

# Hydrogen-Bonding 3D Networks by Polyhedral Organosilanols: Selective Inclusion of Hydrocarbons in Open Frameworks

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Tetrahedral organosilanols  $E[C_6H_4Si(i-Pr)_2OH]_4$  (E = C, 2a; E = Si, 2b) as well as octahedral organosilanols Si<sub>8</sub>O<sub>12</sub>(CH=CHC<sub>6</sub>H<sub>4</sub>SiR<sub>2</sub>OH)<sub>8</sub> (R = *i*-Pr, **5a**; R = Ph, **5b**) have been derived from tetraphenylmethane and -silane (1a,b) and octavinyloctasilsesquioxane (3) designed for self-assembly of 3D hydrogen-bonding networks possessing large porosity. X-ray analyses following crystallization of **2a**,**b** from THF/benzene and either hexane or heptane revealed adamantane-type networks with hydrogen bonds between the silanols of four separate molecules and selective inclusion of hexane or heptane, respectively. Upon changing the mixed solvent to THF/benzene/cyclohexane, X-ray analysis of 2a showed an inclusion compound of composition 2a · 1.5 benzene. TOPOS analyses of **2a** · 1.5 benzene demonstrated a non-adamantane-type framework with **sra** network topology. Crystallization of **5a**,**b** from acetone/benzene followed by X-ray analyses confirmed the production of the inclusion compounds  $5a \cdot 18benzene$  and  $5b \cdot 23benzene$ . The open frameworks of  $5a \cdot 18benzene$ 18benzene and **5b**·23benzene are constructed with zeolitic or fluorite cages, and **ast** or **flu** network topology results, based on the TOPOS program. The packing of benzene molecules in 5a · 18benzene and 5b-23benzene was found to be similar to that of crystals of pure benzene in edge-to-face arrangements. Thus, hydrogen-bonding networks of polyhedral organosilanols have shown selective inclusion of hydrocarbons into large cavities with adjustable porosity and without interpenetration of one network into another.

## Introduction

Self-assembly directed by hydrogen bonding and metal– ligand binding has became a powerful tool for the construction of porous solids, with a three-dimensional (3D) network.<sup>1</sup> Traditionally, self-assembly of well-defined 3D networks with regular porosity has been achieved by connecting the vertices of polyhedral organic building blocks. Derivatives of tetraphenylmethane,<sup>2a-g</sup> -silane,<sup>2h-j</sup> and -adamantane<sup>2e,g,k-m</sup> are useful organic building blocks for production of an adamantane-type network structure. Many examples of such adamantane-type networks exist involving a strongly hydrogen-bonded group such as a carboxylic acid,<sup>2k</sup> borol,<sup>2d</sup> pyridone,<sup>2b</sup> or metal complex.<sup>2a,e</sup> Although silanols are known to form strong hydrogen bonds, there are few networks involving 3D hydrogen-bonded networks of silanols.<sup>3</sup> Herein, polyhedral organosilanols based on tetraphenylmethane (2a) and -silane (2b), as well as octastyryloctasilsesquioxane (5a,b), are used as  $T_d$  and  $O_h$  symmetrical organic building blocks, designed for 3D hydrogenbonding networks. Hydrogen-bonding networks tend to form entangled structures in which two or more independent infinite networks interpenetrate each other.<sup>1d</sup> However, these silanol networks selectively include hydrocarbons in their open frameworks without interpenetration.

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Scheme 1



Table 1. Crystal Data and Data Collection Parameters for 2a · Hexane, 2b · Heptane, and 2a · 1.5Benzene

	<b>2a</b> · hexane	<b>2b</b> · heptane	$2a \cdot 1.5$ benzene
empirical formula	C <sub>55</sub> H <sub>90</sub> O <sub>4</sub> Si <sub>4</sub>	C55H92O4Si5	C <sub>58</sub> H <sub>85</sub> O <sub>4</sub> Si <sub>4</sub>
fw	927.63	957.74	958.61
cryst syst	monoclinic	monoclinic	monoclinic
space group	Pn	Pn	P21/n
a (Å)	12.591(2)	12.700(2)	12.791(2)
$b(\dot{A})$	13.083(3)	13.154(2)	26.646(5)
$c(\dot{A})$	17.732(3)	17.541(3)	17.054(4)
$\alpha$ (deg)	90.00	90.0	90.0
$\beta$ (deg)	90.47(1)	93.05(0)	90.61(1)
$\gamma$ (deg)	90.00	90.0	90.0
volume ( $Å^3$ )	2920.9(10)	2926.2(8)	5812.2(20)
Z	2	2	4
density (calcd) (Mg/cm <sup>3</sup> )	1.055	1.087	1.094
absorp coeff $(mm^{-1})$	0.141	0.156	0.144
$\theta$ range for data collection (deg)	3.11 to 27.69	2.23 to 30.67	3.03 to 27.48
reflns collected	25779	32 296	54 122
indep reflns $(R_{int})$	12431 (0.0574)	13 835 (0.0388)	13 231 (0.1126)
goodness of fit indicator	1.027	1.114	1.035
final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0672, wR2 = 0.1770	R1 = 0.0707, wR2 = 0.1653	R1 = 0.0809, wR2 = 0.2001
R indices (all data)	R1 = 0.0910, wR2 = 0.2018	R1 = 0.0775, wR2 = 0.1735	R1 = 0.1223, wR2 = 0.2284
largest diff peak and hole (e $Å^{-3}$ )	0.778 and -0.268	0.349 and -0.380	0.581 and -0.478

