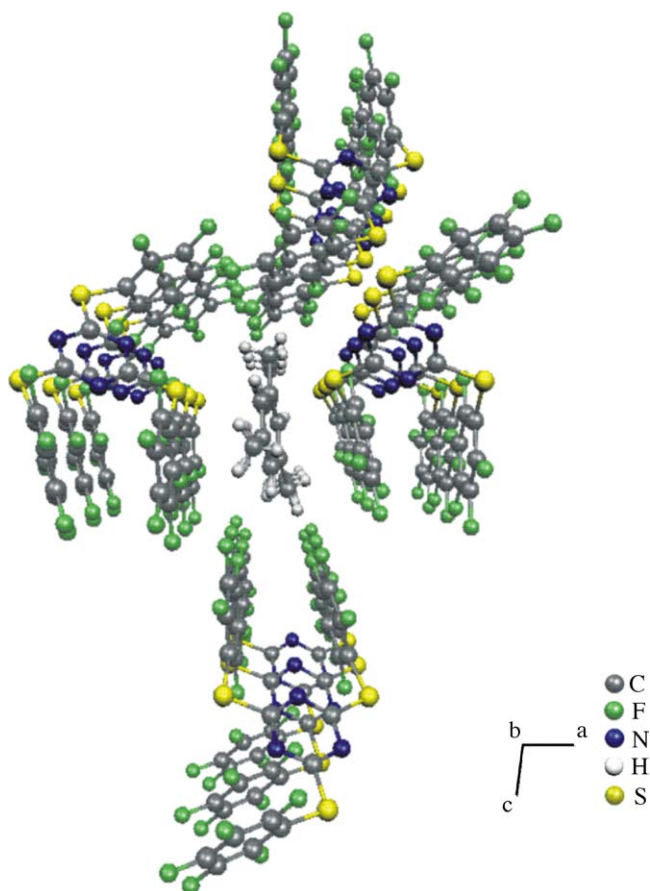


Fig. 2. Channel structure of **2**-mesitylene.

Table 3
Hydrogen bond-type interactions in crystal structures of **1–3**

	Distance (Å)	Angle (°)		
		B···A	D···A	D–B···A
1 -(<i>p</i> -Xylene) _{0.5}	C30–H34A···O1	2.89	3.46	117.75
	C30–H34C···F9	2.68	3.57	150.75
	C30–H34A···F14	2.90	3.65	133.76
	C33–H32···F8	3.09	3.99	159.88
2 -Mesitylene	C64–H64A···F26	2.87	3.86	176.88
	C62–H62C···F25	2.63	3.61	177.66
	C62–H62A···F2	2.68	3.60	155.62
	C59–H59···F27	2.88	3.81	165.46
	C63–H63C···F4	2.91	3.52	103.22
	C53–H53B···F11	2.95	3.87	158.23
	C53–H53A···F17	2.88	3.22	101.55
3	N4–H4···N3	2.12	2.96	174.07
	N6–H5···N2	2.28	3.10	170.00
	N5–H6···F11	2.20	2.99	163.91
3 -Mesitylene	N13–H13A···N6	2.22	3.04	153.74
	N18–H18A···N3	2.25	3.06	153.65
	N17–H17A···F1	2.37	2.98	126.12
	N15–H15A···F16	2.45	3.09	130.58
	C121–H121···F4	2.72	3.49	114.80
	C97–H97A···F16	2.95	3.85	154.31
	C96–H96C···F29	2.90	3.72	142.21
3 -(1,4-Dioxane) _{2.5}	N2–H2···O1	2.10	2.90	160.23

