

Acridinylresorcinol as a Self-Complementary Building Block of Robust Hydrogen-Bonded 2D Nets with Coordinative Saturation. Preservation of Crystal Structures upon Guest Alteration, Guest Removal, and Host Modification

Toshihiro Tanaka,^{†,§} Takashi Tasaki,[‡] and Yasuhiro Aoyama^{*,†,‡}

Contribution from the Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan, and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

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Abstract: Acridinylresorcinol host **3** (9-(3,5-dihydroxy-1-phenyl)acridine) forms such adducts as **3**·(benzene), **3**·(chloroform), **3**·0.5(toluene), and **3**·(isobutyl benzoate). Modified acridinyl host **4** (9-(3,5-dihydroxy-1-phenyl)-4-hydroxyacridine) having an additional OH group on the acridine ring affords such adducts as **4**·(benzene), **4**·(chloroform), **4**·0.5(toluene)·0.5(water), **4**·(methanol)·(water), and **4**·(ethyl acetate). In the crystals, hosts **3** and **4** form hydrogen-bonded (O—H···O—H) poly(resorcinol) chains which are linked together via interchain O—H···N hydrogen bonds to give a coordinatively saturated (O—H···O—H···N) 2D net composed of doubly hydrogen-bonded and antiparallel-stacked, self-complementary cyclic dimer **3**₂ or **4**₂ as a rigidified building block, the otherwise flexible O—H···O—H hydrogen bonds being thereby taken in a cyclophane-like structure. This network turns out to be remarkably well preserved among the above adducts. Guest molecules, which are disordered in many cases, are incorporated in the cavities left. The binding of small polar guests to host **4** is primarily due to hydrogen bonding to the OH group on the acridine ring. The latter therefore acts only as a polarity modifier of preserved cavities. Adduct **3**·(benzene), that is, **3**₂·2(benzene) readily loses one of two guest molecules bound in each cavity to give a microporous half-filled adduct **3**₂·(benzene) which adsorbs 1 mol of benzene to regenerate the starting full adduct without involving a phase change, as confirmed by X-ray powder diffractions and reversible Langmuir-type adsorption/desorption isotherms. The self-complementarity strategy for designing rigid crystal structures is discussed with a particular reference to the possibility of systematic perturbation/variation approaches in crystal engineering.

Introduction

The intermolecular interactions of organic molecules are generally weak. The organic crystal structures are thus sensitive to molecular geometry, that is, size, shape, and functionality.¹ The packing networks of an inclusion compound normally collapse when guest molecules are removed, although there are, in addition to robust metal-coordination networks,^{2–6} a few exceptions where the hosts are small building blocks such as dianin's compounds,⁷ the helical tubuland diols,⁸ and the diaminotriazine derivative.⁹ A common challenge in crystal

engineering may be to find out a rational strategy by which otherwise flexible networks can be made robust enough to define themselves uniquely. This is all we are concerned about here.

* To whom correspondence should be addressed. E-mail: aoyamay@sbchem.kyoto-u.ac.jp.

[†] Kyoto University.

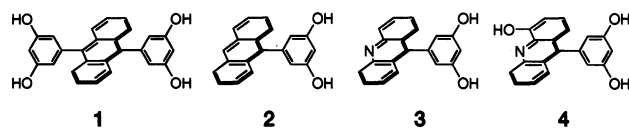
[‡] Kyushu University.

[§] Present address: Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan.

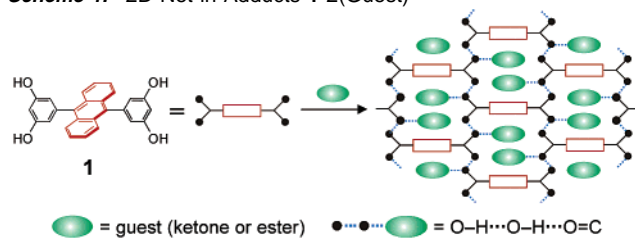
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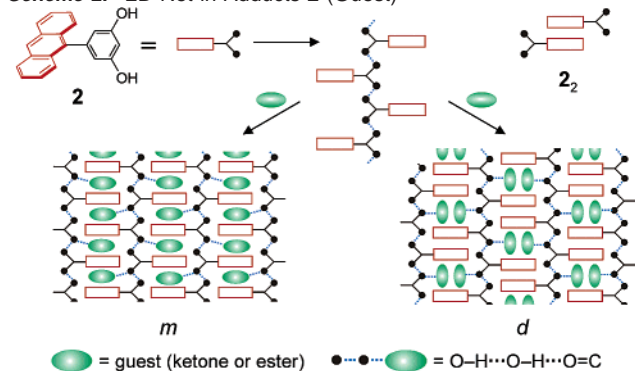
Chart 1. Host Molecules



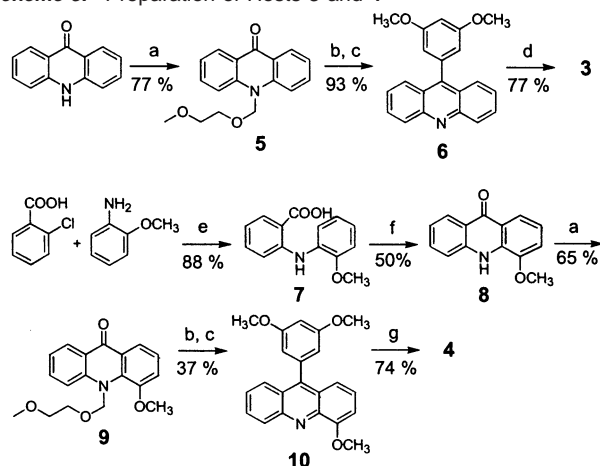
Scheme 1. 2D Net in Adducts 1·2(Guest)



Scheme 2. 2D Net in Adducts 2·(Guest)



The bis(resorcinol) and mono(resorcinol) derivatives of anthracene, **1**¹⁰ and **2**¹¹ (Chart 1), provide typical examples of flexible networks. They afford 1:2 and 1:1 (host-to-guest) adducts with a variety of ketones and esters as guests. Host **1** forms a hydrogen-bonded (O—H···O—H) 2D net (Scheme 1), while host **2** gives 1D chains which are self-assembled into a pseudo 2D net with what we call an either monomeric (*m*) or dimeric (*d*) lattice pattern in a guest-dependent manner (Scheme 2). The network-forming hydrogen bonds are coordinatively unsaturated and become saturated upon guest binding (O—H···O—H···O=C) via host–guest hydrogen bonding, where a remarkable induced-fit adjustment of the network to the guest structures is noted and the network collapses upon guest removal with a phase change to give a nonporous apohost.^{12,13} The present work is concerned about rigidification of the poly(resorcinol) network using acridinylresorcinol host **3** (Chart 1) as a self-complementary building block, where the nitrogen atom

Scheme 3. Preparation of Hosts **3** and **4**^a

^a (a) 2-Methoxyethoxymethyl chloride, NaH, DMF; (b) 3,5-dimethoxyphenylmagnesium chloride, THF; (c) HCl, H₂O; (d) aqueous HBr; (e) K₂CO₃, Cu, C₅H₁₁OH; (f) H₂SO₄; (g) BBr₃, CH₂Cl₂.

acts as a kind of guest. We report here that the resulting 2D net with coordinative saturation (O—H···O—H···N) is remarkably well preserved upon alteration of the guests, partial guest desorption, and polar modification of the host.¹⁴ Thus, the rigid network allows a perturbation of preserved cavities and a systematic variation in guests accommodated therein.^{4a}

Results

Preparation. The network-forming host molecules used in this work are acridinylresorcinol **3** and its 4-acridinyl derivative **4** (Chart 1). Both compounds are obtained from Grignard reactions of the corresponding protected acridone derivatives **5** and **9**, respectively, with dimethoxyphenylmagnesium chloride, followed by deprotection (Scheme 3). 4-Methoxyacridone (**8**) is available from the Ullmann reaction of *o*-chlorobenzoic acid and *o*-anisidine, followed by acid-catalyzed cyclization.

Inclusion Complexation of Host 3. Compound **3** is highly soluble in polar solvents such as methanol and DMF and scarcely so in hydrocarbons such as benzene. Upon recrystallization from benzene/methanol, benzene/DMF, or chloroform/DMF, it exclusively incorporates the less polar component to give 1:1 adduct **3**·(benzene)¹⁵ or **3**·(chloroform). On the other hand, toluene and many other substituted benzenes (*o*-, *m*-, and *p*-), mesitylene, halobenzene (halo = chloro and bromo), alkyl benzoate (alkyl = methyl, ethyl, propyl, isopropyl, and isobutyl), and diphenyl ether) form 1:0.5 (2:1) (host-to-guest) adducts. Cyclohexene and 1,3-cyclohexadiene behave similarly as benzene and afford 1:1 adducts. In marked contrast, cyclohexane and saturated acyclic hydrocarbons (pentane, hexane, heptane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane) are hardly incorporated (guest/**3** < 0.1). At-

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- (15) The simplest way to obtain adduct **3**·(benzene), although not as single crystals, is to reprecipitate host **3** in methanol upon addition of benzene.

