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ARTICLE TYPE

Cocrystallization of Pyrogallol[4]arenes with 1-(2-pyridylazo)-2-naphthol

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Cocrystallizations of pyrogallol[4]arenes and 1-(2-pyridylazo)-2-naphthol (PAN) are investigated herein in order to determine the effect of aliphatic tail-length and solvent on crystal packing, probe orientation, and pyrogallol[4]arene bowl-shape. It is seen that solvent affects the final ratio of PAN to pyrogallol[4]arene, while aliphatic tail-length influences the crystal packing, C−H···π interactions, and overall hydrogen bonding. With an aliphatic tail-length of one carbon atom, there is an atypical bilayer structure. As the aliphatic tail-length increases, the resulting cocrystals have the characteristic bilayer structure as well as an increased number of C−H···π interactions and decreased hydrogen bonding with the PAN molecules.

Introduction

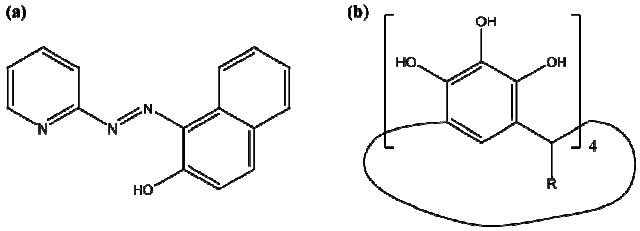
Pyrogallol[4]arenes are a subset of the calixarene family of macrocycles. They have four aromatic groups joined together by –CHR- linkers to form a bowl-shaped molecule. Along the upper-rim of the molecule are twelve hydroxyl groups and at the lower rim, where the aromatic groups join together, are four aliphatic tail groups of a specific length. Herein, pyrogallol[4]arenes will be abbreviated as PgC_x where *x* is the number of carbon atoms in the tail group. The ability of the upper-rim hydroxyl groups to participate in hydrogen bonding and the flexibility of the bowl allow pyrogallol[4]arenes to exhibit diverse structural chemistry. The pyrogallol[4]arenes have been shown to form dimeric and hexameric assemblies along with nanotubes.[1] Metal ions, such as Cu^{2+}, Zn^{2+}, and Ni^{2+}, have also been found to replace the hydroxyl hydrogen atoms at the upper rim, thereby seaming the dimeric or hexameric assemblies with metal ions.[2]

Due to their conical shape, pyrogallol[4]arenes have a cavity that is ideal for host-guest interactions.[3] A variety of guests from small inorganic molecules to drug molecules to ionic liquids, have been found to insert into this cavity.[4,5,6] This ability to act as a host along with its flexibility and affinity towards hydrogen bonding make pyrogallol[4]arenes an ideal candidate for cocrystallizations.

Fluorescent probes are worthwhile candidates for cocrystallization with pyrogallol[4]arenes. Currently, there is little information about the chemical environment inside the pyrogallol[4]arene cavity. Cocrystallizing pyrogallol[4]arenes with fluorescent probes may lead to useful information about the conformational limitations and guest movement with and inside the pyrogallol[4]arene cavity. [7] A few fluorescent probes have been cocrystallized with pyrogallol[4]arenes, but only one study has been done to map the effects of the probe, solvent, and pyrogallol[4]arene aliphatic tail-length on properties of the resulting cocrystals such as the architecture, crystal packing, probe environment, and pyrogallol[4]arene bowl-shape. [8]

Herein, the fluorescent probe chosen for cocrystallization with pyrogallol[4]arenes is 1-(2-pyridylazo)-2-naphthol (PAN). PAN is a fluorescent probe that has been shown to complex with an variety of metal ions. PAN has been encapsulated in cellulose in order to detect mercury in aqueous samples.[9] Further, PAN has been bound to carbon nanotubes and used to detect lead and palladium, and PAN has been used in organic drop microextraction for detecting rare earth elements such as lanthanum, europium, and ytterbium in organic matter.[10,11] PAN has also been used to separate metals ions such as Hg^{2+} and Zn^{2+}.[12]

It has clearly been demonstrated that crystal architecture is determined by intermolecular interactions.[13] The aim of the research herein is to uncover the trends that arise from "fine-tuning" the intermolecular interactions of the pyrogallol[4]arenes cocrystallized with the PAN molecule in order to develop a better understanding of the such interactions (see **Fig. 1**).



1-(2-pyridylazo)-2-naphthol **PgC_x**

Fig. 1 Schematic structures of (a) 1-(2-pyridylazo)-2 naphthol (PAN) and (b) pyrogallol[4]arene.

Experimental

All reagents and solvents were obtained commercially and were

used without further purification. PgC_1, PgC_2, PgC_3, and PgC_3OH were synthesized using a modified method previously described by Gerkensmeier *et al.*[14]

All PAN cocrystals were crystallized by the same method. In a given molar ratio and solvent, PAN and PgC_x were dissolved and mixed together in a 1:1 molar ratio (1.3:1 for cocrystal **8**) (see **Table 1**). They were then sonicated for thirty minutes and left to slowly evaporate to produce orange, prism-shaped or plate-shaped crystals.

Table 1-Amounts of PgC_x and PAN used and solvent used for each cocrystal

Cocrystal	PgC_x	Grams of PgC_x:PAN	Solvent	Solvent Amount (mL)
1	PgC_1	0.1:0.0409	Methanol	15
2	PgC_1	0.1:0.0409	Ethanol	10
3	PgC_1	0.1:0.0409	Isopropanol	15
4	PgC_1	0.1:0.0409	Acetonitrile	20
5	PgC_2	0.05:0.0187	Methanol	10
6	PgC_2	0.05:0.0187	Ethanol/water	10/1
7	PgC_2	0.05:0.0187	Acetonitrile	15
8	PgC_3	1.5:0.0692	Methanol	10
9	PgC_3	0.1:0.0346	Ethanol	15
10	PgC_3	0.1:0.0346	Isopropanol	15
11	PgC_3	0.05:0.0173	Acetonitrile	10
12	PgC_3OH	0.05:0.0318	Methanol	15

Single crystal X-ray data for cocrystals **3**, **10**, and **12** was collected at the ALS using a Bruker Apex II CCD diffractometer with synchrotron radiation, $\lambda = 0.77490$ Å. Single crystal X-ray data for cocrystal **2** was collected at 173 K on a Bruker Apex II CCD diffractometer, using a CuKα radiation source (1.54178Å). Single crystal X-ray data for all other cocrystals was collected at 173 K on a Bruker Apex II CCD diffractometer, using a MoKα radiation source (0.71073 Å).

Results

Unless otherwise noted, all cocrystals are composed of hydrogen bonded, bilayer structures (see **Fig. 2**). Additionally, all hydrogen bonding involving the pyrogallol[4]arene involves only the hydroxyl groups on the upper-rim on the pyrogallol[4]arene or else is noted. Furthermore, all PAN molecules have an intramolecular hydrogen bond donated from the bridge -N–H group to the oxygen atom.

One of the properties examined is the orientation of the PAN molecule. If the probe is outside the bowl of the pyrogallol[4]arene, the probe is said to be exo. When part of the probe is inside the bowl of the pyrogallol[4]arene, the probe is considered to be endo. Unless otherwise noted, the pyridine part of the PAN molecule is the part of the molecule which is located inside the bowl of the pyrogallol[4]arene. A second metric that is analyzed is the cross-sectional distance within the bowl of the pyrogallol[4]arene, the distance between opposing, middle carbon atoms of the upper-rim (see **Fig. 3**). This metric is significant because it describes the shape of the pyrogallol[4]arene bowl. A bowl is referred to as conical with C_{4v} symmetry if the cross-sectional distances are equal; a bowl is referred to as pinched with C_{2v} symmetry if the cross-sectional distances differ by at least 0.75Å.

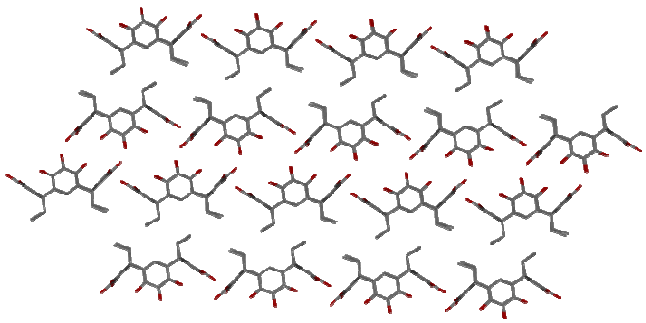


Fig. 2 Typical bilayer structure of pyrogallol[4]arenes.

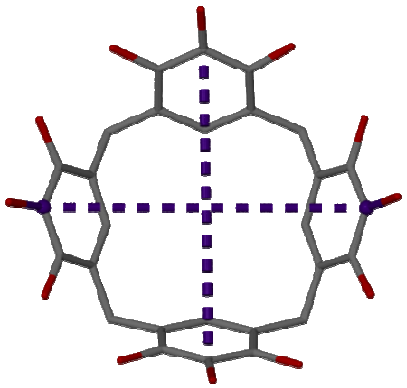


Fig. 3 Distances across the bowl of the pyrogallol[4]arene.

Cocrystal 1

The asymmetric unit of cocrystal **1** contains three PAN molecules, one PgC_1 molecule, one methanol molecule, and one water molecule (see **Fig. 4**). One of the PAN molecules is endo, while the other two are exo (one aligned with the PgC_1 molecule and the other slightly angled). The cross-sectional distances are 6.77 Å and 9.40 Å, which means the bowl of the PgC_1 molecule is pinched (nonsymmetrical). PgC_1 molecules are packed in a bilayer-like structure. However, unlike a typical bilayer structure, adjacent PgC_1 molecules are not orientated in the same direction. A group of two PgC_1 molecules (one oriented with the

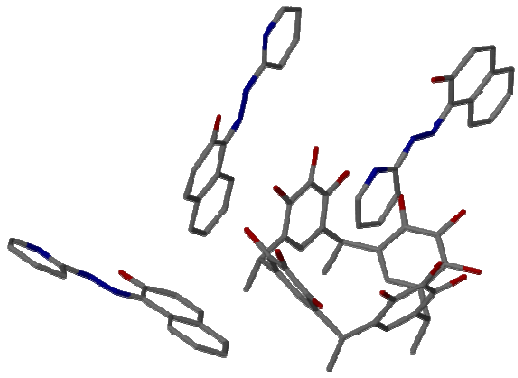


Fig. 4 Asymmetric unit of cocrystal **1**, $C_{32}H_{32}O_{12}\cdot 3C_{15}H_{11}ON_3\cdot CH_3OH\cdot H_2O$. Hydrogen atoms and solvent molecules are removed for clarity.

