Rational molecular design for multicomponent guest inclusion in the solid state: differential binding of small and large aromatic guests

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Tetraarylpyrene H that typifies a host system with three distinct domains for guest inclusion in the solid state is found to include different aromatic guests in the lattice and crystallize as a multicomponent molecular crystal. It is found to exhibit site-selective inclusion of the guests in that the large-sized guests such as biphenyl, anthracene, [2.2]paracyclophane, fluorene and pyrene are included selectively in the trough region, whereas small-sized benzene guest is bound in concave and/or basin regions. These results are of particular importance from the point of view of creating multicomponent molecular crystals based on rational design of the host structure.

Keywords: Host–guest chemistry, inclusion compounds, multicomponent crystals, solid state.

Introduction

CRYSTALLIZATION is a process in which a substance dissolved in a fresh solvent solidifies by assuming certain form and crystal packing. It is a way of purification of an impure organic compound from a suitable solvent or a mixture of solvents. Evidently, it capitalizes on the preferential tendency of a given compound to interact better with itself to yield nuclei that eventually transform into crystals. Although homogeneous growth of two or more different atoms of metals into alloys or inorganic complexes into cocrystals is widely known[1], crystallization of two or more organic compounds together as the so-called cocrystals or multicomponent crystals is not easy, and the growth of multicomponent crystals remains challenging. Given the prominence of organic–inorganic hybrid materials at present in a variety of applications[2], there is no reason to believe that the rational engineering of multicomponent crystals and understanding of their formation should be of invaluable importance in the pharmaceutical industry[3–6] and organic electronics[7,8]. Tremendous work on acids and organic bases such as pyridines, amines, etc. has led to some predictability as to the formation of cocrystals or salts[9–26]. If one excludes this strategy based on organic acids and bases, the literature reveals only scant examples of multicomponent crystals[27–34]. Clearly, engineering the formation of cocrystals or multicomponent crystals is an arduous task. Indeed, there is no readily viable approach to access multicomponent crystals.

In our recent studies[35–37], we have shown that rationally designed, sterically-rigidified tetraarylpyrene **H** (Chart 1) exhibits three domains, i.e. trough, concave and basin, and includes diverse guest molecules in all the three domains depending on the guest compound with which it is crystallized. From a systematic study of a large number of inclusion compounds of **H**, we showed that tetraarylpyrene **H** displays differential guest binding in that the aromatic guests are selectively included in troughs, whereas aliphatic guests are included in the concave region. Indeed, crystallization of the host **H** in the presence of aromatic pyrene and aliphatic cyclooctane guests was shown to lead to site-selective inclusion, and hence the formation of ternary inclusion compounds in a well-defined stoichiometric ratio[36]. We also noted site-selective differentiation even within the aromatic guests, e.g. pyrene–benzene and fluorene–benzene[36]. In a different study, we have shown that analogous, sterically rigid 1,3,5-tris(4-hydroxy-2,6-dimethylphenyl)benzene undergoes hydrogen-bonded self-assembly into honeycomb layers in which the complexes of 18-crown-6 can be bound in a manner reminiscent of Russian dolls[38,39]. Spurred by these results, we wished to establish as to how the host **H** responds, in general, to two different guest molecules of the same kind, i.e. aromatic. In the present study, we have expanded our initial observations on the formation of multicomponent crystals of host **H** with pyrene–benzene and fluorene–benzene[36]. We found that crystallization of **H** with biphenyl (bp), anthracene (an) and [2.2]paracyclophane (cp) in benzene (bz) as the solvent leads likewise to multicomponent ternary inclusion compounds. It has been shown that the host **H** does include all the aromatic guest molecules in a site-selective manner, and forms multicomponent crystals by including the large-sized guests in trough

