# A 20-Å-Thick Interwoven Sheet Consisting of Nanotubes

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Interest in nanotubular materials stems from well-defined applications such as photoelectronic devices, ion exchange, molecular sieves, sensors, biomimetics, catalysts, and artificial storages.[1-7] Significant progress has been made in the tubular materials by the idea of self-assembly of specifically designed building blocks including the flexibility, the length, and the angle,[8-11] even though serendipitous motifs sometimes have been constructed owing to the presence of unpredictable weak interactions.[12,13] We have demonstrated that a series of ($n$-Py)$_2$X ($n$ = 2, 3; X = O, S) linkers are useful tectonics for various functional structures.[14-18] Among various building linkers, the exploitation of silicon-containing pyridine-based units hardly has been explored except for Pd(II) and Pt(II) rhomboids of bis(4-pyridyl)dimethylsilane (Me$_2$Si(4-Py)$_2$ = **L**) reported by Stang's group.[19] The linker possesses a potential bidentate, a tetrahedral angle (N−Si−N, ∼109°), an appropriate bipyridyl length, conformational nonrigidity, and manageable properties. The silver(I) ion has been employed as unique directional units such as linear or T-shape.[20] We report a new conceptual nanotubular sheet constructed by interweaving of two independent [Ag(I)-**L**] undulating networks along with its anion exchangeability and thermal behaviors.

The slow diffusion of AgNO$_3$ with **L** in water/methanol produced colorless crystals.[21] Formation of the product was not significantly affected by the change of the reactant mole ratio, solvents, and the concentrations. The crystalline product is air-stable and insoluble in water and common organic solvents. X-ray characterization[22] on a single crystal has provided a coordination network composed of the building block [Ag$_3$**L**$_4$](NO$_3$)$_3$·H$_2$O (**1**) (Scheme 1). The skeletal structure is the network consisting of Ag and **L** (3:4). Each **L** connects two Ag(I) ions (Ag−N = 2.14(1)−2.34(1) Å) to form an oblong [Ag(I)]$_8$ *80-membered* motif. For the network structure, *two-coordinate Ag(I) and three-coordinate Ag(I) ions* coexist in an 1:2 ratio. The angle around the two-coordinate Ag(I) ion (N−Ag−N = 160.1(6)°) is deviated from the typical two-coordinate angle of 180°, owing to the presence of the weak interaction with a NO$_3^-$ anion (the shortest Ag⋯O, 2.51(4) Å). The other NO$_3^-$ anions exist as simple counteranions. The side view of the network is an undulating sheet to sustain the tetrahedral Si(IV) geometry. One undulating network is *threaded* through the 80-membered rings of another independent identical network, thus forming a polycatenated 2- *nm-thick* (∼20 Å) sheet. The most fascinating feature is that unique *nanotubes* are formed via the two-layer interwoven[23,24] sheets (Figure 1). The tunnel has a 16 × 18 Å$^2$ cross section with a 7 × 8 Å$^2$ square pore. The square pore size and shape are similar to those of the single-walled carbon nanotube. A combination of the geometrically diverse Ag(I) ion with the appropriate length, conformation, angle, and steric effects of **L** seems to afford the formation of the interwoven porous skeleton. The low calculated
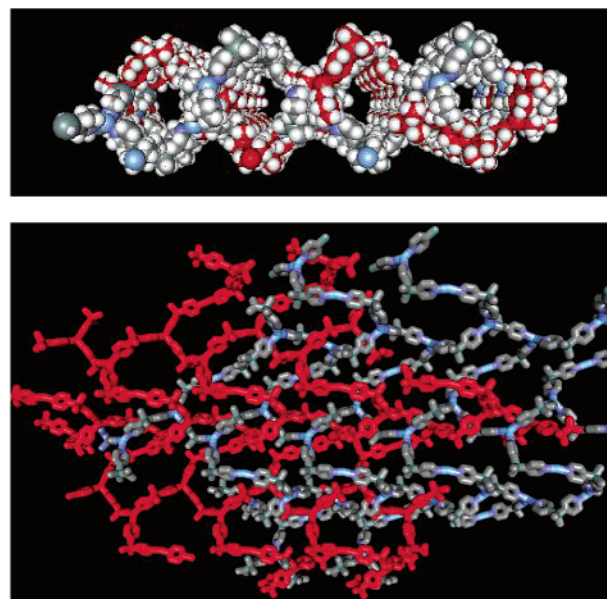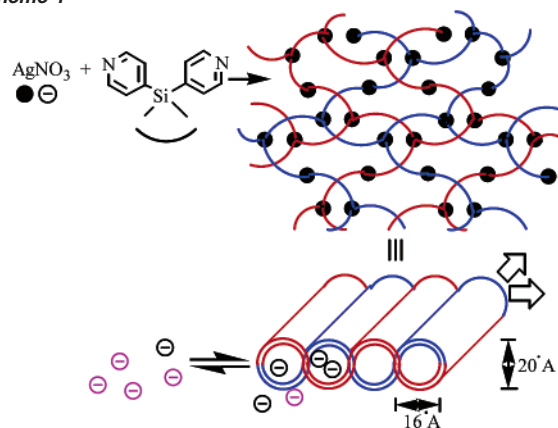


