4,4′-(Fluorene-9,9-diyl)diphenol: a new versatile building block for clathrate type and macrocyclic host–guest inclusion

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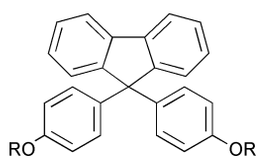
4,4′-(Fluorene-9,9-diyl)diphenol (**1**) is demonstrated to be both an effective clathrate host in itself and a useful construction element to form a rigid macrocyclic host compound **2**. The X-ray crystal structures of **1** and of its inclusion compounds with acetonitrile (1 : 1) and ethanol (1 : 2) as well as the inclusion compound of **2** with dimethyl sulfoxide (1 : 4) and the mixed-guest inclusion compounds of **2** with 2-picoline, 3-picoline or 4-picoline and acetone (2 : 2 : 1) are reported. Inclusion compounds of **1** with acetonitrile and ethanol are studied by thermal analysis.

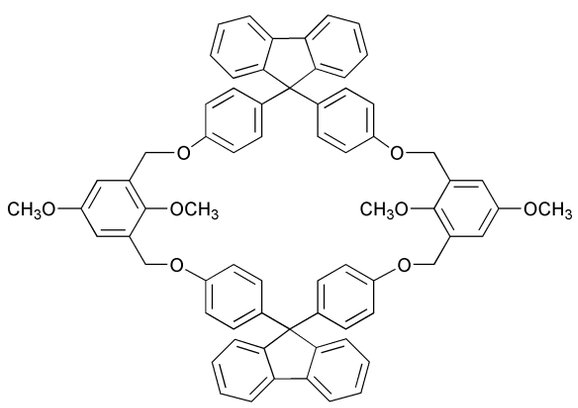
Introduction

Both macrocyclic and noncyclic host compounds are commonly designed by using rigid building blocks in order to stabilize a hollow ring conformation[1] or to support a bulky clathrate structure.[2] Well known construction elements of this type are 2,2′-dihydroxy-1,1′-binaphthyl or 4,4′-dihydroxydiphenylmethane and derivatives of it, which give rise to very efficient crown compounds[3] and cyclophane hosts[4] but also to excellent crystalline inclusion compound formers (clathrands).[5] More building elements along these lines for use as a design module in supramolecular chemistry, including host–guest properties, crystal engineering and other phenomena, are very desirable.[6]

Here we present such a new versatile building block, 4,4′-(fluorene-9,9-diyl)diphenol (**1**), which can be applied for clathrate type and macrocyclic host–guest inclusion in that this compound by itself is capable of forming crystalline inclusions and is shown to be an important constituent of macrocycle **2**, also an efficient inclusion host. We describe the syntheses and the inclusion behavior of **1** and **2**, discuss thermal properties of some inclusion compounds and report the X-ray crystal structures of uncomplexed **1** and of six inclusion compounds involving **1** and **2**.



1 R = H
3 R = CH_3



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Results and discussion

Synthesis

Compound **1** was synthesized by a method analogous to literature procedures[7,8] from fluoren-9-one by treatment with anisole in glacial acetic and sulfuric acid to yield the bis(methyl ether) intermediate **3** which was subjected to ether cleavage with boron tribromide to give **1** in 59% overall yield. Host compound **2** was prepared in 23% yield by macrocyclization reaction from **1** and 2,5-dimethoxy-1,3-bis(bromomethyl)-benzene under high dilution conditions using Cs_2CO_3 in acetone as the solvent–base system.[9] Inclusion compounds of **1** were obtained by simple recrystallization from the respective solvent.

Inclusion properties

As shown in Table 1, the bulky and geometrically well-defined diphenol **1** is a rather efficient host compound, forming crystalline inclusions with solvents of different substance classes including alcohols, amines, ketones, nitriles and other solvents in common use such as DMF, DMSO or 1,4-dioxane. Thus, being indicative of the examples in Table 1, both polar protic and polar aprotic solvents are appropriate guests to form inclusions while apolar solvents apparently are inappropriate. And, what is also manifest from the specified examples, the greatest number of inclusion compounds are formed with amines, showing a particular affinity of **1** for this class of guests.

The stoichiometric ratio favoured in the crystalline inclusions of **1** is 1 : 1 (host : guest). Less frequently encountered stoichiometric ratios are 1 : 2, 2 : 1 and 1 : 3 following a certain dependent relationship between **1** and the size and bulk of the guest molecule within a given solvent class, *i.e.* the larger and bulkier the guest, the lower the stoichiometric ratio to the disadvantage of the guest. For instance, methanol and ethanol yielded

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Table 1 Crystalline inclusion compounds (host : guest stoichiometric ratios) of **1**[a]

With alcohols:	Methanol (1 : 2), ethanol (1 : 2), propan-1-ol (1 : 1), butan-1-ol (2 : 1), butan-2-ol (1 : 1)
With amines:	*n*-Propylamine (1 : 1), *n*-octylamine (1 : 3), cyclopentylamine (1 : 1), *sec*-butylamine (1 : 1), pyrrolidine (1 : 2), morpholine (1 : 2), tri-*n*-propylamine (2 : 1), tri-*n*-butylamine (1 : 3), pyridine (1 : 1)
With ketones:	Acetone (1 : 1), cyclohexanone (1 : 2), 2-methyl-Cyclohexanone (1 : 1)
With nitriles:	Acetonitrile (1 : 1), propionitrile (1 : 1), butyronitrile
With others:	Dimethylformamide (1 : 1), dimethyl sulfoxide (1 : 1), dioxane (2 : 1)