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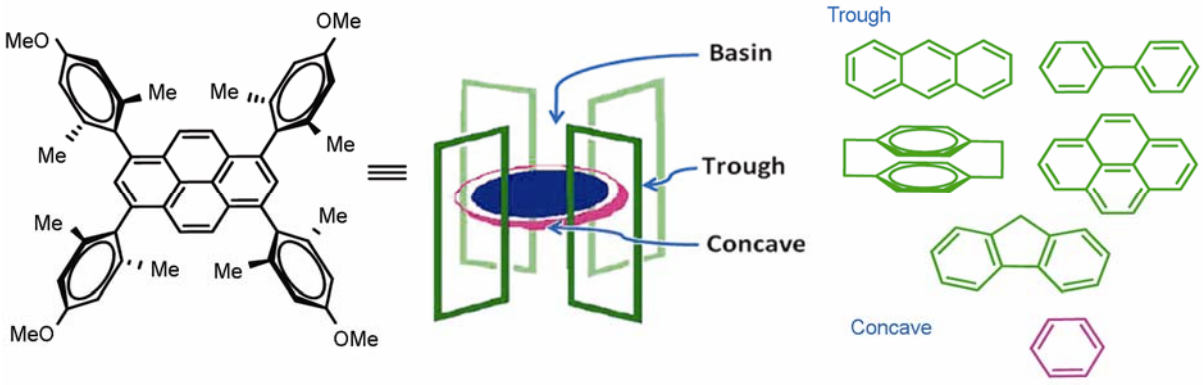

Chart 1. Structures of pyrene host **H** and guest molecules. Also shown is a cartoon drawing that illustrates the various domains for guest inclusion.

Table 1. Multicomponent inclusion compounds, host–guest ratios, identification codes, space groups and location of the guests with respect to different domains of the host

Ternary inclusion compound	Code	Space group	Guest location
Host·benzene (1 : 1)[a]	**H**•bz	$P2_1/c$	Trough/concave
Host·biphenyl (1 : 4)[a]	**H**•bp	$C2/c$	Trough
Host·fluorene·benzene (1 : 1 : 1)[b]	**H**•fl•bz	$P2_1/n$	Trough/concave
Host·pyrene·benzene (1 : 1 : 1)[b]	**H**•py•bz	$P2_1/c$	Trough/concave
Host·anthracene·benzene (1 : 1 : 1)	**H**•an•bz	$P2_1/c$	Trough/concave
Host·biphenyl·benzene (1 : 2 : 3)	**H**•bp•bz	$C2/c$	Trough/concave
Host·[2.2]paracyclophane·benzene (1 : 1 : 2)	**H**•cp•bz	$P\bar{1}$	Trough/concave

[a]From Moorthy *et al.*[35]. [b]From Moorthy *et al.*[36].

regions, and the small-sized benzene in concave and/or basin domains. Clearly, rational design of molecular structure is shown to be fundamental to engineering macroscopic solid-state behaviour, namely lattice inclusion.

Results and discussion

Multicomponent crystals of **H** *and X-ray structure determinations*

The synthesis of tetraarylpyrene host **H** has been reported by us previously[40]. Crystallization of **H** in the presence of stoichiometric amounts of aromatic guests, viz. biphenyl, fluorene, anthracene, pyrene and [2.2]paracyclophane, in benzene by slow evaporation led to crystals in quantitative yields; the crystals were amenable for X-ray crystallographic studies. The intensity data collection and subsequent structure determination revealed that the crystals in all cases contained guests that were employed in addition to benzene, which was used as the solvent.

Table 1 gives the host–guest composition, their identification codes and space groups along with those reported previously by us for **H**•benzene, **H**•biphenyl, **H**•pyrene•benzene and **H**•fluorene•benzene. The crystal data and other details are given in Table 2. In the following are described briefly the crystal packing observed in each case.