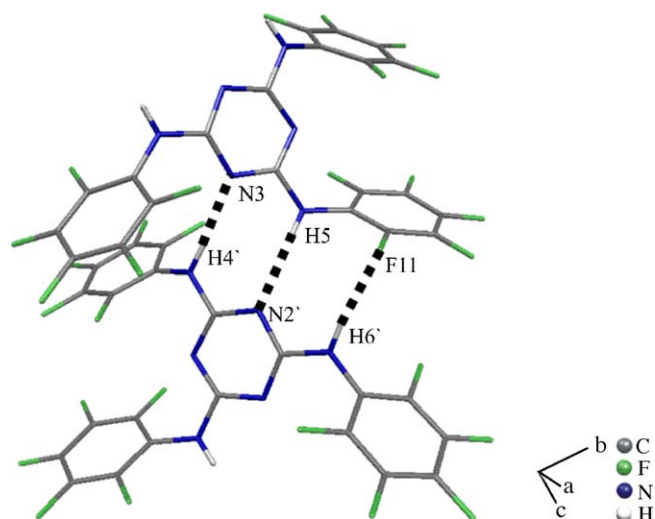


Fig. 3. Motif of hydrogen bond type interactions in the crystal structure of **3**.

difference in the crystal structure of **3** compared to **1** and **2** is caused by the hydrogen atoms of the NH-groups, forming hydrogen bonds between neighbouring triazines (shortest contacts of 2.1 Å) (Table 3), which seem to dominate the structure (Fig. 3). In addition, F···H–N hydrogen bond type contacts were found with a distance of 2.2 Å, being unusually short compared to reported organic fluorine compounds [3]. Measurements of an attractive F···H–N interaction in thrombin derivatives yielded a value of 0.8–1.5 kJ mol⁻¹ [13], which is weak compared to known N–H···N interactions (20–40 kJ mol⁻¹) [14]. A similar kind of interaction pattern was observed in crystal structures of polyfluorophenyl substituted-4,5-dihydropyrazole derivatives, where a slightly larger F···H distance (2.32 Å) was measured [15].

As expected, the particular property of the amino group is also reflected in the inclusion behaviour of **3**, which is broader compared with **1** and **2**, respectively (Table 1). A closer look shows that the host:guest ratios are different in the corresponding inclusions of **3** compared with those of **1** and **2** (except the inclusion of **2** and **3** with mesitylene). Furthermore, 1,4-dioxane was expected to act as guest molecule in the host lattice of **3**. This stimulated the study of inclusions of **3** with mesitylene and 1,4-dioxane.

The inclusion compound of **3** with mesitylene (host–guest 1:1) was crystallized by isothermal evaporation. The structure provides oval channels along the *c*-axis with dimensions of 5.7 × 3.5 Å², built up by four host molecules (Fig. 4a). Two molecules each are connected by N···H hydrogen bonds (N···H: 2.22–2.25 Å) and short F···H contacts (F···H: 2.37–2.44 Å) to form a unit, where two such units are linked by pentafluorophenyl groups showing a close packing of fluorine atoms (F···F: 2.71–2.87 Å). The mesitylene molecules are orientated in the oval channels planar to the pentafluorophenyl substituents of the host showing a centroid–centroid distance of 3.7 Å (Fig. 4b, Table 2).

The inclusion compound of **3** with 1,4-dioxane shows a host:guest ratio of 1:2.5 and crystallizes in the space group *R*3̄.

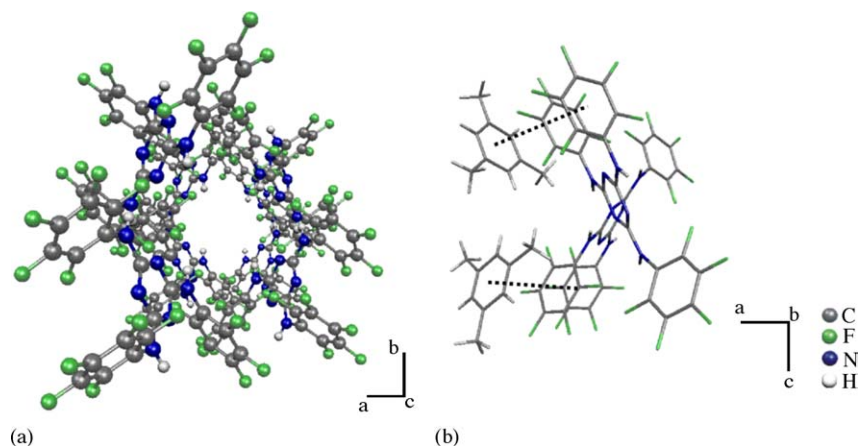


Fig. 4. Crystal structure of **3**-mesitylene: (a) view along the channel of the inclusion; (b) motif showing the host-guest interaction.

