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# Ladder type supramolecular assembly and gas adsorption profile under reduced pressure based on hydrogen bonded *m*-tetraphenyl derivative of anthracene

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**Abstract**—We report a guest adduct X-ray structures and gas adsorption capability of 9,10-bis(4'',4-dihydroxyl-*m*-terphen-5''-yl)anthracene, which is an analogue of anthracene-bis(resorcinol) derivative reported by Aoyama et al. The gas adsorption capability is double scale of guest inclusion than that of anthracene-bis(resorcinol) derivative.

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## 1. Introduction

Hydrogen bonding interactions as well as electrostatic forces, van der Waals, and  $\pi$ – $\pi$  stacking interactions, are the main force for the self-assembly of supramolecular formation, which have recently received much attention because of their versatile functionality such as guest binding with vacancies of defined size and shape to entrap the guest molecule.<sup>1</sup>

Fifteen years ago, a synthesis of bis(resorcinol) derivative of anthracene (**2**), which forms a hydrogen bonded 2D network, has been reported by Aoyama et al. The resulting huge cavities are capable of binding guest molecules.<sup>2</sup> After that, a couple of analogues of resorcinol derivative of anthracene such as stacked porphyrin arrays by hydrogen bonded network,<sup>3</sup> a robust two-dimensional hydrogen bonded network<sup>4</sup> based on anthracene monoresorcinol, have been synthesized in order to evaluate the capability of gas adsorption property, because design of crystal structures is still a tough challenge in materials science and technology.<sup>5</sup> However, these analogues have some problems, which have too small cavity size to entrap two different guest molecules. When de novo

supramolecular architecture was used as molecular reaction flask, the flask should have enough size to incorporate two guest molecules. It would be favorable if a large cavity was constructed by molecular design. Here we present a new bis(resorcinol) derivative of anthracene as a ladder type supramolecular architecture (**1**), in which benzene unit was introduced as a spacer to enlarge a guest incorporated domain. In this study, we succeeded to make a couple of crystal structures, which are **1**·3(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>)·2(*p*-xylene), **1**·3(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>)·2(*p*-xylene), **1**·5(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>), and **1**·4(CH<sub>3</sub>COCH<sub>3</sub>). Also we investigated the gas adsorption profile of **1** with a couple of guest molecules, such as MEK, acetone, EtOAc, and benzene. It was found that gas adsorption capability of **1** shows two times of guest molecules compared with that of **2**, in which two molecules were included in the cavity and another two molecules were trapped between the sheets of ladder like structure. In the system, interactions involving hydroxyl groups have been shown to play an important role in the formation organization.

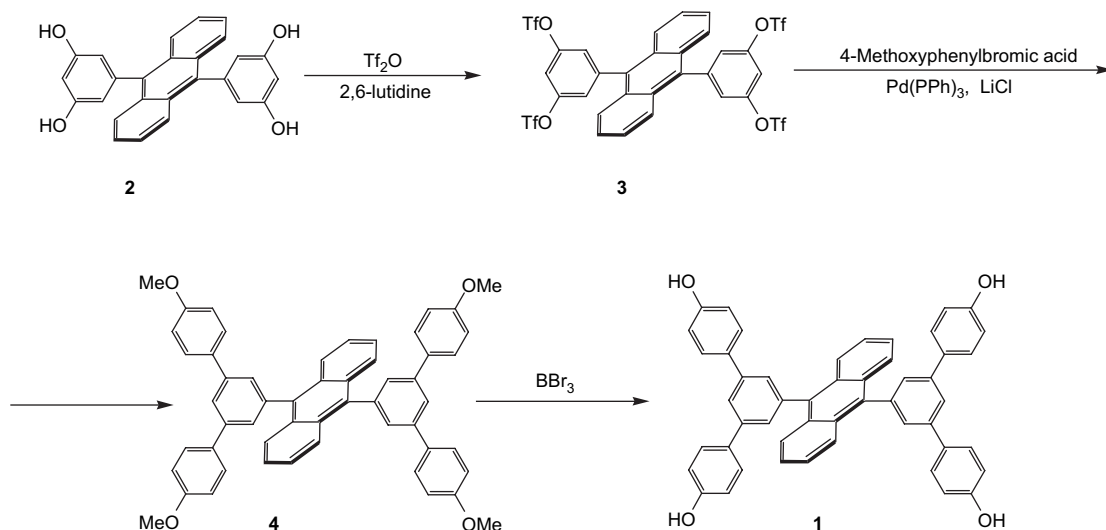
## 2. Results and discussion

### 2.1. The preparation of tetraphenylhydroxyl derivative of anthracene (**1**)

The synthesis of **1** was achieved by three steps in high yields as shown in Scheme 1. The starting material **2** was

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Scheme 1. Preparation of **1**.

synthesized by Aoyama et al. Later, a couple of derivatives of it were prepared to investigate functionalities such as gas sorption and self-assembly formation. Introduction of

benzene unit to **2** was succeeded in Suzuki cross coupling reaction in high yield.<sup>6</sup>

## 2.2. Crystal structures of **1** with several guest molecules

The crystals suitable for X-ray study were obtained by liquid–liquid slow diffusion of a poor solvent into a good solvent of **1** at room temperature as shown in Table 1. In cases of entries 1, 2, 4, and 7 in Table 1, the single crystals were obtained as to be suitable for X-ray analysis. In the other entries 3, 5, 6, and 8, adduct of guest molecular ratios were detected with integration of <sup>1</sup>H NMR, because those crystals were too small for X-ray analysis. Crystal data and parameters of refinement for **1**·3(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>)·2(*p*-xylene), **1**·3(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>)·2(*p*-xylene), **1**·5(CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>), and **1**·4(CH<sub>3</sub>COCH<sub>3</sub>) are summarized in Table 2.