H•bp•bz: With biphenyl as the guest, the host was found to crystallize in the monoclinic crystal system with the space group $C2/c$ in benzene solvent. In the asymmetric unit cell, the host is found to sit on the inversion centre. The benzene guest molecules are found to be highly disordered. Each host molecule is found to accommodate a biphenyl molecule in the trough region via C–H$\cdots\pi$ interaction ($d_{C-H\cdots\pi}$ = 2.86 Å, $D_{C\cdots\pi}$ = 3.79 Å, $\theta_{C-H\cdots\pi}$ = 166.1°). The methyls of the methoxy groups in dimethylanisole moieties of one host form C–H$\cdots\pi$ hydrogen bonds with the aromatic surface of the dimethylanisole moiety of another host molecule ($d_{C-H\cdots\pi}$ = 2.90 Å, $D_{C\cdots\pi}$ = 3.80 Å, $\theta_{C-H\cdots\pi}$ = 153.6°). As a result, all the methoxy groups of the host are situated in the basin regions of the adjoining host molecules via C–H$\cdots\pi$ interactions. The host molecules thus self-assemble into columns down the *b*-axis creating channels which are filled with the disordered benzene molecules (Figure 1). In other words, the host molecules that hold the biphenyl molecules in the trough regions as tweezers sandwich the benzene molecules (Figure 1).

H•an•bz: The crystals were found to be monoclinic ($P2_1/c$) with half a molecule each of the host, anthracene and benzene in the asymmetric unit cell; all the three molecules are found to be located on the inversion centre. The crystal packing shows that the host molecules are connected in the *ab*-plane by C–H$\cdots$O hydrogen-bonds ($d_{C-H\cdots O}$ = 2.69 Å, $D_{C\cdots O}$ = 3.26 Å, $\theta_{C-H\cdots O}$ = 118.5°).

Table 2. Crystal data for multicomponent inclusion compounds of host **H**

Identification code	**H**•bp•bz	**H**•an•bz	**H**•cp•bz
Empirical formula	$C_{94}H_{88}O_4$	$C_{72}H_{66}O_4$	$C_{80}H_{78}O_4$
Formula weight	1281.64	995.25	1103.42
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c* (no. 15)	$P2_1/c$ (no. 14)	*P-1* (no. 2)
a (Å)	33.347(1)	14.484(1)	7.796(2)
b (Å)	14.999(4)	14.247(1)	14.914(3)
c (Å)	14.809(4)	14.795(2)	14.978(3)
α (deg)	90.00	90.00	61.63(1)
β (deg)	90.62(1)	118.22(8)	84.87(1)
γ (deg)	90.00	90.00	89.21(1)
Volume (Å^3)	7407.0(4)	2690.3(5)	1525.4(5)
Z	4	2	1
Calculated density (g/cm^3)	1.149	1.229	1.201
Absorption coefficient (mm^{-1})	0.068	0.074	0.072
F(000)	2736	1060	590
Reflections collected	18696	13694	7871
Independent reflections	3162	3339	3452
Data/restraints/parameters	6488/0/494	4707/0/343	5249/0/379
Goodness-of-fit on F^2	1.038	1.040	1.057
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0633$ $wR_2 = 0.1351$	$R_1 = 0.0514$ $wR_2 = 0.1189$	$R_1 = 0.0634$ $wR_2 = 0.1416$
R indices (all data)	$R_1 = 0.1369$ $wR_2 = 0.1589$	$R_1 = 0.0762$ $wR_2 = 0.1302$	$R_1 = 0.0966$ $wR_2 = 0.1591$