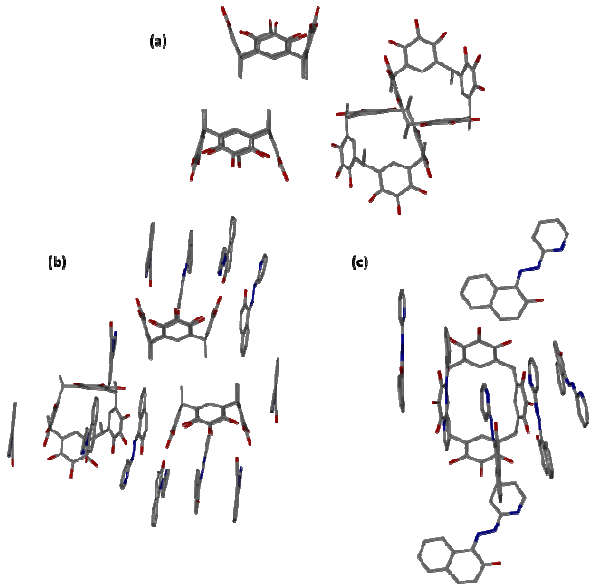


Fig. 5 Packing of cocrystal **1** (a) one unit of PgC_1 packing with PAN molecules removed for clarity, (b) packing of PgC_1 with PAN molecules along the *a*-axis, and (c) along the *c*-axis.

bowl in one direction and the second one directly underneath with the bowl oriented in the opposite direction) is rotated about 30˚ from the adjacent group of PgC_1 molecules (see **Fig. 5**). A PAN molecule is inside the bowl of each PgC_1 molecule, as well as on each side of the exterior of each PgC_1 molecule. Within the structure, there is a complex hydrogen bonding network. In total there are fourteen hydrogen bonds, and the hydroxyl groups of the PgC_1 molecule participates in fourteen (1.86-2.20 Å (O–H···A), 115.9-162.2˚ (O–H···A)). Six of these are intermolecular hydrogen bonds while two are intermolecular hydrogen bonds between hydroxyl groups of adjacent PgC_1 molecules. There is one hydrogen bond donated from a hydroxyl group to a methanol molecule, two hydrogen bonds donated from hydroxyl groups to oxygen atoms of the PAN molecules, and three hydrogen bonds donated from hydroxyl groups to nitrogen atoms of the PAN molecules on the pyridine group. Both the endo PAN molecule and the aligned exo PAN molecule have two hydrogen bonds: one hydrogen bond donated from a hydroxyl group to the nitrogen atom in the pyridine group of the PAN molecule (1.93 Å (O–H···N), 145.2˚ (O–H···N); 1.99 Å (O–H···N), 151.8˚ (O–H···N)), and one hydrogen bond donated from a hydroxyl group to the oxygen atom (1.89 Å (O–H···O), 162.2˚ (O–H···O); 2.00 Å (O–H···O), 158.1˚ (O–H···O)). The third PAN molecule only has one hydrogen bond; a hydrogen bond from a hydroxyl group donated to the nitrogen atom of the pyridine group (1.99 Å (O–H···N), 147.2˚ (O–H···N)). Also found throughout the structure is C–H···π interactions between the aryl groups (centroids) of the PgC_1 molecule and the hydrogen atoms from the pyridine group on the endo PAN molecule (2.75 Å (C–H···π), 156.1˚ (C–H···π); 2.89 Å (C–H···π), 148.7˚ (C–H···π)).

Cocrystal 2

Within the asymmetric unit of cocrystal **2** there are three PAN molecules, two PgC_1 molecules, and four ethanol molecules (see **Fig. 6**). Analogous to cocrystal **1**, one PAN molecule is endo to each PgC_1 bowl and the other PAN molecule is exo and is oriented along the upper-rim of one of the PgC_1 molecules. Arrangement of the exo PAN molecules differs from cocrystal **1**, in that the exo PAN molecules are oriented along two opposing upper-rims of the PgC_1 molecule. The cross-sectional distances are 6.62 Å and 9.48 Å for one PgC_1 molecule and 6.62 Å and 9.56 Å for the second PgC_1 molecule. Similar to cocrystal **1,** the macrocycles do not pack in the typically bilayer arrangement. The pairs of macrocycles (a pair consisting of a top and bottom macrocycle) are rotated from each other at 80˚ (see **Fig. 7**). There is an extensive hydrogen bonding network in the lattice consisting of fifteen hydrogen bonds for the first PgC_1 molecule and sixteen hydrogen bonds for the second PgC_1 molecule (1.85-2.21 Å (O–H···A), 114.3-172.3˚ (O–H···A); (1.83-2.22 Å (O–H···A), 115.0-162.8˚ (O–H···A), respectively). The first PgC_1 molecule has five intramolecular hydrogen bonds between upper-rim hydroxyl groups, and four intermolecular hydrogen bonds between hydroxyl groups of adjacent PgC_1 molecules. There are also two hydrogen atoms donating to one PAN molecule: one hydrogen atom donating to the nitrogen atom of the pyridine group, and one hydrogen atom donating to the oxygen atom. Additionally, two hydroxyl oxygen atoms are accepting hydrogen atoms from two ethanol molecules and four hydroxyl hydrogen atoms are donating to four ethanol oxygen atoms. For the second PgC_1 molecule, the hydrogen bonding scheme changes. There are six intramolecular hydrogen bonds and six intermolecular hydrogen bonds. Furthermore, there is hydrogen bonding to two separate PAN molecules each hydrogen bonding with hydroxyl hydrogen atoms donating to the nitrogen atom in the pyridine group and the oxygen atom. Unlike the first PgC_1 molecule, the second one does not hydrogen bond with solvent molecules. Each of the three PAN molecules have the same hydrogen bonding scheme, hydrogen bonding to only one PgC_1 molecule, and participating in two hydrogen bonds and both are the hydrogen bonds discussed previously, PgC_1 hydroxyl hydrogen atoms

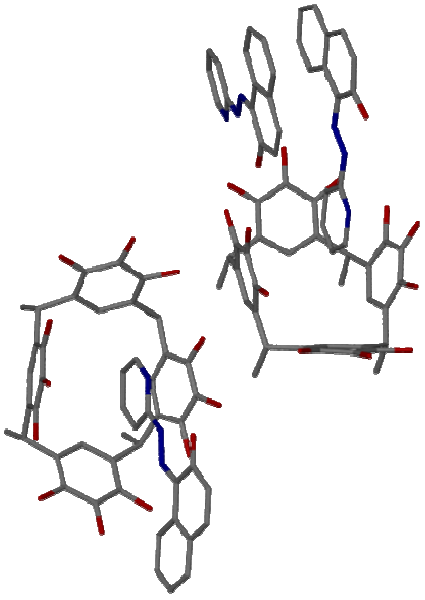


Fig. 6 Asymmetric unit of cocrystal **2**, $2C_{32}H_{32}O_{12}\cdot3C_{15}H_{11}ON_3\cdot4C_2H_5OH$. Hydrogen atoms and solvent molecules are removed for clarity.

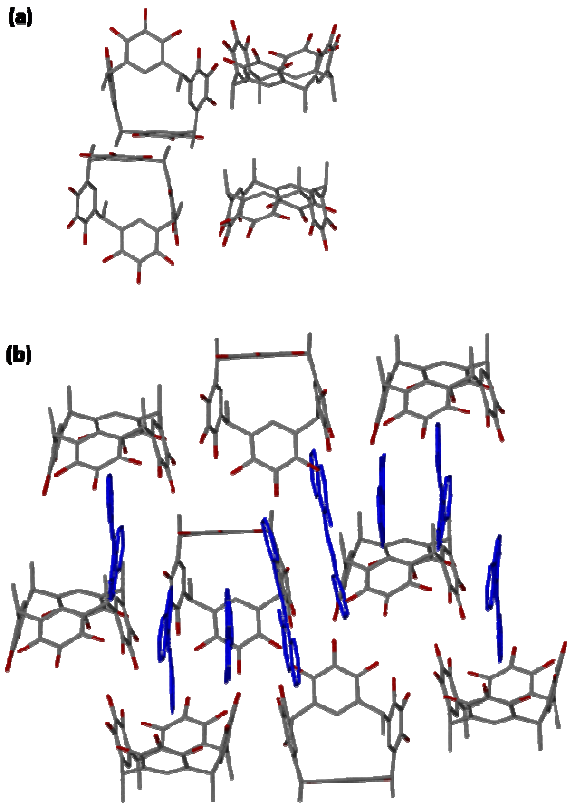


Fig. 7 Crystal packing of cocrystal **2** with (a) one unit of PgC_1 molecules and PAN molecules removed for clarity and (b) packing with PAN molecules (blue).

donating to the nitrogen atom of the pyridine group and the oxygen atom (1.83-2.04 Å (O–H···A), 141.5-162.8˚ (O–H···A)). In addition to the hydrogen bonding of the hydroxyl group and the PAN molecule, the ethanol molecules are participating in hydrogen bonding. Five ethanol molecules hydrogen bond to each other and two PgC_1 molecules (that do not hydrogen bonding to each other), forming a bridge between the two PgC_1 molecules (1.92-2.04 Å (O–H···O), 133.3-171.0˚ (O–H···O)). As well as O–H···O hydrogen bonding, there are also C–H···π interactions throughout the cocrystal network. For the first PgC_1 molecule, two aromatic group are each C–H···π interacting with both a hydrogen atom on the pyridine group of an endo PAN molecule (2.87 Å (C–H···π), 150.1˚ (C–H···π); 2.94 Å (C–H···π), 147.1˚ (C–H···π)) and also with a hydrogen atom on a naphthalene group of an exo PAN molecule (2.57 Å (C–H···π), 163.7˚ (C–H···π); 2.84 Å (C–H···π), 142.9˚ (C–H···π)). Another aromatic group is C–H···π interacting with the hydrogen atom on the tail of an adjacent PgC_1 molecule (2.86 Å (C–H···π), 135.0˚ (C–H···π)). The second PgC_1 molecule has fewer C–H···π interactions than the first molecule: one C–H···π from a hydrogen atom on an endo PAN molecule's pyridine group to an aromatic group, and one from an tertiary hydrogen atom on an adjacent PgC_1 molecule to a centroid (2.83 Å (C–H···π), 156.7˚ (C–H···π); 2.89 Å (C–H···π), 156.7˚ (C–H···π)).

Cocrystal 3

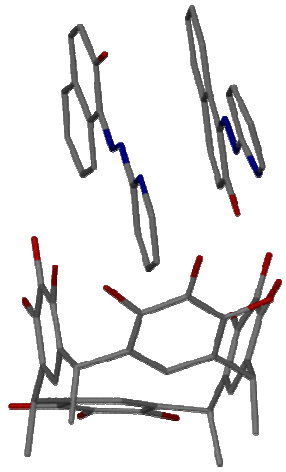


Fig. 8 Asymmetric unit of cocrystal **3**, $C_{32}H_{32}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}3C_3H_7OH$. Hydrogen atoms and solvent molecules are removed for clarity.