Table 1. Crystallization from various conditions

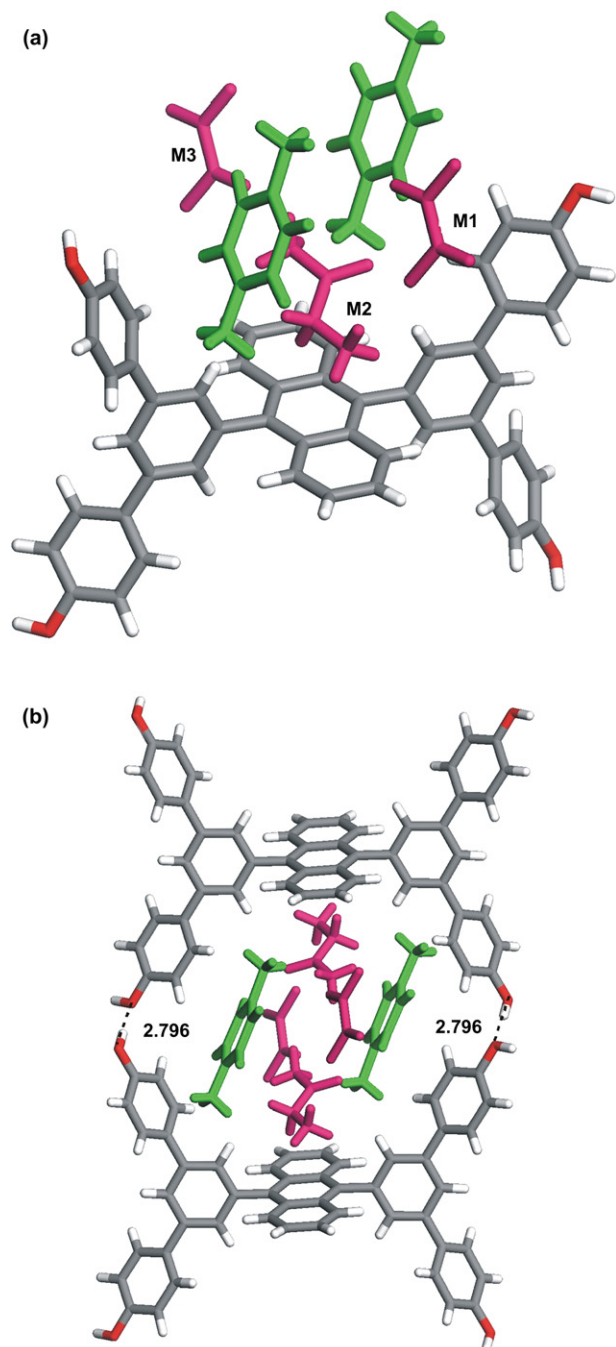
Entry	Guest A (good solvent)	Guest B (poor solvent)	Guest A/host	Guest B/host
1 <sup>a</sup>	MEK	<i>p</i> -Xylene	3	2
2 <sup>a</sup>	AcOEt	<i>p</i> -Xylene	3	2
3	AcOEt	Benzene	—	2
4 <sup>a</sup>	AcOEt	—	5	—
5	Acetone	<i>p</i> -Xylene	2	2
6	Acetone	Benzene	—	2
7 <sup>a</sup>	Acetone	—	4	—
8	Methyl benzoate	—	1	—

<sup>a</sup> The single crystals were obtained as to be suitable for X-ray analysis.

Table 2. Crystal data of **1** with various guest molecules

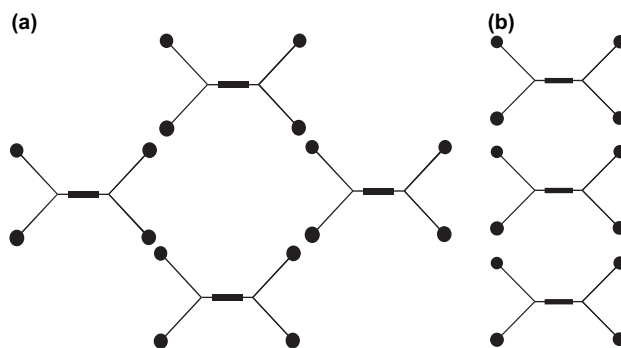
Adduct	<i>p</i> -Xylene MEK	<i>p</i> -Xylene AcOEt	AcOEt	Acetone
Formula	C <sub>78</sub> H <sub>78</sub> O <sub>7</sub>	C <sub>82</sub> H <sub>86</sub> O <sub>12</sub>	C <sub>74</sub> H <sub>82</sub> O <sub>16</sub>	C <sub>62</sub> H <sub>58</sub> O <sub>8</sub>
Formula weight	1127.47	1263.57	1227.45	931.14
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1 21/ <i>m</i> 1
Color	Yellow	Yellow	Yellow	Yellow
Size (mm)	0.600×0.450×0.400	0.800×0.600×0.600	0.500×0.500×0.500	0.500×0.300×0.250
<i>a</i> (Å)	11.7930(5)	11.7863(3)	11.8068(1)	14.3194(4)
<i>b</i> (Å)	11.8241(5)	12.1310(4)	11.8656(3)	9.0878(3)
<i>c</i> (Å)	13.8497(7)	13.864(1)	14.0903(3)	19.4726(6)
$\alpha$ (deg)	75.565(2)	87.451(2)	88.846(2)	90
$\beta$ (deg)	68.929(3)	66.360(3)	67.9064(1)	97.563(1)
$\gamma$ (deg)	61.372(1)	62.936(4)	64.164(5)	90
<i>V</i> (Å <sup>3</sup> )	1574.8(1)	1593.7(2)	1621.57(9)	2512.0(1)
<i>Z</i>	1	1	1	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.189	1.316	1.257	1.231
<i>T</i> (K)	163.2	163.2	163.2	163.2
$\mu$ =(Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.074	0.087	0.088	0.08
No. of reflections measured	14,772	13,945	10,537	20,821
No. of reflections used	7109	7107	6447	5666
No. of variables	457	489	433	374
<i>R</i> <sub>1</sub>	0.033	0.047	0.105	0.055
GOF	1.827	1.709	1.916	1.857
<i>wR</i> <sub>2</sub>	0.2286	0.2127	0.3559	0.2841