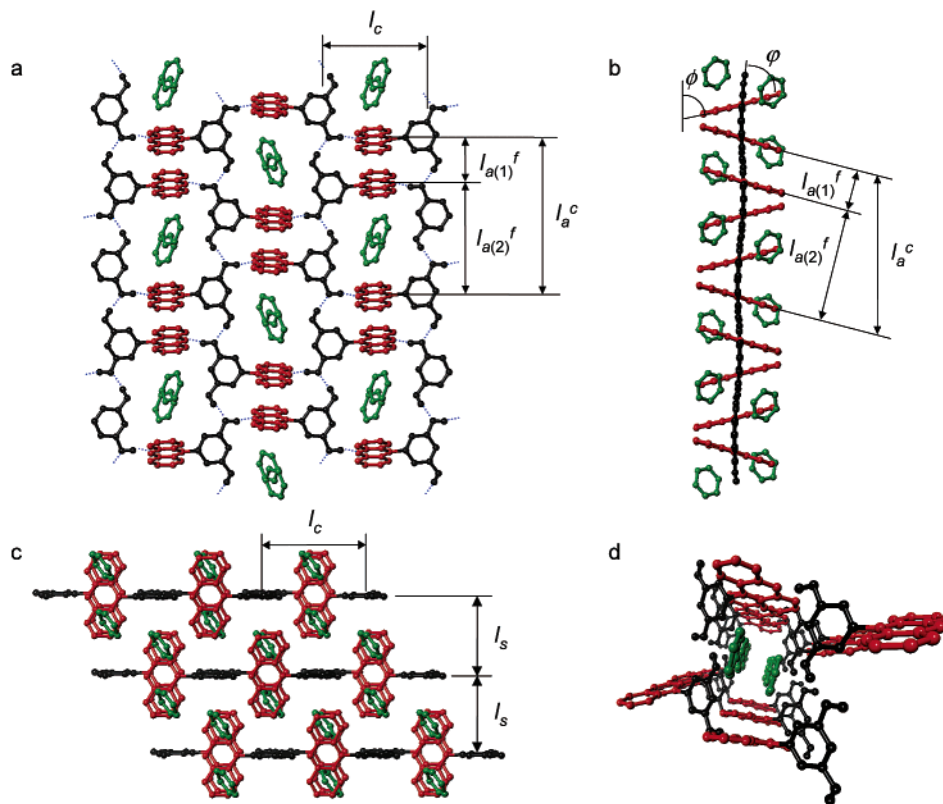
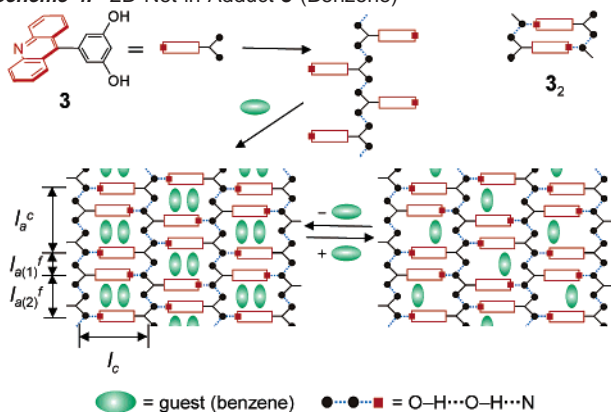


Figure 1. Crystal structure of adduct $3\cdot(\text{benzene})$: front view (a) and side view (b) of a molecular sheet, top view of three adjacent sheets (c), and perspective view along the a axis of the guest-binding cavities (d). l_a , l_c , and l_s are interring, interchain, and intersheet distances, respectively. The acridine rings, resorcinol rings, benzene guests, and hydrogen bonds are shown in red, black, green, and light blue, respectively.

Scheme 4. 2D Net in Adduct $3\cdot(\text{Benzene})$



tempted complexation of small polar guests such as methanol and ethyl acetate only results in recovery of host **3** with little incorporation of the former.

Crystal Structure of Adduct $3\cdot(\text{Benzene})$. The crystal structure of adduct $3\cdot(\text{benzene})$ is shown in Figure 1 and Scheme 4 for a schematic illustration, and the crystal data are summarized in Table 1. Host **3** forms a hydrogen-bonded ($\text{O}-\text{H}\cdots\text{O}-\text{H}$) poly(resorcinol) chain with acridinyl rings sticking out alternately in opposite directions. The chains are linked together via interchain resorcinol–acridine $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds to give a coordinatively saturated ($\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{N}$) 2D net or sheet (front view in Figure 1a and Scheme 4 and side view in Figure 1b); the sheet may also be viewed as arising from an antiparallel dimer (3_2 in Scheme 4) of self-complementary host **3** as a building block. There is little tilting deviation of the resorcinol rings from the sheet (Figure 1b). As

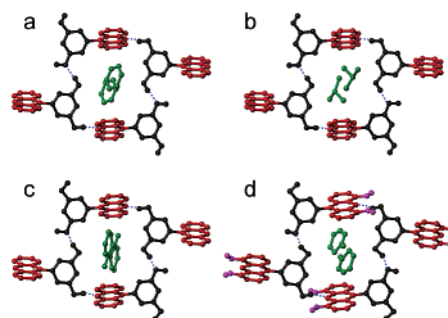


Figure 2. Packing geometry of guest molecules in a cavity of adducts $3\cdot(\text{benzene})$ (a), $3\cdot(\text{chloroform})$ (b), $3\cdot 0.5(\text{isobutyl benzoate})$ (c), and $4\cdot 0.5(\text{toluene})\cdot 0.5(\text{water})$ (d).

a consequence, the tilt angle (ϕ) of the acridine rings with respect to the poly(resorcinol) chain axis is close to the acridine–resorcinol dihedral angle (φ). Each cavity incorporates two benzene molecules which are parallel with each other and perpendicular with respect to the acridine rings, making a T-shaped benzene–acridine $\text{CH}-\pi$ contact (Figure 2a). The sheets are layered in a staggered manner, as shown in the top view of three adjacent sheets in Figure 1c. The guest-binding cavities thereby form intersheet channels (Figure 1d). In Table 2 are summarized characteristic angles and distances, including dihedral (φ) and tilt (ϕ) angles, acridine–acridine interring distances l_a^f (face-to-face) and l_a^c (center-to-center), interchain distance l_c , and intersheet distance l_s in reference to Figure 1 and hydrogen-bond distances $l_{\text{O}-\text{O}}$ and $l_{\text{O}-\text{N}}$.

The crystal structure of adduct $3\cdot(\text{benzene})$ is apparently similar to those of 1:1 adducts of anthracenylresorcinol host **2**, for example, $2\cdot(\text{ethyl acetate})$, in the dimeric (d) lattice pattern

Table 1. Crystallographic Data of Various Adducts

	3•(benzene)	3•(chloroform)	3•0.5(isobutyl benzoate)	3•0.5(benzene) ^a	3•0.5(toluene) ^a
formula	C ₂₅ H ₁₉ NO ₂	C ₂₀ H ₁₄ NO ₂ Cl ₃	C _{24.5} H ₂₀ NO ₃	C ₂₂ H ₁₆ NO ₂	C _{22.5} H ₁₇ NO ₂
formula weight	365.43	406.70	376.43	326.37	333.38
crystal habit and color	orange prisms	orange prisms	orange prisms	orange	orange
crystal system	monoclinic	monoclinic	monoclinic		
space group	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>		
<i>a</i> (Å)	8.866(2)	8.913(2)	8.874(2)	8.8490	8.9000
<i>b</i> (Å)	14.024(2)	13.957(2)	13.998(2)	14.1284	14.0578
<i>c</i> (Å)	15.393(1)	15.099(3)	15.604(1)	15.2494	15.2366
β (deg)	99.34(1)	100.47(1)	97.480(9)	99.528	99.842
<i>V</i> (Å ³)	1888.6(4)	1847.0(5)	1921.8(4)	1880	1878
<i>Z</i>	4	4	4		
<i>d</i> _{calc} (g/cm ³)	1.285	1.462	1.301		
μ (mm ⁻¹)	0.081	0.51	0.086		
<i>T</i> (K)	295	295	295		
no. reflns measured	4811	4595	4899		
no. unique reflns	4347	4258	4423		
	(<i>R</i> _{int} = 0.063)	(<i>R</i> _{int} = 0.025)	(<i>R</i> _{int} = 0.034)		
no. reflns used (<i>I</i> > 3σ(<i>I</i>))	2254	2728	2078		
no. parameters	273	289	268		
reflection/parameter	8.26	9.44	7.75		
<i>R</i> ^b , <i>R</i> _w ^b	0.046, 0.080	0.056, 0.100	0.081, 0.138		
GOF ^b	0.98	1.27	1.70		
final diff four. map (e ⁻ Å ⁻³)	max 0.20, min -0.20	max 0.32, min -0.46	max 0.39, min -0.31		