Contained in the asymmetric unit of cocrystal **3** are two PAN molecules, one PgC_1 molecule, and three isopropanol molecules (see **Fig. 8**). One of the PAN molecules is endo with the other PAN molecule exo and oriented along one of the upper-rims of the PgC_1 bowl. The bowl of the PgC_1 molecule is pinched, cross-sectional distances being 6.20 Å and 10.24 Å. Similar to cocrystals **1** and **2**, cocrystal **3** is an altered bilayer structure. Whereas the typical bilayer structure has individual PgC_x molecules forming the units, cocrystal **3** consists of two PgC_1 molecules creating a pair that acts as a single unit. Along top of the PgC_1 bowl there are four PAN molecules; one endo, two oriented along the upper-rim, and one adjacent to an exo PAN molecule oriented around the upper-rim. They are all oriented with the pyridine groups all at the same end, but each PAN molecule is in a different direction than the one next to it. The

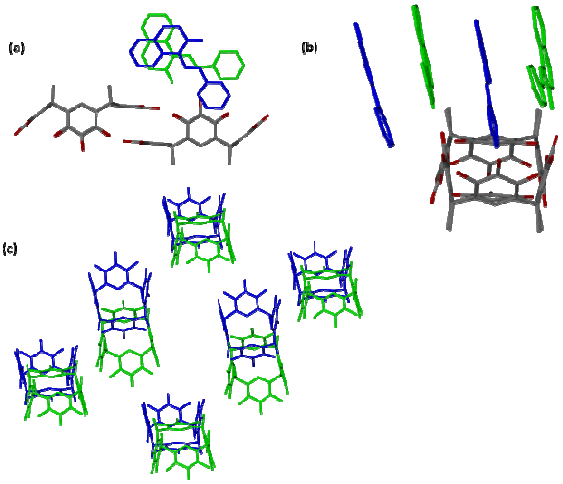


Fig. 9 (a) One unit of the packing motif along the *a*-axis and (b) along the *b*-axis. There is a total of four PAN molecules (blue and green). Blue PAN molecules are oriented in one direction and green PAN molecules in a second direction. (c) The packing of the PgC_1 molecules with the PAN molecules removed for clarity. All hydrogen atoms and solvent molecules are removed for clarity.

two PAN molecules oriented with the upper-rims have the oxygen atom pointed down to the hydroxyl groups of the PgC_1 molecule while the other two PAN molecules have the oxygen atom pointed up away from the PgC_1 molecule's hydroxyl groups (see **Fig. 9**). As with the previous structures, there is an extensive hydrogen bonding network. There are a total of fourteen hydrogen bonds (1.74-2.20 Å (O–H···A), 115.1-171.0˚ (O–H···A)). Three of these are intramolecular hydrogen bonds between the hydroxyl groups. Four hydrogen bonds are intermolecular hydrogen bonding between hydroxyl groups of adjacent PgC_1 molecules. There are four hydrogen bonds donated from hydroxyl hydrogen atoms to PAN molecules, two hydrogen atoms donating to oxygen atoms, and two hydrogen atoms donating to the nitrogen atom of the pyridine group. The final three hydrogen bonds involve isopropanol molecules. Two hydroxyl hydrogen atoms donated to two isopropanol oxygen atoms and one hydroxyl oxygen atom accepts a hydrogen bond from a hydroxyl hydrogen atom on an isopropanol molecule. Unlike previous cocrystals, the solvent does not create a bridge between PgC_1 molecules. Besides the hydrogen bonding already discussed, the PAN molecule on the upper-rim of the PgC_1 bowl is participating in one more hydrogen bond; the oxygen atom is accepting an hydrogen bond from a hydroxyl group of an isopropanol molecule's (1.96 Å (O–H···O), 162.5˚ (O–H···O)).

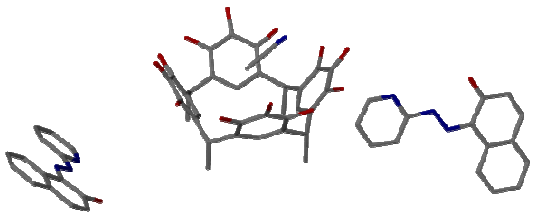


Fig. 10 Asymmetric unit of cocrystal **4**, $C_{32}H_{32}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}2CH_3CN$. Hydrogen atoms and solvent molecules (except for the endo solvent molecule) are removed for clarity.

Additional hydrogen bonding comes from C-H···π interactions. There are three C-H···π interactions involving the aromatic groups of the PgC_1: one from a hydrogen atom on a exo PAN molecule's naphthalene group (2.81 Å (C–H···π), 149.1˚ (C–H···π)), and two from two hydrogen atoms on the endo PAN molecule's pyridine group (2.53 Å (C–H···π), 159.6˚ (C–H···π); 2.83 Å (C–H···π), 119.2˚ (C–H···π)).

Cocrystal 4

In the asymmetric unit cell, there are two PAN molecules, one PgC_1 molecule, and two acetonitrile molecules (see **Fig. 10**). One of the acetonitrile molecules is endo and thus the two PAN molecules are both exo. The bowl-shape is conical with cross-sectional distances of 8.45 Å and 8.54 Å. Again, there is an

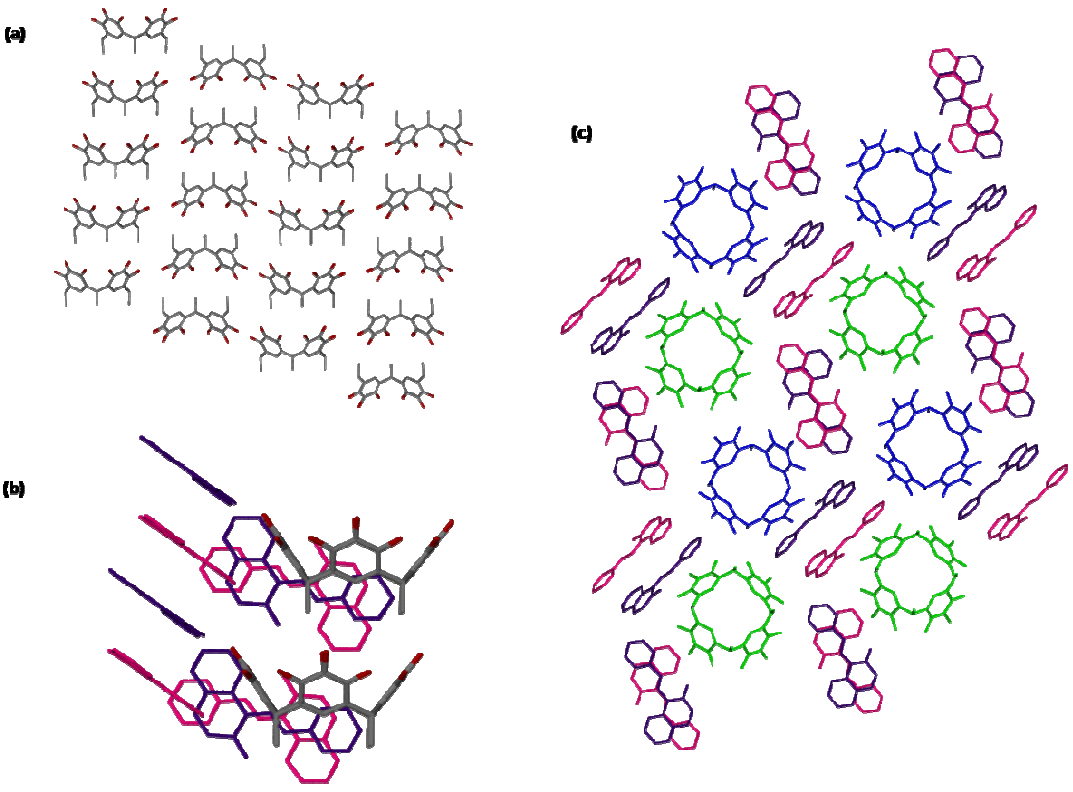


Fig. 11 (a) The packing of PgC_1 with PAN molecules removed for clarity. (b) One unit of the packing motif with PAN molecules (pink and purple). Pink PAN molecules are oriented with the PAN molecule's carbonyl group pointing away from the PgC_1 bowl and purple PAN molecules are oriented with the PAN molecule's carbonyl group pointing toward the PgC_1 bowl. (c) View along the *c*-axis. Blue are PgC_1 molecules with upper-rims facing up and green are PgC_1 molecules with upper-rims facing down. All hydrogens are removed for clarity.

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atypical bilayer structure (see **Fig. 11**). The PgC_1 molecules are stacked inside each other in the same direction to create columns. These columns are arranged in a line in which there is a column of PgC_1 molecules all oriented with the upper-rims facing up, then next to it is a column of PgC_1 molecules all oriented with the carbon tail groups facing up, and then the pattern repeats with a column PgC_1 molecules all oriented with the upper-rims facing up. To the right and the left of the columns are rows of probe molecules. Each PgC_1 molecule in the column has four units surrounding it, two on the adjacent to one of the PgC_1 molecule's aromatic group and two an adjacent aromatic group. Each unit

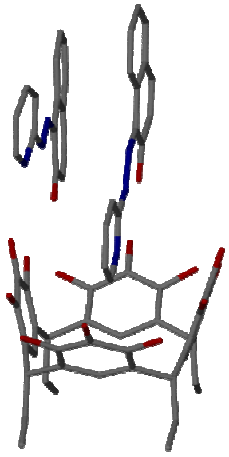

Fig. 12 Asymmetric unit of cocrystal **5**, $C_{36}H_{40}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}CH_3OH$. Hydrogen atoms and solvent molecules are removed for clarity.

consisting of two PAN molecules that are facing opposite directions (one has the carbonyl group pointed towards the PgC_1 molecule and the second has the carbonyl group pointed away from the PgC_1 molecule). One unit has the plane containing the PAN molecule parallel to the plane containing both cross-sectional distances and the second unit has the plane containing the PAN molecule perpendicular to the plane containing both cross-sectional distances. There are eleven hydrogen bonds in which the hydroxyl groups of the PgC_1 molecule are participating (1.84-2.18 Å (O–H···A), 143.6-178.9° (O–H···A)). Four hydrogen bonds are intramolecular bonds between the hydroxyl groups on the upper-rim, two hydrogen bonds are intermolecular bonds, one hydrogen bond is donated from the hydroxyl group to an acetonitrile molecule, two hydrogen bonds are donated from the hydroxyl groups to nitrogen atom in the pyridine group of two PAN molecules, and two hydrogen bonds are donated from the hydroxyl groups to oxygen atoms on two PAN molecules. The two PAN molecules have the same hydrogen bonding scheme: one hydrogen bond donated from a PgC_1 hydroxyl group to the nitrogen atom on the pyridine group (1.89 Å (O–H···N), 155.4° (O–H···N); 1.98 Å (O–H···N), 143.6° (O–H···N)), and one hydrogen bond donated from a PgC_1 hydroxyl group to the oxygen atom (2.01 Å (O–H···O), 161.0° (O–H···O); 2.18 Å (O–H···O), 160.1° (O–H···O)). Three C–H···π bonds are also present between the centroids of the PgC_1 molecule and hydrogen atoms on the endo acetonitrile (2.72-3.04 Å (C–H···π), 113.4-165.0° (C–H···π)).