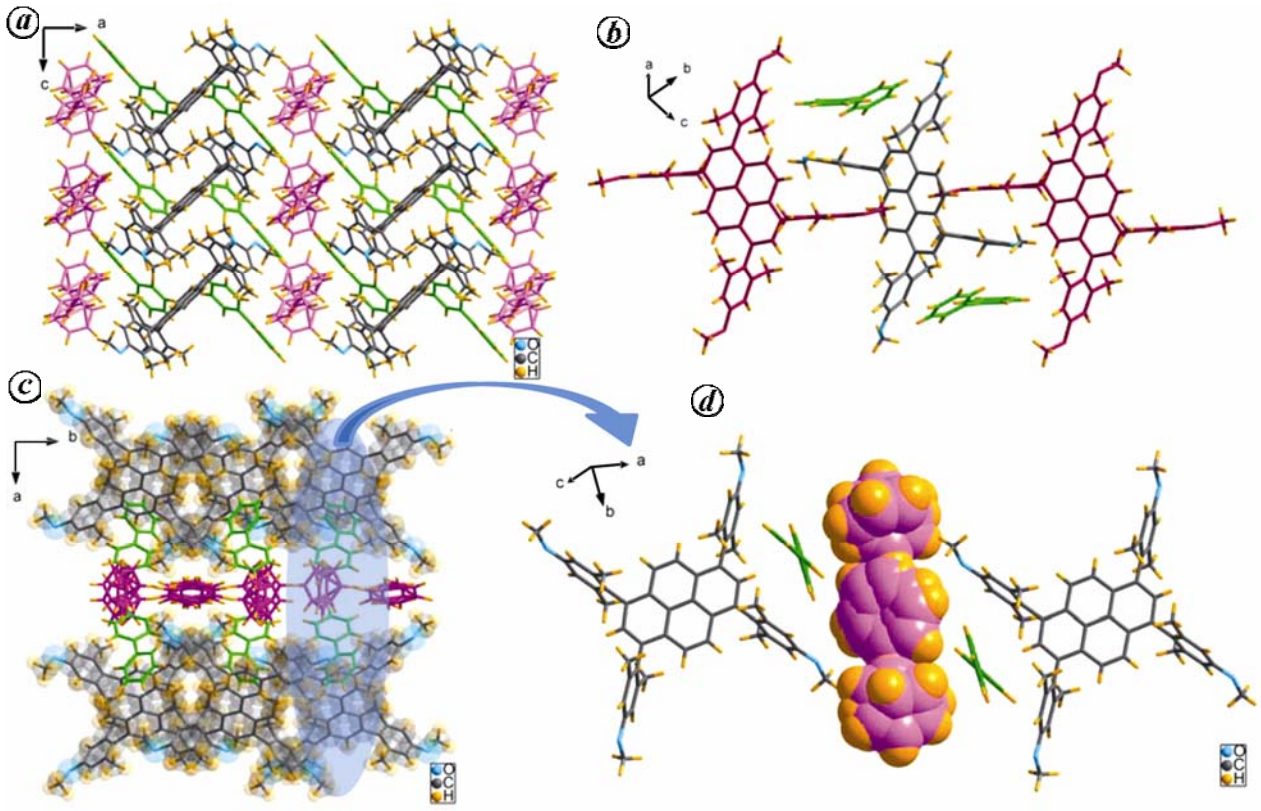

Figure 1. ***a***, Crystal packing diagram of **H**•bp•bz. ***b***, Location of biphenyl guest molecules with respect to the host molecules. ***c***, Host molecules self-assemble to form columns with channels filled with disordered benzene molecules. ***d***, A segment is magnified to highlight the arrangement of **H**, biphenyl (green) and benzene (pink).

