

Crystal Engineering Based on Polymeric Hydrogen-Bonded Supramolecules by Self-Assembling of 9, 10-Bis(3,5-dihydroxyphenyl)anthracene and 2,2',4,4'-Tetrahydroxybenzophenone with Bipyridines

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Abstract: 9, 10-bis(3,5-dihydroxyphenyl)anthracene (BDHA) and 2,2',4,4'-tetrahydroxybenzophenone (THB) are crystallized with bipyridine bases 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bipy-eta), 1,2-di(4-pyridyl)ethylene (dipy-ete), 1,3-di(4-pyridyl)propane (dipy-pra), 4,4'-dipyridyl sulfide (dipy-sul), and 4,4'-dipyridyl disulfide (dipy-dis) to afford molecular complexes (BDHA)·(bipy)₂ **1**, (BDHA)·(bipy-eta)₂ **2**, (BDHA)_{0.5}·(dipy-pra)·CH₃CH₂OH **3**, (BDHA)_{0.5}·(dipy-sul)·H₂O **4**, (BDHA)_{0.5}·(dipy-dis)·CH₃CH₂OH **5** and (THB)·(dipy-ete)₂·H₂O **6**. The crystal structures of **1–6** have been determined by single-crystal X-ray diffraction. All these molecular complexes exhibit polymeric supramolecular structures via O–H···N or O–H···O hydrogen-bonding. **1** and **2** form infinitely rectangular macrocycles linked with one another, whose sizes are *ca.*12.477 Å × 4.802 Å and *ca.*14.575 Å × 4.809 Å, respectively. **3**, **5** and **6** form the one-dimensional zigzag chain structure. **4** forms a ladder structure, and two dipy-sul molecules were included in a frame.

Keywords: Crystal Engineering, crystal structures, polymeric supramolecular structure, hydrogen-bonding

1. Introduction

Crystal engineering has attracted a great deal of interest because of their potential applications, such as in magnetism, catalysis, molecular recognition, ion exchange, small molecule inclusion, nonlinear optics, molecular sensing, and, in general, the rational design of new materials [1-11]. During past few decades, a number of supramolecular architectures have been successfully designed and synthesized through self-assembly from different components by noncovalent, multiple intermolecular interaction [12-14]. Hydrogen bonding is the master key in crystal engineering, supramolecular chemistry, and biological recognition. The directional nature of hydrogen bonds is exploited in the organized self-assembly of molecules in solution and solid state [15-17]. Among many examples, hydrogen bonding between hydroxy and pyridyl is a useful and powerful organizing force and has been utilized for the formation of supramolecules [18-28].

We have recently studied the supramolecular chemistry based on 4, 4'-(9-fluorenylidene)diphenol, 4, 4'-cyclohexylidenebisphenol, bis(2-hydroxy-5-chlorophenyl) sulfide, spirobicomane and adamantane derivatives with bipyridines via O-H...N or O-H...O hydrogen-bonding [29-31]. We will report herein the preparation, and crystal structures of six related acid-base cocrystals based on 9, 10-bis(3,5-dihydroxyphenyl)anthracene (BDHA) and 2,2',4,4'-tetrahydroxybenzophenone (THB) with bipyridine bases 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bipy-eta), 1,2-di(4-pyridyl)ethylene (dipy-ete), 1,3-di(4-pyridyl)propane (dipy-pra), 4,4'-dipyridyl sulfide (dipy-sul), and 4,4'-dipyridyl disulfide (dipy-dis). This provides an opportunity to elucidate the difference in the formation of novel topologies in these six cocrystals. The structures of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (BDHA) and 2,2',4,4'-tetrahydroxybenzophenone (THB) are shown in Chart 1. BDHA is a host system, which has guest-removal, -addition, -exchange properties [32-34], and THB is widely used as an ultraviolet protecting agent [35,36]. Each BDHA and THB molecule has four hydroxy groups, and one bipyridine molecule has two N atoms. Self-assembly via O-H...N between BDHA or THB and bipyridine in EtOH was carried out. We anticipated that 1-D supramolecular hydrogen-bonded polymer would be formed. With this in mind, we prepared six polymeric hydrogen-bonded supramolecules by self-assembling of BDHA or THB with 4,4'-bipyridyl (bipy), 1,2-bis(4-pyridyl)ethane (bipy-eta), 1,2-di(4-pyridyl)ethylene (dipy-ete), 1,3-di(4-pyridyl)propane (dipy-pra), 4,4'-dipyridyl sulfide (dipy-sul), and 4,4'-dipyridyl disulfide (dipy-dis), respectively.

