

Size and Shape Selectivity of Host Networks Built Based on Tunable Secondary Building Units

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By modulating the secondary building units derived from the primary building units, *N*-acylsalicylhydrazides (H_3 -xshz), we have been able to construct isostructural but tunable host networks, $[Mn_6(xshz)_6(dmf)_2(bpea)_2]$, with different cavity sizes and shapes where the secondary building units, $[Mn_6(xshz)_6]$, were linked through exo-bidentate bridging ligand, 1,2-bis(pyridyl)ethane (bpea) to form 3-D networks. With a short length linear *N*-acyl side chain at the primary building unit, the host networks have a 3-D network with three-dimensional cavities. With an appropriate length linear *N*-acyl side chain at the primary building unit, the host network keeps the isostructural 3-D network but with two types of one-dimensional channels of reduced cavity volume. The tuned host networks showed not only size selectivity for the guest molecules but also shape selectivity. While the three-dimensional channeled host showed selectivity depending on the length of the podal guests, the one-dimensional channeled host showed selectivity depending on both the length and/or the podality of the guest molecules.

Introduction

The construction of porous networks¹ is of great interest due to potential applications such as gas absorption,² chiral separation³ and catalysis.⁴ The common strategy for the construction of metal-organic porous networks relies upon the proper programming of the building units made up with metal ions as the corner units and long rigid organic ligands as linkers.⁵ Recently, the strategy of using secondary building units (SBUs) for the construction of highly porous and robust

networks has been very successful.⁶ However, it is still very difficult to modulate the shape and properties of the cavity in the porous networks.⁷ The structural modifications of the building components of the host network usually lead to unpredictable results, frustrating systematic control of such structural features as cavity size and shape.⁸ These obstacles could be surmounted with a host system built on a base of SBUs equipped with the components that can be modulated with retention of the general structural features and supra-molecular connectivity of the host network. One approach is the selection of molecular geometries which naturally not only give rise to porosity but also present sites for modification which is spatially remote from structurally important network linkages.⁹

We recently synthesized a new type of secondary building unit, a metallamacrocycle¹⁰ using a pentadentate ligand,

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N-acetylsalicylhydrazide (ashz^{3-}) and utilized this building unit for the construction of a porous host network, $[\text{Mn}_6(\text{ashz})_6(\text{dmf})_2(\text{bpea})_2]$, **1** (Figure 1a).¹¹ The hexanuclear manganese metallamacrocycle served as a secondary building unit, and the exo-bidentate ligand 1,2-bis(pyridyl)ethane (bpea) served as connection bridges linking these building units (Figure 1b). The network **1** has two types of channels that are interconnected to form three-dimensional channels. The major channels (S_4 channels) with an average diameter of 13.7 Å are along the crystallographic S_4 -improper rotation axes (Figure 1c), and the minor channels (screw channels) with an average diameter of 6.7 Å are along the 4_1 - and 4_3 -screw axes. These channels are connected by bridging channels (BC) to form a three-dimensional channel network, and solvent molecules are packed in the channels of the host network. In addition, we could modulate the secondary building unit, the metallamacrocycle, with retention of the general structural features. Modulation of the *N*-acetyl group of the ligand with different lengths of linear *N*-acyl groups gave isostructural hexanuclear metallamacrocycles where the *N*-acyl groups were located away from the linking sites for the host network formation.¹²

In this study, we attempted to determine whether it is possible to control (1) the cavity size and shape of the host network with retention of the general structural features and supramolecular connectivity using modulated secondary building units and (2) the selectivity for guest molecules based on the size and shape of the cavities of the tuned host networks.

Experimental Section

Materials and Methods. The following were used as received with no further purification: manganese(II) acetate tetrahydrate, 1,2-bis(pyridyl)ethane (bpea), methyl benzoate (*mbz*), isobutyrophenone (*ibp*), ethyl benzoate (*ebz*), propyl benzoate (*pbz*), butyl benzoate (*bbz*), dimethyl phthalate (*dmp*), diethyl phthalate (*dep*), dipropyl phthalate (*dpp*) and dibutyl phthalate (*dbp*) from Aldrich, Inc.; *N,N*-dimethylformamide (*dmf*) from Carlo Erba. A series of pentadentate ligands, *N*-acetylsalicylhydrazide (H_3ashz), *N*-propionylsalicylhydrazide (H_3pshz) and *N*-hexanoysalicylhydrazide (H_3hshz), was prepared according to the literature procedure.¹² $[\text{Mn}_6(\text{ashz})_6(\text{dmf})_2(\text{bpea})_2]$, **1**, was synthesized as previously described.¹¹

C, H, N and Mn determinations were performed at the Elemental Analysis Laboratory of the Korean Institute of Basic Science. Infrared spectra were recorded as KBr pellets in the range 4000–600 cm^{-1} on a BioRad FT-IR spectrometer.

Preparation. Host networks with different sizes and shapes of cavities were prepared by mixing equivalent amounts of manganese(II) acetate tetrahydrate and a corresponding H_3xshz ligand for the generation of the hexanuclear manganese metallamacrocycles as secondary building units and an equivalent amount of bpea as linker ligand in *dmf* solvent.

