

A Robust Two-Dimensional Hydrogen-Bonded Network. Reversible Guest Adsorption/Desorption without a Phase Change

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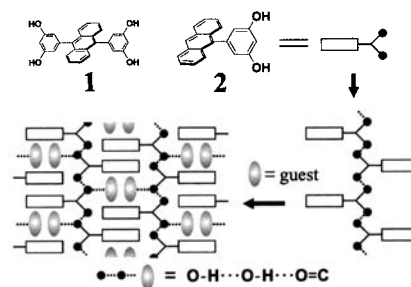
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9-(3,5-Dihydroxyphenyl)acridine (**3**) forms a 1:1 benzene adduct **3**·(benzene) having a novel O–H···O–H···N hydrogen-bonded 2D network. Partial (50%) guest desorption occurs in a reversible manner without undergoing a phase change.

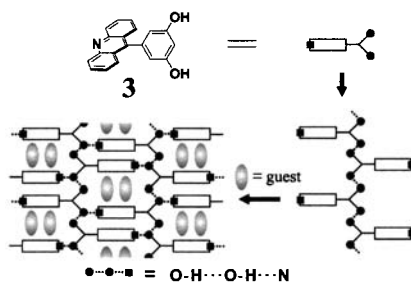
Porosity may in principle be generated in lattice inclusion complexes when the included guest molecules are removed without much affecting the host network. This is the case for some robust metal-coordination polymers, whose porous nature can be deduced on the basis of X-ray powder diffraction patterns and Langmuir-type guest adsorption/desorption isotherms.^{1,2} Hydrogen-bonded networks, on the other hand, are far less robust and can not usually sustain guest-free cavities, pores, or channels. Anthracene-bisresorcinol **1**³ and -monoresorcinol **2**⁴ are typical examples of such hosts. They form 1:2 and 1:1 (host to guest) adducts, respectively, in which the polar guests such as ethyl acetate are included in the cavities provided by the hydrogen-bonded (O–H···O–H) 2-dimensional (2D) or pseudo 2D network via hydrogen bonding (O–H···O–H···O=C), as illustrated in Scheme 1 for adduct **2**·CH₃CO₂CH₂CH₃. Upon guest removal, the network collapses to give a nonporous apohost, which subsequently readsorbs the guest to restore the network. The guest-off and guest-on processes are accompanied by a phase change, as evidenced by different powder diffractions for the guest-on and guest-off species^{3,4} and also by characteristic isotherms having a sharp threshold guest pressure for binding.^{5,6} The present work is concerned about a monoresorcinol derivative of acridine (**3**). We report here that it forms a compact and robust 2D hydrogen-bonded network that is capable of reversible adsorption/desorption of a hydrocarbon guest without undergoing a phase change.

Diol **3** was prepared (70% total yield) by Grignard reaction of N-protected (N–CH₂OCH₂CH₂OCH₃) acridone with 3,5-dimethoxy-1-phenylmagnesium chloride in THF, followed by dehydrative deprotection with HCl in aqueous ethanol and subsequent demethylation in aqueous HBr. Crystallization of host **3** from benzene/DMF or benzene/methanol affords a 1:1 benzene adduct **3**·(benzene), whose X-ray diffraction revealed the following characteristic crystal structure, in reference to Scheme 2 and Figure 1.⁷ (1) Compound **3** forms hydrogen-bonded (O–H···O–H) polyresorcinol 1D chains in a similar manner as compound **2** (Scheme 1). (2) Neighboring chains are linked by resorcinol–acridine hydrogen-bonds (O–H···O–H···N) to give a 2D sheet having stacked acridine dimers. (3) In the resulting cavities, are incorporated two guest (benzene) molecules. (4) The sheets are layered in a staggered manner as in the cases of anthracene hosts **1** and **2**.

When left at room temperature in vacuo for ~3 days, adduct **3**·(benzene) loses 50% of included guest molecules, plausibly one of two in each cavity, to give half-packed adduct **3**·0.5(ben-



Scheme 1.