Three different positions of guest molecules were found. One dioxane molecule (guest 1), involving atom O1, features a centre of symmetry (C_i), while the two remaining dioxane molecules (guest 2 and guest 3) both possess a three-fold inversion axis (C_{3i}). Guest molecules 2 and 3 are stacked alternatively with triazines along the c -axis following an order of guest 2–host–guest 3–host (Fig. 5b). Guest 1 is located between two host molecules in the (a,b)-layer and forms hydrogen bonds with the amino group of the hosts ($O \cdots H$: 2.1 Å, $N-H \cdots O$: 160°), which can be classified as strong interaction [14] (Fig. 5a and Table 3). Thus, each host is surrounded symmetrically by three dioxane molecules. Noteworthy, this relation leads to a three-fold symmetry of the host molecule, which is only seen in this structure. Fluorine interactions could not be observed here, which might be avoided in favour of strong hydrogen bonds.

2.3. Sorption properties

In the previous paper we have described the reversible sorption property of **1**·(*p*-xylene)_{0.5} [11]. Here, desorption of the guest molecules leads to a complete collapse of the channel

structure, which could be rebuilt by sorption of guest molecules from the gas phase.

Inclusion compounds **2**-mesitylene and **3**-mesitylene, obtained by isothermal evaporation, were exposed to the vacuum for 1 h. The resulting solids were analysed by powder X-ray diffraction. Afterwards, these solids were used for sorption experiments, carried out in a closed flask, in which the host (powder) and the guest component (liquid) were kept in open separated glasses. After 4 days of exposure solid phases were analysed by powder X-ray diffraction.

In all three cases, desorption of guest molecules leads to the structure of the corresponding unsolvated host compound, having lost its specific channel architecture (Fig. 6). However, these channel structures were rebuilt by sorption of guest molecules from the gas phase. This occurred at relative low temperatures (performed at 25 and 50 °C) for all three cases indicating a rather low energetic activation to convert the guest free to the channel structure. A comparison of guest free and channel structure showed, that only weak $F \cdots F$ contacts are broken while more intensive host-guest interactions, such as phenyl-perfluorophenyl, $C-H \cdots \pi_F$ or $C-H \cdots O$ contacts, are generated.

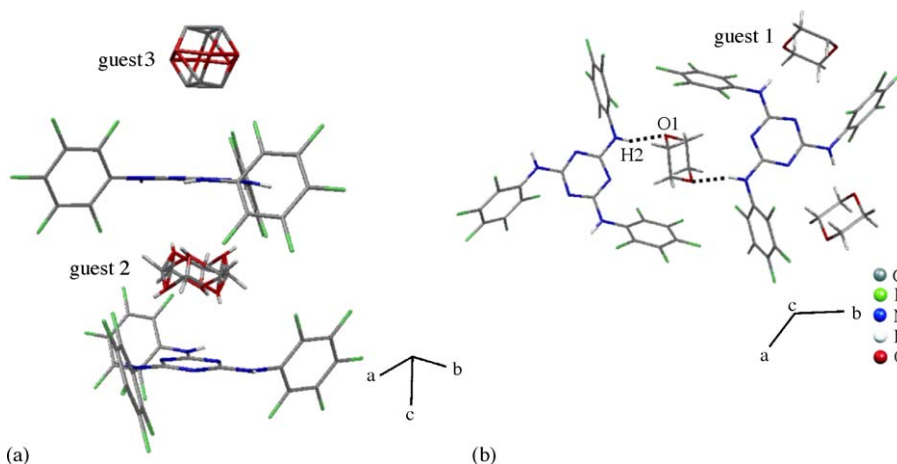


Fig. 5. Crystal structure of **3**·(dioxane)_{2.5}: (a) stacking along the c -axis (order: guest 2–host–guest 3–host); (b) hydrogen bonds of the NH-group with 1,4-dioxane.