[a] The following solvents yielded no crystalline inclusion compounds: propane-1,2-diol, cyclopentanol, cyclohexanol, benzylamine, acetophenone, 3-methylcyclohexanone, 4-methylcyclohexanone, β-butyrolactone, γ-valerolactone, nitromethane, nitroethane, dichloromethane, benzene, toluene, xylenes, cyclohexane.

complexes with 1 : 2 stoichiometry but *n*-propanol and *n*-butanol showed 1 : 1 and 2 : 1 stoichiometry, respectively; cyclohexanone is included with a 1 : 2, but 2-methylcyclohexanone with a 1 : 1, stoichiometric ratio. However, except for some rare cases (including the EtOH compound), there is no simple correspondence between the number of hydrogen donor and acceptor groups of host and guest molecules, suggesting complexity of the supramolecular interaction occurring in the compounds.

In order to learn more about the modes of interaction the new host compound **1** uses for the assemblage of its unsolvated crystalline lattice and for the clathration of polar aprotic and protic guest molecules, we have studied the crystal structures of unsolvated **1**, **1**·MeCN (1 : 1) (**4**) and **1**·EtOH (1 : 2) (**5**).

4 = **1** • MeCN (1:1)
5 = **1** • EtOH (1:2)
6 = **2** • DMSO (1:4)
7 = **2** • 2-picoline • acetone (2:2:1)
8 = **2** • 3-picoline • acetone (2:2:1)
9 = **2** • 4-picoline • acetone (2:2:1)

On the other hand, the macrocycle **2** readily yielded inclusion compounds with DMSO (**6**) and the three picolines (2-, 3-, 4-picoline) (**7**–**9**) when recrystallized from these solvents. The inclusion compounds with the picolines were found to contain an additional stoichiometric amount of acetone coming from the host synthesis, which was entrapped at this early stage and retained, thus leading to mixed guest inclusion compounds of stoichiometric ratio 2 : 2 : 1 (**2** : picoline : acetone), while the inclusion compound of **2** with DMSO revealed an uncommonly high solvent ratio of 1 : 4 (**2** : DMSO), prompting studies of their crystal structures: **2**·DMSO (1 : 4) (**6**), **2**·2-picoline·acetone (2 : 2 : 1) (**7**), **2**·3-picoline·acetone (2 : 2 : 1) (**8**), **2**·4-picoline·acetone (2 : 2 : 1) (**9**).

X-Ray structural studies

Illustrations of the host compounds with crystallographic atomic numbering are shown in Fig. 1. Packing diagrams of unsolvated **1** and host–guest compounds of **1** and **2** are presented in Figs. 2–7. Crystal data and selected experimental and refinement details are given in Tables 2 and 3. Conformational features of the host molecules are listed in Table 4.

The results of the X-ray structural studies involving host compound **1** in unsolvated and clathrated forms showed some common features. One is related to the conformation sustained by **1** in all three structures where the planes of the fluorene backbone and the two phenolic units are twisted nearly perpendicular to each other [Fig. 1(a)].[10] On the other hand, in the packings, the neighboring fluorene moieties have a

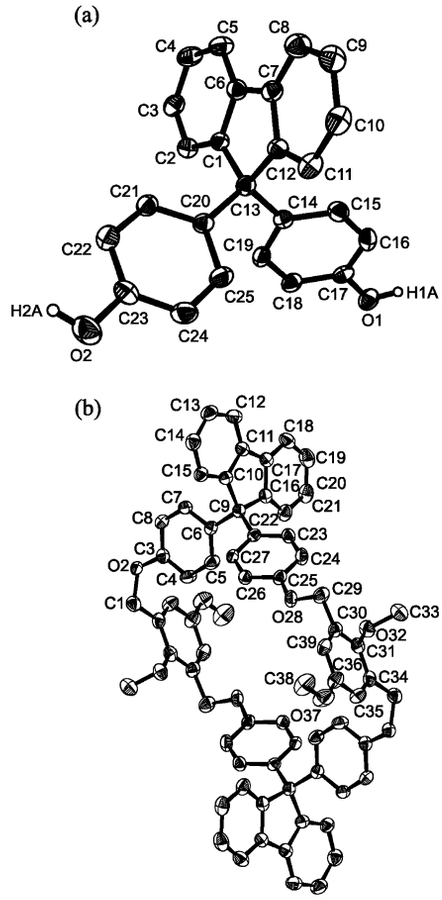

Fig. 1 Perspective views of host compounds **1** (a) and **2** (b) with crystallographic atom numbering.

parallel orientation, suggesting π-stacking interactions between these groups (Figs. 2–4).[11,12] The other common feature is that H bonds exist in all three structures, caused by the phenolic hydroxy groups.[13] Nevertheless, the modes of H bonding revealed in these structures are different depending on the presence and the nature of the guest molecules, making it evident that **1** is able to adapt itself to a varying crystalline environment. This is demonstrated by gradual substitution of host–host to host–guest H bond interactions when going from unsolvated **1** (Fig. 2) *via* the acetonitrile (**4**) (Fig. 3) to the EtOH complex (**5**) (Fig. 4), in this order, corresponding to the increasing H acceptorship and donorship of the guest molecules.

