

Temperature-dependent Penetration of Argon Molecules into Ultramicroporous Tunnel of a Fluoroorganic Molecular Crystal with Alteration of Its Unit Cell Size

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A molecular crystal of octamethylene (*S,S*)-bis(2-hydroxy-3,3,3-trifluoropropanoate) with an ultramicroporous tunnel ($\phi = 2.5\text{--}2.8\text{ \AA}$) starts to adsorb argon ($\phi = 3.6\text{ \AA}$) at 150–140 K with 7% increase of the one direction of the orthorhombic unit cell. The alteration of the unit cell size indicates the penetration of argon into the tunnel and the soft nature of the microporous molecular crystal.

Study on the gas adsorption properties of porous crystal with ultramicropore has been the focus of wide interest.¹ The next target would be construction and utilization of microporous structures with dynamic functions.² To date, a number of crystalline compounds, such as interpenetrated metal assembled frameworks, have shown dynamic functions, gating phenomena in their gas adsorption processes.³

Recently, we prepared an organic crystal with an ultramicropore from the octamethylene (*S,S*)-bis(2-hydroxy-3,3,3-trifluoropropanoate) (**1**) unit molecule.⁴ The molecular crystal has an infinite ultramicroporous tunnel ($\phi = 2.5\text{--}2.8\text{ \AA}$). Figure 1 is a cross section and a bottom view of the tunnel in the crystal. The tunnel is too narrow to allow recrystallizing solvent molecules in it.

The tunnel structure has alternating gates of two facing tri-fluoromethyl (CF_3) groups and rooms surrounded by four CF_3 groups. The tunnel walls have no side holes larger than 1 \AA .⁴ The walls of the tunnel are connected by hydrogen-bonding chains and the floors are made by polymethylene backbones. The tunnel would avoid collapse by a small van der Waals attraction and possible electrostatic repulsion between two negatively charged facing CF_3 groups.⁵

A gas adsorption manometry measurement of the crystal indicated an unexpected argon gas (3.6 \AA diameter⁶) adsorption

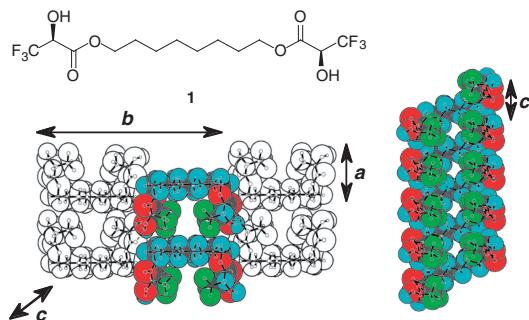


Figure 1. Cross-section view (left) and bottom view (right) of the tunnel structure found in the crystal, which was cooled by a nitrogen flow (120 K). (CCDC No. 246922).⁴ Unit cell size: $a = 8.061(2)$, $b = 22.846(5)$, $c = 5.1730(10)\text{ \AA}$.

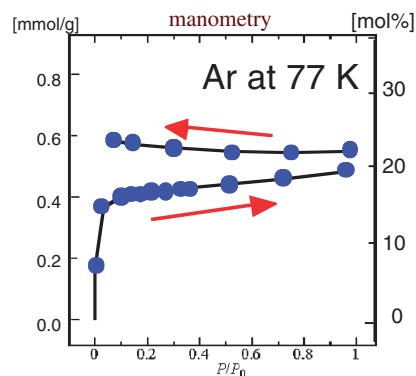


Figure 2. Adsorption-desorption isotherm curve of argon gas at 77 K by the ultramicroporous crystal of **1**, which was observed by BELSORP28SA.

(no less than 20 mol % per unit tunnel molecule). Figure 2 shows the adsorption-desorption isotherm curve of the argon gas into the crystal (needle shaped, 0.05–0.4 mm-length) at 77 K. The curve was characterized by a sharp initial rising, which would be attributed to an initial micropore filling and a large hysteresis in the degassing process. The isotherm curve could be categorized to an IUPAC type I.⁷

A gradual gas adsorption after the initial micropore filling and a large hysteresis even at the low p/p_0 region in the degassing process suggested a slow movement of the argon molecule in the macrolength tunnel.

The crystal should be swelled by penetration of argon molecules into the smaller tunnel. This was confirmed by a change in the unit cell size of the crystal under an argon atmosphere at lower temperature (Figure 3). No such change was observed under an N_2 atmosphere up to 100 K.