$[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2] \cdot x(\text{dmf})$, **2**. A 0.104 g (0.499 mmol) sample of H_3pshz was dissolved in 30 mL of *dmf*. Then, a 0.092 g (0.499 mmol) sample of bpea was added to the solution and stirred for 5 min. When all ligands were dissolved completely, a

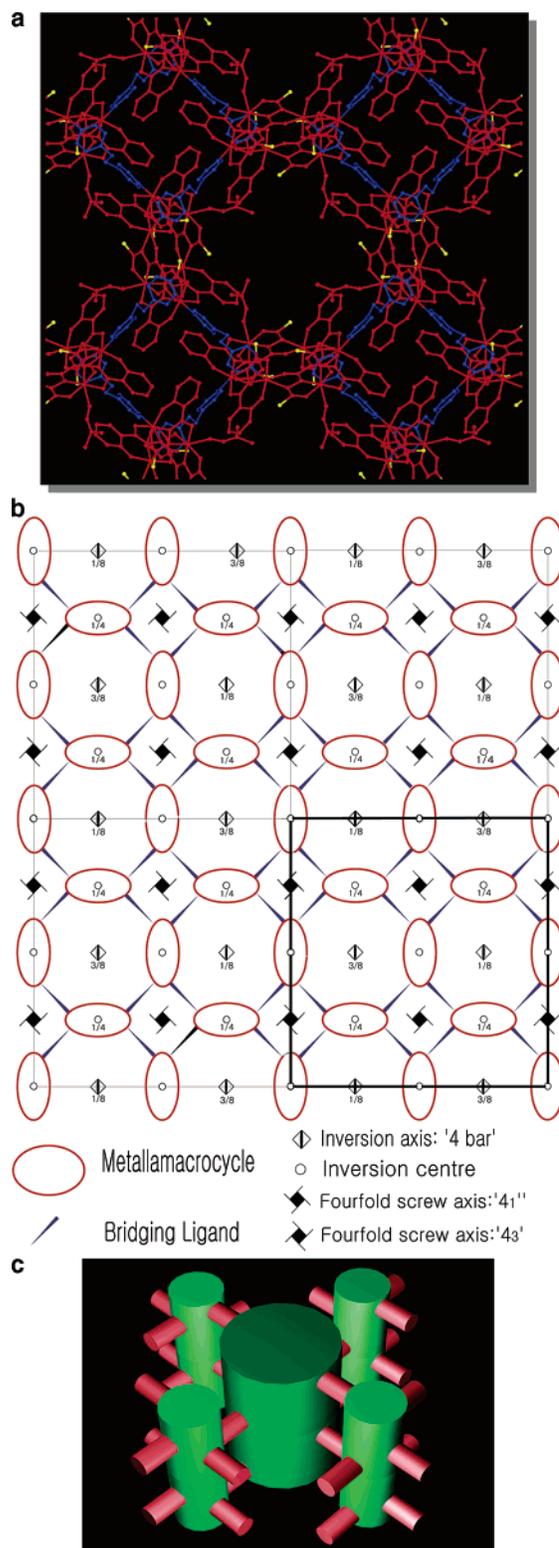


Figure 1. Host network, $[\text{Mn}_6(\text{xshz})_6(\text{dmf})_2(\text{bpea})_2]_n$. (a) The ball-and-stick diagram of the network. Color code: red, metallamacrocycle and *dmf*; blue, bpea; yellow, $-\text{CH}_3$ of the *N*-acyl side chains of the ligands. (b) The schematic diagram of the network. The metallamacrocycles presented as red macrocycles were networked by 4_1 -screw symmetry-related blue exo-didentate bridging ligands bpea. The major channels (S_4 channels) are along the crystallographic 4 inversion axes (S_4 -improper rotation axes) and the minor channels (screw channels) are along the 4_1 - and 4_3 -screw axes. These channels are linked through the bridging channels (BC channels) to form the three-dimensional channel structure. (c) The schematic diagram of the three-dimensional channels of the 3-D networks. S_4 channels and screw channels are interconnected to form a three-dimensional channel.

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Table 1. Summary of Crystal Data and Structure Refinement