Table 1. Crystallographic Data for 1-6

cocrystal	1	2	3	4	5	6
formula	C ₄₆ H ₃₄ N ₄ O ₄	C ₅₀ H ₄₂ N ₄ O ₄	C ₂₈ H ₂₉ N ₂ O ₃	C ₂₃ H ₁₉ N ₂ O ₃ S	C ₂₅ H ₂₃ N ₂ O ₃ S ₂	C ₃₇ H ₃₂ N ₄ O ₆
<i>M_r</i>	706.77	762.91	441.53	403.46	463.57	628.65
Crystal size (mm ³)	0.35 x 0.15 x 0.10	0.70 x 0.40 x 0.10	0.50 x 0.35 x 0.15	0.30 x 0.25 x 0.10	0.60 x 0.40 x 0.35	0.79 x 0.70 x 0.70
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
<i>a</i> (Å)	9.4497(19)	9.1440(18)	9.1264(18)	12.801(3)	9.776(2)	12.233(2)
<i>b</i> (Å)	10.065(2)	9.5925(19)	10.107(2)	12.968(3)	12.530(3)	12.323(3)
<i>c</i> (Å)	10.151(2)	12.159(2)	15.870(3)	26.107(5)	19.178(4)	12.721(3)
<i>α</i> (°)	93.60(3)	92.53(3)	107.16(3)	90	90	68.39(3)
<i>β</i> (°)	103.94(3)	98.09(3)	93.50(3)	100.68(3)	92.57(3)	84.53(3)
<i>γ</i> (°)	108.30(3)	109.22(3)	113.27(3)	90	90	63.89(3)
<i>Z</i>	1	1	2	8	4	2
Volume (Å ³)	879.6(3)	992.4(3)	1258.3(4)	4258.7(15)	2346.8(8)	1595.9(5)
<i>D</i> _{calc} (g cm ⁻³)	1.334	1.280	1.165	1.259	1.312	1.304
<i>μ</i> (mm ⁻¹)	0.086	0.082	0.076	0.178	0.256	0.090
2θ scan range (°)	4.72 - 54.96	4.52 - 54.96	5.14 - 54.6	5.98 - 54.96	5.28 - 50.06	3.46 - 54.94
range <i>h</i>	-12 to 11	-11 to 11	-11 to 10	-16 to 16	-11 to 11	0 to 15
range <i>k</i>	-13 to 13	-12 to 12	-12 to 12	-16 to 16	-14 to 14	-13 to 15
range <i>l</i>	-13 to 13	-15 to 15	-20 to 19	-33 to 33	-22 to 22	-16 to 16
reflns collected	8015	7757	10521	15434	15080	11133
unique reflns	3932	4232	5407	4819	4127	6601
observed reflns	2061	2060	2492	1619	2269	3722
Goodness-of- fit	0.821	1.183	1.120	0.897	0.997	1.043
<i>R</i> 1, w <i>R</i> 2 [<i>I</i> >2σ(<i>I</i>)]	0.0406,0.083 9	0.0545,0.131 2	0.0551,0.116 7	0.0475,0.065 5	0.0458,0.108 5	0.0808,0.237 6

Table 2. Hydrogen Bond Metrics

cocrystal	D-H...A	d(D-H)/Å	d(H...A)/Å	d(D...A)/Å	<(DHA)/	Symmetry
1	O(1)-H...N(1)	0.98(2)	1.80(2)	2.7445(18)	159.4(18)	-x + 2, -y + 2, -z + 1
	O(2)-H...N(2)#2	0.946(18)	1.872(19)	2.8165(18)	175.7(16)	
2	O(1)-H...N(1)	0.99(3)	1.77(3)	2.742(2)	164(2)	-x + 2, -y - 1, -z + 2
	O(2)-H...N(2)#2	1.04(3)	1.68(3)	2.718(2)	173(2)	
3	O(1)-H...N(2)	0.99(3)	1.79(3)	2.764(3)	167(2)	x - 1, y - 2, z - 1
	O(3)-H...N(1)	0.93(3)	1.90(3)	2.818(3)	174(3)	
	O(2)-H...O(3)#2	0.96(4)	1.76(4)	2.713(2)	175(3)	
4	O(1)-H...N(1)	1.02(3)	1.73(3)	2.727(3)	166(2)	x + 1/2, y - 1/2, z
	O(2)-H...O(3)	0.96(3)	1.67(3)	2.628(2)	176(2)	
	O(3)-H...O(1)#2	0.9526(16)	1.8539(17)	2.790(2)	166.95(16)	
5	O(1)-H...O(3)	1.00(2)	1.69(3)	2.683(2)	171.8(2)	x, -y + 1/2, z + 1/2
	O(2)-H...N(1)	1.09(3)	1.71(3)	2.759(3)	159.4(3)	
	O(3)-H...N(2)#2	1.12(3)	1.69(3)	2.801(2)	170.2(2)	
6	O(2)-H...N(1)#3	0.82(3)	1.95(3)	2.765(3)	170.1(2)	x + 1, y - 1, z
	O(3)-H...N(4)	0.82(3)	1.85(3)	2.664(2)	170.3(2)	
	O(4)-H...O(1w)	0.82(3)	1.82(2)	2.638(2)	175.3(3)	
	O(5)-H...O(1)	0.82(3)	1.80(2)	2.528(3)	147.7(3)	

2. Results and Discussion

Synthesis: BDHA (1mmol) and/or THB (1mmol) can be reacted with bipyridines (2mmol) in ethanolic solution at room temperature. Colorless crystals were obtained by slow evaporation of the solvent after a week. The product was (BDHA)·(bipy)₂ **1**, (BDHA)·(bipy-eta)₂ **2**, (BDHA)_{0.5}·(dipy-pra)·CH₃CH₂OH **3**, (BDHA)_{0.5}·(dipy-sul)·H₂O **4**, (BDHA)_{0.5}·(dipy-dis)·CH₃CH₂OH **5** and (THB)·(dipy-ete)₂·H₂O **6**, respectively.