### **Results and Discussion**

Syntheses of  $T_d$  and  $O_h$  Symmetrical Organosilanols (2a,b and 5a,b). Introduction of silanol into the  $T_d$  symmetrical organic building blocks was accomplished as follows: Tetrakis-(4-bromophenyl)methane (1a, E = C) and -silane (1b, E = Si) were synthesized according to the literature methods,<sup>4</sup> treated with *n*-BuLi or *t*-BuLi, and reacted with diisopropylchlorosilane. Subsequent neutral oxidation of the hydrosilyl groups by dimethyldioxirane (DMD) gave the tetrahedral organosilanol derivatives (**2a**,**b**) in 66.7% and 53.3% total yield, respectively, as shown in Scheme 1. For the  $O_h$  symmetrical organic building blocks, octavinyloctasilsesquioxane (**3**), a cubic molecule with a cage-like Si<sub>8</sub>O<sub>12</sub> core and vinyl groups at each vertex, was employed as the starting compound. A Ru-catalyzed silylative coupling reaction<sup>4d</sup> of **3** with 4-(methoxysilyl)styrenes (**4a**,**b**) followed by hydrolysis with HCl afforded the octahedral organosilanol derivatives (**5a**,**b**) in 69.4% and 63.5% total yields, respectively (Scheme 1).

Formation of Hydrogen-Bonding Networks by Tetrahedral Organosilanols (2a,b). Crystallization of the tetrahedral organosilanols from THF/benzene/hexane and THF/benzene/heptane (for details see Experimental Section) provided plates of compounds 2a and 2b. X-ray crystallography established that 2a and 2b are isomorphous (Table 1) and crystallize with composition 2a hexane and 2b heptane, respectively.

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Figure 1. Crystal structures as viewed along the *a*-axis: (a) 2a·hexane, (b) 2b·heptane, and (c) 2a·1.5benzene. Guest hydrocarbons in a cavity are drawn as green molecules. (d) Geometry of hydrogen-bonded silanol tetramer. All ellipsoids are shown at the 30% probability level.



Figure 2. Partial views of the 3D network present in the crystals: (a)  $2a \cdot hexane$  and (b)  $2b \cdot heptane$ . Both views have four network units containing hydrocarbons as guests (green). All substituents on the Si atom are omitted for clarity. (c) dia network of  $2a \cdot hexane$  based on TOPOS analysis. The tetrahedral units of four hydrogen-bonded silanols and tetraphenylmethane are viewed as four-connected nodes.

Even though crystallization occurred in a mixed solvent, the open cavities selectively enclathrated only hexane in **2a** and heptane in **2b**, respectively, as shown in Figure 1a and b. These crystals formed open frameworks, based on four hydrogenbonded silanols, as shown in Figure 2a and b.

The hydrogen-bonded silanols in  $2a \cdot hexane$  and  $2b \cdot heptane$  give rise to cyclic tetramers with distorted tetrahedral geometries, shown in Figure 1d. Hydrogen-bond parameters are also collected in Table 2. The O–O distances (between 2.730(4) and 2.833(4) Å) are indicative of weak to medium strength hydrogen bonding. Although the networks

are constructed from tetraphenylmethane (1) and -silane (2), several minor differences are noteworthy. In particular, the C-C-C bond angles at the core of the tetraphenylmethane (1) in 2a · hexane have values between  $108.2(3)^{\circ}$  and  $111.4(3)^{\circ}$ , whereas the C-Si-C angles at the core of tetraphenylsilane (2) in 2b · heptane varies more widely ( $107.2(1)-114.8(1)^{\circ}$ ), because of the greater flexibility of the four-coordinated silicon atom in 2 as compared to the carbon atom in 1, as shown in Table 3.

This pattern of hydrogen bonding is often found in monosilanols<sup>3</sup> and can be regarded as a bonding motif similar to carboxylic acid dimers<sup>1b,c</sup> and borol dimers.<sup>2d</sup> Assuming the four hydrogen-bonded silanols (synthon R(4)(4) H-bond)<sup>5c-f</sup> and tetraphenylmethane or -silane building blocks (tecton) to be four-connected nodes, the adamantane-type or diamond-type (i.e., dia) net<sup>6</sup> is represented as shown in Figure 2c based on the X-ray crystallographic data of 2a · hexane using the TOPOS program.<sup>5g</sup> It is well known that an adamantanetype network readily enables interpenetration to fill potential cavity space. The adamantane frameworks of  $2a \cdot hexane$  and **2b** heptane contain only four molecules instead of the 10 molecules observed in the corresponding borol derivatives.<sup>2d</sup> Undoubtedly, the smaller size of the adamantane framework and the steric requirements of the bulky substituents on the silicon atoms prevent interpenetration in these networks. In fact, the framework without hexane or heptane is composed of 18% and 22% guest-accessible cavities in the unit cells on the basis of PLATON calculations.

Use of cyclohexane in THF/benzene (for details see Experimental Section) unexpectedly produced needles of  $2a \cdot 1.5$  benzene. The X-ray structure of  $2a \cdot 1.5$  benzene is shown in Figure 1c. The selected bond and hydrogen bond parameters of the tetraphenylmethane core and the silanol tetramer are also collected in Tables 2 and 3. The X-ray crystal structure of  $2a \cdot 1.5$  benzene revealed a four-connected non-adamantane framework possessing two distinct one-dimensional (1D) channels with differing pore sizes, as shown

(6) For the taxonomy of zeolites as well as inorganic, organic, and metal-organic networks, three-letter designations are widely accepted. (a) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. Acc. Chem. Res. 2005, 38, 176. (b) O'Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. Acc. Chem. Res. 2008, 41, 1782. (c) Delgado-Friedrichs, O.; Foster, M. D.; O'Keeffe, M.; Proserpio, D. M.; Treacy, M. M. J.; Yaghi, O. M. J. Solid State Chem. 2005, 178, 2533. (d) http://rcsr.anu.edu.au/home. The proceeding Schläfli symbols are also used in mathematical senses such as in 6<sup>6</sup>-dia, 4<sup>2</sup>.6<sup>3</sup>.8-sra, (4<sup>3</sup>.6<sup>3</sup>)4(6<sup>6</sup>)-ast, and (4<sup>12</sup>.6<sup>12</sup>.8<sup>4</sup>)(4<sup>6</sup>)2-flu. In the text, networks are simply denoted by the three-letter symbols. In those networks, dia is the most common network with a tetrahedral 4-connected node. For example, it is found in the diamond framework. sra is a non-diamondoid 4-connected network. ast is a 4-connected zeolitic network with both tetrahedral and cubic parts, such as AIPO<sub>4</sub>-16 or octadecasil zeolite. flu is a 4- and 8-connected network found in fluorite, CaF<sub>2</sub>.