crystal system	tetragonal	space group	$I4_1/a$
unit cell dimensions ^a	$a = b = 40.6192$,	$c = 17.5391 \text{ \AA}$	
network			final R indices [$I > 2\sigma(I)$] ^b
[Mn ₆ (pshz) ₆ (dmf) ₂ (bpea) ₂ ·y(dmf), 2			$R1^c = 0.0586$, $wR2^c = 0.1537$
[Mn ₆ (hshz) ₆ (dmf) ₂ (bpea) ₂ ·y(dmf), 3			$R1 = 0.0583$, $wR2 = 0.1470$
[Mn ₆ (ashz) ₆ (bpea) ₂ (dmf) ₂ ·x(mbz)·y(dmf), 4			$R1 = 0.0507$, $wR2 = 0.1054$
[Mn ₆ (ashz) ₆ (bpea) ₂ (dmf) ₂ ·x(dep)·y(dmf), 10			$R1 = 0.0788$, $wR2 = 0.2318$
[Mn ₆ (ashz) ₆ (bpea) ₂ (dmf) ₂ ·x(dpp)·y(dmf), 11			$R1 = 0.0437$, $wR2 = 0.0841$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(ibp)·y(dmf), 14			$R1 = 0.0832$, $wR2 = 0.2363$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(ebz)·y(dmf), 15			$R1 = 0.0946$, $wR2 = 0.2693$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(pbz)·y(dmf), 16			$R1 = 0.0914$, $wR2 = 0.2194$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(bbz)·y(dmf), 17			$R1 = 0.0709$, $wR2 = 0.2082$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dmp)·y(dmf), 18			$R1 = 0.0879$, $wR2 = 0.2599$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dep)·y(dmf), 19			$R1 = 0.0883$, $wR2 = 0.2545$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dpp)·y(dmf), 20			$R1 = 0.0946$, $wR2 = 0.2330$
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dbp)·y(dmf), 21			$R1 = 0.0612$, $wR2 = 0.1373$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(mbz)·y(dmf), 22			$R1 = 0.0881$, $wR2 = 0.2314$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(ebz)·y(dmf), 24			$R1 = 0.0551$, $wR2 = 0.1390$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(pbz)·y(dmf), 25			$R1 = 0.0680$, $wR2 = 0.1471$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(bbz)·y(dmf), 26			$R1 = 0.0680$, $wR2 = 0.1414$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dep)·y(dmf), 28			$R1 = 0.1001$, $wR2 = 0.2650$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dpp)·y(dmf), 29			$R1 = 0.0651$, $wR2 = 0.1314$
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂ ·x(dbp)·y(dmf), 30			$R1 = 0.0605$, $wR2 = 0.1245$

^a Average cell parameters of all crystal structures. ^b Structure refinement of the network following modification of the data for the disordered electron density with the SQUEEZE routine. ^c $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

0.123 g (0.502 mmol) sample of manganese(II) acetate tetrahydrate was added to the solution without stirring. The solution was allowed to stand for a week, whereupon dark brown rectangular crystals were obtained (0.167 g, 94.3% yield). Crystals were vacuum-dried. Anal. Calcd for [Mn₆(pshz)₆(bpea)₂(dmf)₂·(H₂O)₃ (C₉₀H₉₈N₁₈O₂₃·Mn₆) (fw = 2129.50): C, 50.76; H, 4.64; N, 11.84; Mn, 15.48%. Found: C, 50.28; H, 4.77; N, 12.59; Mn, 15.1%.

[Mn₆(hshz)₆(bpea)₂(dmf)₂·x(dmf), **3**. **3** was prepared in an analogous manner to that used for **2**. A 0.125 g (0.499 mmol) sample of H₃hshz in 30 mL of *dmf*, 0.092 g (0.499 mmol) of bpea and 0.123 g (0.502 mmol) of manganese(II) acetate tetrahydrate were used. 0.180 g, 91.0% yield. Anal. Calcd for [Mn₆(hshz)₆(bpea)₂(dmf)₂·(H₂O)₃ (C₁₀₈H₁₃₄N₁₈O₂₃Mn₆) (fw = 2381.99): C, 54.46; H, 5.67; N, 10.58; Mn, 13.84%. Found: C, 54.28; H, 5.12; N, 10.57; Mn, 13.7%.

[Mn₆(ashz)₆(bpea)₂(dmf)₂·x(mbz)·y(dmf), **4**. About 7 mL of *mbz* was added to 10 mL of *dmf*, and then 0.097 g (0.500 mmol) of H₃ashz was dissolved in the solution. This was followed by the addition of 0.092 g (0.499 mmol) of bpea to the above solution and stirring for 5 min. When all ligands were dissolved completely, a 0.123 g (0.502 mmol) sample of manganese(II) acetate tetrahydrate was added to the solution without stirring.

[Mn₆(ashz)₆(bpea)₂(dmf)₂·x(guest)·y(dmf), (guest = *ibp*: **5**; *ebz*: **6**; *pbz*: **7**; *bbz*: **8**; *dmp*: **9**; *dep*: **10**; *dpp*: **11**; *dbp*: **12**). **5–12** were prepared in an analogous manner to that used for **4**. About 7 mL of the corresponding guest species was used during each preparation.

[Mn₆(pshz)₆(bpea)₂(dmf)₂·x(guest)·y(dmf), (guest = *mbz*: **13**; *ibp*: **14**; *ebz*: **15**; *pbz*: **16**; *bbz*: **17**; *dmp*: **18**; *dep*: **19**; *dpp*: **20**; *dbp*: **21**). **13–21** were prepared in an analogous manner to that used for **4**. A 0.104 g (0.50 mmol) sample of H₃pshz and 7 mL of the corresponding guest species were used during each preparation.

[Mn₆(hshz)₆(bpea)₂(dmf)₂·x(guest)·y(dmf), (guest = *mbz*: **22**; *ibp*: **23**; *ebz*: **24**; *pbz*: **25**; *bbz*: **26**; *dmp*: **27**; *dep*: **28**; *dpp*: **29**; *dbp*: **30**). **22–30** were prepared in an analogous manner to that used for **4**. A 0.125 g (0.50 mmol) sample of H₃hshz and 7 mL of the corresponding guest compounds were used during each preparation.