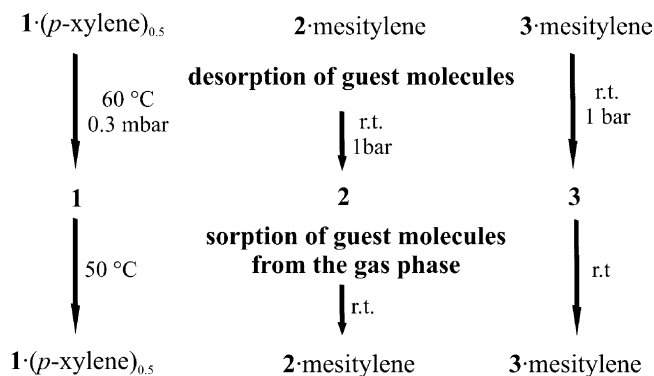


Fig. 6. Reversible sorption properties of the inclusion compounds: **1**·(*p*-xylene)_{0.5}, **2**·mesitylene and **3**·mesitylene.

2.4. Thermogravimetric analysis (TG)

Inclusions of compound **2** showed an onset of desorption of guest molecules already at room temperature. However, inclusions of **1** and **3** featured a higher thermal stability, whereas the onset temperature of desorption for the case of **3** is ordered according to the boiling temperature of the guest. The inclusion compound **3**·(1,4-dioxane)_{2.5} represents an exception since here strong hydrogen bonds act as host–guest interactions.

Inclusions of **1** feature a quite interesting case of thermal stability. Here, the temperature of desorption of guests decreased in the order: *p*-xylene, *p*-chlorotoluene, *p*-methylbenzotrifluoride (Fig. 7a). Thus, exchange of a CH₃ group by a chlorine atom, being roughly of the same size, leads to a decrease of the desorption temperature of about 10 °C, which might be attributed to a loss of hydrogen bonds. This is a suggestive fact that CH₃-groups participate in host–guest interactions (C–H···O and C–H···π_F hydrogen bonds), being confirmed by solid-state NMR [11].

A further type of important host–guest contact, found in inclusions of **2** and **3**, is the phenyl-perfluorophenyl interaction. This kind of interaction is reported to be strong if the phenyl and perfluorophenyl groups are stacked in an alternating manner. However, inclusions of **2** and **3** do not

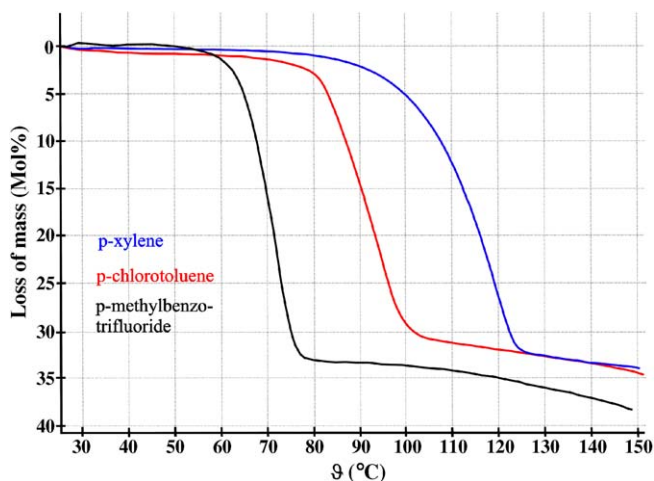


Fig. 7. TG analyses of inclusions of **1**.

form an alternate stacking, which leads to weaker contacts being manifested by the low onset temperature of guest release. Nevertheless, the sum of all the weak interactions affords formation of inclusion compounds.