**Figure 1.** Space-filling side view showing the nanotubes (top) and stick view showing the interwoven sheet (bottom) of **1**. Anions and solvate water molecules were omitted for clarity.

**Scheme 1**



density ($\rho_c$ = 1.55 g cm$^{-3}$) compared to that ($\rho_c$ = 1.80−2.10 g cm$^{-3}$)[14,15,24] of the analogues may be ascribed to the channel structure.

Although the interwoven sheet suggests an ideal porous skeletal structure, it does not by itself prove that the sheet behaves as a nanotunnel. For the cationic nanotunnel, the anion exchange was carried out to reversibly prove the porous properties. Initial evaluation revealed that the anion exchange of **1** with the NO$_2^-$ anion smoothly occurs.[25,26] During the anion exchange, the infrared spectra show the gradual disappearance of intense NO$_3^-$ bands (1352 cm$^{-1}$) and the appearance and growth of new NO$_2^-$ bands

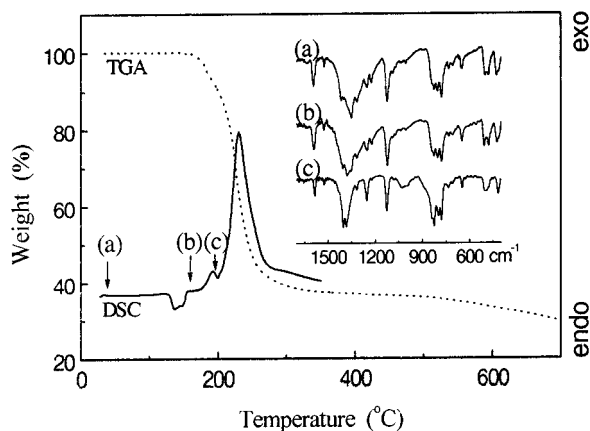* Corresponding author. E-mail: oksjung@kist.re.kr.