Crystal Structure of (BDHA)·(bipy)₂ 1. Single crystals of **1** (Figure 1) were obtained from ethanol solution after slow evaporation of the solvent at ambient conditions and examined using single-crystal X-ray diffraction method. It gave a triclinic crystal lattice with a *P*-1 space group. Selected crystal data and structural refinement parameters of **1** are given in Table 1 and hydrogen bond metrics are given in Table 2.

The crystal structure of **1** is shown in Figure 1a. The crystal consists of only chain frameworks without crystal solvent. The asymmetric unit of **1** consists of one molecule of BDHA and four equivalent halves of bipy forming four different BDHA/bipy heterodimers. One BDHA molecule is alternatively linked with four bipy molecules through four intermolecular O–H...N hydrogen-bondings, thus stacking in an alternating pattern of AB₂AB₂AB₂. The four H atoms in OH groups of BDHA bond to N atoms of bipy molecules to form four intermolecular O–H...N hydrogen-bondings. Figure 1b shows the crystal packing of **1** down the *a* axis and that 1-D supramolecular polymers are packed in a columnar manner to form infinitely rectangular macrocycles, where the neighboring two bipy molecules are nearly parallel to each other. These macrocycles are linked with one another and their sizes are *ca.* 12.477 Å × 4.802 Å. In addition the neighboring macrocycles are also parallel to each other.

Crystal Structure of (BDHA)·(bipy-eta)₂ 2. Single crystals of **2** (Figure 2) were grown from ethanol solution by slow evaporation at room temperature and examined using single-crystal X-ray diffraction method. A triclinic crystal lattice with a *P*-1 space group is identified. Selected crystal data and structural refinement parameters of **2** are given in Table 1 and hydrogen bond metrics are given in Table 2.

The crystal structure of **2** is similar to that of **1** and they belong to the same space group (Table 1). Figure 2a shows the crystal structure of **2**. The asymmetric unit of **2** also consists of one molecule of BDHA and four equivalent halves of bipy-eta forming four different BDHA/bipy-eta heterodimers. One BDHA molecule is alternatively linked with four bipy-eta molecules through four intermolecular O–H...N hydrogen-bondings, thus stacking in an alternating pattern of AB₂AB₂AB₂. Figure 2a also shows the linear geometry with the chain frame bridged by bipy-eta. The four hydrogens in OH groups of BDHA bond to N atoms of bipy-eta molecules to form four intermolecular O–H...N hydrogen-bondings. Figure 2b shows the crystal packing of **2** down the *a* axis. Seen from the direction of the *a* axis, the crystal packing also seems to form infinitely rectangular macrocycles linked with one another, with sizes *ca.* 14.575 Å × 4.809 Å. The macrocyclic sizes of **2** are bigger than those of **1** because bipy-eta is longer than bipy. In each macrocycle, the neighboring two bipy-eta molecules are nearly parallel to each other. Additionally, the neighboring macrocycles have a parallel orientation.

Crystal Structure of (BDHA)_{0.5}·(dipy-pra)·CH₃CH₂OH 3. Single crystals of **3** (Figure 3) were obtained from ethanol solution after slow evaporation of the solvent at ambient conditions and examined using single-crystal X-ray diffraction method. It is associated with a triclinic crystal lattice with a *P*-1 space group. Selected crystal data and structural refinement parameters of **3** are given in Table 1 and hydrogen bond metrics are given in Table 2.

Figure 3a shows the geometry with the chain matrix bridged by dipy-pra and EtOH. One BDHA molecule is alternatively linked with two dipy-pra molecules and two EtOH molecules through O–H...N and O–H...O hydrogen-bondings, respectively. Figure 3b shows the crystal packing of **3** down the *a* axis. Three sorts of hydrogen-bondings form in the crystal packing of **3**: Two H atoms in two OH groups of one BDHA molecule bond to two N atoms of two dipy-pra molecules to form two O–H...N hydrogen-bondings; Two H atoms in the other two OH groups of the BDHA molecule bond to two O atoms of two EtOH molecules to form two O–H...O hydrogen-bondings. The hydrogen in OH group of

the EtOH molecule bonds to N of another dipy-pra molecule to form one O–H...N hydrogen-bonding. This arrangement leads to one-dimensional zigzag chain structure.

Crystal Structure of (BDHA)_{0.5}·(dipy-sul)·H₂O 4. Single crystals of **4** (Figure 4) were grown from ethanol solution after slow evaporation of the solvent at ambient conditions and examined using single-crystal X-ray diffraction method. It is identified as a monoclinic crystal lattice with a *C2/c* space group. Selected crystal data and structural refinement parameters of **4** are given in Table 1 and hydrogen bond metrics are given in Table 2.

Figure 4a shows the geometry with the chain framework bridged by dipy-sul and H₂O. One BDHA molecule is alternatively linked with two dipy-sul molecules and two H₂O molecules through O–H...N and O–H...O hydrogen-bondings, respectively. Figure 4b shows the crystal packing of **4** down the *c* axis. Four sorts of hydrogen-bondings form in the crystal packing of **4**: Two H atoms in two OH groups of one BDHA molecule bond to two N atoms of two dipy-sul molecules to form two O–H...N hydrogen-bondings; Two H atoms in the other two OH groups of the BDHA molecule bond to two O atoms of two H₂O molecules to form two O–H...O hydrogen-bondings; One hydrogen of the H₂O molecule bonds to one O atom in OH group of BDHA to form O–H...O hydrogen-bonding; The another hydrogen of H₂O bonds to N of dipy-sul molecule to form O–H...N hydrogen-bonding. This arrangement leads to a ladder structure, and two dipy-sul molecules were included in a frame.