Figure 1a shows the crystal structure of  $1 \cdot 3\text{MEK} \cdot 2p\text{-xylene}$ . The two *p*-xylene of the guest molecules were located at the parallel and the two MEK of M1 and M3 could not be represented precisely because these molecules were disordered. It was shown that the crystal of adduct of  $1 \cdot 3\text{MEK} \cdot 2p\text{-xylene}$  constructed ladder like network, which was hydrogen bonded with a O...O distance of 2.796 Å, as shown in Figure 1b. Although, it has been reported that supramolecular assembly based on anthracene derivative such as  $2^1$  formed hydrogen bonded network in a cancellous structure depicted, it was recognized that **1** formed different hydrogen

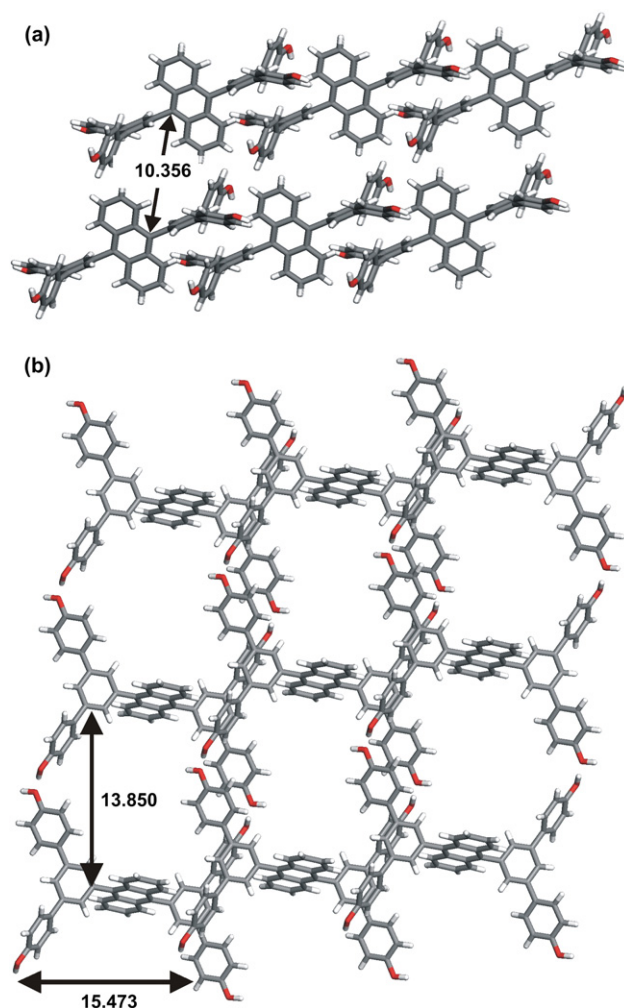


**Figure 1.** (a) Crystal structure of  $1 \cdot 3\text{MEK} \cdot 2p\text{-xylene}$ . The carbons, oxygens, and hydrogens in the host molecules are gray, red, and white, respectively. The *p*-xylene and MEK of the guest molecules are green and pink. (b) Location of host and guest molecules along *a* axis.

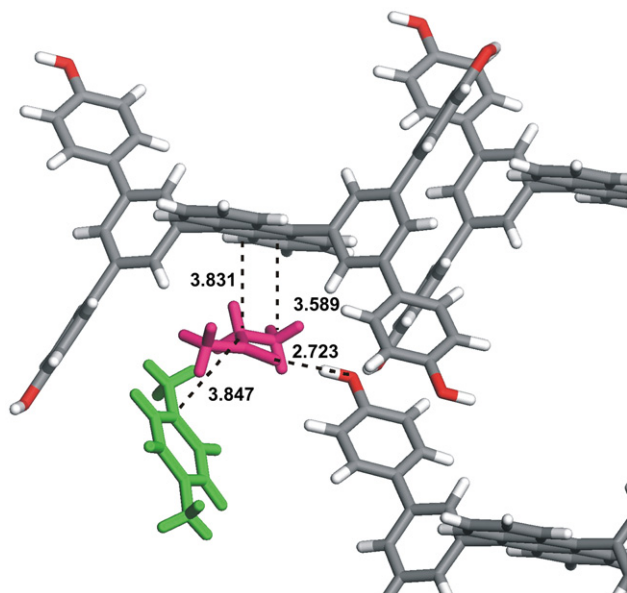
bonded network such as ladder like framework as shown in Scheme 2a and b. Appended moiety linked with anthracene overlapped each other and resulted to make molecular sheet along *c* axis. It was known that two kinds of cavities are present in this structure, which was made from ladder structure and the other from molecular sheet, respectively, as shown in Figure 2a and b. The big cavity was made from ladder structure in parallel with the *bc* plane, of which the longitudinal and lateral direction sizes are 13.850 and 15.473 Å,