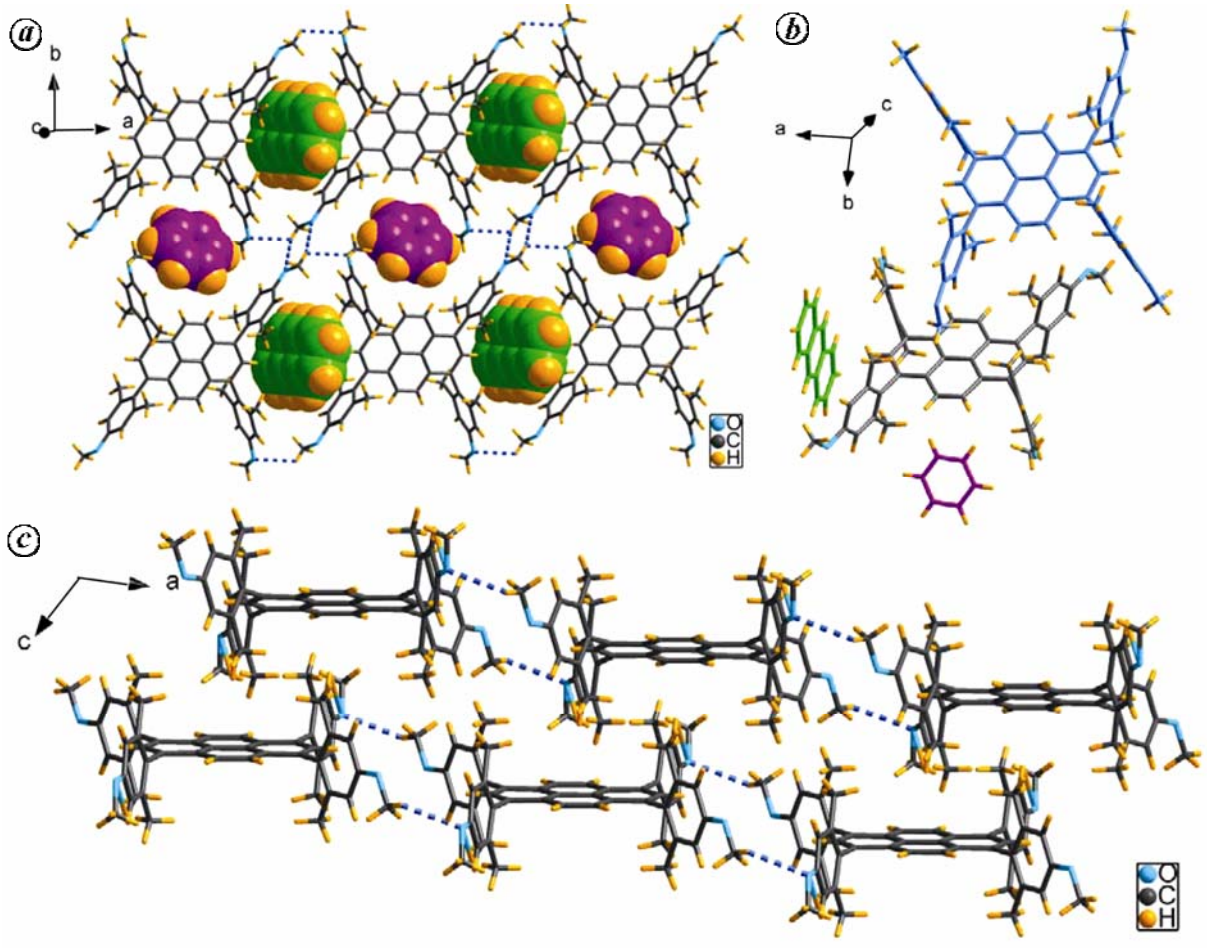

Figure 2. ***a***, C–H···O hydrogen bond-mediated self-assembly into two-dimensional network; notice that the anthracene guest (green) is included in trough, whereas benzene (pink) is found to be located in concave. ***b***, The neighbouring hosts in the layers are supported by C–H···π interactions involving methyl hydrogens of the methoxy group and pyrene π-surface. ***c***, Crystal packing down the *b*-axis without the guests.

Indeed, the host molecules in the layers do not lie in the same plane, but arrange themselves in the form of 'steps' along the *ac*-plane down the *b*-axis (Figure 2 *c*). Consequently, the adjacent layers are offset. The C–H···O hydrogen-bonded self-assembly leads to cavities of two different sizes down the *c*-axis. The anthracene guest molecules are found to occupy the trough region via C–H···π interaction with the host ($d_{C–H...\pi}$ = 2.64 Å, $D_{C...\pi}$ = 3.56, $\theta_{C–H...\pi}$ = 171.3°), whereas benzene molecules are found to be located in the concave region. Furthermore, one observes that the basin region is occupied by part of the host molecule from the adjacent layers; in particular, the methyl of the methoxy group falls on the basin such that all the hydrogens exploit C–H···π interactions (Figure 2b).

