

Cocrystals and Salts of Pyridine-3,5-bis(1-methyl-benzimidazole-2-yl) with Pyromellitic Acid: Aromatic Guest Inclusion and Separation via Benzimidazole–Carboxylic Acid Heterosynthon

Avishek Dey, Saibal Bera, and Kumar Biradha*

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

Supporting Information

ABSTRACT: An arc-shaped molecule pyridine-3,5-bis(1methyl-benzimidazole-2-yl) was shown to form cocrystals and salts with pyromellitic acid (H_4 PMA) which are sustained by COOH…N_{bim}/COO⁻…Hbim heterosynthons. The reaction between these two components in the presence of large aromatic guest molecules resulted in the crystals of salts with aromatic inclusion, while the absence of guests resulted in the H_2O and EtOH solvates of cocrystals. The crystal structures of salts exhibited isostructurality with the inclusion of aromatics such as pyrene, perylene, phenanthrene, and 9-anthraldehyde. The crystal structures of solvates were found to differ significantly despite having similar composition. In all these



structures the –COOH functional group has exhibited significant preference to interact with the benzimidazole moiety over the pyridine moiety. The aromatic guest inclusion was found to occur via cation… π interactions between the protonated benzimidazole and π -cloud of guest molecules. The competitive experiments on guest inclusion reveal that the two-component host system exhibits selective inclusion of perylene or 9-anthraldehyde over other aromatics such as pyrene or phenanthrene.

rystal engineering has emerged as a multidisciplinary area ✓ of research due to its focus on fundamental aspects such as continuous exploration and exploitation of various intermolecular interactions toward the design of novel functional materials with predefined properties. Hydrogen bonds play a dominant role in crystal engineering due to their selectivity and directionality to control the molecular aggregation which defines the properties of a material.¹⁻¹⁰ The exploration of the interactions between various functional groups, supramolecular synthons, that are capable of forming strong hydrogen bonds is very essential for the predictable design of solid state assemblies. $^{11-21}$ In particular, with molecules containing multiple functional groups, it is not clear whether all functional groups act according to the programmed way to form dominant synthons. If not, what happens? Which synthon will prevail? And why? These are the questions that are difficult to answer without ambiguity; of course, some of these questions for tailor-made systems are answered well using hydrogen bonding hierarchy. $^{22-30}$ The design of the cocrystals using supramolecular synthons has gained importance given its applicability in multicomponent molecular hosts, pharmaceuticals, molecular electronics, solid state reactions, and colorimetric indicators. $^{31-38}$ To date, the acid-pyridine synthon is the most utilized one to design cocrystals or salts.³⁹⁻⁴⁸ Recently, we have shown that the acid-pyridine synthon can be successfully utilized to design the two-component hosts for the inclusion and colorimetric detection of poly-aromatic hydrocarbons.34

Along similar lines to acid-pyridine synthon, the studies on acid-imidazole or acid-benzimidazole (bim) synthons have emerged in the recent past due to the greater importance of imidazole/bim moieties in biological systems over pyridine.49-55 For example, the solubility enhancement studies were performed on several drug molecules such as mebendazole, theophilline, omeprazole, etc.^{56–60} The imidazole amine (N-H group) is very basic in bim moiety, and as a result the reaction of R-COOH with bim forms a salt rather than a cocrystal. However, several studies on R-COOH-bim complexes show that the probability of forming a cocrystal increases when the -N-H group in bim is changed to an -N-alkyl group.⁶¹⁻⁶⁷ For example, the Cambridge Structural Database contains 46 structures in which both N-substituted bim and -COOH group are present, and out of these 31 structures contain $\tilde{COO(H)}$... N_{bim} hydrogen bonding. In these 31 structures only eight structures are found to exist as salts and 23 structures exist as neutral structures.^{68,69} This indicates lower basicity of N-alkyl of bim compared to N-H of bim. The pK_{n} calculations also confirm this fact: the bim with N-H is dibasic with pK_a values of 12.25 and 5.79, whereas N-methylated bim is monobasic with a pK_a value of 5.65.^{70,39,16}

Accordingly, in this manuscript we would like to explore the cocrystals of 1, namely, pyridine-3,5-bis(1-methyl-benzimidazole-2-yl),