**Figure 2.** Overlay of TGA and DSC of **1** along with the temperature-dependent IR spectra (KBr).

(1254 cm$^{-1}$). The NO$_3^-$ peaks disappear completely after 5 h (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 [Ag$_3$L$_4$]-(NO$_2$)$_3$, C$_{48}$H$_{56}$N$_{11}$O$_6$Si$_4$Ag$_3$: C, 43.71; H, 4.28; N, 11.68. Found: C, 43.50; H, 4.27; N, 11.50) and IR spectra of the exchanged species are coincident with those of the sample obtained by the direct reaction of AgNO$_2$ with **L**. The reverse exchange of [Ag$_3$L$_4$](NO$_2$)$_3$ with NO$_3^-$ is slow. This fact can be explained by the stronger coordinating ability of NO$_2^-$ than that of NO$_3^-$. On the basis of IR data and elemental analysis it is estimated that after 2 days about 65% exchange has occurred. The present robust compound that maintains structural integrity upon exchange of channel guest anions may be ascribed to the interwoven properties. The thermal properties of **1** are depicted in Figure 2. The thermogravimetric analysis shows a drastic decomposition in the temperature range 200−270 °C and does not exhibit significant weight loss up to 200 °C. An endothermic peak of the differential scanning calorimetric curve around 140 °C was found to be the melting point. The solvate water molecules seem to be evaporated around the melting point (calculated for H$_2$O/**1**: 1.3%). The exothermic peak at 193 °C suggests a prompt structural change without weight loss. In contrast to typical ionic coordination polymers, **1** sharply melts at a relatively low temperature of 140 °C, and is stable up to 185 °C. That is, **1** in the temperature range exists as an ionic liquid that has been attracted attention recently as a recyclable green solvent.[27] To our best knowledge, this is the first 2D ionic liquid. After the ionic liquid was cooled, its IR spectrum was obtained. The IR spectrum (IR(b)) is identical with the original spectrum (IR(a)), suggesting that the interwoven structure is retained during the molten state. Then, the molten **1** is melt-transformed into a new species around 193 °C, followed by drastic decomposition (maximized at 230 °C). Such a procedure is very similar to our previous results on an interwoven structure.[18] Of course, the IR spectra above 193 °C are quite different from the original spectrum (Figure 2, IRc). According to the NO$_3^-$ peak intensity in the IR (c), the free NO$_3^-$ anions begin to decompose, followed by the collapse of the **L** moiety. This fact indicates that the conformation of the highly ordered array is not sustained above 193 °C. These unusual thermal properties, including the ionic liquid, may be attributed to the interwoven structure.

In conclusion, the present compound is an advance 2-nm-thick interwoven sheet consisting of a nanatube architecture. The anion exchangeability demonstrates that small ions within and between the nanotunnel go in and out in aqueous suspension. Such a family of silicon-based bipyridine tectonics appears to have propensity for forming robust framework materials that sustain structural integrity upon exchange or loss of guest molecules. The anion exchange and thermolysis may be devoted to the development of rational synthetic strategies that cannot be approach by general methods. Further experiments will provide more detailed information on the development of tailored organic/inorganic nanomaterials with well-defined structural morphologies.

**Supporting Information Available:** Details of X-ray data of **1**, IR spectra of **1** ,and [Ag$_3$L$_4$](NO$_2$)$_3$ prepared by the direct method and the anion exchange (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) **1**: A methanol solution (6 mL) of Me$_2$Si(4-Py)$_2$ (43 mg, 0.2 mmol) was slowly diffused into an aqueous solution (6 mL) of AgNO3 (34 mg, 0.2 mmol). Colorless crystals of [Ag$_3$(Me$_2$Si(4-Py)$_2$)$_4$](NO$_3$)$_3$·H$_2$O formed at the interface and were obtained in 3 days in 80% yield. Anal. Calcd for C$_{48}$H$_{56}$N$_{11}$O$_9$Si$_4$Ag$_3$·H$_2$O: C, 41.63; H, 4.22; N, 11.12. Found: C, 41.49; H, 4.18; N, 11.14. IR (KBr, cm$^{-1}$): $\nu$(NO$_3$), 1352 (s). With acetone or ethanol instead of the methanol, the same crystals were obtained.

(22) Crystal data for **1**, C$_{48}$H$_{56}$N$_{11}$O$_9$Si$_4$Ag$_3$·H$_2$O: monoclinic, *P*2$_1$, *a* = 19.216-(4) Å, *b* = 16.339(3) Å, *c* = 20.751(5) Å, $\beta$ = 114.05(2)°, *V* = 5950(2) Å$^3$, $\rho_c$ = 1.546 g cm$^{-3}$, *F*(000) = 2800, $\lambda$ = 0.71073 Å, $\mu$ = 1.119 mm$^{-1}$, crystal size 0.20 × 0.30 × 0.35 mm$^3$, *Z* = 2, *R* (*wR2*) = 0.0492 (0.1258) on 6602 reflections with *I* > 2$\sigma$(*I*), GOF = 0.996, 1369 parameters refined. Enraf-Nonius CAD4 diffractometer. Sheldrick, G. M. *SHELXS-97* and *SHELXL-97*, Programs for Structure Determination and Refinement; University of Göttingen: Göttingen, Germany, 1997.

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