In the case of the unsolvated **1**, interaction between the rigid diphenol moieties generates a helical chain of H-bonded molecules (OH · · · O-distance 2.13 Å). Two of these chains wind around each other to form a double-helix suprastructure (Fig. 2). The structure of **4** (1 : 1 inclusion compound with acetonitrile) can be considered as strands of unwound helices kept away from each other by the inserted guest molecules (Fig. 3). The O atom of the phenolic unit is H-bonded to the hydroxy group of the respective neighboring host (OH · · · O-distance 1.80 Å). One of the hydroxy moieties participates in an H bond interaction with a molecule of acetonitrile (OH · · · N-distance 1.88 Å). Compound **5**, including ethanol as guest, crystallizes only in a layer structure (Fig. 4). The layers consist of the host molecules containing the hydroxy groups pointing outwards. This hydrophilic surface is used for binding of the ethanol molecules.

The packing of the four inclusion structures involving the macrocyclic host compound **2** is very similar including also the conformation of the host molecule (Table 4). The conformation of **2** observed in the inclusion compounds **7**–**9** is slightly different to the one in **6** because of the different arrangement of the benzene rings [atoms C(22)–C(27)]. Furthermore, in com-

pounds **7**–**9** the oxygen O(28) works as a double proton acceptor and builds weak C–H···O-interactions with hydrogens H(19A) [C(19A)–H(19A)···O(28)-distance 2.86 Å] and H(20A) [C(20A)–H(20A)···O(28)-distance 2.79 Å] of the spacer unit belonging to the neighbouring host molecule (Fig. 5). The angles O(28)–H(19A)–C(19A) and O(28)–H(20A)–C(20A) are determined as 123.9 and 127.3°, respectively. As a consequence, these weak interactions and the different arrangement of the benzene rings are responsible for the different channels of 8 × 8 Å in **7**–**9** and 8 × 10 Å in **6**. It is obvious that the rigid construction elements of neighbouring macrocycles are located parallel to the channel (Fig. 6). The distances between the host molecules allow the guests to be accommodated. This is clearly shown in Fig. 6 with the DMSO molecules of **6**, being located only on inter-host positions rather than using the host cavity. Moreover, the DMSO molecules are highly disordered. For one of the guest species two, and for the other three, positions could be modelled. Certainly there is H bonding of these guests, but as a result of the high disorder we were unable to make a clear specification. The picoline isomers

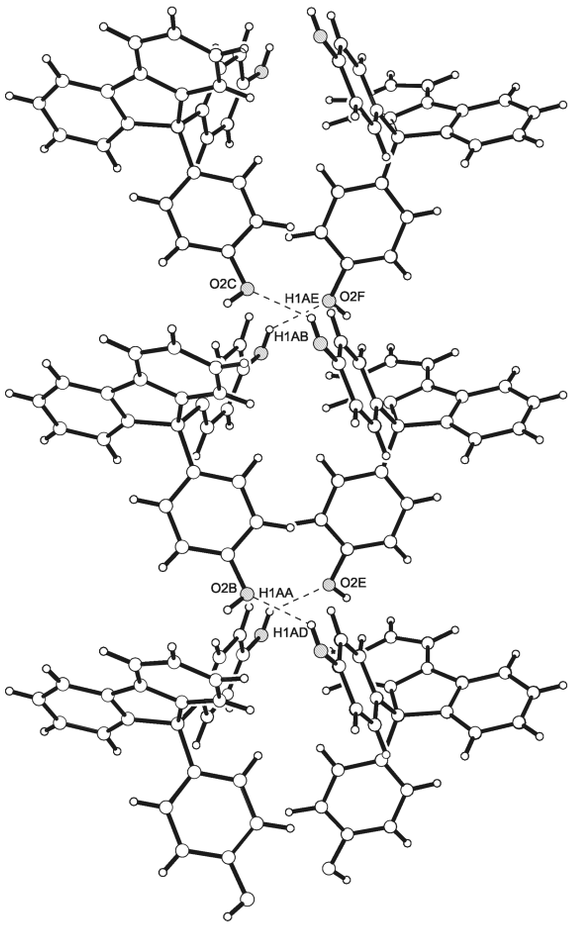

Fig. 2 Packing diagram of **1**. H bonds are drawn as dashed lines, O atoms are shaded.

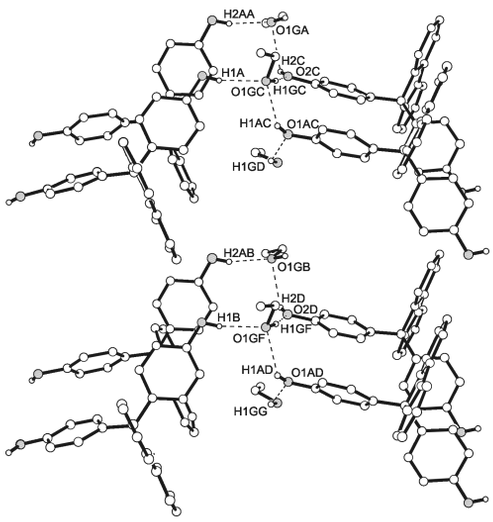

Fig. 4 Packing diagram of **5**. H bonds are drawn as dashed lines, O atoms are shaded. H atoms not involved in H bonding are omitted.