Crystallographic Data Collections and Refinements of Structures. Since most crystals lose their structural solvents of crystallization within a few minutes of exposure to air, they were coated with oil and preliminary examination and data collection were performed at $-100 \text{ }^\circ\text{C}$ with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker SMART CCD equipped with a graphite crystal, incident-beam monochromator. Lp and absorption corrections were applied to the data. All structures were solved by direct methods and refined by full-matrix least-squares calculations with the SHELXTL-PLUS software package (Ver. 5.1).¹³ Structure refinement of the network following modification of the data for the disordered electron density with the SQUEEZE routine led to better refinement.¹⁴

A summary of the crystal and intensity data is given in Table 1. Details of the crystallographic studies are in the Supporting Information.

Results and Discussion

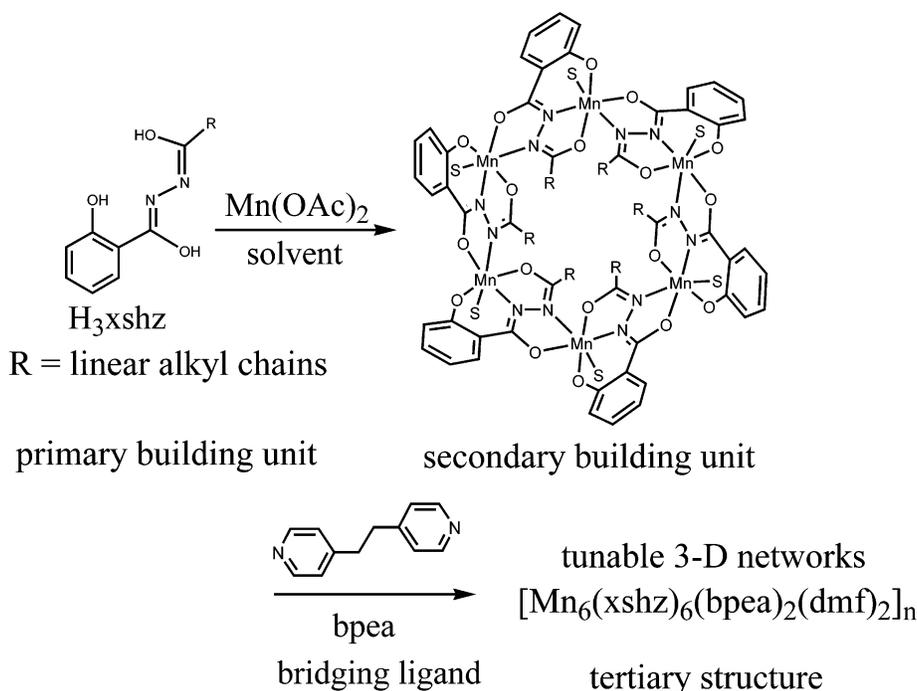
Preparation and Properties of the Tunable Host Networks. The tunable tertiary host networks could be prepared using manganese(II) acetate tetrahydrate and *N*-acetylsalicylhydrazide (H₃xshz) as primary building units for the generation of the modulated secondary building units with bpea in a one pot reaction. The general reaction scheme for the preparation of tunable host networks in *dmf* is given in Scheme 1.

As in host network **1**, the metals were oxidized aerobically to a +3 oxidation state, and the potential trianionic pentadentate ligand, H₃xshz, bridges the metal ions to form a 24-membered hexanuclear metallamacrocyclic. The triple-deprotonated *N*-acetylsalicylhydrazide (*xshz*³⁻) with a linear aliphatic chain could bridge the metal ions using a hydrazide N–N group and form the isostructural secondary building

(13) Sheldrick, G. M. *SHELXTL-PLUS, Crystal Structure Analysis Package*; Bruker Analytical X-ray, Madison, WI, 1997.

(14) Platon program: Spek, A. L. *Acta Crystallogr. Sect. A* **1990**, *46*, 194–201.

Scheme 1



units, the metallamacrocycles. Regardless of the ligands used, all host networks are isostructural. However, depending on the ligands used for modulation of the *SBU*s, the host networks show different cavity dimensionalities.

When we used *N*-propionylsalicylhydrazidate (pshz^{3-}) as a primary building unit, the modulation of the *SBU* was minimal (acetyl to propionyl). Network **2** built based on *N*-propionylsalicylhydrazidate as a primary building unit keeps the general structural features and connectivity of network **1**. The hexanuclear manganese metallamacrocycle, $[\text{Mn}_6(\text{pshz})_6]$, served as a secondary building unit, and the *exo*-bidentate ligand *bpea* served as linker between these secondary building units as in host network **1**. The host network **2** also has a three-dimensional cavity, as in host network **1** (Figure 1). The cavity volume of network **2** (45% of the whole crystal volume)¹⁵ only decreases around 3% compared with that of network **1** (48% of the whole crystal volume). The effect of the propionyl side chain of the pshz^{3-} ligand is minimal on the size and shape of the cavity. The cavity size of the S_4 channel decreases slightly on introduction of the propionyl side chains. The average van der Waals diameter of S_4 channels was estimated to be approximately 13.1 Å (9640 Å³, 33.1%) based on the approximate channel volume per unit cell, 2410 Å³, where the shape of the channel was assumed to be cylindrical. Two propionyl groups in the *SBU* point to the center of the S_4 channel and form part of the neck area of the channel. However, the dimension of the neck of the S_4 channel was not affected by the propionyl side chains, because the neck was formed by a pair of C_2 symmetry-related coordinated *dmf* molecules and of C_2 symmetry-related phenyl groups of the *SBU*s. The largest