Crystal Structure of (BDHA)_{0.5}·(dipy-dis)·CH₃CH₂OH 5. Single crystals of **5** (Figure 5) were grown from ethanol solution after slow evaporation of the solvent at ambient conditions and examined using single-crystal X-ray diffraction method. A monoclinic crystal lattice with a *P2(1)/c* space group is identified. Selected crystal data and structural refinement parameters of **5** are given in Table 1 and hydrogen bond metrics are given in Table 2.

Figure 5a shows the geometry with the chain frame bridged by dipy-dis and EtOH. It is noteworthy that crystals **3** and **5** belong to two different space groups (Table 1). Nevertheless, they have very similar patterns of molecular packing. One BDHA molecule is alternatively linked with two dipy-dis molecules and two EtOH molecules through O–H...N and O–H...O hydrogen-bondings, respectively. Figure 5b shows the crystal packing of **5** down the *a* axis. Three sorts of hydrogen-bondings form in the crystal packing of **5**: Two H atoms in two OH groups of one BDHA molecule bond to two N atoms of two dipy-dis molecules to form two O–H...N hydrogen-bondings; Two H atoms in the other two OH groups of the BDHA molecule bond to two O atoms of two EtOH molecules to form two O–H...O hydrogen-bondings; The hydrogen in OH group of the EtOH molecule bonds to N of another dipy-dis molecule to form one O–H...N hydrogen-bonding. This arrangement leads to one-dimensional zigzag chain structure.

Crystal Structure of (THB)·(dipy-ete)₂·H₂O 6. Single crystals of **6** (Figure 6) were grown from ethanol solution after slow evaporation of the solvent at ambient conditions and examined using single-crystal X-ray diffraction method. It belongs to a triclinic crystal lattice with a *P-1* space group. Selected crystal data and structural refinement parameters of **6** are given in Table 1 and hydrogen bond metrics are given in Table 2.

The crystal structure of **6** is shown in Figure 6a. One THB molecule is alternatively linked with two dipy-ete molecules and one H₂O molecule through O–H...N and O–H...O hydrogen-bondings, respectively. Figure 6b shows the crystal packing of **6** down the *a* axis. Four sorts of hydrogen-

bondings form in the crystal packing of **6**: Two H atoms in two OH groups of one THB molecule bond to two N atoms of two dipy-ete molecules to form two O–H...N hydrogen-bondings; The H atom in the third OH group of the THB molecule bonds to the O atom of one H₂O molecule to form one O–H...O hydrogen-bonding; The H atom in the fourth OH group of the THB molecule bonds to the O atom in carbonyl group of the THB molecule to form the intramolecular hydrogen-bonding. The neighboring two dipy-ete molecules have a parallel orientation. This arrangement leads to one-dimensional zigzag chain structure, and there is one independent dipy-ete molecule along the zigzag chain. In addition the dihedral angle of two six membered aromatic rings in THB molecule is *ca.* 44°, which is in agreement with the published value [35,36].

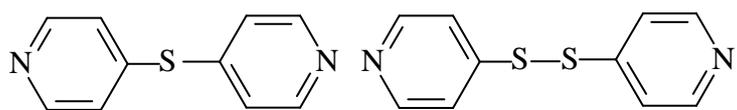
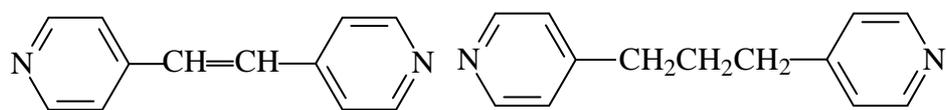
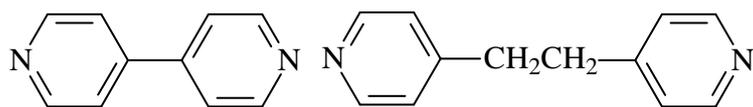
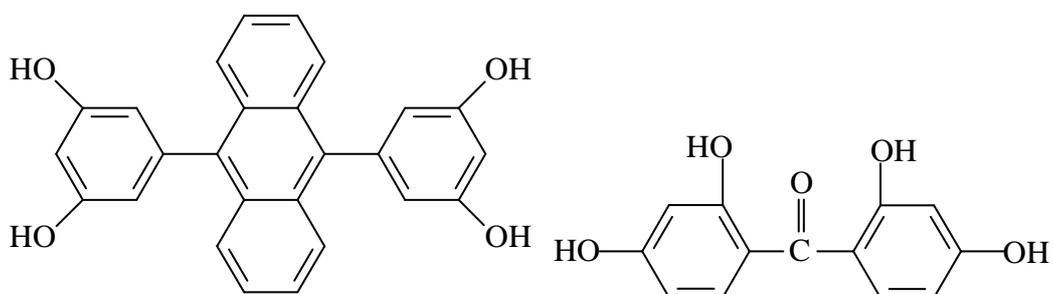
The results of the X-ray structural studies involving host compound BDHA in **1-5** showed one common feature: the conformation was sustained by BDHA in all five structures where the planes of the anthracene backbone and the two phenolic units are twisted nearly perpendicular to each other, and the two phenolic units are nearly parallel to each other (Figures. 1–5) [[32-34]].