	4•(benzene)	4•(chloroform)	4•0.5(toluene)·0.5(H ₂ O)	4•(methanol)·(H ₂ O)	4•(ethyl acetate)	4
formula	C ₂₅ H ₁₉ NO ₃	C ₂₀ H ₁₄ NO ₃ Cl ₃	C _{22.5} H ₁₈ NO _{3.5}	C ₂₀ H ₁₉ NO ₅	C ₂₃ H ₂₁ NO ₅	C ₁₉ H ₁₃ NO ₃
formula weight	381.43	422.69	358.39	353.37	391.42	303.32
crystal habit and color	orange prisms	orange prisms	orange prisms	orange prisms	orange prisms	orange prisms
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>	<i>P</i> ₂ / <i>n</i>
<i>a</i> (Å)	8.986(4)	9.127(2)	9.004(2)	8.923(5)	9.315(4)	7.431(4)
<i>b</i> (Å)	14.010(3)	13.960(1)	14.001(2)	13.966(3)	14.040(4)	9.034(7)
<i>c</i> (Å)	15.591 (3)	15.169(2)	15.273(2)	15.197(4)	14.713 (3)	21.104(4)
β (deg)	99.60 (3)	101.02(1)	100.16(2)	100.84(3)	101.91(2)	92.42(3)
<i>V</i> (Å ³)	1935.3 (9)	1897.1(4)	1895.2(6)	1860.0(1)	1882.8(1)	1415.4(1)
<i>Z</i>	4	4	4	4	4	4
<i>d</i> _{calc} (g/cm ³)	1.309	1.480	1.256	1.262	1.381	1.423
μ (mm ⁻¹)	0.086	0.503	0.085	0.091	0.098	0.097
<i>T</i> (K)	295	295	295	295	295	295
no. reflns measured	4918	4812	4816	4744	4768	3718
no. unique reflns	4445	4355	4354	4288	4320	3250
	(<i>R</i> _{int} = 0.100)	(<i>R</i> _{int} = 0.032)	(<i>R</i> _{int} = 0.085)	(<i>R</i> _{int} = 0.083)	(<i>R</i> _{int} = 0.031)	(<i>R</i> _{int} = 0.071)
no. reflns used (<i>I</i> > 3σ(<i>I</i>))	1839	2043	1619	2107	1542	1089
no. parameters	294	298	263	252	255	217
reflection/parameter	6.26	6.86	6.16	8.36	6.05	5.02
<i>R</i> ^b , <i>R</i> _w ^b	0.054, 0.094	0.057, 0.096	0.072, 0.115	0.075, 0.126	0.082, 0.130	0.074, 0.109
GOF ^b	1.19	1.20	1.46	1.58	1.62	1.36
final diff four. map (e ⁻ Å ⁻³)	max 0.19, min -0.27	max 0.22, min -0.32	max 0.39, min -0.27	max 0.58, min -0.36	max 0.60, min -0.44	max 0.55, min -0.40

^a Cell parameters were derived from analysis of powder diffractions.¹⁹ ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, $GOF = [\sum w(|F_o| - |F_c|)^2 / (\text{no. refls} - \text{no. params})]^{1/2}$.

(Scheme 2). In each case, an antiparallel dimer (**3**₂ or **2**₂) of the host actually serves as a building block. The difference lies in rigidity and selectivity. In the case of **3**₂, the head (O–H) and the tail (N) are hydrogen bonded in a self-complementary manner via an O–H group of another building block to give a rigid cyclophane-like structure (Scheme 4), while **2**₂ (Scheme 2) is a flexible stack, which, depending on the type of guests, readily dissociates into a monomeric (m) lattice pattern. Building blocks **3**₂ and **2**₂ lead to coordinatively saturated and unsaturated networks, respectively, resulting in a remarkable alteration in

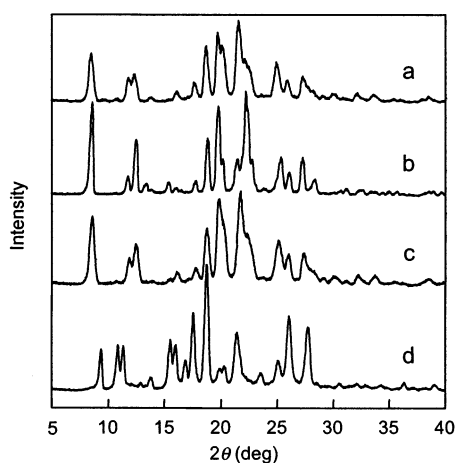
guest-binding selectivities, that is, less polar guests for host **3** and more polar ones for host **2**.

Adducts 3•(Chloroform), 3•0.5(Isobutyl Benzoate), and 3•0.5(Toluene). Chloroform represents less polar nonaromatic guests. Isobutyl benzoate is representative of potential hydrogen-bonding guests as well as substituted benzenes that give rise to the 1:0.5 (2:1) host-to-guest ratio. The crystal structures of adducts **3•(chloroform)** and **3•0.5(isobutyl benzoate)** turn out to be closely related with each other and with that of the benzene adduct described above.¹⁶ They share the chain/sheet/layer motif

Table 2. Characteristic Angles and Distances in the Crystals of Various Adducts^a

	3•(benzene)	3•(chloroform)	3•0.5(isobutyl benzoate)	4•(benzene)	4•(chloroform)	4•0.5(toluene)•0.5(H ₂ O)	4•(methanol)•(H ₂ O)	4•(ethyl acetate)
φ (deg)	71	69	66	73	72	70	68	74
ϕ (deg)	73	76	71	73	76	68	68	76
l_a^c (Å)	14.02	13.96	14.00	14.01	13.96	14.00	13.97	14.04
$l_{a(1)}^f$ (Å)	3.7	3.7	3.7	3.8	3.8	3.8	3.8	3.8
$l_{a(2)}^f$ (Å)	9.7	9.7	9.5	9.7	9.7	9.2	9.0	9.9
l_c (Å)	9.48	9.44	9.46	9.63	9.57	9.52	9.51	9.48
l_s (Å)	7.10	7.01	7.25	7.18	7.10	7.11	7.00	7.07
l_{O-O} (Å)	2.76	2.74	2.75	2.76	2.75	2.75	2.71	2.76
l_{O-N} (Å)	2.68	2.67	2.69	2.81	2.78	2.80	2.77	2.75

^a Definitions are as follows, referring to Figures 1 and 4: φ , acridine–resorcinol dihedral angle; ϕ , tilt angle of acridine rings with respect to a hydrogen-bonded poly(resorcinol) chain; l_a^c , center-to-center interring distance for a neighboring pair of acridine rings along a poly(resorcinol) chain; $l_{a(1)}^f$ and $l_{a(2)}^f$, face-to-face interring distances for neighboring pairs of acridine rings in neighboring poly(resorcinol) chains; l_c , interchain distance; l_s , intersheet distance; l_{O-O} , O–O distance for the hydrogen-bonded O–H···O–H moiety; l_{O-N} , O–N distance for the hydrogen-bonded O–H···N moiety.

**Figure 3.** X-ray powder diffractions for adducts 3•(benzene) (a), 3•0.5(toluene) (b), 3•0.5(benzene) (c), and guest-free apohost 3 (d).

in common, and the cell parameters (a , b , c , β , and V in Table 1) and characteristic angles and distances (Table 2) which define the size and shape of guest-binding cavities are similar for the three (benzene, chloroform, and isobutyl benzoate) adducts, despite a span in the number and type of included guest molecules. An interesting addition in this regard is the 1:0.5 toluene adduct 3•0.5(toluene) in comparison with the 1:1 benzene adduct. Although, unfortunately, the quality of the former adduct is not good enough to allow single-crystal X-ray diffraction, powder-diffraction analyses show that the two adducts are very similar to each other, having almost identical diffraction patterns (Figure 3a and b) and cell parameters (Table 1).

In adduct 3•(chloroform), each cavity incorporates two guest molecules with one of three chlorine atoms pointing to the acridine ring (Figure 2b). Adduct 3•0.5(isobutyl benzoate) exhibits no host–guest hydrogen bonding, as confirmed also by IR spectroscopy showing no complexation-induced shift in $\nu_{C=O}$ for the ester guest. Each cavity binds a single molecule of isobutyl benzoate, which is disordered in two locations with an occupancy of 0.5 each (Figure 2c). This is also true for the toluene adduct as shown below and may reflect a poor packing efficiency of a single guest molecule bound in a big cavity.

Modified Acridinol Host 4 and Its Adducts. As for selectivity, modified acridinol host 4 retains what is characteristic of parent host 3, that is, a remarkable preference for less

polar guests. Competition between ethyl acetate and benzene, toluene, or chloroform, for example, results in an exclusive incorporation of the latter. In its absence, however, host 4, but not 3 (vide supra), is capable of complexing small polar guests such as ethyl acetate and methanol. In addition, water is often co-included. As a result, such adducts as 4•(benzene), 4•(chloroform), 4•0.5(toluene)•0.5(water), 4•(methanol)•(water), and 4•(ethyl acetate) are obtained as single crystals. The IR spectra of the former two anhydrous adducts show a sharp ν_{O-H} absorption at 3250 cm^{-1} for a free OH group assignable to the acridinyl OH. It must therefore be free from hydrogen bonding. Such an absorption is absent in the spectra of the remaining three adducts containing small polar guests. Adduct 4•(ethyl acetate) also shows a $\nu_{C=O}$ at 1710 cm^{-1} , which is shifted by 44 cm^{-1} to a lower wavenumber from that of ethyl acetate as a neat liquid. There is little doubt that these small polar guests are hydrogen bonded to the acridinyl OH group.