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which contains two bim moieties and a pyridine moiety, with a pyromellitic acid (H₄PMA) and exploit them as a two-component host system for the inclusion of poly-aromatic hydrocarbons. We note here that compound 1 has been successfully utilized by us for metal-organic gels and coordination polymers.⁷¹ The arc-like nature of the molecule immobilizes solvent molecules upon coordination with transition metals. Therefore, 1 is of interest given its arc nature that is suitable for creation of voids in their crystal structures. Further, it is of interest to study the competition between the pyridine and bim moieties to form their respective synthons. In this regard, remarkable studies by Aakeroy et al. are noteworthy; it was shown by them that the molecules containing bim and pyridine moieties form ternary cocrystals such that the most acidic -COOH binds with the bim moiety, while less acidic -COOH binds to the pyridine moiety which is in accordance with hierarchy rule.^{22–24} The molecule H₄PMA contains four protons with pK_a values of 1.92, 2.87, 4.49, and 5.63.⁷² It was found by us earlier that the basicity of pyridine containing molecules are good enough to remove two of its protons.^{16,39} In this contribution we would like to address the following aspects: (1) salts or cocrystals? (2) Is it possible to observe both the synthons (I and II) due to the variable pK_3 values of H_4 PMA? (3) If not both, which synthon will prevail? (4) Is it possible to use this two-component system for aromatic inclusion? Does the aromatic inclusion have any influence on the final outcome of salt vs cocrystal? Does the twocomponent host exhibit selective guest inclusion?





RESULTS AND DISCUSSION

The compound **1** was prepared by a condensation reaction between *o*-phenylenediamine and pyridine-3,5-dicarboxylic acid in the presence of polyphosphoric acid followed by methylation

of imine protons.⁷¹ The cocrystallization reaction of 1 with H_4PMA in EtOH resulted in the crystal of EtOH solvate. The repeat of this reaction with the addition of hydrophobic solvents such as phenol, benzonitrile, and nitrobenzene to ethanolic solution of 1 resulted in the formation of crystals of a hydrate of 3. The crystals of guest inclusion complexes (4–7) of 1 with H_4PMA were obtained by reacting 1 and H_4PMA in the solution of ethanol-dichloromethane containing the corresponding guest molecule. Single crystal X-ray diffraction analysis reveals that the crystals of 4–7 exhibit iso-structurality with common formulas of $[(H_4PMA)(H_2PMA)(H1)_2]\cdot 2H_2O$. guest (3). Pertinent crystallographic details are given in Table 1.

 $[(H_4 PMA) \cdot (1)_2] \cdot 2EtOH(2)$

 $[(H_4PMA) \cdot (1)_2] \cdot 2H_2O(3)$

 $[(H_4PMA)(H_2PMA)\cdot(H1)_2]\cdot 2H_2O\cdot pyrene (4)$

 $[(H_4PMA)(H_2PMA)\cdot(H1)_2]\cdot 2H_2O\cdot perylene (5)$

 $[(H_4PMA)(H_2PMA)\cdot(H1)_2]\cdot 2H_2O\cdot phenanthrene (6)$

 $[(H_4PMA)(H_2PMA)\cdot(H1)_2]\cdot 2H_2O\cdot 9$ -anthraldehyde (7)

Solvated Cocrystals. The complex 2 crystallizes in $P\overline{1}$ space group and asymmetric unit contains one molecule of 1, half of H₄PMA, and one ethanol molecule. The C-O and C=O bond lengths of -COOH groups of H₄PMA (1.219(6)) Å and 1.305(6) Å and 1.181(6) Å and 1.294(6) Å) indicate that carboxylic acid groups are not deprotonated; therefore complex 2 is a cocrystal. We note here that the pyridyl moiety is not involved in H-bond formation either with EtOH or with H₄PMA. Each molecule of H₄PMA was surrounded by four molecules of 1 via hydrogen bonds between -COOH groups of bim moiety: among the four COOH groups of H₄PMA, two form synthon-II and other two -COOH groups hydrogen bond to the N atom of bim through ethanol molecules (Figure 1). As a result it forms a hydrogen-bonded onedimensional chain in which two of the bim moieties stack on each other with 3.665 Å. The pyridyl moieties form C-H···N hydrogen bonded cyclic synthon to assemble these onedimensional chains into three dimensions.