For the BDHA molecule, by changing the guest molecule, we can obtain either structurally similar or different supramolecular hydrogen-bonded polymers through interactions of host-guest systems. The conformations of the bipyridines play an important role in the assembly processes. Both bipy and bipy-eta are linear molecules, **1** and **2** form infinitely rectangular macrocycles, whereas dipy-pra, dipy-sul and dipy-dis are V-shaped molecules [the N(1)C(25)N(2) in dipy-pra, N(1)S(1)N(2) in dipy-sul and N(1)S(1)N(2) angles in dipy-dis are 130°, 110° and 105°, respectively] and more flexible than bipy and bipy-eta, **3** and **5** easily form the one-dimensional zigzag chain structure, and **4** forms a ladder structure. For the THB molecule, although dipy-ete is also a linear molecule, it is unfavourable for **6** to form infinitely rectangular macrocycles, but rather a one-dimensional zigzag chain structure because of the intramolecular hydrogen-bonding that occurs in the THB molecule. Such studies are important to crystal engineering. It is possible to obtain novel topologies and extend the study to combinatorial libraries of intermolecular interactions for the exploration of formation of various types of host-guest systems, by changing the guest molecule. Some related experiments are in progress.

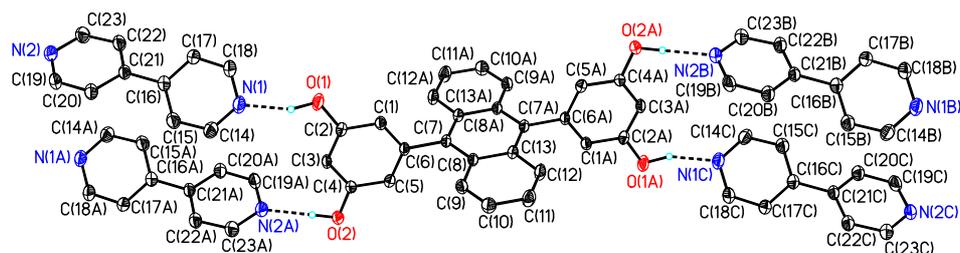
3. Conclusions

In this work, 9, 10-bis(3,5-dihydroxyphenyl)anthracene (BDHA) and 2,2',4,4'-tetrahydroxybenzophenone (THB) are used to construct supramolecular architecture based on crystal engineering. Either similar or different supramolecular hydrogen-bonded polymers would be formed through self-assembly via O–H...N or O–H...O hydrogen-bonding between BDHA and THB with bipyridines. Self-assembling of BDHA with bipy forms infinitely rectangular macrocycles linked with one another, whose sizes are 12.477 Å × 4.802 Å. Self-assembling of BDHA with bipy-eta also forms infinitely rectangular macrocycles linked with one another, whose sizes are 14.575 Å × 4.809 Å. Self-assembling of BDHA with dipy-pra forms the one-dimensional zigzag chain structure. Self-assembling of BDHA with dipy-sul forms a ladder structure. Self-assembling of BDHA with dipy-dis forms the one-dimensional zigzag chain structure. Self-assembling of THB with dipy-ete forms the one-dimensional zigzag chain structure.

Chart 1



a



b

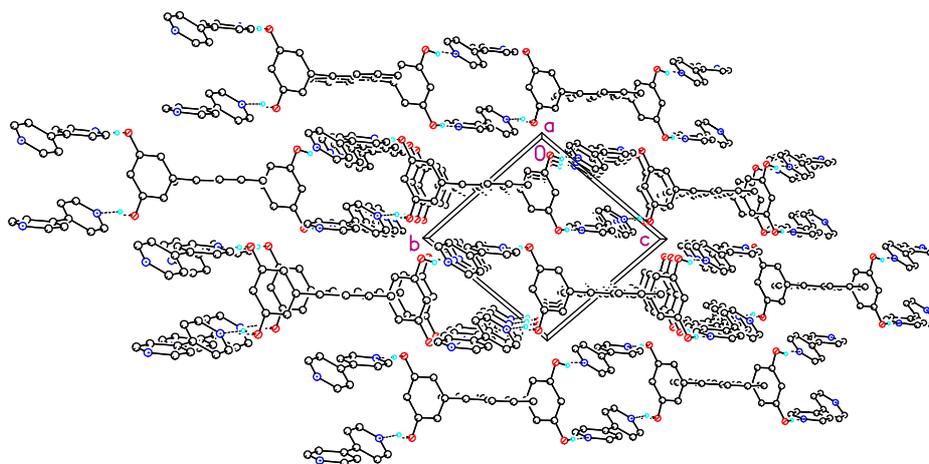
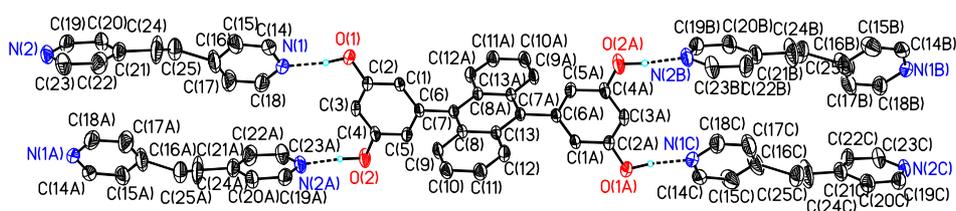