(7) PLATON is a versatile program package for multipurpose crystallography. Other than automatic structure solution, refinement, and geometrical calculations, it calculates the accessible volume ( $V_g$ ). If V is the volume of the unit cell, then the porosity in % is given by 100  $V_g/V$ . (a) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. (b) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194. (c) http://www.cryst.chem.uu.nl/platon.

<sup>(5)</sup> TOPOS is a program package for multipurpose geometrical and topological analysis of crystal structures. It works with crystal structure details and provides automatic determination of network topology and degree of interpenetration. (a) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Cryst.EngComm* **2004**, *6*, 378. (b) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Cryst. Growth* **Des. 2008**, *8*, 519. (d) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Cryst. Growth* **Des. 2008**, *8*, 519. (d) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *Cryst. Growth* **Des. 2008**, *8*, 519. (d) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2008**, *10*, 1822. (e) Baburin, I. A.; Blatov, V. A. *Acta Crystallogr* **2007**, *B63*, 791. (f) Baburin, I. A.; Blatov, V. A.; Carlucci, L.; Cistand, G.; **27008**, *223*, 371. (g) http://www.topos.ssu.samara.ru.

Table 2. Selected Hydrogen Bond Parameters of 2a · Hexane, 2b · Heptane, 2a · 1.5Benzene, 5a · 18Benzene, and 5b · 23Benzene

	О-Н	Н⋯О	00	$O-H\cdots O$
<b>2a</b> · hexane	0.73(4)-0.75(5)	2.02(5)-2.12(5)	2.741(5)-2.828(5)	155(5)-165(4)
2b · heptane	0.71(4) - 0.76(4)	2.09(4) - 2.16(4)	2.730(4) - 2.833(4)	146(4) - 155(4)
$2a \cdot 1.5$ benzene	0.71(4) - 0.76(3)	1.96(3) - 2.12(4)	2.689(4) - 2.795(4)	156(4) - 167(4)
5a · 18benzene	0.74(4) - 0.75(3)	2.03(3) - 2.10(5)	2.758(4) - 2.795(4)	157(5) - 164(4)
5b · 23benzene	0.74(4)-0.75(3)	1.95(4)-1.98(2)	2.669(3)-2.702(2)	161(4)-162(4)

Table 3. Selected Bond Lengths and Angles of Tetrahedral Organic Frameworks in the Crystals of 2a · Hexane, 2b · Heptane, and 2a · 1.5Benzene

	network type	E-C	С-Е-С
$2\mathbf{a} \cdot \text{hexane} (\mathbf{E} = \mathbf{C})$	dia	1.551(5)-1.575(5)	108.2(3)-111.4(3)
$2\mathbf{b} \cdot \text{heptane} (E = Si)$	dia	1.868(4)-1.874(3)	107.2(1)-114.8(1)
$2\mathbf{a} \cdot 1.5$ benzene (E = C)	sra	1.540(4)-1.545(4)	101.7(2)-113.5(2)



Figure 3. (a) Partial view of the 3D network present in  $2a \cdot 1.5$  benzene. The view has four network units containing hydrocarbons as guests (green). All substituents on the Si atom are omitted for clarity. (b) sra network of  $2a \cdot 1.5$  benzene based on TOPOS analysis.

in Figure 1c. The larger channel is occupied by three benzenes, while the smaller channel is completely empty, with a total of 20% guest-accessible volume.

To simplify the framework connectivity, a topological analysis of  $2a \cdot 1.5$  benzene was performed using the TOPOS program. The four-connected node of tetraphenylmethane and the synthon R(4)(4) H-bond by four silanols revealed an **sra** network,<sup>6</sup> as shown in Figure 3b. An analogous topology has been found in metallic and binary inorganic solids such as SrAl<sub>2</sub>, and PBr<sub>5</sub>.<sup>5a,b</sup> Thus fitting the large cyclohexane into the cavities of the adamantane network seems to allow the framework to be changed with inclusion of benzenes.

Formation of Zeolite-Type Hydrogen-Bonding Networks by Octahedral Organosilanols (5a,b). In microporous silicates and zeolites, a number of structures can be built from truncated octahedral (to) or truncated rhombic dodecahedral (trd) cages of silicates and aluminosilicates, commonly referred to as sodalite and octadecasil cages, as shown in Figure 4a and b.<sup>8</sup> These cages have both square and hexagonal faces in their structures. Connecting the square faces of the to structures yields zeolite A, while connecting the hexagonal faces of the to structures yields faujasite zeolite.<sup>8</sup> The trd structures also yield octadecasil zeolite and aluminophosphate molecular sieve AlPO<sub>4</sub>-16 by linking the square faces.<sup>8</sup> The prisms that connect the square faces of to and trd are obviously cubes, as shown in Figure 4c and d. Therefore,



**Figure 4.** Cage units of (a) **to** and (b) **trd** structures. The linkage of (c) **to** and (d) **trd** cages in zeolite A and octadecasil zeolite. Each cage is linked at the square faces of the **to** or **trd** structures together through cubic prisms (yellow).

introducing octasilsesquioxane, having a cubic cage, into the silanol 3D network seems to allow for the expansion of the pore structure in the network and produces zeolite-like frameworks.

Crystallization of octahedral organosilanol derivatives (5a,b) with cubic cages from acetone/benzene (for details see Experimental Section) provided prisms of 5a and 5b, whose X-ray crystallographic analysis confirmed a composition of  $5a \cdot 18$  benzene and  $5b \cdot 23$  benzene, respectively (Table 4). The X-ray structures of  $5a \cdot 18$  benzene and  $5b \cdot 23$  benzene are shown in Figure 5.