X-ray crystallography reveals that all of the adducts contain the same O–H···O–H···N network as described above. Thus, modified host 4 forms a dimeric building block 4₂, the building blocks are assembled into a sheet, and the sheets are layered in a staggered manner in exactly the same way as in the case of parent host 3 (Scheme 4). In no case is the acridinyl OH group involved in the network.¹⁷ In Figure 4 is shown, as an example, the network structure in adduct 4•(ethyl acetate), which is closely related to that of adduct 3•(benzene) shown in Figure 1. This is confirmed in more detail from an inspection of Tables 1 and 2, where a remarkable similarity in the cell parameters and cavity-defining angles and distances among all of the adducts of hosts 3 and 4 is noted. The crystal structures are not simply maintained but actually preserved upon the introduction of an otherwise potential OH group into the host (3 → 4).

Adducts 4•(benzene) and 4•(chloroform) incorporate two guest molecules in each cavity in a similar manner as in 3•(benzene) and 3•(chloroform) (Figure 2a and b). The toluene adduct 4•0.5(toluene)•0.5(water) or 4₂•(toluene)•(water) contains 1 mol of toluene and water per cavity. The toluene is disordered in two locations with a 0.5 occupancy (Figure 2d) in a similar manner as the benzoate guest in adduct 3•0.5(isobutyl benzoate) (Figure 2c), while water is completely disordered. This is also the case for the methanol and water guests in adduct 4•

(16) It is interesting to note that the chloroform adduct dipped in benzene undergoes partial guest exchange while maintaining the single crystallinity.

(17) The acridinyl OH group in all of the adducts of host 4 is disordered in two positions, appearing as either 4-OH or 5-OH. The R values become lowest when the occupancy ratios of 0.36:0.64, 0.40:0.60, 0.35:0.65, 0.74:0.26, and 0.82:0.18 are given to adducts 4•(benzene), 4•(chloroform), 4•0.5(toluene)•0.5(water), 4•(methanol)•(water), and 4•(ethyl acetate), respectively.

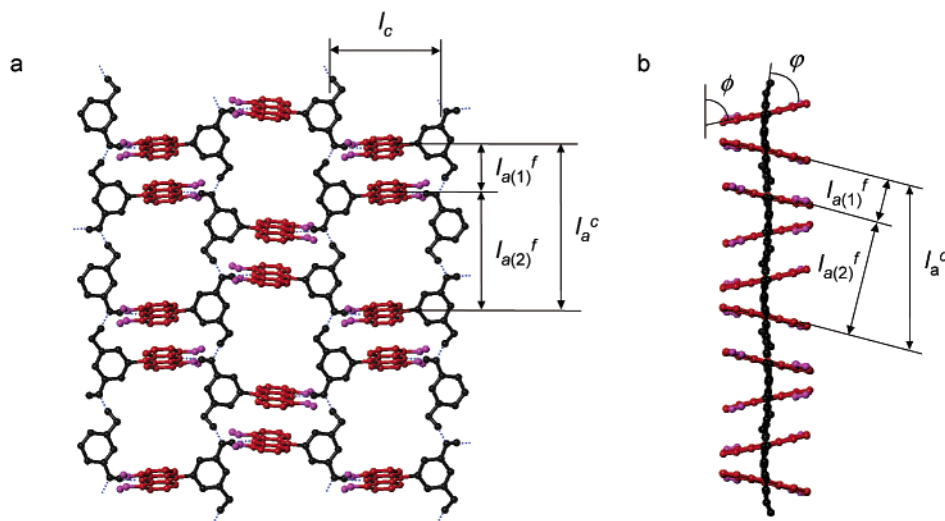


Figure 4. Crystal structure of adduct **4**·(ethyl acetate): front view (a) and side view (b) of a molecular sheet. The colors and the angles and distances have the same meanings as in Figure 1. The acridinyl OH groups are shown in pink. Guest molecules which are disordered are not shown.

(methanol)·(water). In the ethyl acetate adduct, the guest molecules as a whole are disordered again, although the carbonyl oxygen is detected at a distance of 2.75 Å from the oxygen atom of the acridinol. There is little doubt that these small polar guests are hydrogen bonded to the acridinyl OH group. Nevertheless, they are disordered. This may reflect a high degree of conformational flexibility of the O–H···O=C (in the case of ethyl acetate) hydrogen bond and hence, again, a poor packing efficiency for a guest bound in the rigid cavity incapable of induced-fit adjustment.

Microporosity in Half-Filled Benzene Adduct 3·0.5-(Benzene). When left at room temperature in vacuo, benzene adduct **3**·(benzene) or **3**₂·2(benzene) loses one of two guest molecules in each cavity. The resulting half-filled adduct **3**·0.5(benzene) or **3**₂·(benzene) readily regenerates the original full adduct upon uptake of 1 mol (per cavity) of benzene with a Langmuir-type adsorption/desorption isotherm (Figure 5a). The small extent of hysteresis observed may be explained in terms of the so-called capillary condensation. Otherwise, it may be due to developing defects of irreversible nature. The full and half adducts show essentially the same X-ray powder diffractions (Figure 3a and c).¹⁸ These results indicate that the crystal structure is maintained with no phase change during the interconversion of the present full and half adducts, as illustrated in Scheme 4. The cell parameters (derived from analysis of powder diffractions)¹⁹ of the latter, that is, **3**·0.5(benzene), are almost identical with those of the former, that is, **3**·(benzene), as well as not surprisingly with those of the 1:0.5 toluene adduct **3**·0.5(toluene) (Table 1). The half adduct should contain a void equivalent to a molecule of benzene per cavity and must therefore be microporous. A diagnostic Langmuir-type isotherm is not specific to benzene but also applicable to other hydrocarbons such as cyclopentane (~0.6), cyclohexane (~0.5), cyclohexene (~0.5), 2,2-dimethylbutane (~0.25), 2-methylpen-

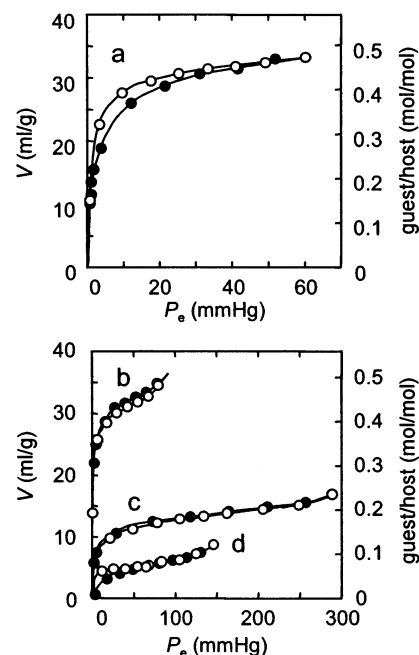


Figure 5. Adsorption (○) and desorption (●) isotherms for gaseous benzene (a), cyclohexene (b), 2,2-dimethylbutane (c), and hexane (d) at 25 °C. The amount of guest adsorbed was calculated from the pressure difference ($P_{\text{cal}} - P_e$), where P_{cal} is the calculated pressure if there were no guest adsorption, and P_e is the observed equilibrium pressure, at which the change in pressure in 9999 s (a) or 3600 s (b–d) had become smaller than 1% of the pressure at that point. All operations were computer-controlled and automatic. V (mL) refers to the standard state.

tane (~0.2), and hexane (~0.1) with varying guest/host ratios, shown in parentheses, at saturation binding (Figure 5b, c, and d for cyclohexene, 2,2-dimethylbutane, and hexane, respectively, as examples).²⁰ The decreasing (guest/host)_{sat} in this order may reflect a compactness or rigidity control of the present guest binding in preserved, rigid micropores.

When heated in vacuo, the benzene adduct loses all of the guest molecules to give a guest-free apohost **3**,²¹ whose X-ray

(18) Simulation (CrystalStructure Analysis Package, Molecular Structure Corp.) based on the crystal structure of benzene full-adduct **3**·(benzene) with a hypothetical occupancy of 0.5 for each benzene molecule in the cavity reproduces the observed powder diffractions of half-adduct **3**·0.5(benzene) very well. These results suggest that the single benzene molecule in the cavity of **3**·0.5(benzene) is disordered in two locations in a similar manner as in toluene adducts **3**·0.5(toluene) and **4**·0.5(toluene)·0.5(water).

(19) Takagi, Y.; Taniguchi, T.; Hori, K. *J. Ceram. Soc. Jpn.* **1993**, *101*, 373–376.

(20) Small polar molecules such as ethyl acetate and acetone are also guests of half-adduct **3**·0.5(benzene) and give Langmuir-type isotherms.

(21) Thermogravimetry indicates that all of the benzene molecules are lost at ≤110 °C.