dimensions of the channel were also not affected by the propionyl side chains, because the largest dimension was formed by a pair of C_2 symmetry-related pyridyl carbon atoms of the *exo*-bidentate bridging ligand and of C_2 symmetry-related phenyl groups of the *SBU*s. The screw channels are along the 4_1 - and 4_3 -screw axes, and the shapes of the channels are helical. The average van der Waals diameter of the channels was estimated to be approximately 6.7 Å (2517 Å³, 8.7%) based on the approximate channel volume per unit cell, 629 Å³, where the shape of the channel was again assumed to be cylindrical. The other propionyl groups in the *SBU* participate in the formation of the short BC channels between the two types of channels.

The introduction of a hexanoyl group in the primary building unit does not change the host network architecture (Figure 2). However, the hexanoyl side chain of the hshz^{3-} ligand not only reduces the cavity size of the host network but also changes the shape and dimensionality of the cavity. The total cavity size of host network **3** decreased to around 33% of the crystal volume. In addition, the hexanoyl side chains fill up the BC channels and result in the separation of the S_4 and screw channels. The average van der Waals diameter of the S_4 channels was reduced to approximately 11.4 Å (7192 Å³, 24.9%) based on the approximate channel volume per unit cell, 1798 Å³. In addition, the hexanoyl side chains affected the dimensions of the neck of the major channel (5.6 Å × 8.3 Å). The neck was formed between two C_2 symmetry-related coordinated *dmf* molecules and a pair of two C_2 symmetry-related hexanoyl groups of the *SBU*s. However, the hexanoyl side chains did not affect the dimensions of the screw channel. The average van der Waals diameter of the screw channels rather slightly increased to 5.8 Å (1860 Å³, 6.4%) based on the approximate channel volume per unit cell, 465 Å³.

(15) The solvent accessible volumes of the host networks were calculated using PLATON program.¹³ The total solvent accessible volume of the network **2** per unit cell was 13014 Å³ (45% of the unit cell volume) and that of **3** per unit cell was 9212 Å³ (33% of the unit cell volume).

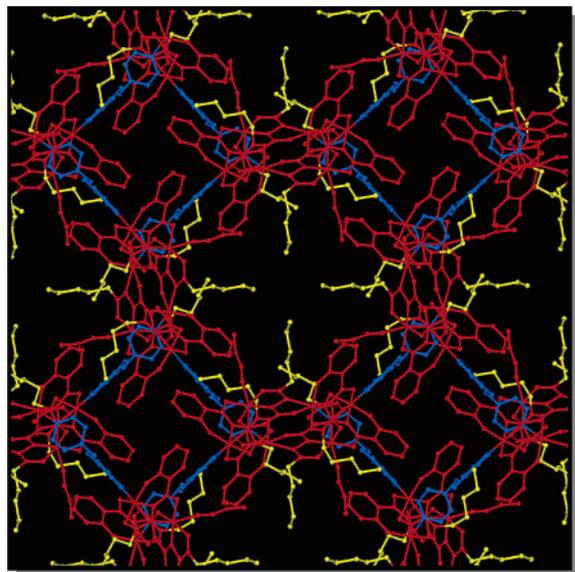


Figure 2. Host network, $[\text{Mn}_6(\text{hshz})_6(\text{dmf})_2(\text{bpea})_2]_n$, **3**. The BC channels are filled with alkyl groups of the *N*-hexanoyl side chain. The S_4 channels and the screw channels are separated by alkyl groups to form different types of one-dimensional channels. Color code: red, metallamacrocycle and *dmf*; blue, *bpea*; yellow, $-(\text{CH}_2)_4\text{CH}_3$ of the *N*-hexanoyl side chain of the H_3 -*hshz* ligand.

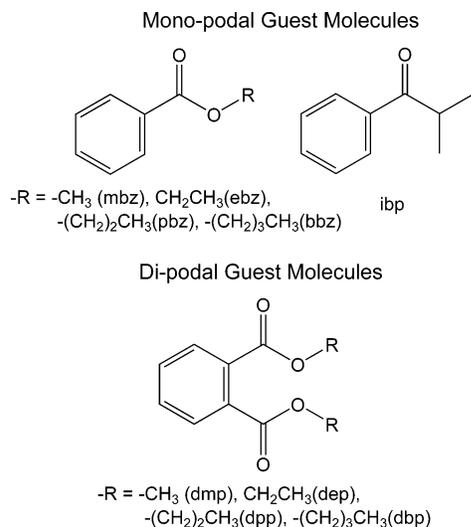


Figure 3. Two types of guest molecules. (Top) The monosubstituted benzenes were used as monopodal guests where the substituents are alkyl ester or isobutanoyl groups. (Bottom) The ortho disubstituted benzenes were used as dipodal guests where the substituents are alkyl ester groups.