In the crystal structures, each octasilsesquioxane cube forms silanol hydrogen bonds with 12 neighboring cubes, resulting in a large cavity where either 18 or 23 benzene molecules were located, as shown in Figure 6a and b. Selected hydrogen bond parameters of the silanol tetramer are listed in Table 2. There is a surprisingly large guest-accessible volume for **5a** and **5b** of 50.9% and 51.0% of the unit cell volume, respectively.

TOPOS analyses of  $5a \cdot 18$  benzene and  $5b \cdot 23$  benzene showed an eight-connected cube with the synthon R(4)(4) H-bond resulting in **ast** networks<sup>6</sup> without interpenetration, as shown in Figure 6c. This network is exhibited by zeolites such as octadodecasil and the ALPO<sub>4</sub>-16 frameworks.<sup>8</sup> If the whole silsesquioxane cube is considered to be an eight-connected node, the network can be further simplified to flu<sup>6</sup> or a fluorite-type of network (Figure 6d). In any case, both the **ast** and **flu** networks are very rare even in metal organic frameworks (MOFs).<sup>10</sup> To the best of our knowledge, these 3D networks are the first hydrogen-bonded replicas of zeolite or fluorite.

<sup>(8) (</sup>a) Baerlocher, Ch.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*, 5th ed.; Elsevier: Amsterdam, 2001. (b) The original date available at http://www.iza-structure.org/databases/.

Table 4. Crystal Data and Data Collection Parameters of
5a · 18Benzene and 5b · 23Benzene

	5a · 18benzene	5b·23benzene
empirical formula	C220H276O20Si16	C149H137O10Si8
fw	3689.85	4624.61
cryst syst	monoclinic	monoclinic
space group	C2/m	C2/m
a (Å)	22.911(3)	26.089(3)
$b(\mathbf{A})$	30.535(3)	29.765(3)
$c(\dot{A})$	18.608(3)	20.783(2)
a (deg)	90.00	90.0
$\beta$ (deg)	124.05(0)	127.19(0)
$\gamma$ (deg)	90.00	90.0
volume ( $Å^3$ )	10786(2)	12857(2)
Z	2	2
density (calcd) (Mg/cm <sup>3</sup> )	1.136	1.195
absorp coeff (mm <sup>-1</sup> )	0.154	0.143
$\theta$ range for data collection (deg)	3.21 to 27.48	3.00 to 27.48
reflns collected	12450	66 958
indep reflns $(R_{int})$	12450 (0.0000)	14838 (0.0394)
goodness of fit indicator	1.206	1.195
final R indices	$R_1 = 0.0937$ .	$R_1 = 0.0668$
$[I \geq 2\sigma(I)]$	$wR_2 = 0.2552$	$wR_2 = 0.1562$
R indices (all data)	$R_1 = 0.1020,$ $wR_2 = 0.2628$	$R_1 = 0.0739,$ w $R_2 = 0.1605$
largest diff peak and hole (e $\text{\AA}^{-3}$ )	0.851 and -0.514	0.353 and -0.308



Figure 5. Crystal structures as viewed along the *a*-axis: (a)  $5a \cdot 18$  benzene and (b)  $5b \cdot 23$  benzene. Guest hydrocarbons in a cavity are drawn as green molecules. All ellipsoids are shown at the 30% probability level.

Packing of Benzene Molecules in Hydrogen-Bonding Networks by Polyhedral Organosilanols. A very interesting part of the crystal structures is the arrangement of the benzene molecules inside the cavities of the hydrogen-bonding networks in these polyhedral organosilanols. Space-filling models of the benzenes within the network structures are shown in Figure 7 to give an open view of the arrangement of the benzene molecules in the unit cell. For comparison, a packing analysis of pure crystalline benzene molecules reveals edge-to-face packing in herringbone layers (Figure 7d).<sup>9</sup>

In the network of  $2a \cdot 1.5$  benzene, three benzenes repeat within the cavity by translation along the *a*-axis, with one



Figure 6. Partial view of the 3D networks present in the crystals: (a)  $5a \cdot 18$  benzene and (b)  $5b \cdot 23$  benzene. Both views have four network units containing hydrocarbons as guests (green). All substituents on the Si atom are omitted for clarity. (c) ast network and (d) flu network of  $5b \cdot 23$  benzene based on TOPOS analyses. The octahedral units of the silesequioxane core are viewed as cubes or eight-connected nodes.

molecule perpendicular to the other two parallel molecules (Figure 7a). However, the perpendicular and parallel benzenes are not overlapped enough to provide optimal edge-toface or face-to-face interactions. In contrast, all 18 benzenes in the  $5a \cdot 18$  benzene network are perpendicularly associated in a cavity to provide optimal edge-to-face interactions similar to that found in pure crystalline benzene (Figure 7b). The larger size of the organosilanol in the network of  $5b \cdot 23$  benzene enables the accommodation of 23 benzenes in a cavity. Some excess benzenes in the unit cell are not perpendicularly associated with neighboring benzenes (Figure 7c). Thus, the surprisingly large cavities of 5a and 5b are supported not only by three-dimensional silanol hydrogen bonding but also by benzene clathrates with edge-to-face interactions.