3. Conclusion

Three perfluorinated triazine compounds differing only in the linking heteroatom (O, S and NH) form inclusions with a number of typical solvent molecules. The alteration of heteroatoms shows an essential effect on crystal structures and inclusion properties.

The crystal structures of the unsolvated hosts of **1** and **2** as well as their inclusion compounds are dominated by a variety of fluorine interactions (phenyl-perfluorophenyl, C–H···F, F···F, C–H···π_F). On the other hand for compound **3**, possessing additional hydrogen atoms, the formation of hydrogen bonds is favoured while fluorine contacts are less apparent. This fact is reflected in the inclusion properties of the host molecules. Here, compounds **1** and **2** include only aromatic solvent molecules, whereas **3** also accepts 1,4-dioxane as a guest may be due to the formation of hydrogen bonds.

Furthermore, a change of the linkage heteroatom effects the sorption properties of the host compounds. Thermogravimetric analysis revealed clear differences between the thermal stability of corresponding inclusions. Particularly, inclusions of **1** featured a decrease of thermal stability with a decreasing number of CH₃-groups of guest molecules, showing that these groups have an essential impact on host–guest interactions. In the case of **2** and **3**, this behaviour could not be observed, as the CH₃-groups of the guest molecules do not directly contribute to the host–guest contacts.

4. Experimental

4.1. General

All starting materials were commercially available and were used without further purification. Melting points (mp) were measured with a Buechi 510. IR spectra of the compounds were analysed with the spectrometer Perkin-Elmer Spectrum One. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at 300.18 and 75.48 MHz, respectively. The chemical shifts are given in ppm (internal standard Me₄Si). ¹⁹F NMR were determined with a Bruker DRX 400 operating at 376.46 MHz (external standard CCl₃F). Acetone-*d*₆ was used as solvent in all NMR measurements. MS spectra were obtained by Perkin-Elmer SCIEX (API QSTAR Pulsar) spectrometer.

4.2. 2,4,6-Tris(pentafluorothiophenoxy)-1,3,5-triazine (**2**)

A 5 g (25 mmol) pentafluorothiophenole and 0.92 g (5 mmol) cyanuric chloride were heated at 140 °C for 15 h. The mixture was washed with hot methanol and purified by column chromatography (SiO₂ 60 [40–63 μm] eluent: chloroform/*n*-hexane 1:1) to yield 16.4% of a white solid. mp: 115 °C;

Table 4
Crystal data for **2**, **3** and their inclusions

	2	2-Mesitylene	3	3·(Dioxane)_{2.5}	3-Mesitylene
Crystallisation method	Isothermal evaporation in <i>n</i> -hexane	Isothermal evaporation in mesitylene	Sublimation	Isothermal evaporation in dioxane	Isothermal evaporation in mesitylene
Empirical formula	C ₂₁ F ₁₅ N ₃ S ₃	C ₃₀ H ₁₂ F ₁₅ N ₃ S ₃	C ₂₁ H ₃ F ₁₅ N ₆	C ₃₁ H ₂₃ F ₁₅ N ₆ O ₅	C ₃₀ H ₁₅ F ₁₅ N ₆
Formular weight (g/mol)	675.42	795.61	624.29	844.55	744.48
<i>T</i> (K)	153	153	373	153	173
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Trigonal	triclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>R</i> $\bar{3}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.1975(3)	21.1449(15)	7.7622(5)	18.255(4)	9.6282(11)
<i>b</i> (Å)	19.8966(8)	7.8900(4)	27.823(3)	18.255(4)	11.9830(11)
<i>c</i> (Å)	24.8044(9)	37.882(3)	10.4393(8)	17.130(4)	26.613(3)
α (°)	90	90	90	90	96.523(8)
β (°)	90	97.024(9)	97.904(6)	90	90.152(8)
γ (°)	90	90	90	120	90.930(8)
<i>V</i> (Å ³)	4539.2(3)	6272.5(7)	2233.1(3)	4943.7(19)	3050.2(6)
<i>Z</i>	8	8	4	6	4
ρ (g cm ⁻³)	1.977	1.685	1.857	1.702	1.621
$2\theta_{\max}$ (°)	59	52	52	59	50
μ (Mo K α) (mm ⁻¹)	0.470	0.355	0.203	0.173	0.163
Measured reflexes	53960	42724	19567	15903	10224
Independent reflexes	6308	12063	3981	2905	10224
<i>R</i> _{int}	0.0454	0.0404	0.0790	0.05	0.1
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0316	0.0341	0.0371	0.042	0.1052
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0777	0.0798	0.0869	0.1144	0.3017
CCDC	290172	290171	290173	290174	290175