Cocrystal 5

Within the asymmetric unit cell of cocrystal **5** there are two PAN molecules, one PgC_2 molecule, and one methanol molecule (see **Fig. 12**). One of the PAN molecules is endo and the other is exo and oriented along one of the PgC_2 molecule's upper-rim. Cross-sectional distances for cocrystal **5** are 6.69 Å and 9.62 Å. The hydroxyl groups of the PgC_2 molecule are involved in thirteen hydrogen bonds (1.85-2.15 Å (O–H···A), 132.6-163.1° (O–H···A)): four intramolecular hydrogen bonds among the upper-rim hydroxyl groups, four intermolecular hydrogen bonds to hydroxyl groups of adjacent PgC_2 molecules, one hydrogen bond donated from a hydroxyl group to a methanol, two hydrogen bonds donated from the hydroxyl groups to the oxygen atom on PAN molecules, one hydrogen bond donated from a hydroxylgroup to a nitrogen atom on the bridge of a PAN molecule, and one hydrogen bond donated from a hydrogen atom on a PAN molecule to a PgC_2 hydroxyl group. Each PAN molecule is participating in two hydrogen bonds. They both are have one intermolecular hydrogen bond donated from a PgC_2 hydroxyl group to the PAN oxygen atom (1.88 Å (O–H···O), 154.4° (O–H···O); 1.93 Å (O–H···O), 163.1° (O–H···O)). The remaining hydrogen bond for the endo

PAN molecule is donated from a hydrogen atom from the pyridine group to a hydroxyl group (1.85 Å (O–H···O), 156.8° (O–H···O)). The last hydrogen bond is from a hydroxyl group on an exo PAN molecule's donating to the nitrogen atom on the

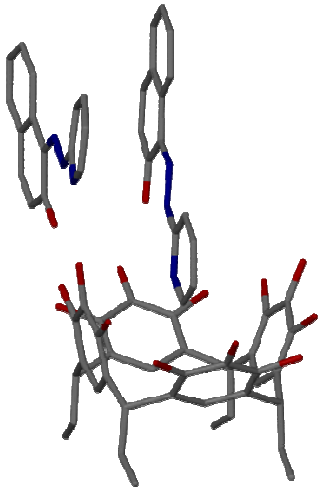

Fig. 13 Asymmetric unit of cocrystal **6**, $C_{36}H_{40}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}H_2O$. Hydrogen atoms and solvent molecules are removed for clarity.

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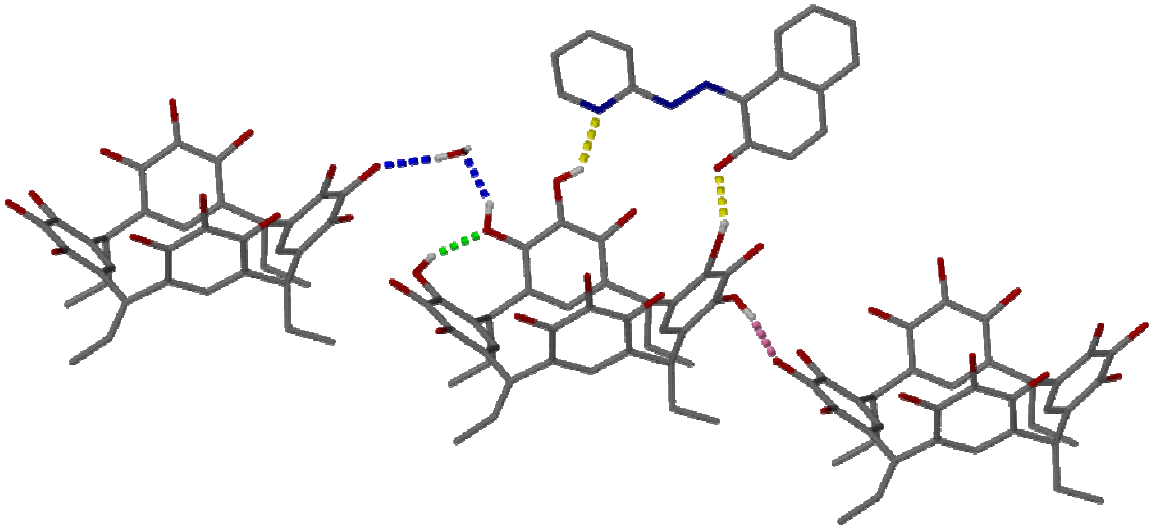

Fig. 14 Types of hydrogen bonding found in cocrystal **6**. Intramolecular hydrogen bonding (dashed green bonds), intermolecular hydrogen bonding (dashed pink bonds), hydrogen bonding with solvent (dashed blue bonds), and hydrogen bonding with a PAN molecule (dashed yellow bond). All hydrogen atoms (unless necessary) are removed for clarity.

PAN's pyridine group (2.20 Å (O–H···O), 132.6˚ (O–H···O)). In addition to the O–H···O hydrogen bonding, there are three C–H···π interactions: two involving the PgC_2 centroids and hydrogen atoms on the pyridine aromatic ring of an endo PAN's (2.77 Å (C–H···π), 151.0˚ (C–H···π); (2.97 Å (C–H···π), 101.1˚ (C–H···π)), and one between the exo PAN's pyridine centroid and an aliphatic tail hydrogen atom (2.84 Å (C–H···π), 148.8˚ (C–H···π)).

Cocrystal 6

The asymmetric unit of cocrystal **6** contains two PAN molecules (one endo and one exo), one PgC_2 molecule, and one water molecule (see **Fig. 13**). One of the aliphatic tails of the PgC_2 molecule is disordered over two positions which are modeled at 87% and 13% occupancies. The bowl of the PgC_2 molecule is pinched with cross-sectional distances of 6.71 Å and 9.59 Å. There are sixteen hydrogen bonds that the PgC_2 molecule is involved in (1.81-2.81 Å (O–H···A), 132.3-168.6˚ (O–H···A)) (see **Fig. 14**). Of the sixteen hydrogen bonds, four are intramolecular hydrogen bonds between the upper-rim hydroxyl groups, two are hydrogen bonds donated to hydroxyl groups of adjacent PgC_2 molecules, two are hydrogen bonds donated from hydroxyl groups of adjacent PgC_2 molecules, one is a hydrogen bond donated to a PAN molecule's nitrogen in the pyridine group, one is a hydrogen bond donated to a nitrogen atom on the bridge of the PAN molecule, two are hydrogen bonds donated to a PAN molecule's oxygen atom, one is a hydrogen bond donated from a hydrogen on the pyridine group of the PAN molecule, one is a hydrogen bond donated to an oxygen atom of a water molecule, and two are hydrogen bonds donated from the hydrogen atoms of the water molecules. Due to the nature of the hydrogen bonding, the water molecules act as bridges between PgC_2 molecules. The two PAN molecules have different hydrogen bonding schemes. Both PAN molecules have intermolecular hydrogen bonding with a hydroxyl hydrogen atom of the PgC_2 molecule donating to the oxygen atoms of the PAN molecules (1.85 Å (O–H···O), 162.5˚ (O–H···O); 1.86 Å (O–H···O), 154.9˚ (O–H···O)). In addition to these two hydrogen bonds, one of the PAN molecules also has a hydrogen bond donated from a PgC_2 hydroxyl group to the nitrogen atom in the pyridine group of the PAN molecule (2.15 Å (O–H···N), 132.3˚ (O–H···N)). The second PAN molecule has two more hydrogen bonds: one hydrogen bond donated from a hydroxyl group of a PgC_2 molecule to the bridge nitrogen atom of the PAN molecule (2.21 Å (O–H···N), 138.9˚ (O–H···N)) and one hydrogen bond donated from a hydrogen on the pyridine group of the PAN molecule to the hydroxyl group of the PgC_2 molecule (1.81 Å (C–H···O), 157.6˚ (C–H···O)). All three, the PgC_2 molecule and two probes, participate in C–H···π bonding. The PgC_2 molecule participates in two C–H···π bonds both donated from hydrogen on the pyridine group of an endo PAN molecule (2.74 Å (C–H···π), 149.2˚ (C–H···π); 2.98 Å (C–H···π), 99.1˚ (C–H···π)). With one of the PAN molecules, one of the hydrogen atoms on an aliphatic chain of a PgC_2 molecule is donating to the centroid of the pyridine (2.76 Å (C–H···π), 150.3˚ (C–H···π)). The second PAN molecules has C–H···π bonding also donated from one of the hydrogen atoms of the aliphatic tail of the PgC_2 molecule, but donated to the centroid of the naphthalene phenyl group without the oxygen of the PAN molecule (2.97 Å (C–H···π), 148.3˚ (C–40 H···π)).

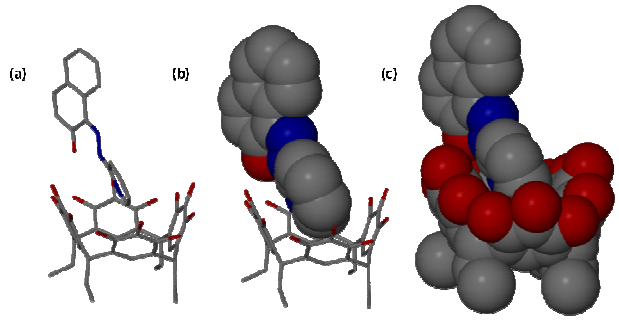

Fig. 15 Asymmetric unit of cocrystal **7**, $C_{36}H_{40}O_{12}\cdot 1C_{15}H_{11}ON_3$ in (a) stick representation, (b) space-filled PAN molecule, and (c) space-filled PAN and PgC_2 molecules. Hydrogen atoms and solvent molecules are removed for clarity.

Cocrystal 7

The asymmetric unit of cocrystal **7** contains one endo PAN molecule and one PgC_2 molecule (see **Fig. 15**). Unlike the other cocrystals, cocrystal **7** does not contain any solvent. The bowl of cocrystal **7** is pinched with cross-sectional distances 7.25 Å and 9.30 Å. There are eleven hydrogen bonds throughout the system (1.91-2.20 Å (O–H···A), 134.2-170.4˚ (O–H···A)): four intramolecular hydrogen bonds between hydroxyl groups, six intermolecular bonds between adjacent hydroxyl groups of the PgC_2 molecules, and one hydrogen bond donated from the hydroxyl hydrogen atom to the PAN molecule's oxygen atom. Both the PgC_2 molecule and the PAN molecule have C–H···π interactions. The hydrogen atoms on the pyridine group of the endo PAN molecule are C–H···π interacting with two centroids of the PgC_2 molecule (2.53 Å (C–H···π), 143.0˚ (C–H···π); (2.65 Å (C–H···π), 124.2 (C–H···π)). Two of the tail hydrogen atoms of the PgC_2 molecule are C–H···π interacting with the aromatic groups of the PAN molecule, each to a different aromatic group of the naphthalene group (2.75 Å (C–H···π), 146.7˚ (C–H···π); (3.00 Å (C–H···π), 142.8˚ (C–H···π)).