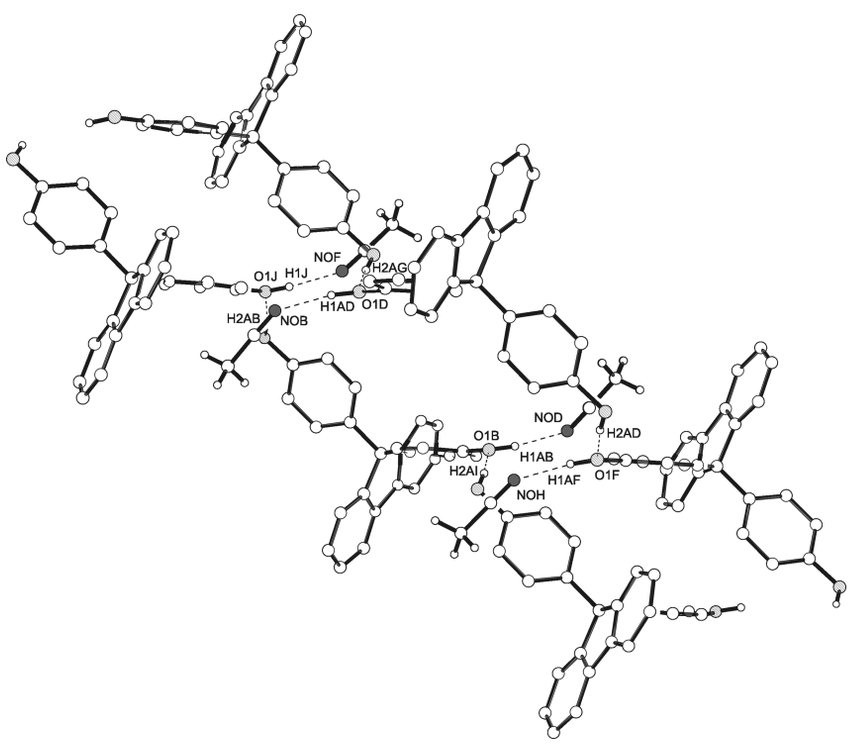

Fig. 3 Packing diagram of **4**. H bonds are drawn as dashed lines, O atoms are shaded, N atoms are in bold. Non-relevant H atoms of the host molecules are omitted for clarity.

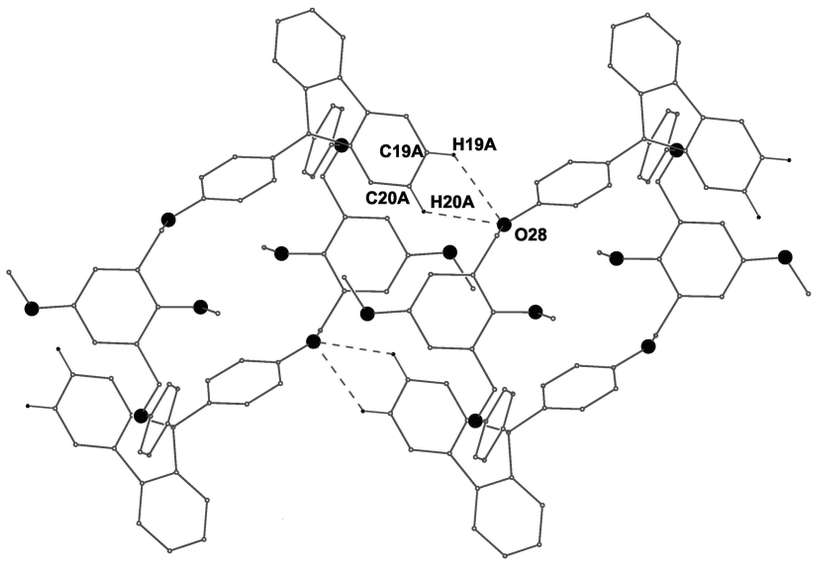

Fig. 5 Host interactions in the inclusion compounds **7**–**9**. H bonds are drawn as dashed lines, O atoms as filled circles. H atoms not involved in H bonding are omitted.

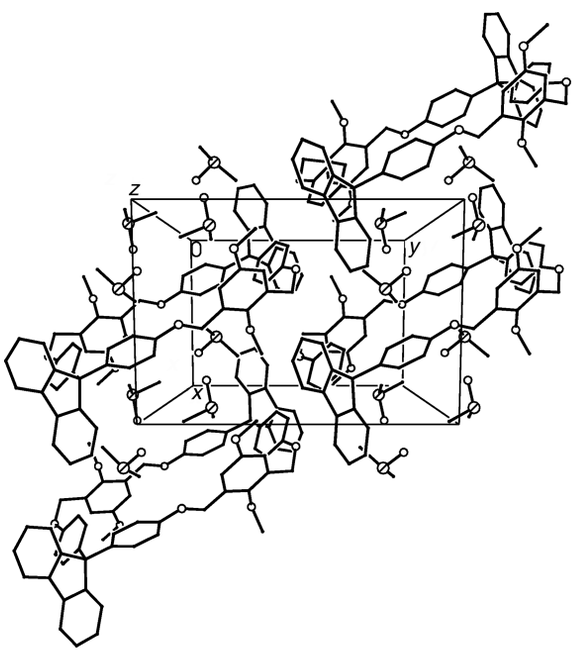

Fig. 6 Packing diagram of **6** viewed along the *z*-axis. O atoms are represented as open circles, S atoms as hatched circles. H atoms are omitted for clarity.