**Scheme 2.** (a) Model of cancellous structure and (b) ladder like structure.

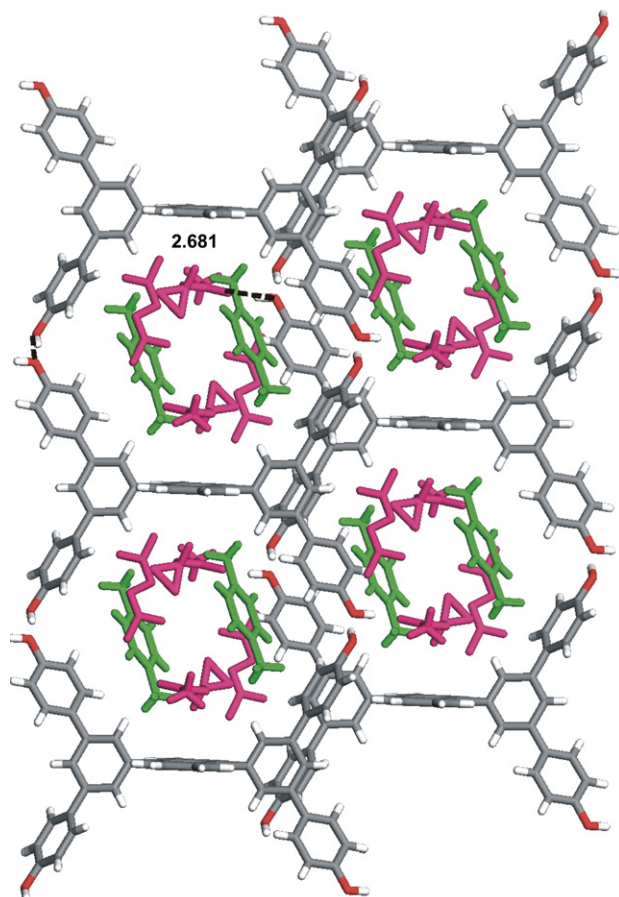


**Figure 2.** (a) Sheet structure along *c* axis. (b) Ladder structure of molecular sheet in parallel with the *bc* plane.



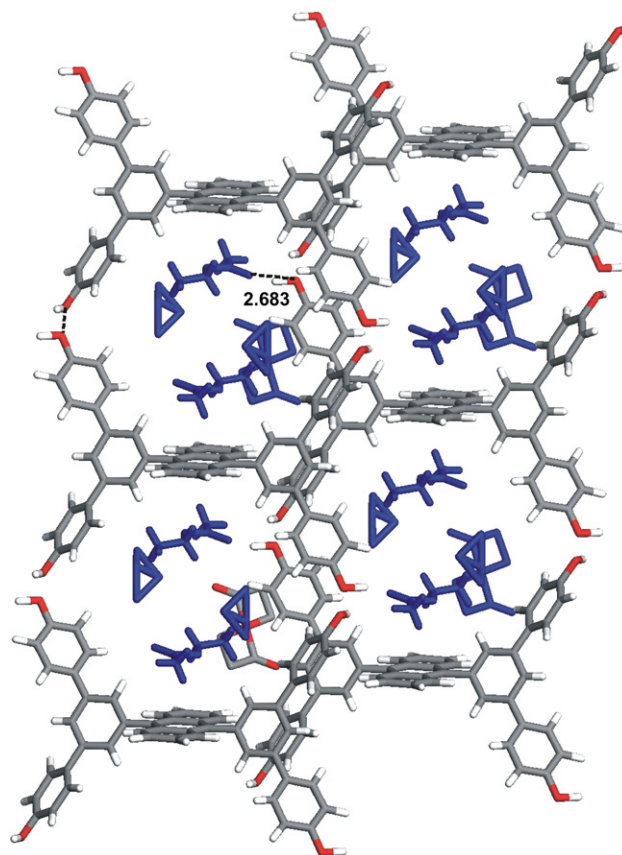
**Figure 3.** Location of host and guest molecules in the crystal. The *p*-xylene and MEK of the guest molecules are green and pink.

respectively. On the other hand, the smaller cavity originated from molecular sheet, of which the distance is 10.356 Å. It was shown that the large cavity included two MEK, and