Table 1. Crystallographic Parameters for the Crystal Structures of 2-7

	2	3	4	5	6	7
formula	$C_{56}H_{52}N_{10}O_{10}$	$C_{52}H_{44}N_{10}O_{10}$	$C_{78}H_{60}N_{10}O_{18}$	$C_{82}H_{62}N_{10}O_{18}$	$C_{76}H_{60}N_{10}O_{18}$	$C_{77}H_{60}N_{10}O_{19}$
mol wt	1025.08	968.97	1425.36	1475.42	1401.34	1429.35
T(K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a (Å)	7.590(3)	8.435(2)	10.741(3)	10.635(4)	10.651(4)	10.625(3)
b (Å)	11.339(5)	10.432(3)	11.454(3)	11.379(4)	11.362(4)	11.428(3)
c (Å)	15.138(6)	13.287(4)	14.658(4)	14.710(5)	14.732(5)	14.773(4)
α (deg)	76.868(14)	81.612(7)	96.553(8)	97.520(11)	96.914(10)	97.149(8)
β (deg)	89.863(13)	75.381(7)	97.070(8)	97.062(12)	96.252(10)	96.088(7)
γ (deg)	75.754(13)	87.175(7)	111.233(8)	109.545(11)	110.223(10)	110.626(7)
$V(A^3)$	1227.8(9)	1119.1(5)	1643.5(7)	1636.3(10)	1638.9(10)	1643.8(7)
Z	1	1	1	1	1	1
$D (mg/m^3)$	1.386	1.438	1.440	1.497	1.420	1.444
$R_1 \left[I > 2\sigma(I) \right]$	0.0670	0.0426	0.0662	0.0697	0.0765	0.0596
wR ₂ (on F ² , all data)	0.1546	0.1356	0.1684	0.1689	0.2057	0.1889



Figure 1. Illustrations for the crystal structure of **2**: (a) onedimensional hydrogen bonding network between **1**, H₄PMA, and EtOH; notice the synthon-**II** and $\pi \cdots \pi$ interactions between bim moieties (encircled); (b) packing of the one-dimensional networks via C-H···N hydrogen bonded cyclic synthons and $\pi \cdots \pi$ interactions (encircled).

The complex 3 crystallizes in a triclinic $P\overline{1}$ space group, and the asymmetric unit is similar to that of 2 albeit a water molecule replaces EtOH. Similar to 2, the C–O and C==O distances (1.208(2) Å and 1.307(2) Å and 1.202(2) Å and 1.300(2) Å) of -COOH groups indicate that it is a cocrystal.

However, the crystal structures differ significantly. Two of the –COOH groups of H₄PMA are directly involved in Hbonding with N atoms of bim and other two –COOH groups are linked with N atoms of pyridine and bim via H-bonding with water molecule. However, the formation of synthons I or II were not observed; although two –COOH groups H-bonded directly to bim, the C=O group hydrogen bonds to pyridyl C-H rather than a C-H group of a bim (Figure 2). As a result each H₄PMA is surrounded by six molecules of 1 via H-bonding and leads to the formation of a three-dimensional hydrogen bonding network. The H₄PMA and bim moieties are stacked on each other with a distance of 3.941 Å leading to the formation of a two-dimensional structure.

Aromatic Guest Inclusion by Cocrystals of 1 and H_4PMA . The repeat of crystallization reactions in the presence of aromatic guest molecules such as of pyrene, perylene, phenanthrene, and 9-anthraldehyde resulted in single crystals of guest inclusion complexes 4–7 respectively. We note here that crystals of 3 were always obtained, despite several tries, in the presence of other guest molecules such as 4-hydroxy benzaldehyde, anthracene, TCNQ, phenazine, naphthalene, triphenylene, biphenyl, nitrobenzene, benzonitrile and *m*-cresol. Single crystal analyses of complexes 4–7 reveal that the guest



Figure 2. Illustrations for the crystal structure of 3: (a) six moieties of 1 surrounding H_4PMA via hydrogen bonding;note the new cyclic synthon which is encircled; (b) hydrogen bonding layers, (c) three-dimensional network structures via assembly of 2D layers.

inclusion complexes exhibit isostructurality. The complexes 4–7 crystallizes in triclinic $P\overline{1}$ space group, and crystal structure analysis reveals that 1 and H₄PMA form a salt to host guest molecules. The asymmetric unit is constituted by one unit each of H1 and H₂O, three half units of H₄PMA, H₂PMA, and guest molecule.