Scheme 2.

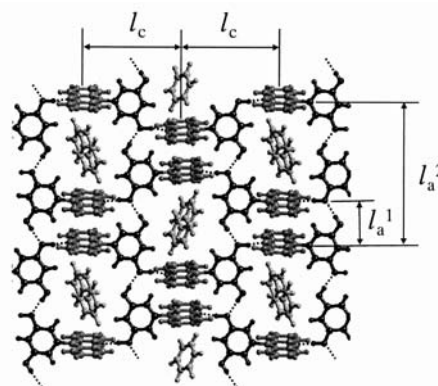


Figure 1. Crystal structure of adduct **3**·(benzene) in reference to Scheme 2, where $l_a^1 = 3.7 \text{ \AA}$, $l_a^2 = 13.5 \text{ \AA}$, and $l_c = 9.46 \text{ \AA}$.

zene),^{8,9} which subsequently adsorbs the benzene guest to regenerate the original full-packed adduct **3**·(benzene) with a Langmuir-type adsorption isotherm (Figure 2, where $V_{\text{sat}} = 40 \text{ mL/g}$ corresponds to 0.5 mole of benzene).¹⁰ In addition, the half-packed and full-packed adducts show essentially the same powder diffractions of comparable intensities (Figures 3a and 3b).⁹ These results indicate that the present guest-off and guest-on processes are free from a phase change. When single crystals

of full adduct are used, single crystallinity is maintained during the desorption of 0.5 mole of benzene. The resultant single-crystalline half adduct $3 \cdot 0.5(\text{benzene})$ shows essentially the same crystal structure as that for the full adduct (Figure 1) with a very slight change in the cell parameters, although the crystal data are rather poor.⁸ The guests also appear as in Figure 1, indicating that the single benzene molecule left in each cavity is disordered and occupies one of two original positions with equal probabilities.⁸

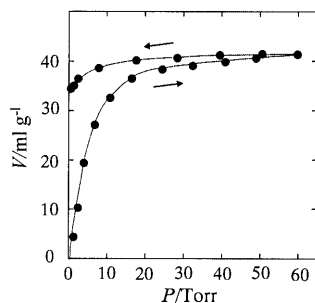


Figure 2. Binding isotherm for gaseous benzene with half-packed adduct $3 \cdot 0.5(\text{benzene})$ at 25 °C. Each point represents a state where the change in 9999 sec (167 min) has become smaller than 1% of the pressure at that point ($\Delta P < 0.01P$). V refers to the standard state.

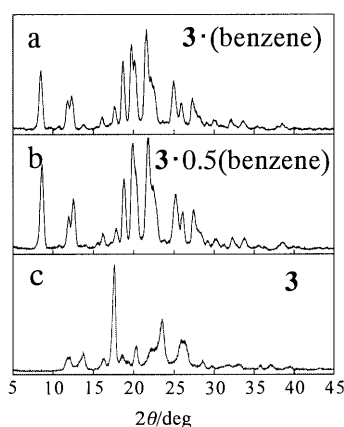
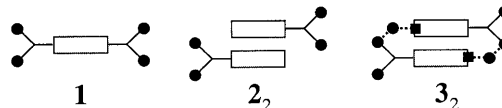


Figure 3. X-ray powder diffraction patterns for the full-packed adduct $3 \cdot (\text{benzene})$ (a), half-packed adduct $3 \cdot 0.5(\text{benzene})$ (b), and apohost 3 (c).