Preparation of the Host–Guest Networks and General Procedures. The host–guest networks were prepared in an analogous manner to that used for the host networks but in the presence of various additional guest molecules. Two types of guest molecules were used for the host–guest interactions (Figure 3). The monosubstituted benzenes were used as monopodal guests, where the substituent is an alkyl ester or isobutanoyl group and the ortho disubstituted benzenes were used as dipodal guests, where the substituents are alkyl ester groups. The monopodal guests used were methyl benzoate, isobutyrophenone, ethyl benzoate, propyl benzoate and butyl benzoate, and the dipodal guests used were dimethyl phthalate, diethyl phthalate, dipropyl phthalate and dibutyl phthalate. The preparation of the host–guest networks was

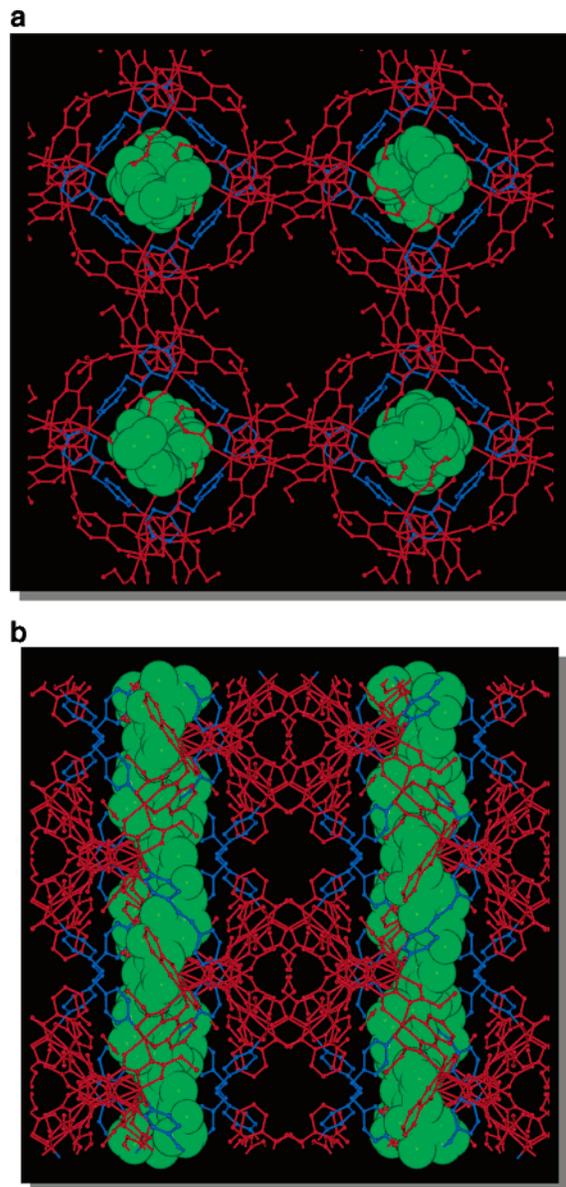


Figure 4. Host–guest network, $[\text{Mn}_6(\text{ashz})_6(\text{bpea})_2(\text{dmf})_2]_n \cdot x(\text{mbz})$, **4**. (a) The view along the crystallographic *c*-axis. The disordered short length monopodal guest *mbz* molecule is observed in the screw channel of the three-dimensional cavity. No ordered guest *mbzs* or solvent *dmfs* are observed in the S_4 channel. (b) The view along the crystallographic *a*-axis. Monopodal guest molecules are aligned along the screw channels.

confirmed by comparing the IR spectra of the host-only network and that of the host–guest network of the freshly prepared sample and using single-crystal X-ray crystallography. The host–guest network showed an additional IR band around $1710\text{--}1727\text{ cm}^{-1}$ for the $\text{C}=\text{O}$ carbonyl group of the bound guest molecules.

Size and Shape Selectivity of the Tunable Host Networks. When the short or medium length monopodal guest molecules (Figure 3) were used as guest molecules, guest molecules could be captured in the three-dimensional cavities of the host network. Figure 4 shows the *mbz*-bound 3-D network host, $[\text{Mn}_6(\text{ashz})_6(\text{bpea})_2(\text{dmf})_2]_n(\text{mbz})_m$. The *mbz* molecules fitted well at the screw channels of the three-dimensional cavities. Two *mbz* molecules were found per

