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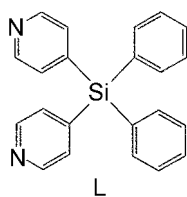
19 Å-Thick Sheet Consisting of Cages

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Interest in nanoporous materials stems from well-defined applications such as photoelectronic devices, ion exchangers, molecular sieves, sensors, biomimetics, catalysts, and artificial storages.¹⁻⁵ Significant progress has been made in the tubular materials by self-assembly of metal halides with specifically designed building blocks,⁶⁻⁸ even though serendipitous motifs have been sometimes constructed owing to the presence of unpredictable weak interactions. Among such building blocks, silicon-containing pyridyl ligands have been used as interesting spacers.⁹⁻¹¹ The exploitation of bis(4-pyridyl)diphenylsilane (L) has been hardly explored except for Pd^{II} and Pt^{II} rhomboids reported by Stang's group.¹² The spacer possesses a potential bidentate, a tetrahedral angle (N-Si-N, ~109°), an appropriate pyridyl length, conformational nonrigidity, and bulkiness. In particular, silver(I) ion has been employed as various directional units such as linear, tetrahedral, or T-shape.¹³ We report a unique 19 Å-thick network consisting of cages along with its physicochemical properties.



Experimental Section

Materials and Measurements. AgClO₄ and NaX (X⁻ = PF₆⁻, NO₃⁻) were purchased from Aldrich and Junsei Chemical Co., respectively, and were used without further purification. The ligand L was prepared by the literature procedure.¹² Elemental microanalyses (C, H, N) were performed on crystalline samples by the Advanced Analysis Center at KIST using a Perkin Elmer 2400 CHN analyzer. Thermal analyses were carried out under a dinitrogen

atmosphere at a scan rate of 10 °C/min using a Stanton Red Croft TG 100. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellets.

Preparation of [Ag^IL₂](ClO₄). A methanol solution (15 mL) of L (85 mg, 0.25 mmol) was slowly diffused into an aqueous solution (15 mL) of AgClO₄·H₂O (28 mg, 0.12 mmol). Colorless crystals of [Ag^IL₂](ClO₄) formed at the interface, and were obtained in 3 days in 80% yield. mp. 110 °C (dec). IR (KBr, cm⁻¹): ν(ClO₄), 1120 (s). Anal. found: C, 59.40; H, 4.17; N, 6.36. Calcd for C₄₄H₃₆N₄O₄ClSi₂Ag: C, 59.76; H, 4.10; N, 6.34.

X-ray Crystallography. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated MoKα radiation (λ = 0.71073 Å) and a CCD detector at ambient temperature. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The structures were solved by the Patterson method (SHELXS 97) and refined by full-matrix least square techniques (SHELXL 97).¹⁴ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated

Table 1. Crystallographic Data for [Ag^IL₂](ClO₄)

formula	C ₄₄ H ₃₆ N ₄ O ₄ ClSi ₂ Ag
f.w.	884.27
space group	C2/c
a, Å	9.529(1)
b, Å	18.928(2)
c, Å	23.969(3)
V, Å ³	4260.6(8)
Z	4
d _{calc} , gcm ⁻³	1.379
μ, mm ⁻¹	0.638
Crystal size (mm ³)	0.05 × 0.2 × 0.3
Completeness to theta = 27.46	98.1%
Data/restraints/parameters	5181 / 0 / 254
R {I > 2σ(I)}	R ₁ = 0.0617
	wR ₂ = 0.1090

$$R_1 = \frac{\sum |F_o| - F_c|}{\sum |F_o|}, wR_2 = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}^{1/2}$$

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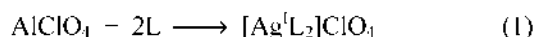
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positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-234705). The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/per/careq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The slow diffusion of AgClO_4 with L in water/methanol produced colorless crystals. Formation of the product was not significantly affected by the change of the reactant mole ratio, solvents, and the concentrations, indicating that the product has a favorable structure. The crystalline product is air-stable and insoluble in water and common organic solvents. X-ray characterization on a single crystal has provided a 2D coordination polymer composed of $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$ unit (eq. 1). Selected bond length and angles are listed in Table 2. The skeletal structure is the network consisting of Ag and L (1 : 2). Four L spacers are



coordinated to a Ag^{I} ion ($\text{Ag-N} = 2.321(5) \text{ \AA} - 2.377(5) \text{ \AA}$) in a tetrahedral arrangement (the bond angles around Ag = $90.8(3)^\circ - 127.2(2)^\circ$) to form a $[\text{Ag}^{\text{I}}]_4$ 40-membered motif. The motif generates about 19 Å-thick network consisting of cages (Figure 1). The unusual thickness may be induced to the presence of diphenyl groups of L. The cage has a $7 \text{ \AA} \times 8 \text{ \AA}$ square pore. Each ClO_4^- anion is nestled as a simple counteranion in a cage (the shortest $\text{Ag} \cdots \text{O} = 4.61 \text{ \AA}$). The