Figure 1 (a) The crystal structure of **1**. Hydrogens were omitted for clarity. (b) The crystal-packing of **1** viewed down the *a* axis. Notice that **1** leads to infinitely rectangular macrocycles, whose sizes are *ca.* 12.477 Å × 4.802 Å.

a



b

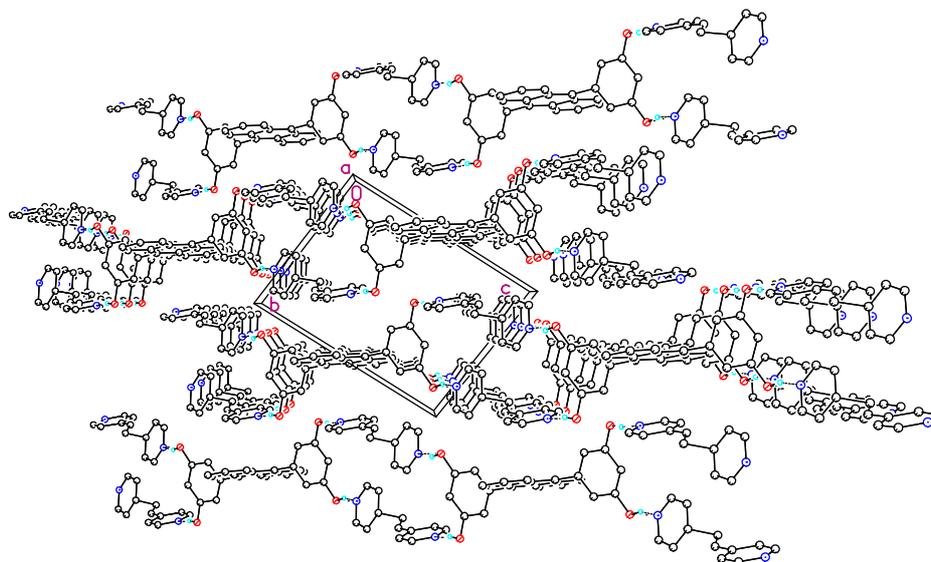
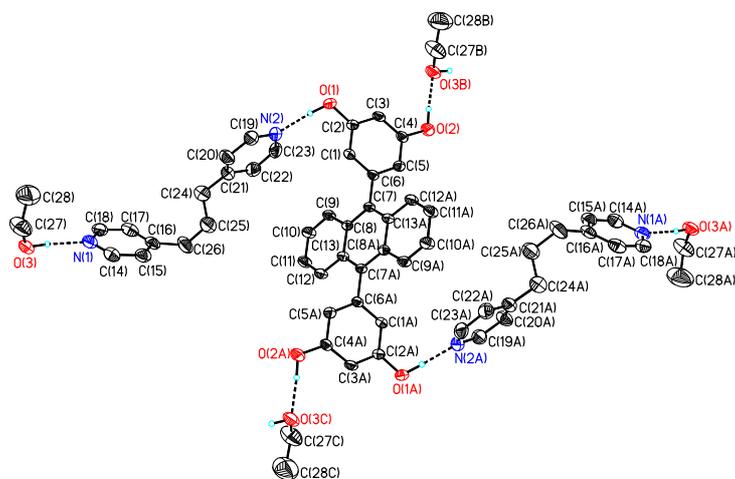


Figure 2 (a) The crystal structure of **2**. Hydrogens were omitted for clarity. (b) The crystal-packing of **2** viewed down the *a* axis. Notice that **2** leads to infinitely rectangular macrocycles, with sizes *ca.* 14.575 Å × 4.809 Å.

a



b

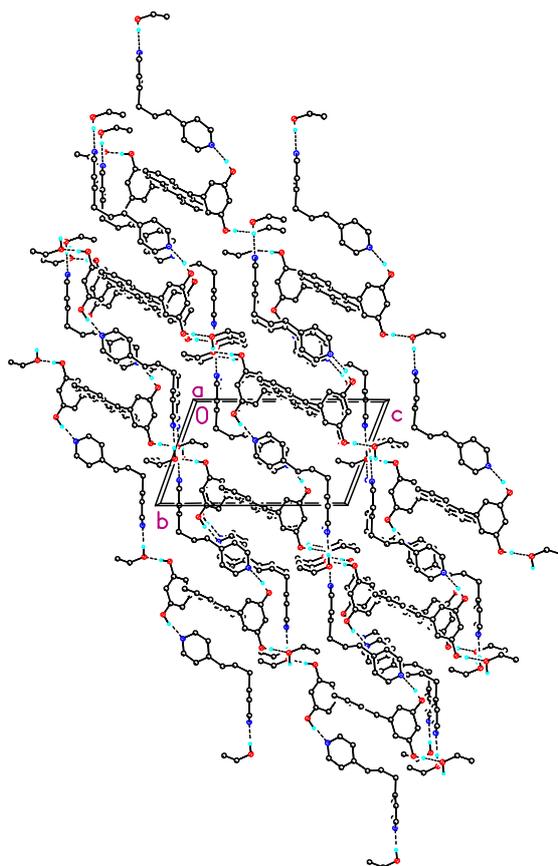
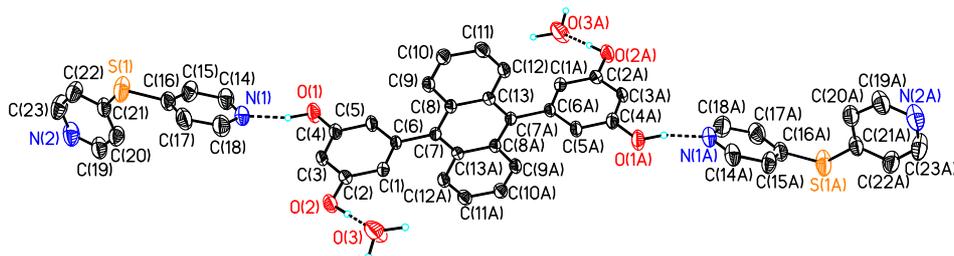