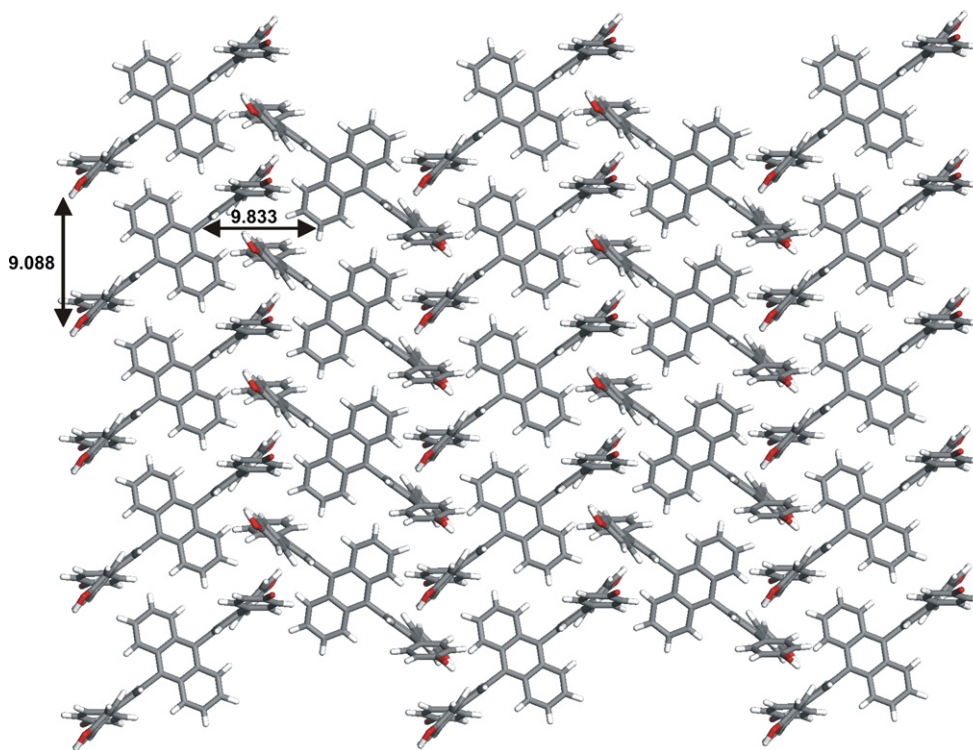


**Figure 4.** Crystal structure of adduct of **1**·3ethylacetate·2*p*-xylene along *b* axis. The carbons, oxygens, and hydrogens in the host molecules are gray, red, and white, respectively. The *p*-xylene and ethylacetate of the guest molecules are green and pink.

small one includes two *p*-xylenes and one MEK. As shown in Figure 3, it was observed as the very interesting location of the guest molecule inclusion in the large cavity, in which there included one MEK that was connected with hydroxylphenyl group of **1** by the hydrogen bonding and CH– $\pi$  interaction with anthracene parts of **1** with a O...O distances of ca. 2.723 Å and 3.589–3.831 Å, respectively. In addition, it was also found that the CH– $\pi$  interaction between MEK and *p*-xylene, which were located in the small cavity, with a distance of ca. 3.847 Å. Another two MEK molecules located in outside of these cavities. It was indicated that the stability of MEK included in the small cavity was not so strong, because this guest molecule has no interaction with surrounding species. It was shown that the conformations of crystal structures of **1**·3ethylacetate·2*p*-xylene and **1**·5ethylacetate were very similar to complex of **1**·3MEK·2*p*-xylene. Figure 4 shows the structure of the adduct of **1**·3ethylacetate·2*p*-xylene, in which one hydrogen bonded ethylacetate was included in the large cavity. The other four guest molecules (two ethylacetate and *p*-xylene) were included in the layer made from the molecular sheet along the [110] direction. It was shown that the O...O distance between ethylacetate and hydroxylphenyl of **1** is 2.681 Å. Figure 5 shows the structure of adduct of **1**·5ethylacetate, in which two of the hydrogen bonded ethylacetate molecules were included in the large cavity and other three guest molecules in the layer made of molecular sheet along direction [110]. The O...O distance between ethylacetate



**Figure 5.** Crystal structure of adduct of **1**·5ethylacetate along *b* axis. The carbons, oxygens, and hydrogens in the host molecules are gray, red, and white, respectively. The ethylacetate of the guest molecule is blue.



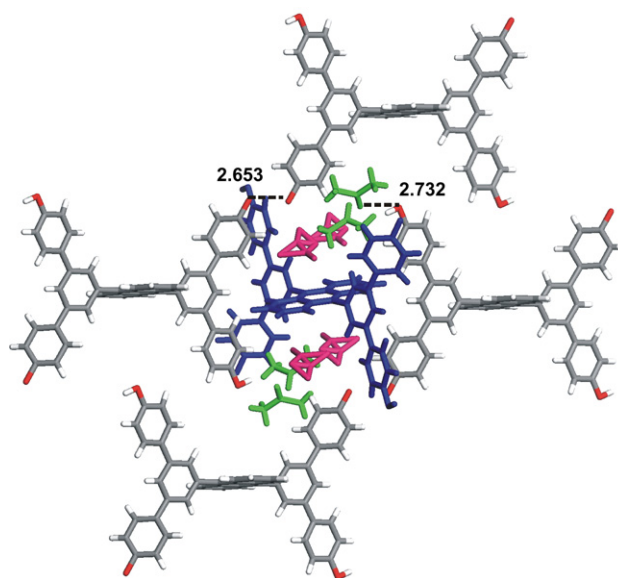
**Figure 6.** Structure of molecular sheet in parallel along direction [10–1].

and hydroxyphenyl of **1** is 2.683 Å. Although the crystal structure of adduct of **1**·4 acetone was formed as a ladder like structure of host assembly, the conformation is different from those of adducts of **1**·3MEK·2*p*-xylene, **1**·3ethylacetate·2*p*-xylene, and **1**·5ethylacetate. It was recognized that the molecular sheet from adduct of **1**·4 acetone formed zigzag structure along direction [10–1] in the crystal as shown in Figure 6. It was shown that the crystal has a very complicated structure, in which four host molecules made the large cavity and one host molecule was included in a different direction from those four host molecules in this resulted cavity as indicated in Figure 7. As a result, a planate sheet structure was formed as a layer, which included four acetone molecules. In this crystal, each host molecule interacted with neighboring host molecule by hydrogen bonding with a O···O distance of 2.653 Å, which made sheet structure with a same direction. In those guest molecules, two acetone molecules were bonded with hydroxyphenyl moiety of **1** by hydrogen bonding with a O···O distance of 2.732 Å. The reason for the formation of the zigzag structure of the complex **1**·4 acetone might be explained by packing of large cavity by neighboring host molecule. It was estimated that it was not enough to fill up such a large cavity with the guest molecules such as *p*-xylene and MEK, because acetone was smaller than those of such guest molecules.