Table 3. Similarity in Longitudinal and Angular Parameters in the Crystal Structures of Various Adducts

parameter	average (maximal deviation in %) ^a		difference in % between ^d			
	[3•(guest)] _{av} ^b	[4•(guest)] _{av} ^c	[3•(guest)] _{av} and [4•(guest)] _{av}	3•(benzene) and 4•(benzene)	3•(benzene) and 3•0.5(benzene)	4•(benzene) and 4•(ethyl acetate)
<i>a</i> (Å)	8.880 (+0.37, -0.35)	9.071 (+2.7, -1.6)	2.1	1.3	0.2	3.6
<i>b</i> (Å)	14.033 (+0.68, -0.54)	13.995 (+0.32, -0.25)	0.3	0.1	0.7	0.2
<i>c</i> (Å)	15.316 (+1.9, -1.4)	15.189 (+2.6, -3.1)	0.8	1.3	0.9	5.8
β (deg)	99.33 (+1.1, -1.9)	100.71 (+1.2, -1.1)	1.4	0.3	0.2	2.3
<i>V</i> (Å ³)	1883 (+2.1, -1.9)	1894 (+2.2, -1.8)	0.6	2.4	0.5	2.8
φ (deg)	69 (+3.4, -3.9)	71 (+3.6, -4.8)	4	3		1
ϕ (deg)	73 (+3.6, -3.2)	72 (+5.3, -5.8)	2	0		4
<i>l</i> _a ^c (Å)	13.99 (+0.2, -0.2)	14.00 (+0.3, -0.3)	~0	0.1		0.2
<i>l</i> _{a(1)} ^f (Å)	3.7 (0, 0)	3.8 (0, 0)	3	3		0
<i>l</i> _{a(2)} ^f (Å)	9.63 (+0.7, -1.4)	9.50 (+4.2, -5.3)	1.4	0		2
<i>l</i> _c (Å)	9.46 (+0.2, -0.2)	9.54 (+0.9, -0.6)	0.9	1.6		1.6
<i>l</i> _s (Å)	7.12 (+1.8, -1.5)	7.09 (+1.2, -1.3)	0.4	1.1		1.5

^a 100•[(max or min) - av]/av, where max, min, and av are the maximal, minimal, and average ([3•(guest)]_{av} or [4•(guest)]_{av}) values among the adducts in concern, respectively. ^b Average value among adducts 3•(benzene), 3•(chloroform), 3•0.5(isobutyl benzoate), 3•0.5(benzene), and 3•0.5(toluene) with respect to *a*, *b*, *c*, β , and *V* and among adducts 3•(benzene), 3•(chloroform), and 3•0.5(isobutyl benzoate) with respect to φ , ϕ , *l*_a^c, *l*_{a(1)}^f, *l*_{a(2)}^f, *l*_c, and *l*_s. ^c Average value among adducts 4•(benzene), 4•(chloroform), 4•0.5(toluene)•0.5(water), 4•(methanol)•(water), and 4•(ethyl acetate). ^d 100•(max - min)/av, where max, min, and av are the larger, smaller, and average ((max + min)/2) values for a pair of adducts in concern, respectively.

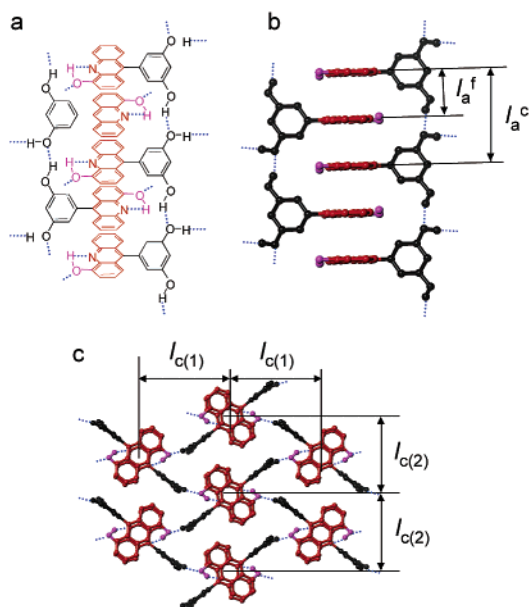


Figure 6. Crystal structure of guest-free apohost **4**: side view of a stacked acridine column (a and b) and top view of columns (*l*_a^f = 3.6 Å, *l*_a^c = 7.43 Å, *l*_{c(1)} = 10.55 Å, and *l*_{c(2)} = 9.03 Å).

powder diffractions (Figure 3d) are different from those of 3•(benzene) and 3•0.5(benzene) (Figure 3a and c). A phase change must have taken place; the network described above is not so robust as to sustain guest-free cavities. So far, host **3** resists to give good single crystals. In the case of modified host **4**, crystals enough to allow single-crystal X-ray diffraction are obtained by sublimation. The crystal structure of apohost **4** is completely nonporous (Figure 6). The acridinol moiety forms an intramolecular O–H•••N hydrogen bond. The resorcinol rings, on the other hand, afford an intermolecular hydrogen-bonded (O–H•••O–H) poly(resorcinol) chain with acridine moieties sticking out in the same direction. A couple of chains come together in such a way as to give a tightly packed (*l*_a^f = 3.6 Å) acridine column (Figure 6a and b). The columns are linked together via intercolumn O–H•••O hydrogen bonds involving the coordinatively unsaturated resorcinol OH groups (O–H•••O–H) and the acridinyl OH groups (O–H•••N) acting

as hydrogen-bond donors and acceptors, respectively (top view of columns in Figure 6c).

Discussion

Coordinative Saturation and Preservation of Crystal Structures. All of the adducts of hosts **3** and **4** investigated here share a common space group (*P*2₁/*n*), and the packing mode of dimeric building block 3₂ or 4₂ is well preserved. The similarity, among adducts, of the cell parameters (*a*, *b*, *c*, β , and *V* in Table 1) and geometrical ones (Table 2) defining the conformation (φ) and orientation (ϕ) of the host molecule and the chain/sheet/layer structures (interring (*l*_a), interchain (*l*_c), and intersheet (*l*_s) distances) becomes clearer when the average values ([3•(guest)]_{av} and [4•(guest)]_{av}) and maximal deviations therein (in percent in parentheses) for the adducts of **3** and **4** are taken (Table 3; columns 2 and 3, respectively). The characteristic angles (φ and ϕ) and lengths (*l*_a, *l*_c, and *l*_s) vary only within $\pm 4\%$ among adducts 3•(guest) and $\pm 6\%$ among 4•(guest), and the cell parameters are constant within $\pm 2\%$ and $\pm 3\%$ for 3•(guest) and 4•(guest), respectively. Moreover, the difference between [3•(guest)]_{av} and [4•(guest)]_{av} is remarkably small ($\leq 4\%$) for all of the parameters (column 4). This is true for any pair of adducts, for example, 3•(benzene) and 4•(benzene) having the same guest with different hosts (column 5), 3•(benzene) and 3•0.5(benzene) having different numbers of guest with the same host (column 6), and 4•(benzene) and 4•(ethyl acetate) having guests of different polarity types with the same host (column 7).

Is there any molecule to which an OH group can be introduced without causing a big change in crystal structures,^{4a} as in the present case of **3** \rightarrow **4**? The acridinyl OH group in host **4** is just a spectator of network formation but is not necessarily “dead”. It is capable of modifying the polarity character of the cavities involving aromatic walls of low to moderate polarity, so that polar guests become accommodable. Such a wide variation in guests as observed here, that is, from benzene, toluene, and chloroform through esters to methanol and water²² in preserved cavities, is hardly met. At the same time, the unprecedentedly high intrinsic apolar/polar (benzene/

(22) When treated with water, adduct 4•(methanol)•(water) readily affords diaquo adduct 4•2(water).

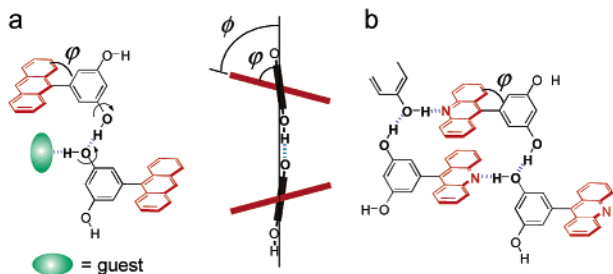


Figure 7. Schematic representation of intermolecular hydrogen bonds in the anthracenyl system (hosts **1** and **2**) (a) and the acridinyl system (hosts **3** and **4**) (b).

methanol, chloroform/DMF, toluene/ethyl acetate, etc.) selectivity of hosts **3** and **4** should not be overlooked. These phenomena are undoubtedly related to each other and may be understood primarily in terms of coordinative saturation of the present network, which gives a low sensitivity, at best, to polar functional groups of the guests and polar modification of the host. However, what is really significant here is the way in which coordinative saturation freezes flexibilities. Before discussing this, we have to spend some time on the reference anthracenyl hosts **1** and **2**.