H•cp•bz: Good quality crystals of **H** with [2.2]paracyclophane were obtained from crystallization of the host **H** in benzene containing paracyclophane. The X-ray crystal structure determination revealed that the crystals belong to the triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit cell is found to contain half molecule each of host and paracyclophane and one molecule of benzene, such that the host : guest : guest ratio is 1 : 1 : 2. The crystal packing diagram reveals that the host molecules self-assemble by C–H···O hydrogen-bonds ($d_{C–H...O}$ = 2.85 Å, $D_{C...O}$ = 3.68 Å, $\theta_{C–H...O}$ = 143.3°) leading to layers in the *bc*-plane as shown in Figure 3 *a*. The trough regions of the host molecule are found to be occupied by [2.2]paracyclophane guests via C–H···π interaction ($d_{C–H...\pi}$ = 2.86 Å, $D_{C...\pi}$ = 3.79 Å, $\theta_{C–H...\pi}$ = 166.1°). The concave regions are found to be occupied by the methoxy moieties of the two neighbouring host molecules present in the same layer. The basin region is found to be filled by the methyl group connected to the aromatic ring of the host present in the adjacent layer. Unlike in the previous two cases, the methyl of the methoxy moiety of the host molecule acting as the guest to the basin region is directed away from the aromatic pyrene surface of the host molecule. The benzene guest is found to be