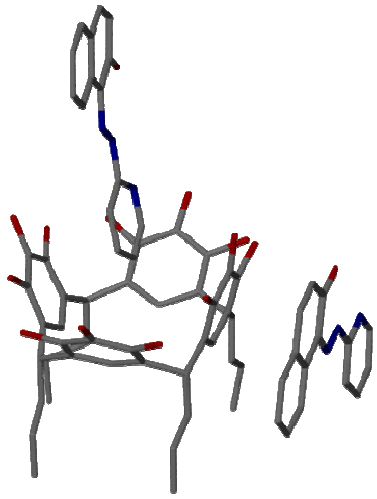

Fig. 16 Asymmetric unit of cocrystal **8**, $C_{40}H_{48}O_{12}\cdot 2C_{15}H_{11}ON_3\cdot 1.5CH_3OH\cdot 1.5H_2O$. Hydrogen atoms and solvent molecules are removed for clarity.

Cocrystal 8

The asymmetric unit of cocrystal **8** contains two PAN molecules (one endo and one exo), one PgC_3 molecule, one and one-half methanol molecules, and one and one-half water molecules (see **Fig. 16**). One methanol and one water molecule are disordered over the same position and each are modeled at 50% occupancy. It is a bilayer structure and the bowl of the PgC_3 molecule is slightly pinched, with cross-sectional distances 6.97 Å and 9.45 Å (see **Fig. 17**). Thirteen hydrogen bonds involve the PgC_3 molecule (1.92-2.20 Å (O–H···A), 134.2-170.4˚ (O–H···A)). Four of these are intramolecular hydrogen bonds around the upper-rim of the PgC_3 molecule, and two are intermolecular hydrogen bonds to hydroxyl groups on adjacent PgC_3 molecules. Six hydrogen bonds involve solvent molecules; four in which hydroxyl

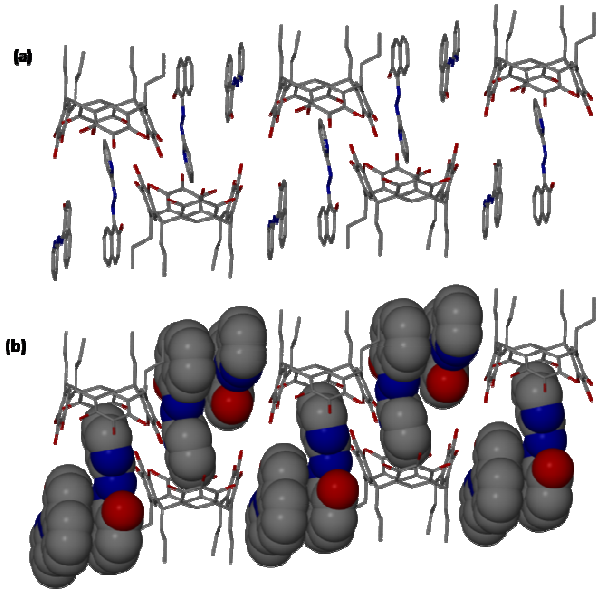

Fig. 17 (a) Packing of cocrystal **8** in stick representation and (b) with PAN molecules in space-filled representation. Hydrogen atoms are removed for clarity.

hydrogen atoms donate to water oxygen atoms and one in which a water's hydrogen atom donates to a hydroxyl group. The hydrogen bonding involving the solvent water causes the water to act like a bridge, joining adjacent PgC_3 molecules together through hydrogen bonding. There is also one hydrogen bond from one hydroxyl hydrogen atom donating to a nitrogen atom in the pyridine group of a PAN molecule. Both PAN molecules are involved in different hydrogen bonding schemes. One of the PAN molecules has hydrogen bond donated from a water hydrogen atom to the oxygen atom of the PAN molecule (1.92 Å (O–H···A), 159.5˚ (C–H··· A)). The other hydrogen bond is the one already discussed previous in which there is hydrogen bonding to the pyridine group from a hydroxyl group of a PgC_3 molecule (2.06 Å (O–H···A), 160.4˚ (O–H···A)). The PgC_3 molecule has quite a few C–H···π interactions. The hydrogen atoms on the pyridine group of the endo PAN molecule C–H···π interacts with three of the aromatic groups of the PgC_3 molecule (2.55-2.88 Å (C–H···π), 112.2-160.3˚ (C–H···π)). There is also a C–H···π interaction between a hydrogen atom on the naphthalene group of an exo PAN molecule to one PgC_3 aromatic group (2.85 Å (C–

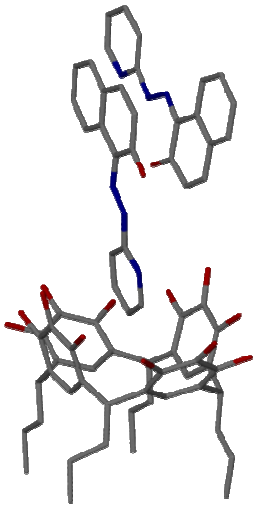

Fig. 18 Asymmetric unit of cocrystal **9**, $C_{40}H_{48}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}C_2H_5OH{\cdot}2H_2O$. Hydrogen atoms and solvent molecules are removed for clarity.

H···π), 167.1˚ (C–H···π)). Finally, there is a C–H···π interaction from a hydrogen atom on a PgC_3 tail to the naphthalene aromatic group, without any attached groups, of the PAN that is hydrogen bonding through the pyridine group.

Cocrystal 9

Contained in the asymmetric unit of cocrystal **9** are two PAN molecules (one exo and one endo), one PgC_3 molecule, one ethanol molecule, and two water molecules (see **Fig. 18**). Cross-sectional distances for the PgC_3 molecule are 6.77 Å and 9.55 Å. The PgC_3 molecules are arranged in a typical bilayer structure with one PAN molecule in the bowl of each PgC_3 moiety. Eighteen hydrogen bonds are donated from and to the PgC_3 molecule (1.88-2.22 Å (O–H···A), 114.5-167.8˚ (O–H···A)) (see **Fig. 19**). Of these, six hydrogen bonds are intramolecular bonds and four are intermolecular bonds. There is one hydrogen bond

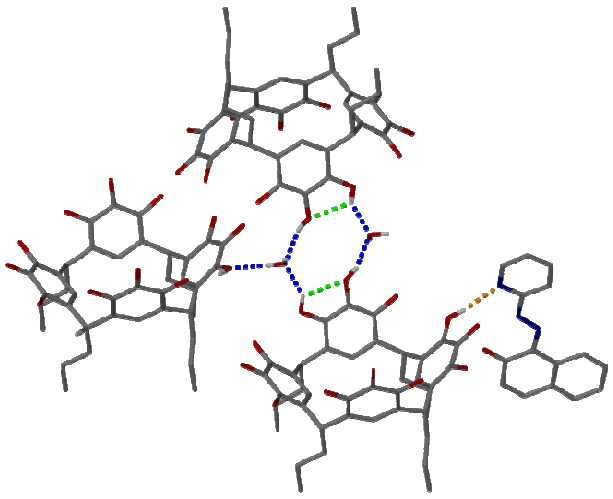

Fig. 19 Types of hydrogen bonding found in cocrystal **9**. Intramolecular hydrogen bonding (dashed green bonds), hydrogen bonding with solvent (dashed blue bonds), and hydrogen bonding with a PAN molecule (dashed orange bond). All hydrogens (unless necessary) are removed for clarity.

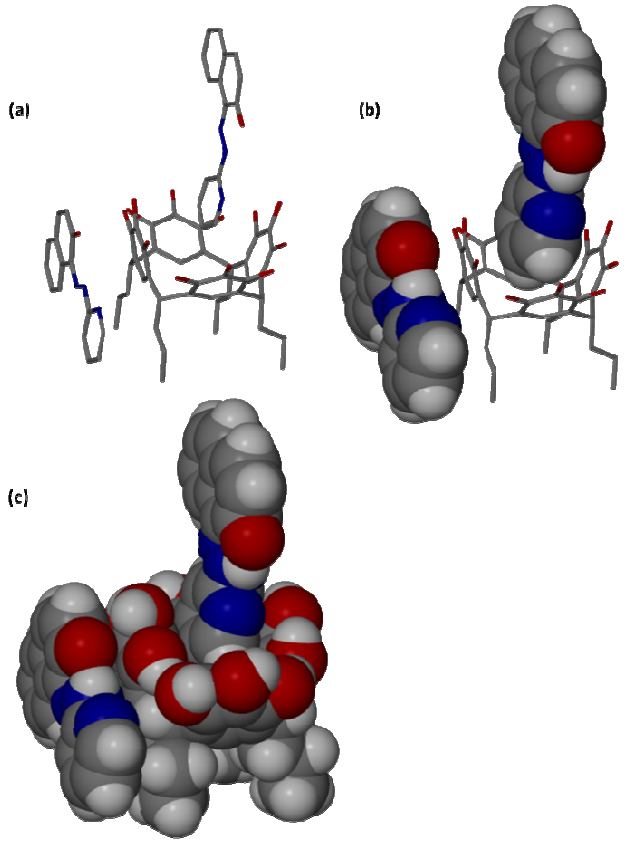

Fig. 20 Asymmetric unit of cocrystal **10**, $C_{40}H_{48}O_{12}{\cdot}2C_{15}H_{11}ON_3{\cdot}C_3H_7OH{\cdot}2H_2O$ in (a) stick representation, (b) PAN molecules in space-filled representation, and (c) both PgC_3 and PAN molecules in space-filled representation. Hydrogen atoms and solvent molecules are removed for clarity.

donated from the hydroxyl group to the nitrogen atom on a pyridine group of the PAN molecule. The remaining hydrogen bonds are to solvent molecules and create a bridge between PgC_3 molecules. Four hydrogen bonds are formed from hydroxyl hydrogen atoms donating to oxygen atoms of four water molecules, one from a water molecule hydrogen bond donating to a hydroxyl group, and one from a hydroxyl hydrogen atom to an ethanol oxygen atom. The two PAN molecules are involved in different hydrogen bonding schemes. The endo PAN molecule is hydrogen bonding from a water molecule to the PAN's oxygen atom (1.82 Å (O–H···O), 152.1˚ (O–H···O)) while the exo PAN molecule has a PgC_3 hydroxyl group donating to the nitrogen atom of the pyridine group (12.13 Å (O–H···N), 157.8˚ (O–H···N)). As with the other cocrystal systems, there is C–H···π bonding. Three C–H···π bonds are from the PgC_3 centroids to three hydrogen atoms on the pyridine aromatic ring of the endo PAN molecule (2.53-2.89 Å (C–H···π), 108.0-165.1˚ (C–H···π)) and one is from hydrogen atom on the naphthalene group of an exo PAN molecule (3.03 Å (C–H···π), 165.2˚ (C–H···π)). The endo PAN molecule does not have any C–H···π hydrogen bonding with PgC_3 aliphatic tail hydrogen atoms, but the exo PAN molecule has two: one from each centroid of the naphthalene group to a PgC_3 tail hydrogen atom (2.77 Å (C–H···π), 148.6˚ (C–H···π); 2.80 Å (C–H···π), 144.5˚ (C–H···π)).