Figure 3 (a) The crystal structure of **3**. Hydrogens were omitted for clarity. (b) The crystal-packing of **3** viewed down the *a* axis. Notice that **3** leads to a zigzag structure.

a



b

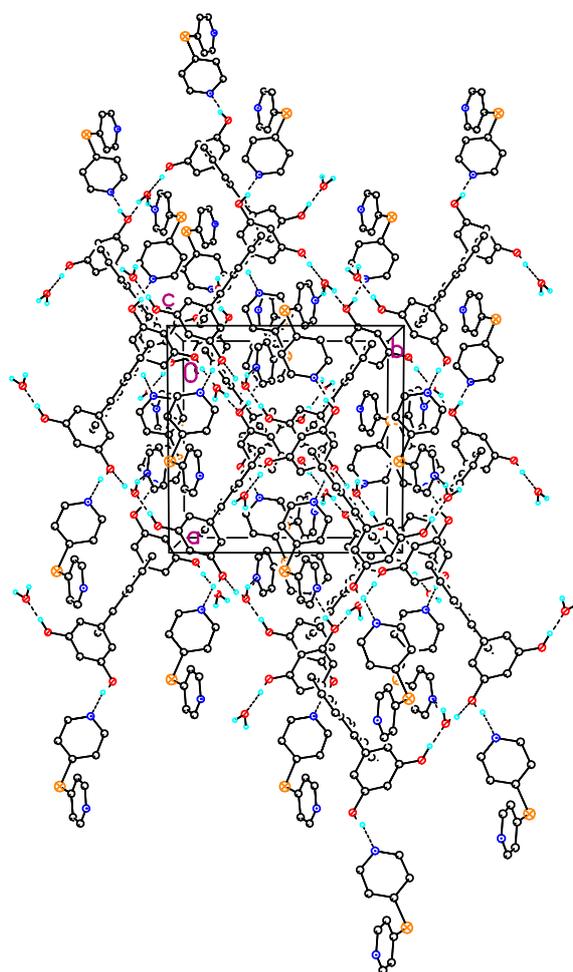
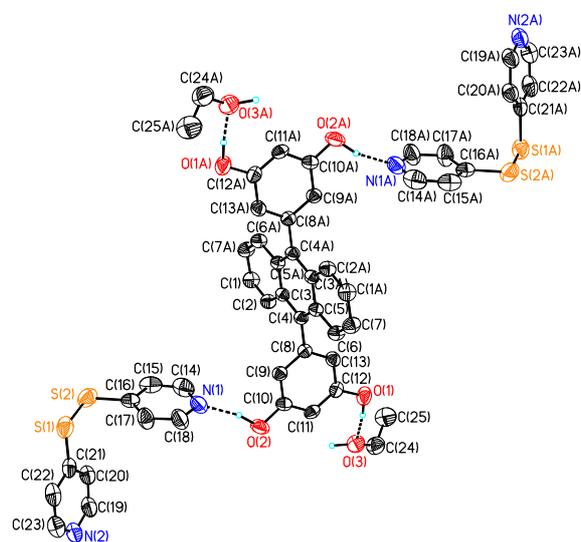


Figure 4 (a) The crystal structure of **4**. Hydrogens were omitted for clarity. (b) The crystal-packing of **4** viewed down the *c* axis. Notice that **4** leads to a ladder structure, and two dipyl-sul molecules were included in a frame.