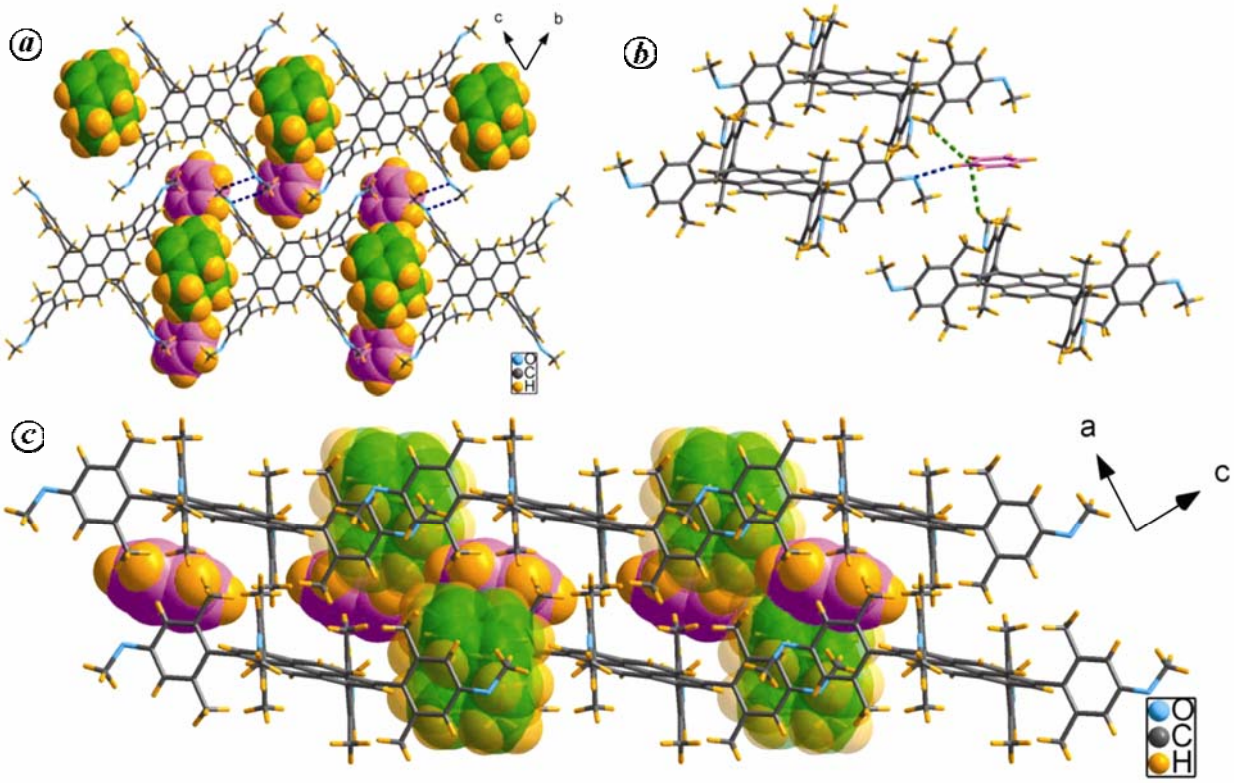

Figure 3. ***a***, Crystal packing in the *bc*-plane. ***b***, One of the host molecules is shown separately to depict the relative arrangement of para-cyclophane (green) in the trough region, whereas a neighbouring host molecule partially occupies the concave region. Notice that benzene is held by the three neighbouring host molecules via two C–H···π interactions (green dotted) and one C–H···O H-bond (blue dotted) of with the benzene molecule (pink). ***c***, The free space between two adjacent layers down the *b*-axis is filled with benzene molecules.

bound by two C–H···π interactions ($d_{C–H\cdots\pi}$ = 2.87 Å, $D_{C\cdots\pi}$ = 3.72 Å, $\theta_{C–H\cdots\pi}$ = 145.7°; $d_{C–H\cdots\pi}$ = 2.89 Å, $D_{C\cdots\pi}$ = 3.76 Å, $\theta_{C–H\cdots\pi}$ = 145.7°) and one C–H···O hydrogen bond ($d_{C–H\cdots O}$ = 2.65 Å, $D_{C\cdots O}$ = 3.44 Å, $\theta_{C–H\cdots\pi}$ = 141.7°) with three neighbouring host molecules, thereby forming a bridge to connect the host molecules together (Figure 3).

Site-selective inclusion and overall generalization

We have earlier shown that the host **H** is a very adaptive system that exhibits kaleidoscopic guest inclusion behaviour in binding a diverse range of guest molecules in the solid state[35–37]. The unique structural features of the host in which the aryl rings lie near orthogonally due to sterics exerted by 2,6-dimethyl rings confer the host system with different domains. Although the aryl rings, i.e. 2,6-dimethyl-4-anisyl rings, are implied to be rigid at the outset, crystal structure analyses of a large number of structures revealed that they do exhibit some torsional flexibility; indeed, they are not perfectly orthogonal, but the angle between the pyrene platform and the plane of the dimethylanisyl ring varies from 68.1° to 89.9° (ref. 35). The little, yet significant torsional flexibility of the aryl rings in conjunction with weak hydrogen bonds with which the host assembles and binds the guest molecules in the solid state seemingly enables the host system to adopt geometries that are complementary to a given guest; the fact that the host system is devoid of any strongly interacting functional groups such as COOH, OH, etc. (J. N. Moorthy and P. Natarajan, unpublished) is evidently advantageous, as the weak interactions may promote looser association of hosts to accommodate guests.

The crystal structures in the present study as well as earlier studies[36,37] point to the fact that the trough domain of the host **H** is particularly well suited to selectively include all aromatic compounds that range from benzene to pyrene[35]. However, the fact that the host does distinguish the shapes and sizes of guests when faced with competition is compellingly revealed from the present study. The previously reported[36] two (**H**•py•bz and **H**•fl•bz) and the presently studied three multicomponent inclusion compounds, cf. Table 1, involving benzene as the small-sized guest reveal that it is not found in the trough region, but in the concave (in H•fl•bz, H•py•bz, H•an•bz, H•cp•bz) and trough as well as concave (in H•bz) regions. The multicomponent crystals **H** with pyrene–benzene, anthracene–benzene and fluorene–benzene exhibit packing similarities in that the large-sized aromatics are found in the trough regions, but the benzene guests in the concave domain; indeed, **H**•py•bz and **H**•an•bz are isostructural.