Cocrystal 10

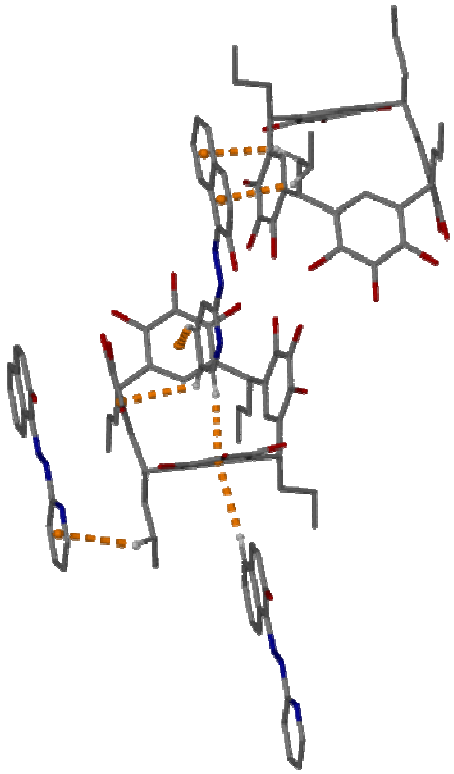

Fig. 21 C–H···π interactions (dashed orange bonds) in cocrystal **10**. Hydrogen atoms and solvent molecules are removed for clarity.

In the asymmetric unit cocrystal **10** there are two PAN molecules (one endo and one exo), one PgC_3 molecule, one isopropanol molecule, and two water molecules (see **Fig 20**). The cross-sectional distances are 6.72 Å and 9.54 Å. There is a similar hydrogen bonding network as with the other cocrystals containing PgC_3. In total, there are seventeen hydrogen bonds in which the PgC_3 participates (1.72-2.21 Å (O–H···A), 114.5-174.9˚ (O–H···A)). The majority of these hydrogen bonds (six) are intramolecular hydrogen bonds between the upper-rim hydroxyl groups. Four of the hydrogen bonds are intermolecular hydrogen bonds from adjacent hydroxyl groups of PgC_3 molecules. Six of the hydrogen bonds are hydroxyl hydrogen atoms donating to solvent molecules, four donated from hydroxyl hydrogen atoms to four water oxygen atoms, one donated from a hydroxyl hydrogen atom to an isopropanol oxygen atom, and one donated from one water hydroxyl hydrogen atom to a hydroxyl oxygen atom of the PgC_3 molecule. As with the previous cocrystals, the water molecules' hydrogen bonds allow it to act as a bridgebetween PgC_3 molecules. The final hydrogen bond involves a hydroxyl hydrogen atom donating to a PAN molecule's nitrogen atom in the pyridine group. Both of the PAN molecules participate in one hydrogen bond. The endo PAN molecule is hydrogen bonding from the hydroxyl hydrogen atom to the nitrogen atom in the pyridine group of the PAN molecule (2.07 Å (O–H···N), 158.1˚ (O–H···N)). The exo PAN molecule accepts a hydrogen bond from a hydroxyl hydrogen atom of a water molecule (1.79 Å (O–H···O), 157.1˚ (O–H···O)). That water molecule is also accepting two hydrogen bonds from hydroxyl hydrogen atoms of two PgC_3 molecules and donating a hydrogen atom to a third hydroxyl oxygen atom of a PgC_3 molecule (1.72-1.94 Å (O–H···O), 145.7-174.9˚ (O–H···O)). There is quite an extensive C–H···π interaction scheme as well as the hydrogen bonding network (see **Fig. 21**). There are four C–H···π interactions to the aromatic rings of the PgC_3 molecule: three from hydrogen atoms on the pyridine aromatic ring of the endo PAN molecule (2.47-2.86 Å (C–H···π), 108.9-163.7˚ (C–H···π)), and one from a hydrogen atom on a naphthalene group of an exo PAN molecule (2.98 Å (C–H···π), 167.1˚ (C–H···π)). Additionally, both of the naphthalene centroids of the endo PAN molecule are C–H···π interacting with hydrogen atom on the same aliphatic tail (but with different hydrogen atoms) (2.75 Å (C–H···π), 148.2˚ (C–H···π); 2.79 Å (C–H···π), 143.9˚ (C–H···π)). The exo PAN molecule is C–H···π interacting with from an aliphatic tail hydrogen atom of a PgC_3 molecule to the pyridine centroid (3.06 Å (C–H···π), 144.3˚ (C–H···π)).

Cocrystal 11

There is one endo PAN molecule, one PgC_3, one acetonitrile, and two water molecules in the asymmetric unit of cocrystal **11** (see **Fig. 22**). The cross-sectional distances are 6.78 Å and 9.56 Å In total, there are twelve hydrogen bonds in which the PgC_3 is participating in (1.92-2.21 Å (O–H···A), 114.8-169.7˚ (O–H···A)). Of the twelve hydrogen bonds, five are intramolecular hydrogen bonds between the hydroxyl groups on the upper-rim, four are intermolecular hydrogen bonds between the hydroxyl groups adjacent PgC_3 molecules, two are hydroxyl hydrogen atoms donating to water molecules, and one is a hydrogen bond involving hydrogen atom on the PAN pyridine group donating to the oxygen atom of a hydroxyl group of a PgC_3 molecule. Once again, the water molecules act as a bridge, connecting PgC_3 molecules through hydrogen bonding. Additional hydrogen bonding comes from two C–H···π interactions from two PgC_3 aromatic centroids to hydrogen atoms on the pyridine group of the endo PAN molecule (2.78 Å (C–H···π), 165.5˚ (C–H···π); 2.84 Å (C–H···π), 115.2˚ (C–H···π)). The PAN molecule also

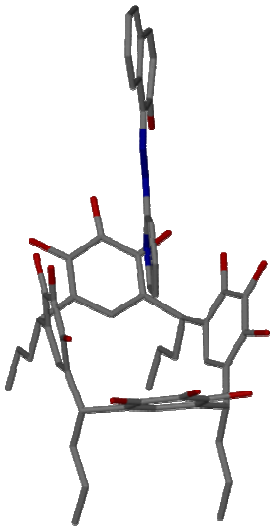

Fig. 22 Asymmetric unit of cocrystal **11**, $C_{40}H_{48}O_{12}{\cdot}C_{15}H_{11}ON_3{\cdot}CH_3CN{\cdot}2H_2O$. Hydrogen atoms and solvent molecules are removed for clarity.

participates in C–H···π interactions. Two aliphatic tail hydrogen atoms (from two different, adjacent PgC_3 molecules) are donating to the centroids of the naphthalene group (2.90 Å (C–H···π), 149.0˚ (C–H···π); 2.98 Å (C–H···π), 166.3˚ (C–H···π)).

Cocrystal 12

Within the asymmetric unit cell of cocrystal **12** there is one endo PAN molecule, one PgC_3OH molecule, and one ethanol molecule (see **Fig. 23**). The bowl is pinched-shaped with cross-sectional distances of 7.67 Å and 9.21 Å. In total, there are fifteen hydrogen bonds in which the upper-rim hydroxyl groups are participating in (1.80-2.19 Å (O–H···O), 148.2-170.4˚(O–H···O)). There are four intramolecular hydrogen bonds between the upper-rim hydroxyl groups, four intermolecular hydrogen bonds between upper-rim hydroxyl groups of adjacent PgC_3OH

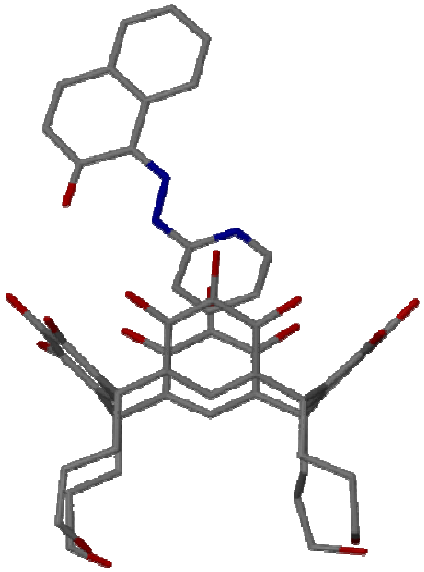

Fig. 23 Asymmetric unit of cocrystal **12**, $C_{40}H_{48}O_{16}{\cdot}C_{15}H_{11}ON_3{\cdot}C_2H_5OH$. Hydrogen atoms and solvent molecules are removed for clarity.

molecules, five intermolecular hydrogen bonds between the upper-rim hydroxyl groups to hydroxyl groups at the end of the carbon tail groups of adjacent PgC_3OH molecules, one hydrogen bond between an upper-rim hydroxyl hydrogen atom and the nitrogen atom on the pyridine group of the PAN molecule, and one hydrogen bond from an upper-rim hydroxyl hydrogen atom to the bridging nitrogen atom on the same PAN molecule. The hydroxyl groups on the end of the PgC_3OH molecule tail groups are also involved in hydrogen bonding (1.72-2.03 Å (O–H···O), 132.3-170.4˚ (O–H···O)). There is one intramolecular hydrogen bond between aliphatic tail hydroxyl groups, three intermolecular hydrogen bonds to upper-rim hydroxyl groups on adjacent PgC_3OH molecules, two hydrogen bonds to two ethanol molecules, and one hydrogen bond to the oxygen atom of a PAN molecule. The PAN molecule is also involved in hydrogen bonding (1.86-2.10 Å (O–H···O), 132.8-170.4˚ (O–H···O)). Besides the PAN hydrogen bonding already discussed previously when describing the hydrogen bonding of the PgC_3OH, there is an intramolecular hydrogen bond between the hydrogen atom on the bridging nitrogen atom and the oxygen atom. In addition to the C–H···O hydrogen bonding, there are also four C–H···π bonds. Three are from hydrogen atoms on the pyridine group of the endo PAN molecule to the centroids of the PgC_3OH molecule (2.44-2.87 Å (C–H···π), 125.5-143.7˚ (C–H···π)). The fourth C–H···π is from the hydrogen atom on the naphthalene group of the PAN molecule (the aromatic group without and groups attached) to the centroid of the pyridine group of a second PAN molecule (2.97 Å (C–H···π), 107.0˚ (C–H···π)).

Discussion

Cocrystals containing the PAN molecule, show a wide range of characteristics that appear to be influenced by solvent and aliphatic tail-length. First, aliphatic tail-length plays a significant role in the resulting architecture of the cocrystal. One of the most significant differences is in the bilayer structure. With PgC_1

Table 2 Number of C–H···π interactions involving PgC_x molecules and PAN molecules

Cocrystal	PgC_x Endo C–H···π interactions	PgC_x Exo C–H···π interactions	PAN 1	PAN 2	PAN 3
1	1	1	0	0	0
2	1	2	0	0	0
	1	2			
3	2	1	0	0	N/A
4	3	0	0	0	N/A
5	2	0	1	0	N/A
6	2	0	1	1	N/A
7	2	0	2	N/A	N/A
8	3	1	0	1	N/A
9	3	1	0	2	N/A
10	3	1	2	1	N/A
11	1	0	2	N/A	N/A
12	3	0	1	N/A	N/A

molecules, the crystal network is an atypical bilayer structure. The PgC_1 molecules are angled from each other as in cocrystal **1** and **2**, pack in pairs to form a single unit as in cocrystal **3**, or pack in columns as in cocrystal **4**. Increasing the aliphatic tail-length to two and three carbon atoms, leads to cocrystals packed in the typical bilayer arrangement.