a



b

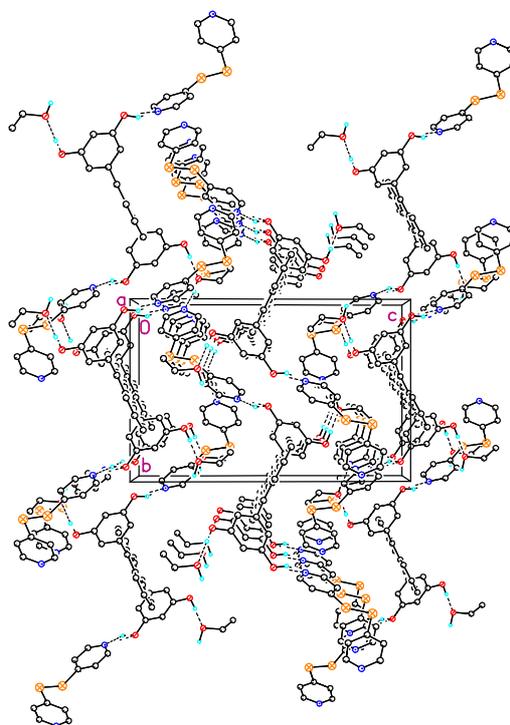
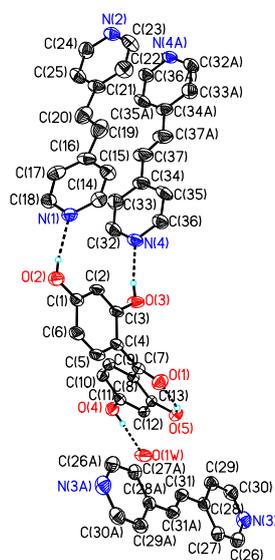


Figure 5 (a) The crystal structure of **5**. Hydrogens were omitted for clarity. (b) The crystal-packing of **5** viewed down the *a* axis. Notice that **5** leads to a zigzag structure.

a



b

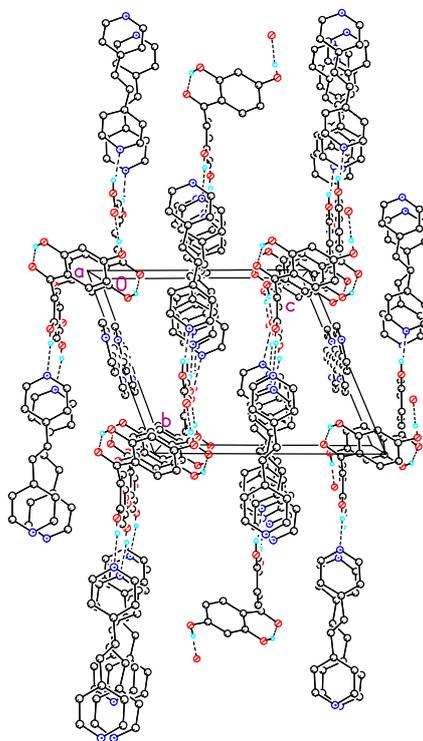


Figure 6 (a) The crystal structure of **6**. Hydrogens were omitted for clarity. (b) The crystal-packing of **6** viewed down the *a* axis. Notice that **6** leads to a zigzag structure.

4. Experimental Section

All materials (including BDHA and THB) were obtained from commercial suppliers (ACROS ORGANICS and TOKYO KASEI KOGYO CO., LTD) and used without further purification.

4.1. Syntheses of cocrystals 1-6

(BDHA)·(bipy)₂ 1. An ethanolic solution of 4,4'-bipyridine (31.2 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (39.4 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₄₆H₃₄N₄O₄: C, 78.17 (78.41); H, 4.85 (4.72).

(BDHA)·(bipy-eta)₂ 2. An ethanolic solution of 1,2-bis(4-pyridyl)ethane (36.8 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (39.4 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₅₀H₄₂N₄O₄: C, 78.72 (78.94); H, 5.55 (5.71).

(BDHA)_{0.5}·(dipy-pra)·CH₃CH₂OH 3. An ethanolic solution of 1,3-di(4-pyridyl)propane (39.6 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (39.4 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₂₈H₂₉N₂O₃: C, 76.17 (76.06); H, 6.62 (6.76).

(BDHA)_{0.5}·(dipy-sul)·H₂O 4. An ethanolic solution of 4,4'-dipyridyl sulfide (37.6 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (39.4 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₂₃H₁₉N₂O₃S: C, 68.47 (68.60); H, 4.75 (4.65).

(BDHA)_{0.5}·(dipy-dis)·CH₃CH₂OH 5. An ethanolic solution of 4,4'-dipyridyl disulfide (44.0 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 9, 10-bis(3,5-dihydroxyphenyl)anthracene (39.4 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₂₅H₂₃N₂O₃S₂: C, 64.72 (64.56); H, 5.00 (4.95).

(THB)·(dipy-ete)₂·H₂O 6. An ethanolic solution of 1,2-di(4-pyridyl)ethylene (36.4 mg, 0.2 mmol) was slowly added to a 20 ml ethanolic solution of 2,2',4,4'-tetrahydroxybenzophenone (24.6 mg, 0.1 mmol) with stirring for 2 hours at room temperature, colorless crystals were obtained by slow evaporation of the solvent after a week. Anal. calcd % (found %) for C₃₇H₃₂N₄O₆: C, 70.63 (70.50); H, 5.13 (5.26).

4.2. X-ray Crystallographic Analyses

The diffraction data for **1-6** were collected on a Rigaku RAXISRAPID automated diffractometer at room temperature using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and successive difference maps (SHELXS 97) [37] and refined by full-matrix least squares on F^2 using all unique data (SHELXL 97) [38]. The non-hydrogen atoms were refined

anisotropically. Hydrogen atoms in these structures were placed in the ideal positions or located from the differential Fourier map. Crystal data and experimental details for the crystals of **1-6** are given in Table 1. Hydrogen bond metrics are given in Table 2. All bond distances and angles of the molecule are normal [18-28].

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