#### Conclusions

In summary, the crystal structures of **2a,b** and **5a,b** with hydrocarbons are the first examples of adamantane-type, SrAl<sub>2</sub>-type, zeolite-type, and fluorite-type packing motifs formed by silanol hydrogen bonding. Depending on the pore size, hydrocarbons were included in the open frameworks without interpenetration of the networks. Furthermore, as a guest hydrocarbon perpendicular stacking of the benzene cluster is found in the pores of **5a** and **5b**. Having established this silanol hydrogen-bonded framework, we are currently investigating covalent organic frameworks (COFs) as well as MOFs based on polyhedral organosilanols with the aim of achieving structural integrity during removal of the guest molcules.<sup>11</sup>

<sup>(9)</sup> Crystal structures of pure benzene: (a) Cox, E. G.; Cruickshank,
D. W. J.; Smith, J. A. S. *Proc. R. Soc. London* **1958**, *A247*, 1. (b) Bacon,
G. E.; Curry, N. A.; Wilson, S. A. *Proc. R. Soc. London* **1964**, *A279*, 98.
(c) Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; Pople, J. A. *Proc. R. Soc. London* **1987**, *A414*, 47.

<sup>(10)</sup> Metal organic frameworks (MOFs) with octadecasil network:
(a) Gädara, F.; Gömez-Lor, B.; Iglesias, M.; Snejko, N.; Gutiërrez-Puebla, E.; Monge, A. *Chem. Commun.* 2009, 2393. MOF with fluorite network: (b) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* 2004, *43*, 971.

<sup>(11)</sup> Preliminary experiments show that the adamantane-type network of 2b does not remain ordered under cryogenic (77 K) nitrogen adsorption conditions.



Figure 7. Crystal structures as viewed along the *b*-axis (left) and *c*-axis or *ac*-plane (right): (a)  $2a \cdot 1.5$ benzene, (b)  $5a \cdot 18$ benzene, (c)  $5b \cdot 23$ benzene, and (d) pure benzene.<sup>9a</sup> Benzene molecules are shown as space-filling models for clarity of the stacking.

## **Experimental Section**

General Information. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>29</sup>Si NMR spectra were recorded at room temperature using JEOL JNM-ECP 500 or JNM-EX 400 spectrometers. Low-resolution EI mass spectra were recorded on a JEOL JMS-AX505H mass spectrometer, and MALDI-TOF mass spectra were measured on a Shimadzu AXIMA-CFR mass spectrometer using angiotensin II and insulin  $\beta$  for accurate mass calibration. High-resolution mass spectra (ESI) were recorded on a JEOL JMS-T100LC mass spectrometer. The standard substance Yokudelna (purchased from JEOL) was used for calibration. HPLC (GPC) purification was performed using a Japan Analytical Industry LC-908. Starting materials and reagents were purchased from Sigma-Aldrich, Wako, TCI, and Kanto. Tetrahydrofuran (THF), hexane, and benzene were distilled from sodium benzophenone ketyl. Methanol was distilled from magnesium methoxide, and toluene was distilled from lithium aluminum hydride (LAH). Tetrakis-(4-bromophenyl)methane,<sup>4a</sup> tetrakis(4-bromophenyl)silane,<sup>4c</sup> dimethyldioxirane (DMD),<sup>4e</sup> octavinyloctasilsesquioxane,<sup>4f</sup> 4-chlorostyrene,<sup>4g</sup> and RuH(CO)(PCy<sub>3</sub>)<sub>2</sub><sup>4h,i</sup> were prepared according to literature methods.

Synthesis of Diisopropylchlorosilane. Magnesium turnings (12.2 g, 500 mmol) were added to anhydrous Et<sub>2</sub>O (50 mL), and a few drops of 1,2-dibromoethane was added for activation of the magnesium surface. A solution of 2-chloropropane (47.6 mL, 520 mmol) in Et<sub>2</sub>O (250 mL) was added dropwise over 2 h at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at room temperature. To this Grignard reagent was added dropwise trichlorosilane (25.2 mL, 250 mmol) in 200 mL of Et<sub>2</sub>O over 2 h and stirred overnight using a dry ice/ methanol trap over the reaction vessel. The reaction mixture was Schlenk filtered with a glass filter, and the solvent was removed in vacuo. The resulting mixture was fractionally distilled to give 16.7 g (111 mmol) of diisopropylchlorosilane (44.2%): bp 136-8 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.47 (t, J = 1.8 Hz, 1H), 1.12-1.03 (m, 2H), 0.97 (d, J = 7.3 Hz, 6H), 0.92 (d, J = 7.3 Hz, 6H)6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 17.31, 16.97, 13.81; MS (EI) m/z calcd for C<sub>6</sub>H<sub>15</sub>ClSi (M)<sup>+</sup> 150, found 150.

Synthesis of Diphenylchlorosilane. Magnesium turnings (5.35 g, 220 mmol) were added to anhydrous THF (10 mL), and a few drops of 1,2-dibromoethane was added for activation of the magnesium surface. A solution of chlorobenzene (20.3 mL, 200 mmol) in THF (100 mL) was added dropwise over 1 h. After complete addition, the reaction mixture was refluxed overnight. This Grignard reagent was added dropwise to a solution of trichlorosilane (10.2 mL, 100 mmol) in 100 mL of THF over 3 h and stirred overnight using a dry ice/methanol trap over the reaction vessel. The solvent was removed in vacuo and redissolved in 100 mL of hexane. The reaction mixture was Schlenk filtered with a glass filter, and the solvent was removed under reduced pressure. The resulting mixture was fractionally distilled to give 18.0 g (82.4 mmol) of diphenylchlorosilane (82.4%): bp 96-8 °C/0.4 mmHg; <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.79 (d, J = 7.9 Hz, 4H), 7.58 (t, J = 7.5 Hz, 2H), 7.53  $(t, J = 7.5 \text{ Hz}, 4\text{H}), 5.88 (s, 1\text{H}); {}^{13}\text{C} \text{ NMR} (125 \text{ MHz}, \text{CDCl}_3) \delta$ 134.49, 131.90, 131.05, 128.28; MS (EI) *m/z* calcd for C<sub>12</sub>H<sub>11</sub>ClSi  $(M)^+$  218, found 218.