It interesting to note here that only one bim moiety of 1 was protonated, and similarly one of the two H₄PMA gets deprotonated. The H₄PMA exhibits nonplanar geometry as the -COOH (C-O: 1.192(3) Å, 1.198(3) Å and C=O: 1.290(3), 1.291(3) Å) groups make some angles with central C₆ ring, while the H₂PMA exhibits planar geometry as the $-COO^-$ (C-O: 1.234(3) Å and 1.265(3) Å) and -COOH (C=O: 1.213(3) Å and C-O: 1.273(3) Å), which are ortho to each other, engage in intramolecular O-H···O hydrogen bonds (Figure 3). The Hbim and bim moieties of 1 were found to be easily distinguished by their stacking interactions. The Hbim



Figure 3. Illustration for the crystal structures of 4–7: (a) 2Dhydrogen bonding layer between H₄PMA, H₂PMA, and H₂O, (b) connecting 2D-layers of H₄PMA-H₂PMA-H₂O into a three-dimensional network by the moieties of H1 (synthon-II encircled); (c) weak $\pi \cdots \pi$ and C–H···N interactions between the moieties of H1.

moiety forms stacks with guest molecules via cation… π interactions, while the bim moiety involved in self-stacking interactions (3.190 Å). We note here that the N-Me group, in particular, forms shorter interactions with the guest molecules: the distances between N⁺ of the NMe to one of the centroid of aromatic ring of the guests are 3.589, 3.994, and 3.985 Å in 4, 5, and 7 respectively. This observation indicates that the positive charge is located more on the NMe group than on the N–H group of bim moiety. The analysis on C–N distances using the entries in CSD indicates that the difference between two C–N distances (N(1)–C(1)–N(2), Scheme 2)) is much smaller

Scheme 2. Protonation of bim and Resonance in Hbim



(0.016 Å) than that of the nonprotonated bim (0.048 Å).⁷³ This observation reveals that protonated bim exhibits more delocalization of the double bond than the nonprotonated one. However, C1–N1 was found to be always longer than C1–N2 in both cases: by 0.016 Å in the case of protonated bim and by 0.048 Å in the case of the neutral one.

The H_4PMA and H_2PMA linked by H_2O molecules via $O-H\cdots O$ hydrogen bonds to form a two-dimensional layer



Figure 4. Illustrations for the guest inclusion in the crystal structures of 4–7: inclusion of (a) pyrene, (b) perylene, (c) phenanthrene, and (d) 9-anthraldehyde with in the 2D-layer of $H_4PMA-H_2PMA-H_2O$. (e) Cation… π interactions between Hbim and pyrene molecule.

containing cavities (16.505 Å and 11.196 Å). The size of the cavities found to be a perfect fit for the guest molecules, which nearly lie in the plane of the layer (Figure 4). These layers are interconnected by H1 via N–H···O and O–H···N hydrogen bonds to form a hydrogen bonded three-dimensional network. The neutral –COOH is engaged in the formation of synthon-II, while –COO⁻ hydrogen bonds with Hbim (–N–H···O) but does not form the C–H···O of synthon-II. The pyrene guest molecules are located without any disorder in complexes 4, and only –CHO groups of 9-anthraldehyde exhibited disorder in complex 5 6 and 7 were found to be severely disordered.

D

Mechanochemical Grinding Reactions. Recently, synthesis of cocrystals or salts by mechanochemical dry or wet grinding had gained importance given their facile synthesis and green route.^{74–77} In the past, it was shown in our laboratory the dry/wet grinding of the components as an alternate process to produce such materials.³⁴ Therefore, dry grinding and solvent drop assisted grinding experiments with 1, H₄PMA, and aromatic guest molecules were carried out. It was found that even for these systems it is an effective methodology to produce salts similar the ones that are observed by the conventional crystallization reactions. The similarities between these materials were confirmed by the observed colors and comparing powder diffraction patterns (See Supporting Information).