Self-Complementary Building Block and Network Rigidity. The flexibility of the anthracenyl system arises, in reference to Figure 7a, from the conformational (φ) and orientational (ϕ) freedom of the host, the rotational freedom around the C–OH bond which governs the orientation of the key intermolecular hydrogen bond (O–H...O–H) and hence that of guest molecule bound via hydrogen bonding thereto, and the conformational freedom of the guest. They cooperate or manipulate to give the best induced-fit adjustment to the guest molecules with varying size and shape. Thus, the crystal structures (cell constants, geometrical parameters (φ , ϕ , l_a (anthracene–anthracene), l_c , and l_s), and even crystal system and space group), and hence powder diffractions as well, of adducts **1**·2(guest) and **2**·(guest) are rendered highly guest-dependent,²³ although the strict stoichiometry (1:2 for **1** and 1:1 for **2**) and similar network motifs (Scheme 1 or 2) are shared by the adducts. Guest molecules are generally well-packed and well-positioned without undergoing crystallographic disorder.

In the case of self-complementary hosts **3** and **4**, the key intermolecular hydrogen bond (O–H...O–H) as well as the nitrogen atom as a guest are contained in a π -stacked ($l_{a(1)}$)^f = 3.7 Å in **3**₂ and 3.8 Å in **4**₂ (Table 2)) cyclophane-like structure (Figure 7b). The molecular conformation, that is, dihedral angle (φ), must be fixed at a certain narrow range (actually, $\varphi \cong 69^\circ$ in **3**·(guest) and 71° in **4**·(guest), Table 3) to allow simultaneous

(23) A selected comparison is among adducts **1**·2(4-heptanone), **1**·2(6-undecanone), and **1**·2(ethyl acetate). Adduct **1**·2(4-heptanone): monoclinic, $P2_1/n$, $a = 8.973$ Å, $b = 13.739$ Å, $c = 15.320$ Å, $\beta = 104.11^\circ$, $V = 1831.8$ Å³, $Z = 2$, $d = 1.13$ g/cm³. Adduct **1**·2(6-undecanone): monoclinic, $P2_1/n$, $a = 9.375$ Å, $b = 13.519$ Å, $c = 17.547$ Å, $\beta = 92.36^\circ$, $V = 2222.2$ Å³, $Z = 2$, $d = 1.10$ g/cm³. Adduct **1**·2(ethyl acetate): monoclinic, $P2_1/n$, $a = 12.847$ Å, $b = 9.579$ Å, $c = 13.343$ Å, $\beta = 115.24^\circ$, $V = 1485.2$ Å³, $Z = 2$, $d = 1.276$ g/cm³. Another comparison is among adducts **1**·2(methyl benzoate), **1**·2(ethyl benzoate), and **1**·2(isobutyl benzoate). Adduct **1**·2(methyl benzoate): monoclinic, $C2/c$, $a = 13.396$ Å, $b = 20.395$ Å, $c = 13.918$ Å, $\beta = 117.012^\circ$, $V = 3387.9$ Å³, $Z = 4$, $d = 1.31$ g/cm³, $\varphi = 72.4^\circ$ and 58.3° , $l_a^c = 13.40$ Å, $l_a^f = 13.35$ Å, $l_c = 10.20$ Å, $l_s = 6.20$ Å. Adduct **1**·2(ethyl benzoate): monoclinic, $P2_1/n$, $a = 9.033$ Å, $b = 13.885$ Å, $c = 15.244$ Å, $\beta = 104.32^\circ$, $V = 1852.5$ Å³, $Z = 2$, $d = 1.25$ g/cm³, $\varphi = 72.4^\circ$, $l_a^c = 13.89$ Å, $l_a^f = 12.43$ Å, $l_c = 9.77$ Å, $l_s = 6.83$ Å. Adduct **1**·2(isobutyl benzoate): monoclinic, $P2_1/n$, $a = 9.534$ Å, $b = 13.479$ Å, $c = 15.572$ Å, $\beta = 100.77^\circ$, $V = 1966.0$ Å³, $Z = 2$, $d = 1.27$ g/cm³, $\varphi = 89.8^\circ$, $l_a^c = 13.48$ Å, $l_a^f = 12.22$ Å, $l_c = 9.86$ Å, $l_s = 7.40$ Å.

hydrogen-bonding and π -stacking interactions. With such a fixation of φ , the orientation of the hydrogen bond will also be fixed if a preferred linear O–H...O bond is assumed. This, in turn, fixes the relative geometry of the two resorcinol rings linked by the hydrogen bond and hence the inter(building block) geometry including the tilt angle (ϕ) and interrering (l_a) and interchain (l_c) distances. Thus, the flexibility-causing freedoms associated with anthracenyl hosts **1** and **2** are mostly frozen here. The structure of the derived 2D network (Scheme 4) is self-definable or autodetermined as far as it is formed. With the present included guests as a space filler, such a network is in fact formed with little guest-dependence and with no interference by such polar guests as esters, methanol, and water, which are either rejected by host **3** or bound only to the spectator OH group of host **4**. Varying host/guest ratios and crystallographic disorder of the guests are reminiscent of the incapability of the host network to adjust to guest structures.^{3,9}

Langmuir-type Adsorption/Desorption of Organic Guests. Pores may be generated in some robust metal-coordination polymers when included guest molecules including labile metal–ligands are removed without much affecting the host network.^{2–6} The microporosity of such guest-off materials can be demonstrated on the basis of maintenance of the phase during the guest-on/guest-off process in concern. This is usually done by referring to similar X-ray powder diffractions (XRPD) of the guest-off and guest-on species and to Langmuir-type adsorption/desorption isotherms²⁴ for small, inert guests such as N₂ and CH₄.^{2,3,25,26} In particular cases, microporosity can be demonstrated directly by single-crystal X-ray diffraction.^{2c} Hydrogen-bonded networks, on the other hand, are far less robust and collapse in the absence of guests. Exceptional cases are some 3D hydrogen-bonded networks which accommodate various guests with different host/guest ratios and survive (partial) guest desorption, as demonstrated mainly on the basis of powder-diffraction evidence.^{8,9} The present half-filled adduct **3**·0.5(benzene) or **3**₂·(benzene) provides a novel example of hydrogen-bonded microporous materials in that (1) a 2D network is involved and (2) the microporosity is evidenced on criteria of both XRPD and isotherm. This is probably the first demonstration of stoichiometric and reversible Langmuir-type adsorption/desorption of such a sizable organic molecule as benzene as a guest and a metal-free organic solid as an adsorbent.

Concluding Remarks

To summarize, self-complementary hosts **3** and **4** form a coordinatively saturated 2D net, which is well preserved upon

(24) Sigmoidal or threshold-type isotherms are observed in the case when complexation is accompanied by a phase change. For a comprehensive discussion, see ref 12. Also see: (a) Dewa, T.; Aoyama, Y. *Chem. Lett.* **2000**, 854–855. (b) Ariga, K.; Endo, K.; Aoyama, Y.; Okahata, Y. *Colloids Surf., A* **2000**, *169*, 177–186. (c) Matsuura, K.; Ariga, K.; Endo, K.; Aoyama, Y.; Okahata, Y. *Chem.-Eur. J.* **2000**, *6*, 1750–1756. (d) Dewa, T.; Saiki, T.; Imai, Y.; Endo, K.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2123–2127. (e) Naito, M.; Sasaki, Y.; Dewa, T.; Aoyama, Y.; Okahata, Y. *J. Am. Chem. Soc.* **2001**, *123*, 11037–11041. (25) (a) Fletcher, A. J.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J.; Kepert, C. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10001–10011. (b) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158–5168. (c) Rujiwatra, A.; Kepert, C. J.; Claridge, J. B.; Rosseinsky, M. J.; Kumagai, H.; Kurmoo, M. *J. Am. Chem. Soc.* **2001**, *123*, 10584–10594. (26) (a) Yaghi, O. M.; Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571–8572. (b) Reineke, T. M.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2590–2594. (c) Eddaoudi, M.; Li, H. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397. (d) Chen, B. L.; Eddaoudi, M.; Hyde, S. T.; O’Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021–1023.

alteration of the guests, partial (but not complete) loss of guest, and polar modification of the host. The rigidity of the network originates in the cooperation of self-complementary hydrogen bonding and π -stacking, which leads to a highly structure-regulating cyclophane-like motif. In this regard, dimeric building blocks **3**₂ and **4**₂ may represent a supramolecular synthon of C=C double bonds used as a conformation-fixed building block of covalent architectures. In principle, the self-complementarity strategy is applicable not only to the OH group, a commonest network former in crystal engineering, but also to other functionalities such as amine, amide, and ligated metal ion, and thus provides a new tool of designing crystal structures, especially rigid crystal structures.

Perturbation or variation may also be a key word of this work. It is only through a systematic variation in guests in preserved cavities that the guest-binding selectivity can be rigorously evaluated. The role of the acridinyl OH group in modified host **4** is a kind of *substituent effect*.^{4a} Various substituents might also be introduced as selectivity-controllers, as sensing chromophores or fluorophores, or as catalytic sites. The perturbation methods play key roles in establishing structure–property correlations in solution chemistry. This is, however, not the case for molecular crystals, because perturbation, for example, different substituents or different guests, often lead to different crystal structures. To exaggerate, one crystal structure represents one chemistry. The real significance of this work, we believe, lies in that it refers to the possibility of such a perturbation approach in crystal engineering.