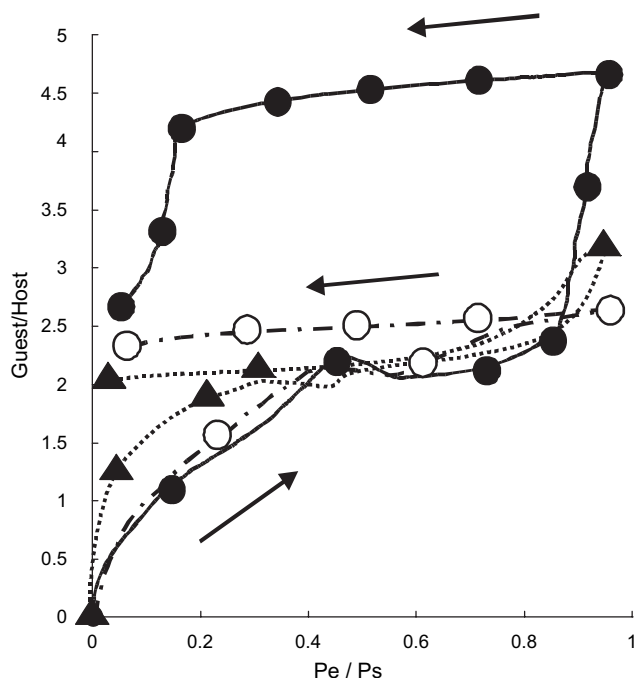
### 2.3. Guest binding to apohost of **1**

Heating at 100 °C in vacuo an adduct of **1**·3MEK·2*p*-xylene resulted in a complete loss of guest molecules. The resulting apohost **1** is non-crystalline as judged by its powder X-ray diffraction pattern, and small specific surface  $A_{\text{BET}}$  is below

10 m<sup>2</sup>/g obtained by an adsorption isotherm of N<sub>2</sub> at 77 K. In spite of this condensed nature, an apohost which is capable of crystalline phase guest addition and removal would be noteworthy. Binding isotherms for gaseous guests with apohost is shown in Figure 8, where molar ratio of guest bound to the apohost used is plotted against guest pressure at 25 °C for the adsorption. On adsorption of ethylacetate within the saturation vapor pressure ( $P_s=114$  Torr), at the beginning, ca. two molecules per host are absorbed into the apohost,

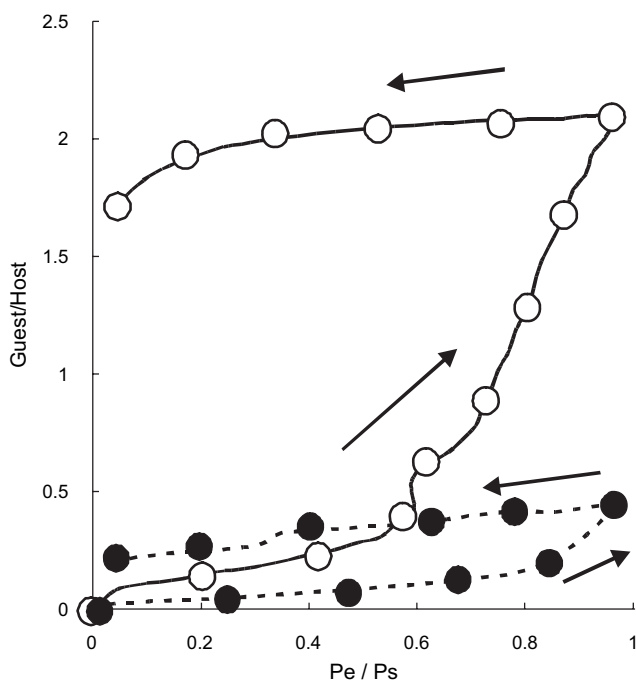


**Figure 7.** Location of among host and guest molecules. Included a host molecule in a different direction is blue. Acetone outside the large cavity is green. Acetone inside the large cavity is pink.



**Figure 8.** Binding isotherms for non-polar guest molecules of acetone (●), ethylacetate (○), and MEK (▲) adsorption at 25 °C with apohost as 1.

in which hydrogen bonded network might be formed. And then, more adsorption of guests was recognized, in which the guest molecules might be included in the sheet structure. Not only ethylacetate but also other guests such as acetone, MEK can also be bound under similar condition. It was observed that two molecules were adsorbed first and then removal of guests was observed. On the other hand, a different phenomenon was observed in the case of acetone



**Figure 9.** Binding isotherms for molar ratio of guest molecules of *n*-hexane (●) and benzene (○) adsorption at 25 °C with apohost as 1.

used as a guest, two and half acetone molecules' adsorption was seen. It might be due to small molecular size of acetone. When vapor pressure was reduced, there remained two guest molecules. It was suggested that remaining two molecules are bounded by hydrogen bonding. On the other hand, non-polar guest molecules such as *n*-hexane and benzene were also studied. It was recognized that benzene was adsorbed in a ratio of two molecules as shown in Figure 9. It might be caused by the affinity between aromatic rings.

### 3. Conclusion

In this study, it was shown that 9,10-bis(4'',4-dihydroxyl-*m*-terphen-5''-yl)anthracene (**1**) can get ladder like hydrogen bonding network in the presence of guest molecules, which has a column structure.

It was shown that there are two kinds of cavities, which contains ladder framework and sheet framework. It was observed that four or five guest molecules were adsorbed in the system, which is twice as high as that of anthracene-bis(resorcinol) derivatives. It was confirmed that two molecules, which bonded with **1** by hydrogen bonding, were included in the ladder framework, and the other two or three molecules were included in the space obtained from the sheet framework. It is undergoing to study catalysis by the apohost, because the host can entrap both polar and non-polar substances, which might accelerate a reaction.

### 4. Experimental

#### 4.1. General

9,10-Bis(3,5-dihydroxyl-1-phenyl)anthracene (**2**) was synthesized as reported previously.<sup>2</sup> <sup>1</sup>H NMR spectra were obtained with Bruker DPX 300 spectrometer. IR spectra were obtained with a Perkin-Elmer SPECTRUM 2000 spectrophotometer. X-ray powder diffractions were obtained with Rigaku RAD-PC X-ray diffractometer (30 kV, 20 mA, Cu K $\alpha$  radiation with  $\lambda=1.5418$  Å).