DRS Study. The optical absorption of the complexes 2-7 were measured using an UV-vis spectrometer. The crystals of the complexes 2-7 are colorless, colorless, off-white, deep yellow, colorless, and yellow, respectively. The solid-state diffuse reflectance spectra (DRS) of the complexes indicate different absorption edges reflecting their different colors observed (Figure 5) in the solid state. The absorption edges



Figure 5. DRS for the complexes 1-7.

of 2, 3 4, 5, 6, and 7 are located at around 335, 330, 362, 456, 357, and 434 nm, respectively. The absorption edges of 4–7 are found to be blue-shifted compared to their corresponding guest molecules by 15 nm (377 nm, pyrene), 24 nm (480 nm, perylene), 21 nm (378 nm, phenanthrene), 49 nm (483 nm, 9-anthraldehyde) respectively. The solid state structures indicate cation… π interactions with distances between N⁺ of the NMe to one of the centroid of aromatic ring of the guests of 3.589 Å, 3.994 and 3.985 Å in 4, 5, and 7 respectively. It can be noted that the complex 4 has a shorter cation… π interaction and exhibits less blue shift compared to the other two complexes. However, with respect to the neutral 1 (335 nm) all are found to be red-shifted 27, 121, 22, and 99 nm in the complexes 4–7 respectively.

Separation of Guest Molecule. Competitive guest encapsulation studies were carried out by complexing 1 with H_4PMA in the presence of a mixture of two guest molecules, for example, 9-anthraldehyde and anthracene, phenanthrene and perylene, pyrene and perylene, 9-anthraldehyde and phenanthrene or perylene and naphthalene. Preferential uptake of one guest molecule over the other was observed and easily identified by the color of the crystals. It is interesting to note here that host system can effectively capture 9-anthraldehyde from the mixtures of 9-anthraldehyde and anthracene or 9-anthraldehyde and phenanthrene and perylene from phenanthrene and perylene or pyrene and perylene, perylene and naphthalene systems. The preferential inclusions of 9-anthraldehyde and perylene over other aromatic molecules could be attributed to size and shape selectivity of the host system. In the case of 9-anthraldehyde, the -CHO group is acting as an anchor to attach the host system for the inclusion, whereas for perylene the bigger aromatic cloud as well as its curved shape could be the driving forces over the inclusion of other aromatics. The preferential uptakes of guest molecules has also been verified by recording the ¹H NMR of the bulk samples which reveals the presence of only one of the guest molecules from the above pairs, namely, 9-anthradehyde or perylene.

CONCLUSIONS

The benzimidazole and pyridine containing molecule 1 with H₄PMA was shown to form hydrate and ethanol solvates of cocrystals 2 and 3. Interestingly, a small change, namely, addition of hydrophobic solvent, in crystallization conditions was found to result in the two solvates. The -COOH groups have shown a propensity for the formation of synthon II over I, which is in accordance with interaction hierarchy principle. However, the repeat of these reactions in the presence of a large aromatic guest such as pyrene, perylene, phenanthrene, and 9-anthraldehyde resulted in the formation of salts. In other words, the presence of an electron-rich guest promoted the deprotonation of H₄PMA by forming strong cation... π interactions between N⁺-Me and the aromatic moiety of the ring. The crystal structures of 4-7 help in understanding the resonance structure of the bim moiety. In summary, the results indicate that H₄PMA and 1 can form a two-component organic host which can accommodated large aromatic guest molecules. The selective inclusion of guest molecules from the mixture of guest indicates their utility for the separation of mixtures.

EXPERIMENTAL SECTION

All the chemicals, such as *o*-phenylenediamine, pyridine-3,5-dicarboxylic acid, polyphosphoric acid (PPA), methyl iodide, 9-anthraldehyde, pyromellitic acid, pyrene, perylene, and phenanthrene, were purchased from local chemical suppliers and used without purification with the exception of tetrahydrofuran (THF), which was dried over sodium and benzophenone before use. NMR spectra were recorded on a Bruker DRX200 spectrometer, and IR spectra were recorded on a PerkinElmer Instrument Spectrum Rx Serial No. 73713. Melting points were taken using a Fisher Scientific melting point apparatus, Cat. No. 12-144-1. The diffuse reflectance spectra (DRS) were recorded with a Cary model 5000 UV–vis-NIR spectrophotometer.