Experimental Section

General Procedures. THF was distilled from benzophenone ketyl and dichloromethane from calcium hydride. Other solvents for preparative purposes and as guests were dried by standard methods. TLC and column chromatography were carried out with silica gel 60 F₂₅₄ plates (Merck) and Wakogel C-200 (Wako), respectively. Melting points were measured on a Yanako MP-500D melting point apparatus. Microanalyses were performed at the microanalysis center of Kyushu University. NMR and IR spectra were taken on a Bruker DPX 400 spectrometer and a JASCO IR-810 spectrophotometer, respectively. Mass spectra were obtained with a JEOL JMS-700/700S spectrometer. Thermogravimetry was performed by using a Seiko Denshi TG/DTA 220U thermal analysis system at a heating rate of 10 °C/min, in a similar manner as described.¹² Binding isotherms were recorded with a BELSORP 18 automated gas adsorption apparatus, in a similar manner as reported.¹² X-ray powder diffractions were obtained with a Rigaku diffractometer RINT 2000V.

N-(2-Methoxyethoxymethyl)-9-acridone (5).²⁷ A DMF solution (250 mL) of 9(10H)-acridone (9.76 g, 50.0 mmol) was added to sodium hydride (2.40 g, 60% in oil), which had been repeatedly washed with hexane, and the mixture was stirred at room temperature under nitrogen for 30 min. To the resulting mixture was added dropwise 2-methoxyethoxymethyl chloride (8.0 g, 64 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature, treated with water, and extracted with ethyl acetate. The extract was washed successively with water and aqueous NaCl, dried on Na₂SO₄, and evaporated. The residue was chromatographed. The main component eluted with ethyl acetate was dried at 80 °C in vacuo to give *N*-protected acridone **5** (10.9 g, 38.5 mmol, 77%) as a pale-yellow solid: mp 180–181 °C. TLC *R*_f = 0.43 (ethyl acetate). ¹H NMR (DMSO-*d*₆): δ 3.26 (s, 3H, OCH₃), 3.53 and

3.81 (both t, both 2H, OCH₂CH₂O), 5.84 (s, 2H, NCH₂O), 7.36 (m, 2H, Ar–H), 7.80–7.94 (m, 4H, Ar–H), 8.31 (dd, 2H, Ar–H). Found: C, 72.31; H, 6.25; N, 5.09%. Calcd for C₁₇H₁₇NO₃: C, 72.07; H, 6.05; N, 4.94%.

9-(3,5-Dimethoxyphenyl)acridine (6).²⁸ Into a solution of *N*-protected acridone **5** (3.85 g, 13.6 mmol) in THF (60 mL) was added dropwise under nitrogen at –77 °C a THF solution (27 mL) of 3,5-dimethoxyphenylmagnesium chloride, obtained from magnesium (1.09 g, 44.9 mmol) and 1-chloro-3,5-dimethoxybenzene (5.17 g, 30.0 mmol) in the presence of dibromoethane (100 μ L). The mixture was stirred at room temperature for 24 h, treated successively with aqueous HCl and aqueous K₂CO₃, and extracted with chloroform. The crude product was chromatographed after usual workup. The main component eluted with chloroform was washed with methanol and dried at 100 °C in vacuo to give dimethoxy derivative **6** (4.01 g, 12.7 mmol, 93%) as a pale-yellow solid: mp 199–200 °C. TLC *R*_f = 0.25 (CHCl₃). ¹H NMR (CDCl₃): δ 3.83 (s, 6H, OCH₃), 6.59 (d with *J* = 2.2 Hz, 2H, Ar–H), 6.67 (t with *J* = 2.2 Hz, 1H, Ar–H), 7.40–7.50 (m, 2H, Ar–H), 7.70–7.80 (m, 4H, Ar–H), 8.27 (d with *J* = 8.7 Hz, 2H, Ar–H). Found: C, 79.72; H, 5.43; N, 4.46%. Calcd for C₂₁H₁₇NO₂: C, 79.98; H, 5.43; N, 4.44%.

9-(3,5-Dihydroxyphenyl)acridine (3).²⁹ A mixture of dimethoxy derivative **6** (1.60 g, 5.06 mmol) and concentrated hydrobromic acid (47% HBr, 100 mL) was refluxed under nitrogen for 2 h. The mixture was allowed to cool to room temperature, neutralized with aqueous K₂CO₃, and extracted with ethyl acetate. The crude product was chromatographed after usual workup. The main component eluted with ethyl acetate was taken in methanol, reprecipitated upon addition of diethyl ether, and dried at 170 °C in vacuo to give dihydroxy compound **3** (1.11 g, 3.86 mmol, 77%) as pale-yellow powders: mp > 280 °C (dec). TLC *R*_f = 0.65 (ethyl acetate). ¹H NMR (DMSO-*d*₆): δ 6.26 (d with *J* = 2.0 Hz, 2H, Ar–H), 6.44 (t with *J* = 2.0 Hz, 1H, Ar–H), 7.52–7.57 (m, 2H, Ar–H), 7.75 (d with *J* = 8.7 Hz, 2H, Ar–H), 7.81–7.86 (m, 2H, Ar–H), 8.18 (d with *J* = 8.7 Hz, 2H, Ar–H), 9.60 (s, 2H, OH). ¹³C NMR (DMSO-*d*₆): δ 102.38, 108.30, 124.00, 125.83, 126.48, 129.12, 130.15, 136.69, 146.90, 148.06, 158.42. MS (FAB+) (*M* + *H*)⁺ = 288. Found: C, 79.45; H, 4.67; N, 4.73%. Calcd for C₁₉H₁₃NO₂: C, 79.43; H, 4.56; N, 4.88%.

4-Methoxy-9(10H)-acridone (8).³⁰ Anthranilic acid derivative **7** was obtained in a yield of 88% by Ullmann reaction of *o*-chlorobenzoic acid and *o*-anisidine.³¹ A mixture of compound **7** (80.1 g, 0.33 mol) and concentrated sulfuric acid (200 mL) was stirred at 100 °C under atmosphere for 4 h. Hot water (80–90 °C, 1 L) was added slowly, and the mixture was stirred at 100 °C for further 1 h and allowed to cool. Insoluble materials were recovered by filtration and taken in an aqueous solution (800 mL) of Na₂CO₃ (61 g, 0.57 mol). The mixture was stirred at 100 °C for 5 min. Insoluble materials were recovered by filtration and washed with water and then with hot methanol, and dried at 100 °C in vacuo to give acridone derivative **8** (37.3 g, 0.166 mol, 50%) as a pale-green solid. ¹H NMR (DMSO-*d*₆): δ 4.04 (s, 3H, OCH₃), 7.16–7.21 (m, 1H, Ar–H), 7.22–7.27 (m, 1H, Ar–H), 7.33 (d with *J* = 2.0 Hz, 1H, Ar–H), 7.66–7.72 (m, 1H, Ar–H), 7.80 (d with *J* = 2.0 Hz, 1H, Ar–H), 7.93 (d with *J* = 2.0 Hz, 1H, Ar–H), 8.20 (d with *J* = 2.0 Hz, 1H, Ar–H), 11.21 (s, 1H, NH).

N-(2-Methoxyethoxymethyl)-4-methoxy-9-acridone (9).²⁷ This compound was obtained (yield, 65%) as a yellow solid in a similar manner as parent acridone derivative **5**. Compound **9**: mp 95–96 °C. TLC *R*_f = 0.72 (ethyl acetate). ¹H NMR (DMSO-*d*₆): δ 3.18 (s, 3H,

(27) *N*-Alkylation was performed according to the procedures shown in: (a) Whitten, J. P.; Matthews, D. P.; McCarthy, J. R. *J. Org. Chem.* **1986**, *51*, 1891–1894. (b) Zeng, Z. J.; Zimmerman, S. C. *Tetrahedron Lett.* **1988**, *29*, 5123–5124. (c) McConnaughie, A. W.; Jenkins, T. C. *J. Med. Chem.* **1995**, *38*, 3488–3501.

(28) Grignard reactions were carried out according to the procedures shown in ref 27a,b.

(29) Deprotection with HBr was carried out according to the procedures shown in: (a) King, F. E.; Sherred, G. A. *J. Chem. Soc.* **1942**, 415–416. (b) Hartshorn, S. L.; Baird, S. L., Jr. *J. Am. Chem. Soc.* **1946**, *68*, 1562–1563.

(30) Cyclization was performed according to the procedure shown in: Brockmann, H.; Muxfeldt, H.; Haese, G. *Chem. Ber.* **1957**, *90*, 44–49.

(31) For the general procedure of Ullmann reactions, see: Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613–632.