Synthesis of Tetrakis[4-(diisopropylhydrosilyl)phenyl]methane. A solution of tetrakis(4-bromophenyl)methane (1a) (3.60 g, 5.66 mmol) in anhydrous THF (250 mL) was added to n-BuLi in hexanes (19.2 mL, 1.60 M, 31.7 mmol) at -78 °C and stirred for 1 h. Then diisopropylchlorosilane (6.20 mL, 35.8 mmol) was added dropwise over 1 h and then warmed to ambient temperature overnight. The solvent was removed in vacuo, and the residue was redissolved in chloroform. The resulting salt was filtered, and the filtrate was evaporated to afford the crude product. The crude product was purified by gel permeation chromatography to give 2.34 g (3.02 mmol) of tetrakis[4-(diisopropylhydrosilyl)phenyl]methane (53.3%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, J = 8.1 Hz, 8H), 7.18 (d, J = 8.1 Hz, 8H), 3.97 (t, J =3.0 Hz, 4H, 1.28-1.22 (m, 8H), 1.11 (d, J = 7.3 Hz, 24H),  $1.03 \text{ Hz}, 1.03 \text{ H$ (d, J = 7.3 Hz, 24H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  147.39, 134.53, 131.53, 130.53, 65.15, 18.76, 18.64, 10.78; MS (MALDI-TOF, matrix: DHB) calcd for  $C_{49}H_{76}Si_4Na$  (M + Na<sup>+</sup>) 799, found 799.

Synthesis of Tetrakis[4-(diisopropylhydrosilyl)phenyl]silane. The reaction of tetrakis(4-bromophenyl)silane (1b) (2.00 g, 3.06 mmol), *t*-BuLi in pentanes (22.5 mL, 1.60 M, 37.1 mmol), and diisopropylchlorosilane (3.60 mL, 21.3 mmol) was performed in a similar manner to that described above and gave 1.62 g (2.04 mmol) of tetrakis[4-(diisopropylhydrosilyl)phenyl]silane (66.7%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.54–7.52 (br, 16H), 3.94 (t, J = 3.0 Hz, 4H), 1.26–1.21 (m, 8H), 1.08 (d, J = 7.3 Hz, 24H), 1.01 (d, J = 7.3 Hz, 24H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  135.76, 135.43, 134.82, 134.78, 18.70, 18.60, 10.71; MS (MALDI-TOF, matrix: DHB) calcd for C<sub>48</sub>H<sub>76</sub>Si<sub>5</sub>Na (M + Na<sup>+</sup>) 815, found 815.

Synthesis of Tetrakis[4-(diisopropylhydroxysilyl)phenyl]methane (2a). To a solution of tetrakis[4-(diisopropylhydrosilyl)phenyl]methane (0.290 g, 0.366 mmol) in anhydrous carbon tetrachloride (20 mL) was added dimethyldioxirane in acetone solution (30.0 mL, 0.300 M, 9.00 mmol). The resulting mixture was stirred for 1 h and then evaporated to afford 0.321 g (0.366 mmol) of **2a** (99.9%):

<sup>1</sup>H NMR (500 MHz, THF- $d_8$ )  $\delta$  7.46 (d, J = 8.1 Hz, 8H), 7.16 (d, J = 8.1 Hz, 8H), 4.87 (s, 4H,), 1.14–1.07 (m, 8H), 1.03 (d, J = 7.1 Hz, 24H), 0.95 (d, J = 7.1 Hz, 24H); <sup>13</sup>C NMR (125 MHz, THF- $d_8$ )  $\delta$  148.40, 134.28, 134.23, 131.30, 66.22, 17.95, 17.65, 13.81; HRMS (ESI) calcd for C<sub>49</sub>H<sub>76</sub>O<sub>4</sub>Si<sub>4</sub>Na (M - Na<sup>+</sup>) 863.4718, found 863.4674.

Synthesis of Tetrakis[4-(diisopropylhydroxysilyl)phenyl]silane (2b). The reaction of tetrakis[4-(diisopropylhydrosilyl)phenyl]silane (0.590 g, 0.738 mmol) and dimethyldioxirane (DMD) in acetone (30.0 mL, 0.300 M, 9.00 mmol) was performed in a similar manner to that described above and gave 0.663 g (0.737 mmol) of **2b** (99.9%): <sup>1</sup>H NMR (500 MHz, THF- $d_8$ )  $\delta$  7.60 (d, J = 7.8 Hz, 8H), 7.55 (d, J = 7.8 Hz, 8H), 5.04 (s, 4H), 1.18–1.11 (m, 4H), 1.01 (d, J = 7.2 Hz, 24H), 0.93 (d, J = 7.2 Hz, 24H); <sup>13</sup>C NMR (125 MHz, THF- $d_8$ )  $\delta$  139.39, 136.04, 135.76, 134.41, 17.80, 13.68; HRMS (ESI) calcd for C<sub>48</sub>H<sub>76</sub>O<sub>4</sub>Si<sub>5</sub>Na (M + Na<sup>+</sup>) 879.4488, found, 879.4467.

Synthesis of 4-(Diisopropylhydrosilyl)styrene. Magnesium turnings (1.46 g, 60.0 mmol) were added to anhydrous THF (5 mL), and a few drops of 1,2-dibromoethane was added to activate the magnesium surface. A solution of 4-chlorostyrene (6.00 mL, 50.0 mmol) in THF (45 mL) was added dropwise over 1 h. The reaction mixture was stirred for 2 h at 60 °C and then cooled to room temperature. A solution of diisopropylchlorosilane (10.4 mL, 60.0 mmol) in 20 mL of THF was added, and the mixture stirred for 1 h. The solvent was removed in vacuo, and the residue redissolved in 50 mL of hexane. The reaction mixture was washed with 100 mL of water, and the organic layer was dried over magnesium sulfate. The solution of crude product was concentrated and purified on a silica gel short column with hexane as the eluent to give 7.91 g (36.2 mmol) of 4-(diisopropylhydrosilyl)styrene (72.4%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 6.81 (dd, J = 17.6, 10.9 Hz, 1H), 5.89 (d, J =17.6 Hz, 1H), 5.35 (d, J = 10.9 Hz, 1H), 4.08 (t, J = 3.1 Hz, 1H), 1.40-1.30 (m, 2H), 1.19 (d, J = 7.3 Hz, 6H), 1.12 (d, J = 7.3 Hz,6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.25, 136.94, 135.74, 133.80, 125.48, 114.06, 18.67, 18.48, 10.75; MS (EI) m/z calcd for  $C_{14}H_{22}Si(M)^+$  218, found 218.