Synthesis of 1. Compound 1 was synthesized using the reported procedures.⁷¹ Pyridine-3,5-dicarboxylic acid (3.0 g, 17.96 mmol) and *o*-phenylenediamine (3.879 g, 35.92 mmol) were added to polyphosphoric acid (PPA) and mixed thoroughly to make a paste. The mixture was then heated slowly to 190–200 °C and stirred for 3–4 h; the mixture was allowed to cool to about 100 °C. The resultant green-colored viscous crude mixture was poured into a large volume of rapidly stirred cold water, and it was neutralized with an aqueous ammonia solution to make the solution slightly basic. The insoluble residue was collected by filtration and washed with water until the residue part became base free. The product was dried under a vacuum and recrystallized from hot methanol. The crystalline powder was isolated with a good yield (70%). mp >290 °C.

A total of 1.158 g of sodium hydride (95%) was added to a stirred dry THF solution (40 mL) of the above compound (3.0 g, 9.6 mmol) in a 100 mL round-bottom flask, under a nitrogen atmosphere, over 30 min through a side arm. Methyl iodide (2.72 g, 19.2 mmol) was

Table 2. Hydrogen Bonding Parameters in the Crystal Structures of 2–7

complexes	interaction	H…A (Å)	D…A (Å)	D-H…A (deg)
2	O−H…N	1.80(4)	2.700(4)	167(4)
	O−H…O	1.66(4)	2.583(5)	167(4)
	С–Н…О	2.58	3.428(8)	146
		2.49	3.420(6)	162
		2.47	3.199(5)	133
3	O−H…N	2.08(3)	2.881(2)	173.7(19)
	O−H…O	1.84(2)	2.780(2)	175.4(17)
	С–Н…О	1.67(2)	2.621(2)	159.5(18)
		1.48(2)	2.572(2)	172.9(19)
		2.56	3.254(2)	132
		2.56	3.407(3)	152
4	$C-H\cdots O^{a}$	2.30	2.690(6)	105
	С–Н…О	2.29	2.691(5)	105
		2.46	3.311(5)	147
		2.40	3.319(6)	168
		2.44	3.220(6)	141
		2.35	3.299(6)	172
5	O−H…O	1.83(5)	2.812(5)	164(4)
	$O-H\cdots O^{a}$	1.87(5)	2.772(5)	171(4)
	N–H…O	1.82(4)	2.594(5)	179(7)
	$C-H\cdots O^{a}$	1.27(4)	2.416(4)	168(5)
	С−Н…О	1.77	2.614(4)	165
		1.78	2.635(5)	170
		2.28	2.677(5)	105
		2.29	2.684(5)	105
		2.58	3.327(6)	137
		2.39	3.309(7)	169
		2.58	3.378(6)	144
6	O−H…O	1.83(5)	2.812(5)	164(4)
	$O-H\cdots O^{a}$	1.87(5)	2.772(5)	171(4)
	N–H…O	1.82(4)	2.594(5)	179(7)
	$C-H\cdots O^{a}$	1.27(4)	2.416(4)	168(5)
	С−Н…О	1.77	2.614(4)	165
		1.78	2.635(5)	170
		2.28	2.677(5)	105
		2.29	2.684(5)	105
		2.58	3.327(6)	137
		2.39	3.309(7)	169
		2.58	3.378(6)	144
7	О-Н…О	1.81(3)	2.599(3)	175(3)
	O−H…N	1.86(3)	2.784(3)	161(2)
	N–H…O	1.86(3)	2.807(3)	172(2)
	$C-H\cdots O^{a}$	1.65(3)	2.601(3)	170(3)
	С–Н…О	1.73(3)	2.628(3)	175(2)
		2.29	2.683(3)	105
		2.27	2.667(3)	105
		1.95	2.493(11)	115
		2.45	3.345(4)	155
		2.44	3.365(4)	170
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added to this solution dropwise. The reaction mixture was stirred overnight, quenched with water, and then poured into 400 mL of water. After the solution was stirred for 30 min, a pale yellow precipitate was collected by filtration, washed repeatedly with water, and dried in a vacuum for 24 h. The crude product was recrystallized from methanol and kept for slow evaporation at room temperature. After 2 days, the compound 1 was collected via filtration with a good yield (85%). mp 244 °C