OCH₂CH₂OCH₃), 3.37–3.41 and 3.45–3.50 (both m, both 2H, OCH₂-CH₂O), 3.96 (s, 3H, Ar-OCH₃), 5.77 (s, 2H, NCH₂O), 7.27–7.38 (m, 2H, Ar-H), 7.44–7.48 (m, 1H, Ar-H), 7.76–7.82 (m, 1H, Ar-H), 7.84–7.89 (m, 2H, Ar-H), 8.17–8.21 (m, 1H, Ar-H). Found: C, 69.16; H, 6.06; N, 4.52%. Calcd for C₁₈H₁₉NO₄: C, 68.99; H, 6.11; N, 4.47%.

9-(3,5-Dimethoxyphenyl)-4-methoxyacridine (10).²⁸ This compound was obtained (yield, 37%) as a yellow solid in a similar manner as parent acridine derivative **6**. Compound **10**: mp 186–187 °C. TLC $R_f = 0.36$ (CHCl₃). ¹H NMR (DMSO-*d*₆): δ 3.84 (s, 6H, Dmp-OCH₃; Dmp = dimethoxyphenyl), 4.19 (s, 3H, Acr-OCH₃; Acr = acridinyl), 6.58 (d with $J = 2.3$ Hz, 2H, Dmp-H), 6.73 (t with $J = 2.3$ Hz, 1H, Dmp-H), 7.19 (d with $J = 8.7$ Hz, 1H, Acr-H), 7.40–7.45 (m, 2H, Acr-H), 7.51–7.57 (m, 1H, Acr-H), 7.63–7.66 (d, 1H, Acr-H), 7.79–7.85 (m, 1H, Acr-H), 8.22 (d with $J = 8.7$ Hz, 1H, Acr-H). Found: C, 76.01; H, 5.61; N, 3.94%. Calcd for C₂₂H₁₉NO₃: C, 76.50; H, 5.54; N, 4.06%.

9-(3,5-Dihydroxyphenyl)-4-acridinol (4).³² Into a dichloromethane solution (250 mL) of trimethoxy derivative **10** (6.96 g, 20.2 mmol) was added dropwise slowly a solution (40 mL) of BBr₃ (28.3 mL, 88.3 mmol) in dichloromethane (40 mL) at 0 °C. After the addition was complete, the mixture was further stirred at room temperature for 12 h, treated with water, and extracted with ethyl acetate. The crude product was chromatographed after usual workup. The main component eluted with ethyl acetate was dried at 100 °C in vacuo to give trihydroxy compound **4** (4.54 g, 15.0 mmol, 74%) as yellow powders: mp > 230 °C (dec). TLC $R_f = 0.57$ (ethyl acetate). ¹H NMR (DMSO-*d*₆): δ 6.24 (d with $J = 2.0$ Hz, 2H, Dhp-H; Dhp = dihydroxyphenyl), 6.42 (d with $J = 2.0$ Hz, 1H, Dhp-H), 7.09–7.18 (m, 2H, Acr-H; Acr = acridinyl), 7.35–7.40 (m, 1H, Acr-H), 7.52–7.57 (m, 1H, Acr-H), 7.73 (d with $J = 8.6$ Hz, 1H, Acr-H), 7.81–7.86 (m, 1H, Acr-H), 8.24 (d with $J = 8.8$ Hz, 1H, Acr-H), 9.60 (s, 2H, Dhp-OH), 9.82 (bs, 1H, Acr-OH). ¹³C NMR (DMSO-*d*₆): δ 158.37, 152.60, 146.87, 146.21, 140.14, 139.97, 129.94, 129.02, 126.63, 126.48, 126.02, 124.82, 124.36, 116.33, 109.26, 108.20, 102.31. MS (FAB+) ($M + H$)⁺ = 304. Found: C, 75.09; H, 4.32; N, 4.56%. Calcd for C₁₉H₁₃NO₃: C, 75.24; H, 4.32; N, 4.62%.

Adducts and Apohost. Adducts were obtained by recrystallization of hosts **3** and **4** in one of three ways. In method A, the guest vapor was allowed to diffuse into a solution of the host in methanol, DMF, or ethyl acetate. In method B, a solution of the host in methanol/guest or ethyl acetate/guest was left open to allow methanol or ethyl acetate to evaporate gradually. In method C, a solution of the host in guest was left open to allow the solvent (guest) to evaporate gradually. The compositions of the adducts were determined by ¹H NMR integration, elemental analyses, and thermogravimetry. Adduct **3**•(benzene) (method A with DMF or methanol) as orange prisms. Found: C, 82.07; H, 5.26; N, 3.81%. Calcd for C₂₅H₁₉NO₂: C, 82.17; H, 5.24; N, 3.83%. Adduct **3**•0.5 (toluene) (method B with methanol) as orange prisms. Found: C, 80.69; H, 5.26; N, 4.04%. Calcd for C_{22.5}H₁₇NO₂: C, 81.06; H, 5.14; N, 4.20%. Adduct **3**•(chloroform) (method A with DMF) as orange prisms.³³ Found: C, 60.07; H, 3.71; N, 3.76%. Calcd for C₂₀H₁₄Cl₃NO₂: C, 59.07; H, 3.47; N, 3.44%. Adduct **3**•0.5 (isobutyl benzoate) (method B with methanol) as orange prisms. Found: C, 77.88; H, 5.32; N, 3.73%. Calcd for C_{24.5}H₂₀NO₃: C, 78.17; H, 5.36; N, 3.72%. Adduct **4**•(benzene) (method B with ethyl acetate) as orange prisms. Found: C, 78.81; H, 5.04; N, 3.64%. Calcd for C₂₅H₁₉NO₃: C, 78.72; H, 5.02; N, 3.67%. Adduct **4**•(chloroform) (method A with ethyl acetate) as

orange prisms. Found: C, 56.97; H, 3.43; N, 3.26%. Calcd for C₂₀H₁₄Cl₃NO₃: C, 56.83; H, 3.34; N, 3.31%. Adduct **4**•0.5(toluene)•0.5(water) (method B with ethyl acetate) as orange prisms. Found: C, 75.09; H, 5.17; N, 3.74%. Calcd for C_{22.5}H₁₈NO_{3.5}: C, 75.39; H, 5.06; N, 3.91%. Adduct **4**•(methanol)•(water) (method C) as orange prisms. Found: C, 68.35; H, 5.11; N, 3.90%. Calcd for C₂₀H₁₉NO₅: C, 67.98; H, 5.42; N, 3.96%. Adduct **4**•(ethyl acetate) (method C) as orange prisms. Found: C, 70.28; H, 5.42; N, 3.39%. Calcd for C₂₃H₂₁NO₅: C, 70.58; H, 5.41; N, 3.58%.

Treatment of full-adduct **3**•(benzene) at 250 mmHg at room temperature for 3 days gave the half-adduct **3**•0.5(benzene). Single crystals of apohost **4** were obtained by sublimation when adduct **4**•(ethyl acetate) was heated at 180 °C in vacuo (1 mmHg) for 3 days.

X-ray Crystal Structure Determinations. Diffraction data were collected on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). Single crystals were mounted on a glass fiber. A linear absorption correction was applied in each case. The intensities of three standard reflections were monitored after every 150 reflections were taken; the decay of intensities was within 2%. The intensity data collected by using the ω - 2θ scan technique were corrected for both Lorentz and polarization effects. The unit-cell parameters used for refinement were determined by least-squares calculations on the setting angles of 25 reflections.

The structures were solved by a combination of the direct method using SIR92 program and the Fourier techniques using DIRDIF99. Non-hydrogen atoms of hosts **3** and **4** were refined anisotropically. The hydroxyl hydrogen atoms in the resorcinol rings were located by difference Fourier maps, and the rest in the host molecules were introduced at calculated positions (C–H = 0.95 Å). All of these hydrogen atoms were refined isotropically. Non-hydrogen and hydrogen atoms of guests benzene and chloroform were refined anisotropically and isotropically, respectively, in a similar manner as those in the hosts. Non-hydrogen atoms in other guests were refined isotropically. The weighting scheme $w^{-1} = [\sigma^2(F_o) + (0.0005F_o)^2]$ was employed for all of the adducts. Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography.³⁴ Calculations were performed by using the CrystalStructure crystallographic software package of the Molecular Structure Corp., and the crystal structures were visualized by using the Cerius2 set of computer programs of Molecular Simulation Inc.

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Supporting Information Available: X-ray structural information for adducts **3**•(benzene), **3**•(chloroform), **3**•(isobutyl benzoate), **4**•(benzene), **4**•(chloroform), **4**•0.5(toluene)•0.5(water), **4**•(methanol)•(water), and **4**•(ethyl acetate) and apohost **4**, including tables of crystal and refinement data, atomic coordinates and thermal parameters, bond lengths and angles, anisotropic displacement values, torsion angles, nonbonded contacts out to 3.60 Å, and thermal ellipsoid figures (PDF). They are also available in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(32) Deprotection with BBr₃ was performed according to the procedure shown in: Bonner, T. G.; Bourne, F. J.; McNally, S. J. *Chem. Soc.* **1960**, 2929–2934.

(33) On standing, adduct **3**•(chloroform) gradually loses some of the included guest molecules.

(34) Creagh, D. C.; McAuley, W. J. In *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Vol C.