A unifying view of the crystal structures of hosts **1**, **2**, and **3** is that an X-shaped tetraol acts as a building block; a covalent molecule **1**, an anti-parallel π -stacked dimer **2**, or an O–H...N hydrogen-bonded supramolecular cyclophane **3**. They all form 1:2 (building block to guest) adducts having a similar hydrogen-bonded 2D network. The building blocks **1**, **2**, and **3** differ in size, rigidity/flexibility, and coordinative saturation/unsaturation after forming a network. The flexible and unsaturated hosts **1** and **2** bind two polar guests, which are simultaneously desorbed with a concomitant collapse of the network. The less flexible and saturated host **3** adsorbs a pair of hydrocarbon guests, which are removed in a stepwise manner, where the crystal structure is maintained upon desorption of the initial half. Some 3D hydrogen-bonded networks are claimed, based mainly on X-ray powder-diffraction evidence, to be robust

enough to survive (partial) guest removal.^{11, 12} The present system may be novel in that (1) its 2D network is shown, (2) the phase-preserving guest adsorption/desorption is evidenced on the ground of both powder diffractions and adsorption isotherms, and (3) the similarity in the single-crystal X-ray structures of guest-on and guest-off species is referred to.



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References and Notes

- a) M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, and S. Kitagawa, *Angew. Chem. Int. Ed. Engl.*, **36**, 1725 (1997).
b) S. Noro, S. Kitagawa, M. Kondo, and K. Seki, *Angew. Chem. Int. Ed.*, **39**, 2082 (2000).
- a) H. Li, M. Eddaoudi, T. L. Groi, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 8571 (1998).
b) H. Li, M. Eddaoudi, M. Okeeffe, and O. M. Yaghi, *Nature*, **402**, 276 (1999).
- K. Endo, T. Sawaki, M. Koyanagi, K. Kobayashi, H. Masuda, and Y. Aoyama, *J. Am. Chem. Soc.*, **117**, 8341 (1995).
- K. Endo, T. Ezuhara, M. Koyanagi, H. Masuda, and Y. Aoyama, *J. Am. Chem. Soc.*, **119**, 499 (1997).
- T. Dewa, K. Endo, and Y. Aoyama, *J. Am. Chem. Soc.*, **120**, 8933 (1998).
- T. Dewa and Y. Aoyama, *Chem. Lett.*, **2000**, 854.
- Crystallographic data for $3 \cdot (\text{benzene})$: formula = $\text{C}_{25}\text{H}_{19}\text{NO}_2$, fw = 365.43, monoclinic, $P2_1/n$, $a = 8.866(2)$ Å, $b = 14.024(2)$ Å, $c = 15.393(1)$ Å, $\beta = 99.34(1)^\circ$, $V = 1888.6(4)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.324$ g cm⁻³. The final R factor was 0.043 ($R_w = 0.064$) for 2258 unique reflections out of 4811 with $I > 3\sigma(I)$ and GOF = 1.34.
- Found: C, 80.51; H, 4.96; N, 4.08%. Calcd for $\text{C}_{22}\text{H}_{16}\text{NO}_2$: C, 80.96; H, 4.94; N, 4.29%. The composition of 1:0.5 (host to guest) was independently confirmed by ¹H NMR. Crystallographic data: monoclinic, $P2_1/n$, $a = 8.8731(9)$ Å, $b = 14.002(2)$ Å, $c = 15.307(2)$ Å, $\beta = 99.581(4)^\circ$, $V = 1875.1(3)$ Å³, $Z = 4$, $d_{\text{calcd}} = 1.156$ g cm⁻³, $R = 0.131$, $R_w = 0.204$, GOF = 2.27 for 2067 unique reflections out of 3223 with $I > 3\sigma(I)$ after assigning an occupancy of 0.5 for each of two disordered benzene molecules in the cavity.
- Thermogravimetry (TG) of adduct $3 \cdot (\text{benzene})$ at 0.1 °C/min shows non-resolved desorption of two benzene molecules at 25–110 °C. The resulting guest-free apohost **3** with powder diffractions shown in Figure 3c shows practically no affinity to benzene.
- The apparent hysteresis observed may simply be a kinetic consequence of slow desorption.
- P. B. Brunet, M. Simard, and J. D. Wuest, *J. Am. Chem. Soc.*, **119**, 2737 (1997).
- A. T. Ung, D. Gizachew, R. Bishop, M. L. Scudder, I. G. Dance, and D. C. Craig, *J. Am. Chem. Soc.*, **117**, 8745 (1995).