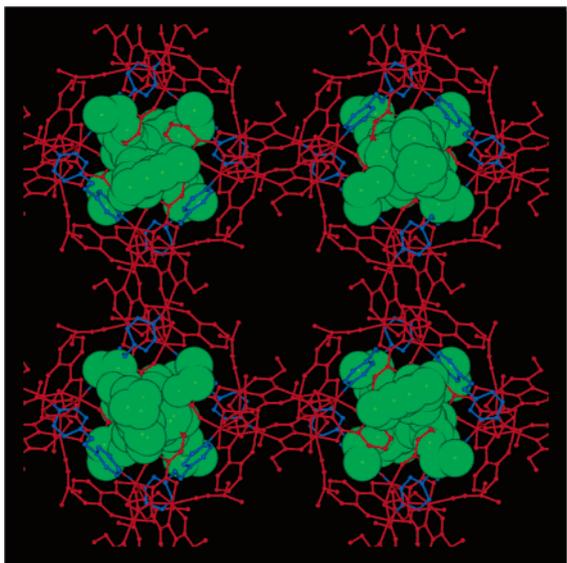


Figure 5. Host-guest network, $[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2]_n \cdot x(\text{dep})$, **19**. The view along the crystallographic *c*-axis. The disordered medium length dipodal guest *dep* molecule is observed in the screw channel of the three-dimensional cavity. While one-pode is aligned along the screw axis, the other pod is aligned along the BC channel. No ordered guest *mbzs* or solvent *dmfs* are observed in the S_4 channel.

4_1 - or 4_3 -screw pitch. There were no H-bonding interactions between the host and guest, *mbz* in the screw channel area, only the van der Waals interaction was observed. However, no ordered guest or solvent molecules were discovered at the S_4 channels. The cavity size of the S_4 channel is too large for the ordered arrangement of the guest or solvent molecules. The monopodal guest molecule with the slightly bulkier isobutanoyl side group, *ibp*, also fitted well at the screw channels of the three-dimensional cavities, as did the *mbz* guest molecule in the three-dimensional cavity of the host network.

When the short or medium length dipodal molecules were used as guest molecules, guest molecules could also be captured in the three-dimensional cavities of the host cavities. Figure 5 shows the *dep*-bound 3-D network host, $[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2]_n(\text{dep})_m$. The *dep* molecules fitted well at the screw channels in the three-dimensional cavities. Two *dep* molecules were found per 4_1 - or 4_3 -screw pitch. While one pod of the dipodal guest molecule was aligned along the screw channel, the other pod was aligned along the BC channel.

When the long length podal guests, either monopodal or dipodal molecules, were used as guest molecules, the guest molecules could not be fitted at the screw channels. Figure 6 shows the *dpp*-bound 3-D network host, $[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2]_n(\text{dpp})_m$. The partially defined *dpp* molecules were only found at the S_4 channels. No ordered *dpp* molecules were found at the screw channels. The host networks with three-dimensional cavities could capture short length monopodal or dipodal guest molecules at their screw channels. However, the long length monopodal or dipodal guest molecules could not be fitted at their screw channels.

Figure 7 shows the *mbz*-bound 3-D network host with two types of one-dimensional cavities, $[\text{Mn}_6(\text{hshz})_6(\text{bpea})_2(\text{dmf})_2]_n$

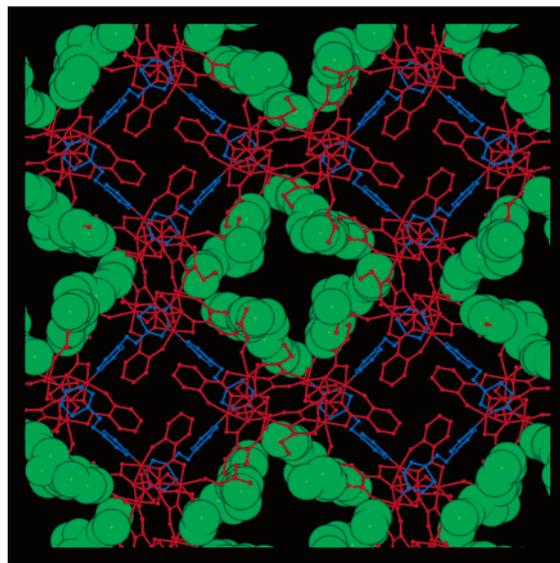


Figure 6. Host-guest network, $[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2]_n \cdot x(\text{dpp})$, **20**. The view along the crystallographic *c*-axis. The partly resolved long length dipodal guest *dpp* molecule and/or *dmf* are observed in the S_4 channel of the three-dimensional cavity. No guest molecules are observed in the screw channels, and the partly resolved long length dipodal guest molecules are observed only in the S_4 channels.

$(\text{mbz})_m$. The *mbz* molecules at the screw channels fitted well in the cavities. Two *mbz* molecules were found per 4_1 - or 4_3 -screw pitch. No ordered guest molecules were discovered at the S_4 channels. All guest or solvent molecules were disordered at the S_4 channels. Similar behavior was observed when the medium-length *ebz* molecules were used as guest molecules. When the long length monopodal molecules such as *ppz* and *bbz* or any dipodal molecules were used as guest molecules, these guest molecules could not fit at the screw channels and were observed only at the S_4 channels.

Table 2 summarizes the host-guest interactions of tunable host networks based on the size and shape of the host and guest molecules. The three-dimensional cavities of 3-D networks can host either monopodal or dipodal guests in their screw channels in a fairly ordered fashion if the podal lengths of the guests are short or medium. The one-dimensional cavities of 3-D networks can only host the short or medium length monopodal guests in their screw channels in a fairly ordered fashion, and no dipodal guests were observed in the screw channels.