Changing the tail-lengths also causes the C–H···π interactions to alter (see **Table 2**). As the tail-length increases, the amount of C–H···π interaction to the endo PAN molecules increases. Of thecocrystals involving PgC_1 (cocrystals **1-4**), cocrystals **1** and **2** have only one C–H···π interaction with the endo PAN molecule and cocrystal **3** has two C–H···π interactions. Additionally, there is at least one C–H···π interaction to an exo PAN molecule. Increasing the tail-length by one in turn increases the C–H···π interactions with the endo PAN molecule by one; all cocrystals containing PgC_2 (cocrystals **5-7**) have two C–H···π interactions to the endo PAN molecule. However, unlike the cocrystals with PgC_1, there are no C–H···π interactions with exo PAN molecules. Further increasing the tail-length from two carbon atoms to three carbon atoms (cocrystals **8-11**) causes the C–H···π interactions to the endo PAN molecule to increases to three interactions. Additionally, similar to cocrystal **1**, there is at least one C–H···π interaction with an exo PAN molecule.

Not only does increasing the tail-length change the C–H···π interactions, it also alters the hydrogen bonding scheme. As the

Table 3 Number of hydrogen bonds between PgC_x molecules and solvent molecules.

Cocrystal	Hydrogen bonds to solvent molecules	Hydrogen bonds to water molecules	Solvent Bridging
1	1	0	No
2	4	0	Yes
	0	0	No
3	3	0	No
4	1	0	No
5	1	0	No
6	3	N/A	Yes
7	N/A	N/A	N/A
8	0	6	Yes
9	2	5	Yes
10	1	5	Yes
11	0	2	Yes
12	0	0	Yes

tail-length increases, the presence of hydrogen bonding solvent-bridging also increases (see **Table 3**). With cocrystals of PgC_1 (cocrystals **1-4**), the solvent does not act as a bridge between PgC_1 molecules, except with cocrystal **2**. With cocrystals ofPgC_2 (cocrystals **5-7**), cocrystal **5** does not have solvent-bridging, but cocrystal **6** does have it. All of the cocrystals with PgC_3 (cocrystals **8-11**) have solvent that acts as a bridge between PgC_3 molecules. Furthermore, with PgC_3, there are more than double the amount of hydrogen bonds involving the PgC_3 hydroxyl groups and water molecules (*ca.* 5-6 hydrogen bonds) compared to the PgC_3 hydroxyl groups hydrogen bonding with the main solvent (*ca.* 1-2 hydrogen bonds). Out of the solvents used, the methanol cocrystals (cocrystals **1**, **5**, and **8**) and acetonitrile cocrystals (cocrystals **4** and **11**) have the least number of hydrogen bonds between the solvent and the pyrogallol[4]arenes (*ca*. 0-1 hydrogen bonds). Another aspect of the hydrogen bonding scheme that alters as the tail-length is increased is the number of hydrogen bonds to the PAN molecules (see **Table 4**). As the tail-length increases, the number of hydrogen bonds to PAN molecules decreases. With the exception of cocrystal **7**, there are four or five hydrogen bonds to PAN molecules with cocrystals of PgC_1 and PgC_2 (cocrystals **1-7**). However, when the tail length is increased to three carbon atoms, there is only one hydrogen bond to a PAN molecule (cocrystals **8-11**). The hydrogen bonding scheme is a probable explanation for the PgC_1

Table 4 Types and number of hydrogen bonds involving PgC_x molecules.

Cocrystal	Intramolecular Hydrogen Bonds	Intermolecular Hydrogen Bonds	PAN/PgC_x Hydrogen Bonds	Total Hydrogen Bonds
1	6	2	5	14
2	5	4	2	15
	6	6	4	16
3	3	4	4	14
4	4	2	4	11
5	4	4	4	13
6	4	4	5	16
7	4	6	1	11
8	4	2	1	13
9	6	4	1	18
10	6	4	1	17
11	5	4	1	12
12	4	4	2	22

molecules packing in an atypical bilayer whereas PgC_2 and PgC_3 molecules pack in a more typical bilayer arrangement. It seems the PgC_1 molecules are more likely to hydrogen bond with the PAN molecules than to other PgC_1 molecules (as a percentage of total bonds, about 25%-36% are hydrogen bonds between PgC_1 and PAN molecules) whereas it is not the case with the PgC_2 and PgC_3 molecules (percentage of total bonds is 5%-8% for PgC_3).

Along with influencing the hydrogen bonding scheme, solvent appears to affect the final ratio of PAN to pyrogallol[4]arene in the final structure (see **Table 5**). In methanol (cocrystals **1**, **5**, and **8**), the ratio of PAN to pyrogallol[4]arene is either 3:1 or 2:1. With isopropanol as the solvent (cocrystals **3** and **10**), the ratio is constant at 2:1. The ethanol cocrystals (cocrystals **2**, **9**, and **12**) are seen to prefer a lower ratio of PAN to pyrogallol[4]arene with ratios of 1.5:1, 2:1, and 1:1 respectively. Cocrystals with acetonitrile (cocrystals **4** and **11**) also appear to favour lower PAN to pyrogallol[4]arene ratios (2:1 and 1:1, respectively). The bowl shape of the pyrogallol[4]arenes remains consistent with the cocrystals. However, only cocrystal **4** has a symmetrical bowl while the rest are pinched with cross-sectional distances of *ca.* 6.7 Å and 9.5 Å. Thus, it does not appear that solvent or tail-length affect the shape of the bowl, but rather whether solvent or probe is endo determines the bowl shape.

Table 5 Solvent and the final ratio of PAN to pyrogallol[4]arene

Cocrystal	Solvent	Ratio PAN:PgC_x
1	Methanol	3:1
2	Ethanol	1.5:1
3	Isopropanol	2:1
4	Acetonitrile	2:1
5	Methanol	2:1
6	Water	2:1
7	No solvent	1:1
8	Methanol	2:1
9	Ethanol	2:1
10	Isopropanol	2:1
11	Acetonitrile	1:1
12	Ethanol	1:1

Conclusion

In summary, twelve cocrystals of PAN and pyrogallol[4]arenes of varying aliphatic tail-length have been examined. The flexibility of the pyrogallol[4]arenes was demonstrated by the ability to cocrystallize with PAN in different solvent media. Trends arise as to how solvent and aliphatic tail-length influence the final cocrystals. The aliphatic tail-length of the pyrogallol[4]arene molecules is seen to affect several properties, most notably the bilayer architecture, C–H···π interactions, and hydrogen bonding scheme. Cocrystals with PgC_1 pack in an atypical bilayer structure and have the fewest C–H···π interactions with the endo PAN molecule and the most hydrogen bonds to PAN molecules. As the aliphatic tail-length increases, the bilayer structure becomes more standard, the number of C–H···π interactions with the endo PAN molecule increases, and hydrogen bonds to PAN molecules decreases. In contrast, solvent plays a role in the final ratio of PAN to pyrogallol[4]arene. Methanol solvent is seen to yield a higher ratio (3:1 or 2:1) whereas ethanol and acetonitrile yield a lower ratio (2:1 or 1:1).

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Supplementary Information

Single crystal X-ray crystallographic information files (CIF) are available for all cocrystals. Crystallographic information files are also available from the Cambridge Crystallographic Data Center (CCDC) upon request (http://www.ccdc.cam.ac.uk, CCDC deposition numbers 1002494-1002500; 1002506-1002510).

Notes and references

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†Crystallographic data –

Cocrystal 1: $C_{78}H_{71}O_{17}N_9$, M = 1406.44, orange prism, a = 22.950(4) Å, b = 14.573(5) Å, c = 17.549(5) Å, β = 104.677(2)˚, space group $C2/c$, V = 13469(5) Å^3, Z = 8, D_c = 1.39 g/cm^3, F_{000} = 5904, MoKα radiation, λ = 0.71073 Å, T = 100K, 15605 reflections collected. Final *GooF* = 0.990, *R1* = 0.062, *wR2* = 0.126, *R* indices based on reflections with I (refinement on F^2), 956 parameters, no restraints. Lp and absorption corrections applied, μ = 0.099 mm^{-1}.

Cocrystal 2: $C_{117}H_{121}O_{31}N_9$, M = 2149.23, orange plate, a = 17.5240(4) Å, b = 17.9622(4) Å, c = 18.5524(4) Å, α = 99.369(1)˚, β = 100.579(1)˚, γ = 110.010(1)˚, space group P -1, V = 5230.5(2) Å^3, Z = 2, D_c = 1.37 g/cm^3, F_{000} = 2268, CuKα radiation, λ = 1.54178 Å, T = 100K, 18823 reflections collected. Final *GooF* = 1.066, *R1* = 0.056, *wR2* = 0.173, *R* indices based on reflections with I (refinement on F^2), 1479 parameters, 36 restraints. Lp and absorption corrections applied, μ = 0.825 mm^{-1}.

Cocrystal 3: $C_{71}H_{78}O_{17}N_6$, M = 1287.39, orange plate, a = 29.924(1) Å, b = 19.7720(7) Å, c = 23.7677(9) Å, β = 116.033(2)˚, space group $C2/c$, V = 12635.5(8) Å^3, Z = 8, D_c = 1.35 g/cm^3, F_{000} = 5456, synchrotron radiation, λ = 0.77490 Å, T = 100K, 11646 reflections collected. Final *GooF* = 1.047, *R1* = 0.057, *wR2* = 0.156, *R* indices based on reflections with I (refinement on F^2), 859 parameters, no restraints. Lp and absorption corrections applied, μ = 0.108 mm^{-1}.

Cocrystal 4: $C_{66}H_{60}O_{14}N_8$, M = 1189.22, orange plate, a = 7.3273(6) Å, b = 16.733(1) Å, c = 23.611(3) Å, α = 85.742(2)˚, β = 83.946(2)˚, γ = 86.963(2)˚, space group P -1, V = 2867.7(6) Å^3, Z = 2, D_c = 1.38 g/cm^3, F_{000} = 1248, MoKα radiation, λ = 0.71073 Å, T = 100K, 12730 reflections collected. Final *GooF* = 0.986, *R1* = 0.046, *wR2* = 0.098, *R* indices based on reflections with I (refinement on F^2), 811 parameters, no restraints. Lp and absorption corrections applied, μ = 0.098 mm^{-1}.

Cocrystal 5: $C_{67}H_{66}O_{15}N_6$, M = 1195.26, orange plate, a = 12.646(1) Å, b = 15.636(2) Å, c = 16.887(2) Å, α = 64.978(2)˚, β = 81.891(2)˚, γ = 68.093(2)˚, space group P -1, V = 2806.9(6) Å^3, Z = 2, D_c = 1.41 g/cm^3, F_{000} = 1260, MoKα radiation, λ = 0.71073 Å, T = 100K, 10865 reflections collected. Final *GooF* = 1.023, *R1* = 0.058, *wR2* = 0.151, *R* indices based on reflections with I (refinement on F^2), 809 parameters, 6 restraints. Lp and absorption corrections applied, μ = 0.101 mm^{-1}.