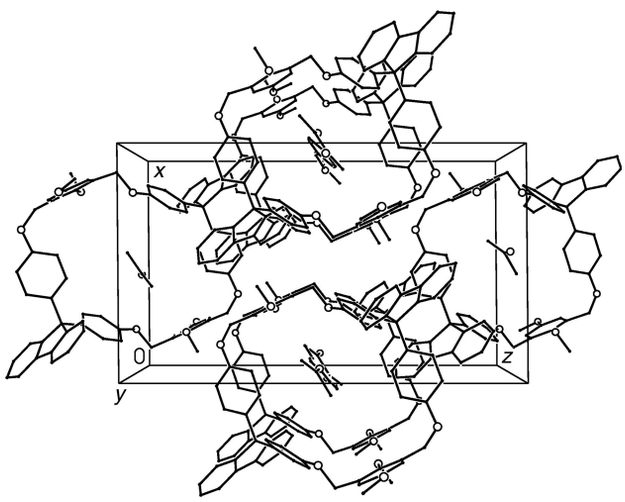

Fig. 7 Packing diagram of **9** viewed along the *y*-axis. Hetero atoms are represented as open circles. H atoms are omitted for clarity.

occupy the same position in the lattice as the DMSO guests in **6** (Fig. 7). However, the other guest species, which are the molecules of acetone in **7**–**9**, are diagonally enclosed in the cavity of every second host molecule where they do not maintain hydrogen bonding to the host.

The acetone–picoline interactions in **7**–**9** were analysed. As illustrated in Fig. 8, only in **9** [Fig. 8(c)] is a typical van der Waals contact[11,14] between the acetone and 4-picoline molecules [N(5G)···O(3A) = 2.78 Å] found. As a consequence, the distance between two picolines surrounding an acetone molecule is the shortest in **9**. Making a comparison between **9** and **7** it is obvious that the methyl groups of the picolines in both structures point at each other so that 2-picoline [Fig. 8(a)] is unable to have close contact with acetone. None of these features can be found in **8** [Fig. 8(b)]. There are no relevant interactions between acetone and 3-picoline. The distance between two 3-picoline molecules is, at 10.96 Å, the largest one compared to 2- and 4-picoline in their corresponding inclusion compounds. This is caused by the C–H···π-interaction

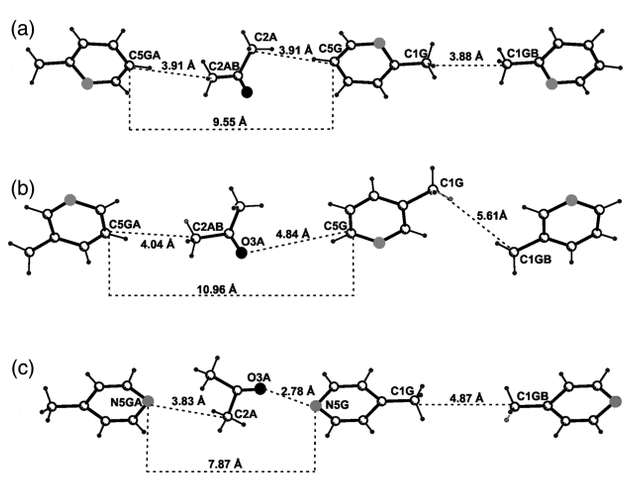

Fig. 8 Modes of contacts involving acetone and isomeric picoline molecules in **7** (a), **8** (b) and **9** (c).

found between the hydrogen H(21A) of the host and the aromatic system of the 3-picoline [C(21)–H(21A)···centroid of 3-picoline-distance 2.82 Å]. Within the series of the picoline isomers, 2- and 4-picoline are more symmetrical than 3-picoline

Table 2 Details of crystals, data collections and final refinement for host **1** and its inclusion compounds

Compound	**1**	**4**	**5**
Crystal data			
Empirical formula	$C_{25}H_{18}O_2$	$C_{25}H_{18}O_2 \cdot C_4H_3N$	$C_{25}H_{18}O_2 \cdot 2C_2H_6O$
M_r/g mol^{-1}	350.39	415.46	442.53
Temperature/K	133(2)	133(2)	298(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P22_12_1$	$P2_1/n$	$P2_12_12_1$
Unit cell dimensions			
a/Å	9.054(3)	11.338(3)	11.281(3)
b/Å	10.761(3)	12.733(3)	17.888(3)
c/Å	18.539(3)	14.245(3)	23.950(3)
α/°	90	90	90
β/°	90	94.45(3)	90
γ/°	90	90	90
V/Å^3	1806.3(8)	2050.3(8)	4833.0(2)
Z (formula)	4	4	8
D_c/g cm^{-3}	1.289	1.258	1.204
μ/mm^{-1}	0.635	0.628	0.636
F(000)	736	812	1852
Reflections collected	1971	4014	5510
Reflections observed	1687	3648	3579
Refinement			
R_1 [$I > 2\sigma(I)$]	0.0494	0.0414	0.0638
wR_2 (F^2)	0.1241	0.1066	0.1612

and therefore the arrangement with the face-to-face methyl groups is probably the most comfortable in the lattice. Presumably 3-picoline also tries to fit into the lattice in the same way but is forced by the interaction with the host to a differing structure.