IR (KBr): ν_{\max} (cm⁻¹) 1644 (perfluorinated arom.), 1490 (triazine), 1259 (C–F), 1099(s), 984 (s), 870/835 (s). ¹³C NMR (acetone-*d*₆): δ = 103.0 (C1, t, ²*J*_{CF} = 20.5 Hz), 137.0 (C2, d, ¹*J*_{CF} = 254.5 Hz), 143.6 (C4, d, ¹*J*_{CF} = 257.0 Hz), 147.0 (C3, d, ¹*J*_{CF} = 252.7 Hz). ¹⁹F NMR (acetone-*d*₆): δ = –132.2 (F1, d), –150.65 (F3, t), –163.1 (F2, dd). MS *m/z* (rel. int.): 675 (28.8) [*M*]⁺, 476 (41.4) [*M*–SC₆F₅]⁺, 251 (37.4) [*M*–434]⁺, 199 (100) [SC₆F₅], 155 (66.1) [*M*–520]⁺.

4.3. 2,4,6-Tris(pentafluorophenamino)-1,3,5-triazine (**3**)

5 g (27.3 mmol) pentafluoroaniline and 0.72 g (3.9 mmol) cyanuric chloride in 30 ml *n*-decane were heated at 100 °C for 15 h. The mixture was washed with hot *n*-hexane and recrystallized from benzene to yield 37.2% of a white solid. mp: 172 °C; IR (KBr): ν_{\max} (cm⁻¹) 3224–2951 (N–H), 1595 (perfluorinated arom.), 1497 and 1445 (triazine), 1367 (C–F), 1099 (s), 999 and 977 (s). ¹H NMR (acetone-*d*₆): δ = 8.6 (H–N, s). ¹³C NMR (acetone-*d*₆): δ = 114.9 (C1, t, ²*J*_{CF} = 15.6 Hz), 136.6 (C2, d, ¹*J*_{CF} = 274.0 Hz), 139.0 (C4, d, ¹*J*_{CF} = 249.1 Hz), 143.3 (C3, d, ¹*J*_{CF} = 241.5 Hz), 166.9 (N–C–N, s). ¹⁹F NMR (acetone-*d*₆): δ = –146.7 (F1, d), –160.2 (F3, t), –166.5 (F2, s). MS: *m/z* (rel. int.): 624 (4.8) [*M*]⁺, 397 (100) [*M*–(N–C(NHC₆F₅)–N)]⁺, 182 (36.5) [NH(C₆F₅)], 155 (48.2) [*M*–469]⁺.

4.4. X-ray structure determination

Single crystals of the reported compounds were obtained by isothermal evaporation, cooling of a saturated solution or sublimation. The used methods for each crystal are summarized

in Table 4. The intensity data were recorded on a Stoe IPDS diffractometer. The structures were solved by direct methods using the programme SHELXS-97 [16]. The refinement and all further calculations were carried out using SHELXL-97 [17]. In cases where it was possible to locate the H-atoms from Fourier difference maps, they were refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F₂. The corresponding crystallographic data are summarized in Table 4. CCDC reference numbers 290, 171–175.

4.5. Thermogravimetric analysis

Thermogravimetric data were measured with a Mettler Toledo TGA 50.

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