Synthesis of 4-(Dipenylhydrosilyl)styrene. The reaction of magnesium (2.19 g, 90.0 mmol), 4-chlorostyrene (9.60 mL, 80.0 mmol), and diphenylchlorosilane (15.7 mL, 80.0 mmol) was performed in a similar manner to that described above and gave 20.5 g (71.6 mmol) of 4-(dipenylhydrosilyl)styrene (89.5%): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d, J = 7.3 Hz, 4H), 7.54 (d, J = 8.0 Hz, 2H), 7.41–7.37 (m, 4H), 7.35 (t, J = 7.3 Hz, 4H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.47 (s, 1H), 5.26 (d, J = 10.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.90, 136.69, 136.06, 135.77, 133.27, 132.83, 129.81, 128.05, 125.82, 114.73; MS (EI) m/z calcd for C<sub>20</sub>H<sub>18</sub>Si (M)<sup>+</sup> 286, found 286.

Synthesis of 4-(Diisopropylmethoxysilyl)styrene (4a). To anhydrous methanol (20 mL) at -78 °C was added sodium metal (0.920 g, 40.0 mmol), and the solution was warmed to ambient temperature over 1 h. Stirring was continued for an additional 2 h until the sodium is fully dissolved. 4-(Diisopropylhydrosilyl)styrene (4.37 g, 20.0 mmol) in THF (40 mL) was added dropwise and stirred for 18 h at 40 °C. Trimethylchlorosilane (6.35 mL, 50 mmol) in THF (10 mL) was added to the reaction mixture and stirred for an additional hour. The solvent and volatiles were removed in vacuo and redissolved in 40 mL of hexane. The resulting salt was filtered, and the filtrate was evaporated to afford 4.43 g (17.8 mmol) of 4a (89.2%): <sup>1</sup>H NMR  $(500 \text{ MHz}, C_6D_6) \delta 7.54 \text{ (d}, J = 7.8 \text{ Hz}, 2\text{H}), 7.31 \text{ (d}, J = 7.8 \text{ Hz}, 2\text{Hz})$ 2H), 6.60 (dd, J = 17.9, 11.0 Hz, 1H), 5.67 (d, J = 17.9 Hz, 1H), 5.10 (d, J = 11.0 Hz, 1H), 3.45 (s, 3H), 1.21 (sept, J = 7.3 Hz)2H), 1.11 (d, J = 7.3 Hz, 6H), 1.05 (d, J = 7.3 Hz, 6H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 138.83, 137.36, 135.21, 134.22, 125.93, 114.16, 51.82, 17.67, 17.46, 12.37; MS (EI) m/z calcd for C<sub>15</sub>H<sub>24</sub>OSi (M)<sup>+</sup> 248, found 248.

**Synthesis of 4-(Diphenylmethoxysilyl)styrene (4b).** The reaction of methanol (40 mL), sodium metal (2.76 g, 120 mmol), and

4-(diphenylhydrosilyl)styrene (17.2 g, 60.0 mmol) was performed in a similar manner to that described above and gave 18.5 g (58.5 mmol) of **4b** (97.5%): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$ 7.74 (d, J = 7.6 Hz, 4H), 7.68 (d, J = 8.0 Hz, 2H), 7.25 (d, J =8.0 Hz, 2H), 7.22–7.17 (m, 6H), 6.55 (dd, J = 17.5, 10.9 Hz, 1H), 5.63 (d, J = 17.5 Hz, 1H), 5.08 (d, J = 10.9 Hz, 1H), 3.50 (s, 3H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  139.50, 137.16, 136.11, 135.80, 134.62, 134.10, 130.29, 128.23, 126.12, 114.66, 51.58; MS (EI) m/z calcd for C<sub>21</sub>H<sub>20</sub>OSi (M)<sup>+</sup> 316, found 316.

Synthesis of Octakis[4-(diisopropylmethoxysilyl)styryl]octasilsesquioxane. Octavinyloctasilsesquioxane (3) (0.252 g, 0.399 mmol) and RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (36.3 mg, 50.0 µmol) were added to an anhydrous toluene solution (6.4 mL) of 4-(diisopropylmethoxysilyl)styrene (4a) (1.58 g, 6.38 mmol) under an N<sub>2</sub> atmosphere and stirred for 72 h at 80 °C. The solvent was evaporated and the crude product purified by gel permeation chromatography to give 0.663 g (0.277 mmol) of octakis[4-(diisopropylmethoxysilyl)styryl]octasilsesquioxane (69.4%): <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ )  $\delta$  7.66 (d, J = 19.2 Hz, 8H), 7.36 (d, J = 7.8 Hz, 16H), 7.29 (d, J = 7.8 Hz, 16H), 6.57 (d, J = 19.2 Hz, 8H), 3.30 (s, 24H), 1.05 (sept, J = 7.3 Hz,16H), 0.96 (d, J = 7.3 Hz, 48H), 0.89 (d, J = 7.3 Hz, 48H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>) δ 150.29, 138.45, 135.93, 135.29, 126.65, 118.29, 51.81, 17.64, 17.44, 12.33; MS (MALDI-TOF, matrix: 3-aminoquinoline) m/z calcd for  $C_{129}H_{193}N_2O_{20}Si_{16}$  (M +  $C_9H_9N_2$ )<sup>+</sup> 2538, found 2538.