#### 4.2. Synthesis

**4.2.1. Preparation of triflate derivative of 9,10-bis(3,5-dihydroxyl-1-phenyl)anthracene (3).** To a CH<sub>2</sub>Cl<sub>2</sub> solution containing **2** (3.24 g, 8.25 mol) cooled in an ice bath, 2,6-lutidine (19.06 mL, 80.25 mmol) and trifluoromethane sulfonic anhydride (14.7 mL, 80.25 mmol) were added and stirred for 6 h at room temperature. The reaction mixture was concentrated in vacuo and the obtained residue was extracted with chloroform. The chloroform layer was washed with water, saturated copper sulfate solution, water, and saturated saline. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to crude product, which was washed with ethanol and filtered to give a triflate derivative 9,10-bis(3,5-dihydroxyl-1-phenyl)anthracene (6.77 g, 89% yield).

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>):  $\delta$  8.260 (s, 2H, phenyl-H), 7.825–7.833 (d, 4H, phenyl-H), 7.519 (m, 8H, anthracene-H).

**4.2.2. Preparation of 9,10-bis(4'',4-dimethoxyl-*m*-terphen-5''-yl)anthracene (4).** To a solution containing **3** (2.00 g, 2.17 mmol), 4-methoxyphenyl boronic acid (1.46 g, 9.54 mmol), LiCl (2.21 g, 52.1 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.01 g, 0.87 mmol) in a mixture of 25 mL of ethanol, 150 mL of dioxane was added in the condition of light shielding. 2 M Na<sub>2</sub>CO<sub>3</sub> (4.25 g, 40.1 mmol) in aqueous solution (20 mL) was added drop-wise to the reaction mixture. The reaction mixture was stirred at 90 °C for 24 h. Then, the reaction mixture was concentrated to remove organic solvents and extracted with chloroform. The organic layer was washed with diluted hydrochloric acid, water, saturated sodium bicarbonate water, water, and saturated saline, and then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The mother liquid was concentrated and the obtained residue was washed with ethanol, filtered, and dried in vacuo to give pure 9,10-bis(4'',4-dimethoxyl-*m*-terphen-5''-yl)anthracene (1.57 g, 95.7% yield).

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>): δ 8.06 (s, 2H, phenyl-H), 7.77–7.83 (m, 12H, phenyl-H), 7.63 (q, 4H, anthracene-H), 7.02–7.056 (d, 8H, phenyl-H), 3.80 (s, 12H, OCH<sub>3</sub>).

<sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>): δ 159.0 (s), 140.9 (s), 139.4 (s), 136.5 (s), 132.6 (s), 129.4 (s), 127.9 (s), 127.3 (s), 125.0 (s), 114.0 (s), 54.9 (s).

**4.2.3. Preparation of 9,10-bis(4'',4-dihydroxyl-*m*-terphen-5''-yl)anthracene (1).** To a solution containing **3** (13.7 g, 18 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (125 mL) cooled in an ice bath, boron tribromide (23.4 g, 93.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL) was added drop-wise in the condition of light shielding. The reaction mixture was stirred for 12 h. Then, the reaction mixture was cooled in an ice bath and treated with 300 mL of water to quench excess of BBr<sub>3</sub>. After CH<sub>2</sub>Cl<sub>2</sub> was removed in vacuo, the aqueous layer was extracted with EtOAc. The organic layer was washed with saturated sodium bicarbonate water, water, and saturated saline, and then the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. The organic layer was concentrated under reduced pressure to give oily residue. The residue was treated with activated carbon, filtered, and then purified with silica gel flush column chromatography. Elution with EtOAc gave fractions containing corresponding product, which was concentrated to remove solvent and resulting product was treated with a mixture of EtOAc and chloroform to give **1** (12.2 g, 96.1% yield) as precipitates.

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 9.58 (s, 4H, phenyl-H), 7.98 (s, 2H, phenyl-H), 7.76–7.79 (m, 4H, anthracene-H), 7.67 (d, 8H, phenyl-H), 7.55 (d, 4H, phenyl-H), 6.88 (d, 8H, phenyl-H).

<sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub>): δ 157.6 (s), 141.3 (s), 139.4 (s), 136.9 (s), 130.7 (s), 129.5 (s), 127.9 (s), 128.4 (s), 126.8 (s), 125.9 (s), 123.2 (s), 116.0 (s), 79.3 (s).

IR (KBr): 3342, 1610, 1598, 1513, 1229, 1175, 1106, 829, 787, 759 cm<sup>-1</sup>.

### 4.3. Crystal data of **1** with solvents

The crystals suitable for X-ray study were obtained by liquid–liquid slow diffusion of a poor solvent into a good

solvent of **1** at room temperature. All measurements of X-ray data were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer.

**4.3.1. Crystal data of 1·3MEK·2*p*-xylene.** C<sub>78</sub>H<sub>78</sub>O<sub>7</sub>, *M*=1127.47, yellow, crystal dimensions 0.60×0.45×0.40 mm, triclinic, space group *P*-1, *a*=11.7930(5), *b*=11.8241(5), *c*=13.8497(7) Å, α=75.565(2), β=68.929(3), γ=61.372(1) deg, *V*=1574.8(1) Å<sup>3</sup>, *Z*=1, Mo Kα radiation ρ<sub>calc</sub>=1.189 g cm<sup>-3</sup>, *T*=163.2 K, numerical absorption correction, μ(Mo Kα)=0.074 cm<sup>-1</sup>, data collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 14,772 measured reflections, 7116 unique reflections (*R*<sub>int</sub>=0.0847), 4991 observed reflections (*I*>3.00σ(*I*)), 457 parameters, *R*=0.033, *wR*=0.2286, refine against |*F*|, GOF=1.827. All crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 632059. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail:deposit@ccdc.cam.ac.uk).