Thermal analysis

The thermal gravimetry (TG) and differential scanning calorimetry (DSC) traces for the inclusion compounds **4** and **5** are shown in Fig. 9. The weight loss data derived from the TG traces for **4** and **5** are in good agreement with the stoichiometric ratios (1 : 1 and 1 : 2, respectively) obtained from ^{1}H NMR integration and X-ray diffraction. The acetonitrile inclusion compound **4** [Fig. 9(a)] decomposes in two overlapping steps during a linear temperature scan with an onset temperature of decay of 120 °C, which is much higher than the boiling point of acetonitrile (81.6 °C). This may be interpreted as steric hindrance of the guest release effected by the crystalline matrix. The DSC trace for **4** shows two endotherms corresponding to the two steps of decomposition and is suggestive of a pseudo-polymorphic phase transition.[15] In contrast, the ethanol inclusion compound **5** [Fig. 9(b)] decays in a single step around the boiling point of ethanol and the DSC trace shows a broad endotherm.

Conclusions

Attachment of two *p*-hydroxyphenyl groups to position 9

Table 3 Details of crystals, data collections and final refinement for inclusion compounds of host **2**

Compound	**6**	**7**	**8**	**9**
Crystal data				
Empirical formula	$C_{70}H_{56}O_8 \cdot 4\ C_2H_6OS$	$2C_{70}H_{56}O_8 \cdot 2C_6H_7NC_3H_6O$	$2C_{70}H_{56}O_8 \cdot 2C_6H_7N \cdot C_3H_6O$	$2C_{70}H_{56}O_8 \cdot 2C_6H_7N \cdot C_3H_6O$[a]
M_r/g mol^{-1}	1337.66	2294.74	2294.74	2294.74
Temperature/K	293(2)	183(2)	183(2)	183(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a/Å	9.475(2)	12.902(7)	12.815(3)	12.804(2)
b/Å	13.591(2)	10.930(2)	10.963(3)	10.892(2)
c/Å	26.899(4)	21.704(6)	21.673(4)	21.865(4)
α/°	90	90	90	90
β/°	100.00(1)	90.39(3)	90.14(2)	90.47(3)
γ/°	90	90	90	90
V/Å^3	3411(1)	3037(2)	3045(1)	3049(2)
Z (formula)	2	2	2	2
D_c/g cm^{-3}	1.302	1.225	1.251	1.247
μ/mm^{-1}	1.794	0.081	0.081	0.080
F(000)	1416	1212	1212	1210
Reflections collected	6776	6407	6502	6419
Reflections observed	3737	4124	3200	4835
Refinement				
R_1 [$I > 2\sigma(I)$]	0.1260	0.0832	0.1124	0.0859
wR_2 (F^2)	0.3329	0.2377	0.3045	0.2505

[a] For inclusion compound **9** the atom C2G was not modelled as a nitrogen atom because of a high temperature factor.

Table 4 Selected torsion angles of the host molecule **2** in the inclusion compounds **6**–**9**

Selected torsion angles/°	**6**	**7**	**8**	**9**
C(31)–C(34)–C(1)–O(2)	122.0(5)	146.9(3)	148.4(5)	−146.9(3)
C(34)–C(1)–O(2)–C(3)	81.5(6)	84.0(4)	84.1(6)	83.2(3)
C(1)–O(2)–C(3)–C(4)	−2.8(8)	−15.0(5)	−15.7(7)	−14.8(4)
C(5)–C(6)–C(9)–C(22)	31.0(7)	32.9(4)	32.8(7)	43.9(4)
C(6)–C(9)–C(22)–C(23)	−128.4(6)	−139.3(3)	−139.0(5)	−152.8(3)
C(24)–C(25)–O(28)–C(29)	3.8(8)	−28.0(5)	−26.6(8)	−29.0(5)
C(25)–O(28)–C(29)–C(30)	−173.4(5)	148.9(3)	148.5(5)	149.7(3)
O(28)–C(29)–C(30)–C(31)	−178.4(5)	−89.9(4)	−90.2(6)	89.3(4)