Synthesis of Octakis[4-(diphenylmethoxysilyl)styryl]octasilsesquioxane. The reaction of 4-(dipenylmethoxysilyl)styrene (4b) (1.02 g, 3.22 mmol) and octavinyloctasilsesquioxane (3) (0.128 g, 0.202 mmol) in the presence of RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (23.4 mg, 32.2  $\mu$ mol) was performed in a similar manner to that described above and gave 0.376 g (0.128 mmol) of octakis[4-(diphenylmethoxysilyl)styryl]octasilsesquioxane (63.5%): <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.60 (d, J = 19.2 Hz, 8H), 7.56 (d, J = 6.5 Hz, 32H), 7.49 (d, J = 7.8 Hz, 16H), 7.24 (d, J = 7.8 Hz, 16H), 7.13–7.04 (m, 48H), 6.52 (d, J = 19.2 Hz, 8H), 3.34 (s, 24H); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  150.07, 139.01, 136.19, 135.74, 134.38, 130.32, 129.27, 128.22, 126.77, 118.73, 51.58; MS (MALDI-TOF, matrix: 3-aminoquinoline) *m*/*z* calcd for C<sub>177</sub>H<sub>161</sub>N<sub>2</sub>O<sub>20</sub>-Si<sub>16</sub> (M + C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>)<sup>+</sup> 3082, found 3082.

Synthesis of Octakis[4-(diisopropylhydroxysilyl)styryl]octasilsesquioxane (5a). Octakis[4-(diisopropylmethoxysilyl)styryl]octasilsesquioxane (0.240 g, 0.100 mmol) was stirred at room temperature for 2 h in a 1:9 mixture of 1 M HCl/THF (5 mL). Then 5 mL of chloroform was added, and the organic layer was washed 5 mL of water. Evaporation of the solvent from the mixture gave 0.228 g (0.100 mmol) of **5a** in quantitative yield: <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.64 (d, J = 8.3 Hz, 16H), 7.61 (d, J = 8.3 Hz, 16H), 7.53 (d, J = 19.2 Hz, 8H), 6.55 (d, J = 19.2 Hz, 8H), 4.90 (br, 8H), 1.19 (sept, J = 7.3 Hz, 16H), 1.05 (d, J = 7.3 Hz, 48H), 0.96 (d, J = 7.3 Hz, 48H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  150.39, 138.96, 138.41, 135.37, 126.70, 118.02, 17.63, 17.31, 13.29; <sup>29</sup>Si NMR (100 MHz, acetone $d_6$ )  $\delta$  3.91, -77.68; HRMS (ESI) m/z calcd for C<sub>112</sub>H<sub>168</sub>NaO<sub>20</sub>Si<sub>16</sub> (M + Na)<sup>+</sup> 2303.8335, found 2303.8367.

Synthesis of Octakis[4-(diphenylhydroxysilyl)styryl]octasilsesquioxane (5b). The reaction of octakis[4-(diphenylmethoxysilyl)styryl)octasilsesquioxane (0.147 g, 50.0  $\mu$ mol) in a 1:9 mixture of 1 M HCl/THF (5 mL) was performed in a similar manner to that described above and gave 0.141 g (50.0  $\mu$ mol) of 5b in quantitative yield: <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.67–7.58 (m, 64H), 7.50 (d, J = 19.3 Hz, 8H), 7.43 (t, J = 7.3 Hz, 16H), 7.37 (t, J = 7.3 Hz, 32H), 6.54 (d, J = 19.3 Hz, 8H), 6.06 (br, 8H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  150.25, 139.12, 138.83, 137.15, 136.08, 135.59, 130.55, 128.55, 127.04, 118.66; <sup>29</sup>Si NMR (100 MHz, acetone- $d_6$ )  $\delta$  –16.37, –77.83; HRMS (ESI) m/z calcd for C<sub>160</sub>H<sub>136</sub>Na<sub>2</sub>O<sub>20</sub>Si<sub>16</sub> (M + 2Na)<sup>2+</sup> 2870.5729, found 2870.5708.

X-ray Crystal Structure Determination for All Crystals. The recrystallization procedures for 2a hexane, 2b heptane, 2a 1.5benzene, 5a 18benzene, and 5b 23benzene were performed

as follows: Single crystals suitable for X-ray crystallography were obtained from THF/benzene/hexane or cyclohexane (2a) or THF/benzene/heptane (2b) in 1:1:1 ratios, and acetone/benzene (5a,b) in 1:10 ratios. The "THF/benzene/hexane" notation signifies that the compound was dissolved in the first solvent and then precipitated with successive addition of the second and third solvents. The "acetone/benzene" notation indicates that the compound was dissolved in the first solvent and then precipitated with addition of the second solvent.

All reflections were measured on a Rigaku Mercury diffractometer using a CCD camera. The structures were solved by direct methods (SHELXS-97<sup>12</sup> and SIR 2004<sup>13</sup>) using WinGX v1.70.01 as an interface.<sup>14</sup> The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method (SHELXL-97).<sup>12</sup> Hydrogen atoms were placed at calculated positions and kept fixed. In subsequent refinement, the function  $\sum w(F_o^2 - F_c^2)^2$  was minimized, where  $|F_o|$  and  $|F_c|$  are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as  $R_1 = \sum (||F_o| - |F_d|) / \sum |F_o|$ and  $wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$ . Crystal data and data collection parameters are listed in Tables 1 and 4.

The kind and quantity of guest solvent molecules were roughly estimated by <sup>1</sup>H NMR spectroscopy of dissolved samples. Their location within the cavity was easily determined by normal difference Fourier synthesis. The small size of the cavities in **2a**,**b** and the perpendicular packing of benzenes in **5a**, **b** sufficiently ordered the guest solvent molecules. Nevertheless, some of the disordered benzenes were restrained to be regular and planar by fixing their bond lengths, and the sums of the population parameters of the disordered benzenes were constrained to P1 + P2 = 1.

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**Supporting Information Available:** X-ray data for all crystals are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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