**4.3.2. Crystal data of 1·3ethylacetate·2*p*-xylene.** C<sub>82</sub>H<sub>86</sub>O<sub>12</sub>, *M*=1263.57, yellow, crystal dimensions 0.80×0.60×0.50 mm, triclinic, space group *P*-1, *a*=11.7863(3), *b*=12.1310(4), *c*=13.864(1) Å, α=87.451(2), β=66.360(3), γ=62.936(4) deg, *V*=1593.7(2) Å<sup>3</sup>, *Z*=1, Mo Kα radiation, ρ<sub>calc</sub>=1.316 g cm<sup>-3</sup>, *T*=163.2 K, numerical absorption correction, μ(Mo Kα)=0.087 cm<sup>-1</sup>, data collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 13,945 measured reflections, 7114 unique reflections (*R*<sub>int</sub>=0.0896), 7107 observed reflections (*I*>3.00σ(*I*)), 489 parameters, *R*=0.047, *wR*=0.2127, refine against |*F*|, GOF=1.709. All crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 632062. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail:deposit@ccdc.cam.ac.uk).

**4.3.3. Crystal data of 1·5ethylacetate.** C<sub>74</sub>H<sub>82</sub>O<sub>16</sub>, *M*=1227.45, yellow, crystal dimensions 0.50×0.50×0.50 mm, triclinic, space group *P*-1, *a*=11.8068(1), *b*=11.8656(3), *c*=14.0903(3) Å, α=88.846(2), β=67.9064(1), γ=64.164(5) deg, *V*=1621.57(9) Å<sup>3</sup>, *Z*=1, Mo Kα radiation, ρ<sub>calc</sub>=1.257 g cm<sup>-3</sup>, *T*=163.2 K, numerical absorption correction, μ(Mo Kα)=0.088 cm<sup>-1</sup>, data collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 10,537 measured reflections, 6453 unique reflections (*R*<sub>int</sub>=0.1578), 6447 observed reflections (*I*>3.00σ(*I*)), 433 parameters, *R*=0.105, *wR*=0.3559, refine against |*F*|, GOF=1.916. All crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 632060. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail:deposit@ccdc.cam.ac.uk).

**4.3.4. Crystal data of 1·4 acetone.** C<sub>62</sub>H<sub>58</sub>O<sub>8</sub>, *M*=931.14, yellow, crystal dimensions 0.50×0.30×0.25 mm, monoclinic, space group *P*-1 21/*n*1, *a*=14.3194(4), *b*=9.0878(3), *c*=19.4726(6) Å, β=97.563(1) deg, *V*=2512.0(1) Å<sup>3</sup>, *Z*=2, Mo Kα radiation, ρ<sub>calc</sub>=1.231 g cm<sup>-3</sup>, *T*=163.2 K, numerical absorption correction, μ(Mo Kα)=0.08 cm<sup>-1</sup>, data

collections using Rigaku RAXIS-RAPID imaging plate diffractometer, 20,821 measured reflections, 5666 unique reflections ( $R_{\text{int}}=0.1139$ ), 374 observed reflections ( $I>3.00\sigma(I)$ ), 374 parameters,  $R=0.055$ ,  $wR=0.2841$ , refined against  $|F|$ , GOF=1.857. All crystallographic data of the crystals have been deposited at the Cambridge Crystallographic Data Center in CIF format CCDC no. 632061. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail:deposit@ccdc.cam.ac.uk).

#### 4.4. Gas absorption measurements of 1

The isotherm measurements for EtOAc, acetone, MEK, benzene, and *n*-hexane were performed at 298 K by using an automatic volumetric adsorption apparatus (BELSORP 18SP-V; BEL Inc.). In the sample chamber (ca. 15 mL) maintained at  $25.0\pm 0.1$  °C was placed apohost as 1·3MEK·2*p*-xylene complex (ca. 200 mg), which has been pretreated at 60 °C at  $<10^{-3}$  Torr for 5 h just prior to use. The larger gas chamber (176.36 mL) with a pressure gauge was kept at  $50\pm 0.1$  °C. Helium gas at certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The change in pressure allowed an accurate determination of volume of the total gas phase. Host–guest complexation was monitored in a similar manner by using a guest vapor in place of He. The amount of guest adsorbed was calculated readily from the pressure difference ( $P_{\text{cal}}-P_{\text{e}}$ ), where  $P_{\text{cal}}$  is the calculated pressure if there were no guest adsorption, as in the case of helium, and  $P_{\text{e}}$  is the observed equilibrium pressure, as which the change in pressure in 600 s had

become smaller than 1% of the pressure at the point. All operations were computer-controlled and automatic. The specific surface areas ( $A_{\text{BET}}$ ) were obtained by using the same apparatus. The adsorption isotherm for N<sub>2</sub> at 77 K cannot fit well with BET equation,  $P_{\text{e}}/V(P_{\text{e}}-P_{\text{s}})=1/V_{\text{m}}C+[(C-1)/V_{\text{m}}C](P_{\text{e}}/P_{\text{s}})$ , where  $P_{\text{s}}$  is saturation vapor pressure of N<sub>2</sub> at 77 K and is 760 Torr,  $V$  (mL/g) is the amount (in terms of volume in the standard state) of N<sub>2</sub> adsorbed per gram of adsorbent,  $V_{\text{m}}$  is saturation monolayer coverage, and  $C$  is a constant.

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