In all of the five multicomponent crystals involving benzene and other large-sized aromatic guests, the latter are invariably found to be bound in the troughs. This attests to the fact that the aromatic guests that are larger in size than benzene are preferably accommodated in trough regions, whereas aliphatic or benzene guests are utilized in filling the space to achieve close packing. In the absence of other larger guests, solvent benzene itself is found to be bound in all the three domains[35,36]. The ternary cocrystals of **H**•bp•bz exhibit packing similarity with those of the binary crystals of **H**•bp. Indeed, crystal packing in the latter is almost similar to that shown in Figure 1 (ref. 35). The analysis of crystal structures of the multicomponent crystals shows that the large-sized aromatic guests bound in troughs are held by C–H$\cdots\pi$ interactions involving the C2 hydrogen of the host pyrene, which falls into the π-expanse of the included guest. Insofar as the crystal packings of all the multicomponent compounds of **H** are concerned, it is the weak C–H···O hydrogen bonds and C–H$\cdots\pi$ interactions that are involved in the crystal lattice stabilization[41].

A variety of host systems that are devoid of strongly interacting functional groups are known that bind the guest molecules[42,43]. For example, tetraarylporphyrin has long been shown to include a number of guest molecules[44,45]. Likewise, other host systems that exhibit guest entrapment based on weak interactions include perhydrotriphenylene, triphenylmethane, etc.[43]. What is it that actually causes the pyrene host **H** described herein to exhibit differential guest binding? The answer lies in the reduced symmetry of tetraarylpyrene when compared with other host systems, e.g. tetraarylporphyrin, which seemingly imparts distinct topological features to bind two or more different guests. Thus, the nuance for inclusion of two or more guest molecules evidently lies in the rational design of molecular structure that is programmed for the given cause.

Conclusion

The unique topological features of the host **H** that permit three distinct domains for guest inclusion are exploited to demonstrate accessibility of multicomponent lattice inclusion crystals with a definite stoichiometry of the components. The host **H** is found to exhibit site-selective inclusion of the aromatic guests. The binding of guests in trough domain of the host is differentiated by the sizes of the aromatic guests. Thus, the large-sized aromatic guests, i.e. biphenyl, fluorene, anthracene, pyrene and [2.2]paracyclophane, are found to be selectively bound in the trough domain, whereas small-sized benzene guest is included in other regions of the host, i.e. concave and basin. The results clearly show that rational molecular design constitutes a definite approach to multicomponent molecular crystals.

General procedure for synthesis of multicomponent crystals

A mixture of host **H** (0.1 mmol) and solid guest (0.2 mmol) was dissolved in a minimum amount of benzene (2–3 ml). Slow evaporation of the resultant solution over a period of one week led to colourless crystals quantitatively. Crystals were isolated by filtration and washed with pet. ether–diethyl ether (50 : 50, 2 ml) mixture.

X-ray crystal structure determination

Good-quality crystals of the inclusion compounds of **H** were mounted in glass capillaries, cooled to 100 K, and the intensity data were collected on a Bruker Nonius SMART APEX CCD detector system with Mo-sealed Siemens ceramic diffraction tube ($\lambda = 0.71073$) and a highly oriented graphite monochromator operating at 50 kV and 30 mA. The data were collected on a hemisphere mode and processed with SAINTPLUS. Empirical absorption corrections were made using SADABS. The structures were solved by direct methods using SHELXTL package and refined by full matrix least-squares method based on F^2 using SHELX97 program[46]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the ideal positions with fixed isotropic U values and were riding with their respective non-hydrogen atoms.

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