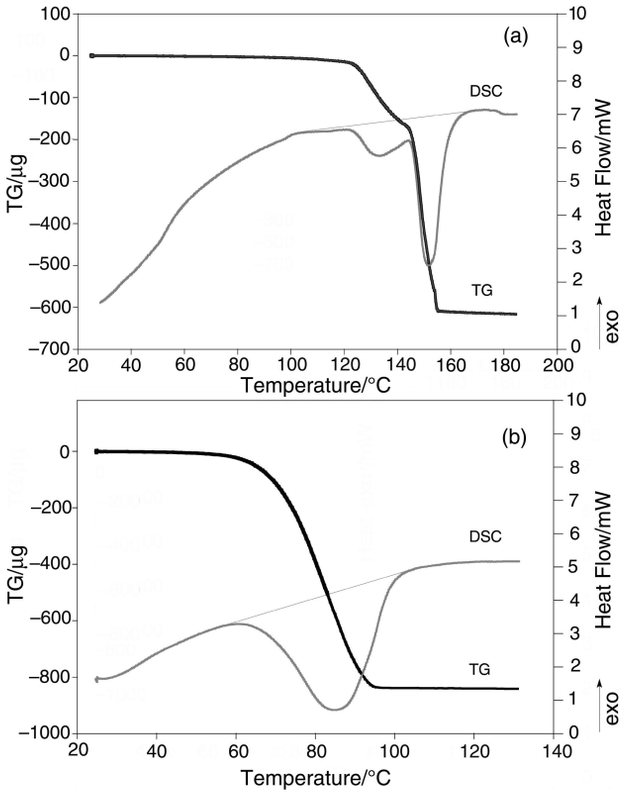

Fig. 9 Thermograms (TG and DSC) for **4** (a) and **5** (b).

of a fluorene base unit yielded a new versatile construction element which proved useful in crystalline inclusion and macrocyclic host chemistry. Both the simple diphenol **1** and the macrocycle **2** derived from **1** form inclusion compounds with a variety of uncharged molecules of protic dipolar and aprotic dipolar nature, but with a preference for amines and alcohols, while apolar compounds were found to be inefficient.

The structural versatility of the new host types based on this modular building unit is demonstrated by the crystal structures of unsolvated **1** and its inclusion compounds with MeCN (**4**) and EtOH (**5**), the inclusion compound of **2** with DMSO (**6**) or of the mixed-guest inclusion compounds of **2** with 2-picoline, 3-picoline and 4-picoline including additional acetone (**7**–**9**), making it evident that these hosts are able to adapt to a varying crystalline environment governed by H-bonding and π-stacking interactions. A similar case is perhaps the compound 1,1-bis-(4-hydroxyphenyl)cyclohexane.[16] Nevertheless, due to the high conformational rigidity and the favorable arrangement of the phenolic functions united with the stacking behavior of the planar fluorene moiety,[12] the present compound is superior in its structural properties, and a number of uses in host–guest chemistry [1a,2a] and crystal engineering [14,17] starting from this module or its potential modifications may be imagined.[6] Thus, the phenols are a class of compounds still promising in supramolecular design.[13] Work is also being continued on replacing the rather insignificant methoxy groups of **2** by more attractive functions in order to improve the binding behavior of the host.[4,18]

Experimental

Synthesis

General methods and materials. Mps were determined with a Reichert hot-stage apparatus. IR spectra were recorded on a Perkin-Elmer FT-IR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on Brücker MSL 300 and MSL 400 spectrometers for solutions in $CDCl_3$ with $SiMe_4$ as internal standard. Microanalyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the TU Bergakademie Freiberg. For column chromatography, silica gel (0.04–0.06 mm) was used. Solvents were dried by standard procedures. Starting compounds (fluoren-9-one, anisole) and reagents (boron tribromide, hydrobromic acid) were purchased from Merck.

Host compound 1. *9,9-Bis(4-methoxyphenyl)fluorene* ***3***. To glacial acetic acid (10 ml, 0.17 mol) was added under vigorous stirring sulfuric acid (96%, 5 ml, 0.1 mol). After cooling the mixture to 15 °C, thioglycolic acid (3 drops) was added, followed by a mixture of anisole (27.3 ml, 0.25 mol) and fluoren-9-one (9.0 g, 0.05 mol) which was added dropwise at the given temperature. Stirring was continued at room temperature for 4 d. Then water was added and the mixture was extracted with diethyl ether. The ethereal extract was washed free from acid with aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4) and evaporated to give the crude product as an orange–yellow oil which was subjected to steam distillation in order to free it from anisole. Recrystallization from ethanol yielded 60% of **3** as colourless crystals: mp 126 °C (Found: C, 85.57; H, 5.70. Calc. for $C_{27}H_{22}O_2$: C, 85.69; H, 5.86%); ν_{max} (KBr)/cm^{-1} 3072w, 3037w, 2833m, 1607vs, 1509vs, 1250vs, 823s; δ_H (300 MHz) 3.73 (6 H, s, OCH_3), 6.72, 7.10 (4 H, d, $^3J_{(H,\ H)} = 8.8$ Hz, Ar), 7.23–7.77 (8 H, m, Ar); δ_C (75 MHz) 55.18, 64.17, 113.53, 120.09, 126.00, 127.28, 127.64, 129.16, 138.12, 139.96, 151.88, 158.31; *m*/*z* (GC-MS) 378 (M^+).