Table 2. Relevant Bond Distances (Å) and Angles ($^\circ$) of $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$

Ag-N(1)	2.321(5)	Ag-N(1)#1	2.321(5)
Ag-N(2)#2	2.377(5)	Ag-N(2)#3	2.377(5)
Si(1)-C(17)	1.851(7)	Si(1)-C(11)	1.851(6)
Si(1)-C(8)	1.875(6)	Si(1)-C(3)	1.882(6)
N(2)-Ag#4	2.377(5)		
N(1)-Ag-N(1)#1	115.0(3)	N(1)-Ag-N(2)#2	98.65(19)
N(1)#1-Ag-N(2)#2	127.2(2)	N(1)-Ag-N(2)#3	127.2(2)
N(1)#1-Ag-N(2)#3	98.7(2)	N(2)#2-Ag-N(2)#4	390.8(3)
C(17)-Si(1)-C(11)	110.5(3)	C(17)-Si(1)-C(8)	111.1(3)
C(11)-Si(1)-C(8)	108.9(3)	C(17)-Si(1)-C(3)	109.5(3)
C(11)-Si(1)-C(3)	111.2(3)	C(8)-Si(1)-C(3)	105.5(3)
C(1)-N(1)-C(5)	115.6(6)	C(1)-N(1)-Ag	121.0(5)
C(5)-N(1)-Ag	119.6(4)	C(10)-N(2)-C(6)	115.0(6)
C(10)-N(2)-Ag#4	127.5(5)	C(6)-N(2)-Ag#4	114.9(4)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+1/2$; #2 $x+1/2, y+1/2, z$; #3 $-x+1/2, y+1/2, -z+1/2$; #4 $x-1/2, y-1/2, z$

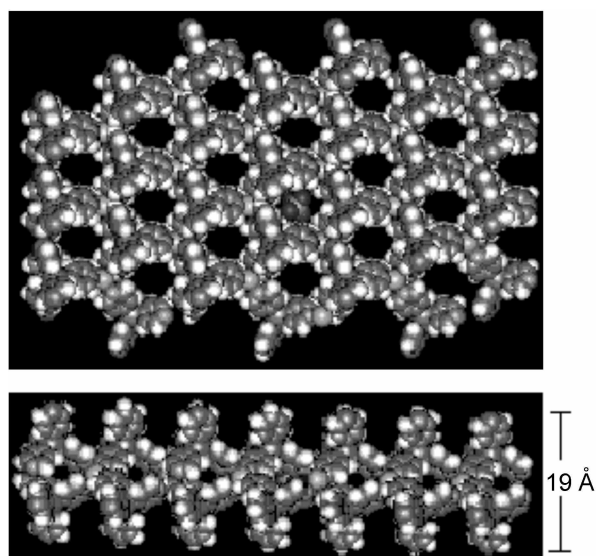
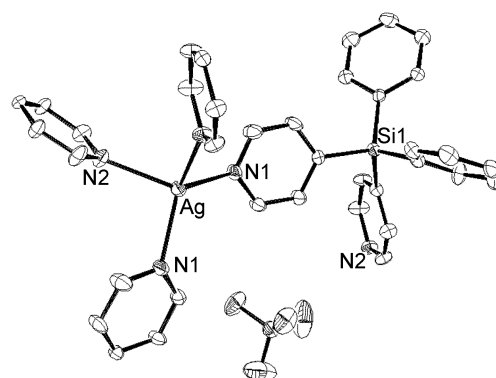
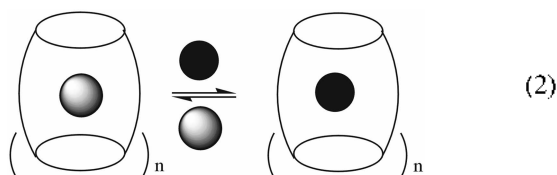