The crystal was put in a thin glass capillary, which was filled

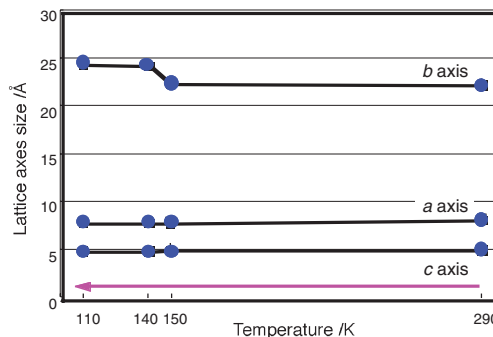


Figure 3. The effect of temperature decrease to the unit cell sizes of **1** under an argon atmosphere.

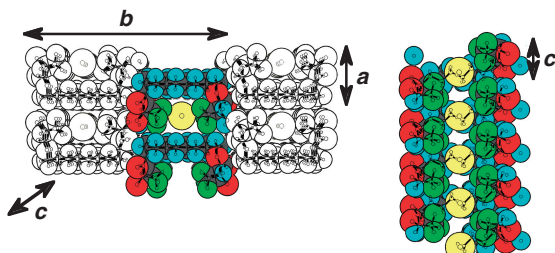


Figure 4. Cross-section view (left) and bottom view (right) of the tunnel with argon (pale yellow sphere) observed at 105 K (CCDC No. 256312).⁸ Unit cell size: $a = 7.986(1)$, $b = 24.535(4)$, $c = 5.0851(5)$ Å.

with argon gas. Then the capillary was cooled by a nitrogen flow and kept at that temperature for 3 h prior to the single crystal X-ray diffraction measurements. The crystal systems, orthorhombic, were identical throughout the examined temperatures. The unit cell size was not changed from room temperature (293 K) to 150 K. Then, it changed sharply at 140 K. The length of the b axis was increased by around 7.4% from 22.8 Å at 150 K to 24.4 Å at 140 K. Meanwhile, that of the a and the c axes was slightly decreased (<0.1 Å).

To confirm an existence of argon molecules in the crystal, single crystal X-ray analysis at 105 K was done. The analysis gave a molecular structure of the crystal of **1** bearing argon molecules, as shown in Figure 4. The argon atom was found at the center of the room surrounded by the four CF_3 groups, and occupancy of the room by the argon molecule was estimated to be 67 mol % (0.67 molecule/room). This incomplete occupation of the rooms by the argon resulted in a large R residual of the analysis.⁸ Longer precooling of the crystal at <140 K for further stuffing of argon into the tunnel caused cracks in the crystal.

We found that the expansion of the b axis was caused by a much more vertical orientation of the polymethylene chain to the direction of the hydrogen-bonding chain (c axis) (Figure 4) than that of vacant one (Figure 1).

A notable feature of the present argon gas penetration into the ultramicroscopic tunnel of the fluoroorganic molecular crystal is the small extent of stabilization of the argon molecule, in spite of the narrow tunnel width, whereas the unit cell size alteration was started at 150–140 K. Here, the boiling point of argon is 87 K.⁹ Thus, the crystal stabilizes the argon molecules only at 53–63 K (<1.3 kcal/mol).¹⁰ This small extent of the thermal stabilization would be due to a small van der Waals interaction of the lattice molecule and destabilization by possible lattice strain. Moreover, this small stabilization would allow argon molecules to go deeply into the tight-fitted tunnel-type pore.

Controlled gas loading, storage and release promoted by external conditions and stimulation is of interest in nano science.¹¹ Such material with a sharp response may have potential applicability such as a molecular valve. For the purpose, the gating phenomenon would be a key item to control the gas loading and release.⁴ The cooperative opening of the gates in the crystal, controlled by the temperature, needs further study on its dynamics and mechanisms.⁴ We are now studying this phenomenon in depth for a series of gaseous molecules and a series of tunnel crystals.

We thank The Japan Energy Corporation for a fluorinated

compound. This work was financially supported by The Mazda Foundation Research Grant, JST Innovation Plaza Hiroshima, and Okayama University Grant. We thank the VBL of Okayama University for X-ray crystal diffraction measurements and analysis.

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- Tentative structural analysis result for Ar-adsorbed crystal. (CCDC No. 256312) $\text{C}_{14}\text{H}_{20}\text{Ar}_{0.67}\text{F}_6\text{O}_6$, $M_r = 425.02$, orthorhombic, $a = 7.9865(14)$, $b = 24.635(4)$, $c = 5.0851(5)$ Å, $V = 1000.5(3)$ Å³, $T = 105$ K, space group $P2_12_12$ (# 18), $Z = 2$, $\mu(\text{Mo K}\alpha) = 2.49 \text{ cm}^{-1}$, 1395 reflections measured, 924 unique, The final $R = 0.179$, $\text{GOF} = 1.130$, Residual electron density = $0.34/-0.40 \text{ e}\text{\AA}^{-3}$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-246922 and CCDC-256312. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.jp).
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