4,4′-(Fluorenyl-9,9-diyl)diphenol ***1***. Into a stirred solution of **3** (8.0 g, 21.3 mmol) in dry dichloromethane (150 ml) was dropped, at −15 °C, 80 ml of a 1 M solution of boron tribromide (85.2 mmol) in dry dichloromethane. The mixture was allowed to warm to room temperature, stirred for 2 d, hydrolyzed with ice–water, extracted with diethyl ether, washed free from acid ($NaHCO_3$, water) and dried (Na_2SO_4). Evaporation of the ether and recrystallization from ethanol yielded colourless crystals, determined as the inclusion compound of **1** with ethanol (1 : 2). Desolvation was brought about by drying the inclusion crystals for 4 h at rt under vacuum (12 Torr) to give 98% of solvent free **1** as a colourless solid: mp 115 °C (Found: C, 85.26; H, 5.19. Calc. for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18%); ν_{max} (KBr)/cm^{-1} 3459vs, 3065w, 1623vs, 1511vs, 1434vs, 1251vs, 829s; δ_H (300 MHz) 4.55 (2 H, s, OH), 6.66, 7.04 (4 H, d, $^3J_{(H,\ H)} = 8.8$ Hz, Ar), 7.11–7.73 (8 H, m, Ar); δ_C (75 MHz) 115.02, 120.13, 126.01, 127.36, 127.67, 129.41, 138.36, 139.99, 151.80, 154.25; *m*/*z* (DCI, pos., methane) 350 (M + H)$^+$.

Host compound 2. 2,5-Dimethoxy-1,3-bis(bromomethyl)-benzene was prepared by bromination of 2,5-dimethoxy-1,3-bis(hydroxymethyl)benzene with hydrobromic acid as described.[19]

Solutions of **1** (2.6 g, 7.5 mmol) in dry acetone (250 ml) and of 2,5-dimethoxy-1,3-bis(bromomethyl)benzene (2.4 g, 7.5 mmol) in dry acetone (250 ml) were added dropwise and simultaneously over 8 h to a suspension of caesium carbonate (7.5 g, 23 mmol) in dry acetone (1 l) under reflux.[9] The reaction mixture was filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, eluent: chloroform) and recrystallization from acetone to yield 23% of **2** as a colourless solid: mp > 300 °C (Found: C, 82.41; H, 5.55. Calc. for $C_{70}H_{56}O_8$: C, 82.01; H, 5.51%); ν_{max} (KBr)/cm^{-1} 3062m, 2933s, 2835m, 1607s, 1509w; δ_H (400 MHz) 3.75 (6 H, s, CH_3), 3.78 (6 H, s, CH_3), 5.10 (8 H, s, CH_2), 6.78–7.77 (36 H, m, Ar); δ_C (100.6 MHz) 54.99, 62.56, 63.45, 63.83, 113.58, 113.86, 119.54, 125.50, 126.81, 127.07, 128.64, 130.95, 137.88, 139.31, 148.68, 150.99, 155.60, 156.59; *m*/*z* (DCI, pos., methane) 1025 (M + H)$^+$.

Crystalline inclusion compounds. The host compound **1** was dissolved under heating in a minimum amount of the respective

guest solvent. After storage for 12 h at room temperature, the crystals which formed were collected. The host–guest stoichiometric ratios were determined by ^{1}H NMR integration. Data for each compound are given in Table 1.

Crystallography

Sample preparation, structure solution and refinement. Single crystals of diffraction quality of pure **1** were obtained by dissolving the host in benzene and those of **4** and **5** in acetonitrile and ethanol, respectively. The inclusion compounds of the host **2** were obtained by offering an excess of the corresponding picoline isomer. The additional guest acetone being accommodated is due to the crystallization of **2** from acetone although the host compound was dried. Therefore the inclusion compound **7** has 2-picoline and acetone as guests, **8** has 3-picoline and acetone, and **9** 4-picoline and acetone, while **6** includes dimethyl sulfoxide only. Since all of the inclusion compounds, except **5** and **6**, proved labile, the crystals were measured under low temperature conditions on a CAD 4 diffractometer using Cu-Kα radiation (1.5418 Å) for **1**, **4**–**6** and Mo-Kα radiation (0.71073 Å) for **7**–**9**. During the data collection three reference reflections were monitored periodically to check crystal stability. Crystal data and structural refinements for inclusion compounds of **1** are given in Table 2 and of **2** in Table 3. All structures were solved by direct methods using SHELX-86[20] and refined by full matrix least-squares with SHELX-93.[21] For all structures host non-hydrogen atoms were treated anisotropically. The hydrogen atoms were subjected to constrained refinement, with isotropic temperature factors given to hydrogen atoms of the same kind. The disorder of the DMSO molecules in **6** and the picoline molecules in **7**–**9** is responsible for the high *R*-values given in Table 3.

Supplementary data. Lists of fractional atomic coordinates with isotropic (for H atoms) or equivalent isotropic displacement parameters (for C and O atoms), and of covalent bond distances and bond angles (Tables 5–25) have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.† Further experimental details as well as lists of the anisotropic displacement parameters (Tables 26–32) and of the $F_{obs} - F_{calc}$ values are available directly from one of the authors (E. W.)

Thermal analysis

Simultaneous and isothermal differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a TG-DSC 111 (SETARAM) using open aluminium crucibles, sample weights of about 4 mg, a linear heating rate of 5 K min^{-1} and argon at 1 l h^{-1} as purge gas for all measurements. Crystals were taken from the mother liquor, blotted dry on filter paper, and transferred into the crucibles for weighing and measuring.

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† CCDC reference numbers 150561–150567. See http://www.rsc.org/suppdata/p2/b0/b008451o/ for crystallographic files in .cif or other electronic format.

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