The host networks with three-dimensional or one-dimensional cavities are not stable in air or in solution other than in the mother liquor. They lose their crystallinities within a day in air or within a few minutes in organic solvent. However, the bound guests at the screw channels generally increase the stability of the host-guest networks in air. The *dep*-bound 3-D network host, $[\text{Mn}_6(\text{pshz})_6(\text{bpea})_2(\text{dmf})_2]_n(\text{dep})_m$, showed remarkable stability in air. Even after exposure in air for more than a month, the guest bound host crystals diffract significantly. Unfortunately, even these crystals lose their crystallinities when soaked in organic solvent.

By modulation of the *SBU*s derived from the primary building units, we could construct isostructural but tunable

Table 2. Guest Molecules in the Host Networks

host network	monopodal guests					dipodal guests			
	<i>mbz</i>	<i>ibp</i>	<i>ebz</i>	<i>pbz</i>	<i>bbz</i>	<i>dmp</i>	<i>dep</i>	<i>dpp</i>	<i>dbp</i>
[Mn ₆ (ashz) ₆ (bpea) ₂ (dmf) ₂], 1	(4 ₁ , S ₄) ^a	(4 ₁ , S ₄) ^a	(4 ₁ , S ₄) ^c	(S ₄) ^d	(S ₄) ^d	(4 ₁ , S ₄) ^c	(4 ₁ , S ₄) ^a	(S ₄) ^b	(S ₄) ^d
[Mn ₆ (pshz) ₆ (bpea) ₂ (dmf) ₂], 2	(4 ₁ , S ₄) ^c	(4 ₁ , S ₄) ^a	(4 ₁ , S ₄) ^a	(S ₄) ^b	(S ₄) ^b	(4 ₁ , S ₄) ^a	(4 ₁ , S ₄) ^a	(S ₄) ^b	(S ₄) ^b
[Mn ₆ (hshz) ₆ (bpea) ₂ (dmf) ₂], 3	(4 ₁ , S ₄) ^a	(4 ₁ , S ₄) ^c	(4 ₁ , S ₄) ^a	(S ₄) ^b	(S ₄) ^b	(S ₄) ^d	(S ₄) ^b	(S ₄) ^b	(S ₄) ^b

^a Guest molecules at the screw channels were confirmed by X-ray crystallography. ^b IR spectrum indicated the presence of the guest molecules at the channel cavities. However, no ordered guest molecules were observed at the screw channels in the crystal structure. ^c IR spectrum indicated the presence of the guest molecules at the channel cavities, but the presence of the guest molecules at screw channels was not confirmed by X-ray crystallography. ^d IR spectrum indicated the presence of the guest molecules at the channel cavities, but the absence of the guest molecules at screw channels was not confirmed by X-ray crystallography.

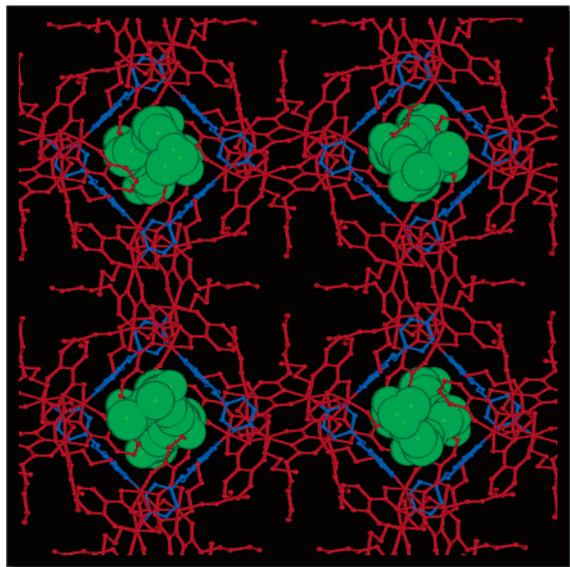


Figure 7. Host–guest network, [Mn₆(hshz)₆(bpea)₂(dmf)₂]_n·x(*mbz*), **22**. The view along the crystallographic *c*-axis. The disordered short length monopodal guest *mbz* molecule is observed in the screw channel of the one-dimensional cavity. Monopodal guest molecules are aligned along the screw channels.

host networks with different cavity sizes and shapes. With *N*-acetyl salicylhydrazidate or *N*-propionyl side chains at the

primary building unit, the host networks have a 3-D network with three-dimensional cavities. With *N*-hexanoyl side chains at the primary building unit, the host network keeps the isostructural 3-D network but with two types of one-dimensional channels of reduced cavity volume.

The tuned host networks showed not only size selectivity for the guest molecules but also shape selectivity. While the three-dimensional channeled host showed selectivity depending on the length of the podal guests, the one-dimensional channeled host showed selectivity depending on both the length and/or the podality of the guest molecules.

In this study, we could construct tunable host networks based on modulation of the *SBU*s, and these host networks showed guest selectivity based on the shapes and dimensionalities of the tuned host cavities.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination and details on the crystallographic studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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