Synthesis of Cocrystals of 2-7. Crystallization of 2. The cocrystals of 2 were synthesized by direct mixing of 2 mL of ethanolic

solutions of 1 (10 mg, 0.0295 mmol) and H_4PMA (7.4 mg, 0.0295 mmol). After 2 days, colorless single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 232 °C. FT-IR (KBr): 3294, 3055, 2868, 2482, 1700, 1522, 1477, 1364, 1332, 1233, 1109, 1053, 951, 885, 821, 755, 652, 583, 552, 471, 436 cm⁻¹.

Crystallization of **3**. The cocrystals of 3 were synthesized by direct mixing of 2 mL of ethanol/phenol mixture solution of **1** (10 mg, 0.0295 mmol) with the 2 mL solution of H₄PMA (7.4 mg, 0.0295 mmol) in ethanol. After 2 days, colorless single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 206 °C. FT-IR (KBr): 3057, 2437, 1698, 1488, 1366, 1333, 1288, 1233, 1111, 1020, 951, 885, 821, 755, 706, 653, 584, 554, 471, 438 cm⁻¹.

Crystallization of 4. The crystals of 3 were synthesized by direct mixing of 2 mL ethanolic solution of 1 (10 mg, 0.0295 mmol) and H₄PMA (7.4 mg, 0.0295 mmol) with the 3 equiv of pyrene guest in DCM solution. After 2 days, off-white single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 166 °C. FT-IR (KBr): 3394, 3037, 2778, 2370, 1909, 1718, 1463, 1343, 1305, 1281, 1149, 1109, 911, 889, 845, 820, 758, 706, 652, 602, 577, 538, 504 cm⁻¹.

All other crystallizations were carried out in a similar way.

Crystallization of 5. Three equivalents of perylene guest was used instead of pyrene in this reaction. After 2 days, deep yellow single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 216 °C. FT-IR (KBr): 3407, 3054, 2366, 1918, 1720, 1697, 1463, 1341, 1304, 1239, 1107, 886, 811, 755, 706, 652, 601, 579, 542 cm⁻¹.

Crystallization of **6**. Three equivalents of phenanthrene guest was used instead of pyrene in this reaction. After 2 days, colorless single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 178 °C. FT-IR (KBr): 3366, 3098, 2927, 2764, 2365, 1909, 1723, 1666, 1463, 1345, 1300, 1282, 1150, 1107, 915, 890, 823, 763, 706, 652, 603, 579, 540 cm⁻¹.

Crystallization of **7**. Three equivalents of 9-anthraldehyde guest was used instead of pyrene in this reaction. After 2 days, yellow single crystals suitable for X-ray diffraction were obtained with 60% yield. mp 190 °C. FT-IR (KBr): 3366, 3098, 2927, 2764, 2365, 1909, 1723, 1666, 1463, 1345, 1300, 1282, 1150, 1107, 915, 890, 823, 763, 706, 652, 603, 579, 540 cm⁻¹.

Crystal Structure Determination. All the single crystal data were collected on a Bruker-APEX-II CCD X-ray diffractometer that uses graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at room temperature (293 K) by the hemisphere method. The structures were solved by direct methods and refined by least-squares methods on F² using SHELX-97.⁷⁸ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. The H atoms attached to the O atom or N atoms are located and refined using the riding model. In the case of crystal structure **5**, the perylene was located initially; however it was removed in the final refinement, using the Platon squeeze option,⁷⁹ due to the higher thermal motions and disorder which cannot be modeled. Similarly in the crystal structure **6**, phenanthrene exhibited heavy disorder that cannot be modeled; therefore the final refinement was conducted without phenanthrene using Platon squeeze option.

ASSOCIATED CONTENT

Supporting Information

FT-IR spectra of the complexes 1-7, TGA thermograms for the complexes 2-7, calculated and experimental PXRD patterns for the complexes 2-7, ¹H NMR of guest separation. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: +91-3222-282252. Tel: +91-3222-283346. E-mail: kbiradha@chem.iitkgp.ernet.in.

Notes

The authors declare no competing financial interest.

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