Cocrystal 6: $C_{66}H_{64}O_{15}N_6$, M = 1181.23, orange prism, a = 12.576(1) Å, b = 15.566(2) Å, c = 16.818(2) Å, α = 65.345(2)˚, β = 82.005(2)˚, γ = 68.245(2)˚, space group P -1, V = 2778.6(6) Å^3, Z = 2, D_c = 1.41 g/cm^3, F_{000} = 1244, MoKα radiation, λ = 0.71073 Å, T = 100K, 10579 reflections collected. Final *GooF* = 1.041, *R1* = 0.061, *wR2* = 0.141, *R* indices based on reflections with I (refinement on F^2), 813 parameters, no restraints. Lp and absorption corrections applied, μ = 0.101 mm^{-1}.

Cocrystal 7: $C_{51}H_{51}O_{13}N_3$, M = 4322.2, orange plate, a = 15.986(3) Å, b = 13.950(3) Å, c = 19.675(4) Å, β = 99.924(3)˚, space group $P2_1/c$, V = 4322(1) Å^3, Z = 4, D_c = 1.41 g/cm^3, F_{000} = 1928, MoKα radiation, λ = 0.71073 Å, T = 100K, 6713 reflections collected. Final *GooF* = 1.017, *R1* = 0.049, *wR2* = 0.11, *R* indices based on reflections with I (refinement on F^2), 617 parameters, 4 restraints. Lp and absorption corrections applied, μ = 0.102 mm^{-1}.

Cocrystal 8: $C_{71.5}H_{79}O_{17}N_6$, M = 1294.41, orange plate, a = 12.453(3) Å, b = 15.858(3) Å, c = 19.087(6) Å, α = 110.506(4)˚, β = 94.181(4)˚, γ = 110.339(3)˚, space group P -1, V = 3228.1(14) Å^3, Z = 2, D_c = 1.33 g/cm^3, F_{000} = 1372, MoKα radiation, λ = 0.71073 Å, T = 100K, 14230 reflections collected. Final *GooF* = 1.067, *R1* = 0.068, *wR2* = 0.178, *R* indices based on reflections with I (refinement on F^2), 913 parameters, 49 restraints. Lp and absorption corrections applied, μ = 0.096 mm^{-1}.

Cocrystal 9: $C_{72}H_{80}O_{17}N_6$, M = 1301.42, orange prism, a = 12.657(1) Å, b = 15.762(1) Å, c = 18.771(2) Å, α = 109.665(1)˚, β = 92.113(1)˚, γ = 111.920(1)˚, space group P -1, V = 3214.3(5) Å^3, Z = 2, D_c = 1.35 g/cm^3, F_{000} = 1380, MoKα radiation, λ = 0.71073 Å, T = 100K, 13987 reflections collected. Final *GooF* = 1.047, *R1* = 0.048, *wR2* = 0.123, *R* indices based on reflections with I (refinement on F^2), 889 parameters, 46 restraints. Lp and absorption corrections applied, μ = 0.096 mm^{-1}.

Cocrystal 10: $C_{73}H_{82}O_{17}N_6$, M = 1315.45, orange plate, a = 12.618(3) Å, b = 15.758(3) Å, c = 18.702(4) Å, α = 109.763(3)˚, β = 92.291(3)˚, γ = 112.029(3)˚, space group P -1, V = 3184.(1) Å^3, Z = 2, D_c = 1.37 g/cm^3, F_{000} = 1396, synchrotron radiation, λ = 0.77490 Å, T = 100K, 13007 reflections collected. Final *GooF* = 1.036, *R1* = 0.062, *wR2* = 0.167, *R* indices based on reflections with I (refinement on F^2), 887 parameters, 1 restraints. Lp and absorption corrections applied, μ = 0.109 mm^{-1}.

Cocrystal 11: $C_{57}H_{66}O_{15}N_4$, M = 1047.14, orange plate, a = 18.733(2) Å, b = 12.849(1) Å, c = 22.432(2) Å, β = 106.873(1)˚, space group $P2_1/c$, V = 5166.7(9) Å^3, Z = 4, D_c = 1.346 g/cm^3, F_{000} = 2224, MoKα radiation, λ = 0.71073 Å, T = 100K, 11637 reflections collected. Final *GooF* = 1.031, *R1* = 0.060, *wR2* = 0.147, *R* indices based on reflections with I (refinement on F^2), 700 parameters, no restraints. Lp and absorption corrections applied, μ = 0.098 mm^{-1}.

Cocrystal 12: $C_{57}H_{65}O_{18}N_3$, M = 1080.12, orange prism, a = 11.849(1) Å, b = 12.75(1) Å, c = 18.287(2) Å, α = 84.294(2)˚, β = 85.839(2)˚, γ = 63.720(2)˚, space group P -1, V = 2463.5(5) Å^3, Z = 2, D_c = 1.46 g/cm^3, F_{000} = 1144, synchrotron radiation, λ = 0.77490 Å, T = 100K, 13132 reflections collected. Final *GooF* = 1.039, *R1* = 0.063, *wR2* = 0.165, *R* indices based on reflections with I (refinement on F^2), 759 parameters, 2 restraints. Lp and absorption corrections applied, μ = 0.131 mm^{-1}.

1. (a) M. Busi, M. Laurenti, G. G. Condorelli, A. Motta, M. Favazza, I. L. Fragalà, M. Montalti, L. Prodi and E. Dalcanale, *Chem. Eur. J.*, 2007, **13**, 6891-6898; (b) S. J. Dalgarno, G. W. V. Cave and J. L. Atwood, *Angew. Chem. Int. Ed.*, 2006, **45**, 570-574; (c) O. V. Kulikov, M. M. Daschbach, C. R. Yamnitz, N. Rath and G. W. Gokel, *Chem. Commun.*, 2009, 7497-7499; (d) R. Pinalli, V. Cristini, V. Sottili, S. Geremia, M. Campagnolo, A. Caneschi and E. Dalcanale, *J. Am. Chem. Soc.*, 2004, **126**, 6516-6517.
2. (a) S. J. Dalgarno, N. P. Power, J. E. Warren and J. L. Atwood, *Chem. Commun.*, 2008, 1539-1541; (b) S. J. Dalgarno, N. P. Power and J. L. Atwood, *Coord. Chem. Rev.*, 2008, **252**, 825-841; (c) P. Jin, S. J. Dalgarno and J. L. Atwood, *Coord. Chem. Rev.*, 2010, **254**, 1760-1768; (d) P. Jin, S. J. Dalgarno, J. E. Warren, S. J. Teat and J. L. Atwood, *Chem. Commun.*, 2009, 3348-3350; (e) R. M. McKinlay, G. W. V. Cave and J. L. Atwood, *Proc. Nat. Acad. Sci.*, 2005, **102**, 5944-5948; (f) R. M. McKinlay, P. K. Thallapally and J. L. Atwood, *Chem. Commun.*, 2006, 2956-2958; (g) R. M. McKinlay, P. K. Thallapally, G. W. V. Cave and J. L. Atwood, *Angew. Chem. Int. Ed.*, 2005, **44**, 5733-5736; (h) N. P. Power, S. J. Dalgarno and J. L. Atwood, *Angew. Chem. Int. Ed.*, 2007, **46**, 8601-8604.
3. S. J. Dalgarno, N. P. Power and J. L. Atwood, *Chem, Commun.*, 2007, 3447-3449.
4. (a) A. V. Mossine, H. Kumari, D. A. Fowler, A. K. Maerz, S. R. Kline, C. L. Barnes and J. L. Atwood, *Isr. J. Chem.*, 2011, **51**, 840-842; (b) A. V. Mossine, H. Kumari, D. A. Fowler, A. Shih, S. R. Kline, C. L. Barnes and J. L. Atwood, *Chem. Eur. J.*, 2012, **18**, 10258-10260,
5. (a) D. A. Fowler, J. Tian, C. L. Barnes, S. J. Teat and J. L. Atwood, *CrystEngComm*, 2011, **13**, 1446-1449; (b) H. Kumari, J. Zhang, L. Erra, L. J. Barbour, C. A. Deakyne and J. L. Atwood, *CrystEngComm*, 2013, **15**, 4045-4048.

6. (a) D. A. Fowler, J. L. Atwood and G. A. Baker, *Chem. Commun.*, 2013, **49**, 1802-1804; (b) D. A. Fowler, S. J. Teat, G. A. Baker and J. L. Atwood, *Chem. Commun.*, 2012, **48**, 5262-5264; (c) D. A. Fowler, C. R. Pfeiffer, S. J. Teat, C. M. Beavers, G. A. Baker, and J. L. Atwood, *CrystEngComm*, 2014, **16**, 6010-6022; (d) D. A. Fowler, C. R. Pfeiffer, S. J. Teat, G. A. Baker, and J. L. Atwood, *Cryst. Growth Des*, 2014, **14**, 4199-4204.
7. E. S. Barrett, T. J. Dale and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2007, **129**, 3818-3819.
8. (a) S. J. Dalgarno, D. B. Bassil, S. A. Tucker and J. L. Atwood, *Angew. Chem. Int. Ed*. 2006, **45**, 7019-7022; (b) S. J. Dalgarno, S. A. Tucker, D. B. Bassil and J. L. Atwood, *Science*, 2005, **309**, 2037-2039; (c) K. K. Kline, D. A. Fowler, S. A. Tucker and J. L. Atwood, *Chem. Eur. J.*, 2011. (d) C. R. Pfeiffer, D. A. Fowler, and J. L. Atwood, *Cryst. Growth Des*. 2014, **14**, 4205-4213.
9. J. H. Poplin, R. P. Swatloski, J. D. Holbrey, S. K. Spear, A. Metlen, M. Gratzel, M. K. Nazeeruddin and R. D. Rogers, *Chem. Commun.*, 2007, 2025-2027.
10. (a) A. Mohadesi, Z. Motallebi and A. Salmanipour, *Analyst*, 2010, **135**, 1686-1690; (b) N. Tavakkoli, S. Habibollahi and M. Keshavarzianpour, *Desal. Water Treat.*, 2013, **52**, 350-356.
11. S. Chen, X. Cheng, Y. He, S. Zhu and D. Lu, *Microchim. Acta*, 2013, **180**, 1479-1486.
12. S. Nabi, A. Alim, A. Islam and M. Amjad, *J. Sep. Sci.*, 2005, **28**, 2463-2467.
13. P. Bombicz, T. Gruber, C. Fischer, E. Weber and A. Kalman, *CrystEngComm*, 2014.
14. T. Gerkensmeier, W. Iwanek, C. Agena, R. Fröhlich, S. Kotila, C. Näther and J. Mattay, *Eur. J. Org. Chem.*, 1999, **19**, 2257-2262.