Figure 1. An ORTEP drawing of the unit of $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$ (top). Top view space-filling of the infinite structure (middle). Side view of the infinite structure (bottom).

two intraplanar $\text{Ag} \cdots \text{Ag}$ distances are 18.93 and 9.53 Å. The inner part of the nanometer-thick sheet is consisted of hydrophilic Ag, N, O atoms, and the outer part is covered by the hydrophobic phenyl groups. A combination of the tetrahedral geometry of Ag^{I} ion and Si^{IV} with the appropriate length, conformation, angle, and bulkiness of L seems to afford the formation of the porous skeleton. The low calculated density ($\rho_c = 1.38 \text{ g cm}^{-3}$) compared to that ($\rho_c = 1.80\text{--}2.10 \text{ g cm}^{-3}$)¹⁵ of the analogs may be ascribed to the vacant porous structure. The face-to-face (π - π) stackings between/among aromatic rings do not exist within the skeletal structure and even between interplates.

For the cationic skeletal structure, the anion exchange¹⁵ (see the reference 15 for the detailed exchange procedure) was carried out to prove the porous properties. Initial evaluation revealed that the anion exchange of $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$ with PF_6^- anion smoothly occurs (eq. 2). During the anion exchange, the infrared spectra show the gradual disappearance of intense ClO_4^- bands (1120 cm^{-1}) and the appearance and growth of new PF_6^- bands (840 cm^{-1} and 558 cm^{-1}). The ClO_4^- peaks disappear completely after 1 day (Supporting information). The other peaks of the

spectrum remain virtually unchanged, suggesting that the skeleton is retained after the anion exchange. The elemental analysis (Anal. Calcd for $[\text{Ag}^{\text{I}}\text{L}_2](\text{PF}_6)$, $\text{C}_{44}\text{H}_{36}\text{N}_3\text{F}_6\text{PSi}_2\text{Ag}$: C, 56.84; H, 3.90; N, 6.03. Found: C, 56.40; H, 3.88; N, 6.06) is consistent with the expected structure. However, the anion exchange of $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$ with NO_3^- or SO_4^{2-} was not carried out in a similar condition. Such results indicate that the exchangeability is ascribed to the electronic properties of anions. $[\text{Ag}^{\text{I}}\text{L}_2](\text{ClO}_4)$ is not thermally robust, and is collapsed around 110 °C (Supporting information). Such thermal properties may be attributed to the conformational constraint and the long Ag-N bond distance.



In conclusion, the unique 2 nm-thick porous network has been synthesized. This network is significant as a rare example of metalloid nano-plate covered by the organic group with a periodic array of cages. Further experiments will provide more detailed information on the development of the deep porous molecular networks.

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References

- Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.
- Khazanovich, N.; Granja, J. R.; McRee, D. E.; Milligan, R. A.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 6011.
- Meissner, R. S.; Rebek, Jr., J.; de Mendoza, J. *Science* **1995**, *270*, 1485.
- Yao, Z.; Postma, H. W. C.; Balents, L.; Dekker, C. *Nature* **1999**, *402*, 273.
- Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
- Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049.
- Fenniri, H.; Mathivanan, P.; Vidale, K. L.; Sherman, D. M.; Hallagna, K.; Wood, K. V.; Stowell, J. G. *J. Am. Chem. Soc.* **2001**, *123*, 3854.
- Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304.
- Jung, O.-S.; Kim, Y. J.; Kim, K. M.; Lee, Y.-A. *J. Am. Chem. Soc.* **2002**, *124*, 7906.
- Jung, O.-S.; Lee, Y.-A.; Kim, Y. J. *Chem. Lett.* **2002**, 1096.
- Jung, O.-S.; Lee, Y.-A.; Kim, Y. J.; Hong, J. *Cryst. Growth Des.* **2002**, *2*, 497.
- Schmitz, M.; Leininger, S.; Fan, J.; Arif, A. M.; Stang, P. J. *Organometallics* **1999**, *18*, 4817.
- Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1998**, *46*, 173.
- Sheldrick, G. M. *SHELXS-97: A Program for Structure Determination*; University of Göttingen: Germany, 1997; Sheldrick, G. M. *SHELXL-97: A Program for Structure Refinement*; University of Göttingen: Germany, 1997.
- Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, J. K.; Chae, H. K. *J. Am. Chem. Soc.* **2000**, *122*, 9921.