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A Three-Dimensional Synthetic Metallic Crystal Composed of Single-Component Molecules
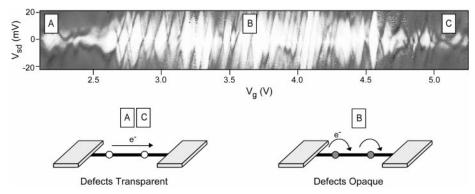
Fig. 3. Gray-scale plot of differential conductance (dI/dV_{sd}) of device D2 as a function of V_{sd} and V_g at $T = 4.2$ K. In this panel, white corresponds to zero conductance, and black corresponds to 40 μS. In regions A and C, the defects in the nanotube are tuned to transparency. In region B, the defects are tuned to result in strong electron scattering.

scattering resonances of the lower defect. If $r_1 = 0$ away from the scattering resonances, the observed resistance change yields $r_1 \sim 0.7$ at the peak of the scattering resonance. Because r_1 may not be zero off resonance, this estimate represents an upper bound for r_1. A similar analysis of defects in other samples indicates that the reflection coefficients of defects range from 0.5 to 0.7 at room temperature. The V_{tip}-induced ε_{loc} change is estimated to be ~ 50 meV/V from the comparison of the V_{tip} and V_g scans (*28*), which indicates that the resonance peaks in Fig. 2B are separated by ~ 0.5 eV in their energy positions. Both the value of r and the energy separation between resonances compare favorably with theoretical predictions for various few-atom defects in SWNTs (*11, 15–17*).

The present finding indicates that the defects in metallic nanotubes act as gate-tunable electron scatterers and SWNTs with defects can be the basis for new types of electronic devices (*14*). One example for such devices is demonstrated here by the formation of an intratube quantum dot by two defects. A gray-scale differential conductance plot measured from device D2 at temperature $T = 4$ K is shown in Fig. 3 as a function of V_{sd} and V_g. At the V_g ranges designated as regions A and C, the electron scattering by defects is minimal. In this region, the low-bias conductance of D2 never reaches zero, irrespective of V_g, and the nanotube acts as a metallic wire. In the V_g range designated as region B, on the other hand, defects act as strong electron scatterers, and the nanotube section between two defects turns into a quantum dot, as illustrated by the well-known Coulomb-blockade patterns in Fig. 3 (*29*). This dot exhibits a charging energy around 20 meV, just as expected for a quantum dot that is ~ 120 nm in length (*3*). Unlike nanotube dots reported previously, the barriers that form the intratube quantum dot can be tuned by adjusting V_g, illustrating the unique potential of defect manipulation in molecular electronic applications of SWNTs.

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23. Degenerately doped silicon wafers with a 1-μm oxide layer were dipped in a 0.1 mM solution of Fe(NO$_3$)·9(H$_2$O) in isopropanol, rinsed in hexane, and then dried. The wafers were placed in a furnace and heated under argon [600 standard cubic centimeters per minute (sccm)] and hydrogen (400 sccm) to the reaction temperature (700° to 900°C). Nanotubes were grown by flowing ethylene at 0.5 sccm for 6 min.
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28. The V_g scan (Fig. 3) shows that ~ 12 electrons per volt are added to the nanotube in the Coulomb-blockade region. The chemical potential change (~ 50 meV/V) is obtained by multiplying the number of electrons added by the mean level spacing (~ 4 meV for a 120-nm-length tube, assuming spin degeneracy). The comparison between the V_g and V_{tip} scans shows that a back gate and the AFM tip have similar local electrostatic coupling.
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30. This work was supported by the Air Force Office of Scientific Research and NIH (C.M.L.), NSF and the Office of Naval Research (M.T.), and the Dreyfus Foundation and Harvard University (H.P.).

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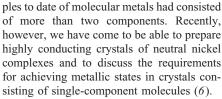# A Three-Dimensional Synthetic Metallic Crystal Composed of Single-Component Molecules

Hisashi Tanaka,[1] Yoshinori Okano,[1] Hayao Kobayashi,[1] Wakako Suzuki,[2] Akiko Kobayashi[2]*

Molecular metals normally require charge transfer between two different chemical species. We prepared crystals of [Ni(tmdt)$_2$] (tmdt, trimethylenetetrathiafulvalenedithiolate) and carried out crystal structure analyses and resistivity measurements. The analyses and measurements revealed that these single-component molecular crystals are metallic from room temperature down to 0.6 kelvin. Ab initio molecular orbital calculations suggested that π molecular orbitals form conduction bands. The compact molecular arrangement, intermolecular overlap integrals of the highest occupied and lowest unoccupied molecular orbitals, and tight-binding electronic band structure calculation revealed that [Ni(tmdt)$_2$] is a three-dimensional synthetic metal composed of planar molecules.

Semiconducting properties in phthalocyanine and condensed aromatic hydrocarbons were found around 1950 (*1, 2*), and one-dimensional molecular metals were discovered around 1970 (*3, 4*). Ever since the discovery of the organic superconductor (TMTSF)$_2$PF$_6$ (TMTSF, tetramethyltetraselenafulvalene) in

1980 (*5*), an extremely large number of molecular conductors have been developed. Until recently, however, a difficult problem in the metallization of molecular crystals had remained unsolved. In contrast to typical inorganic metals composed of single elements, such as sodium and copper, all of the exam-

ples to date of molecular metals had consisted of more than two components. Recently, however, we have come to be able to prepare highly conducting crystals of neutral nickel complexes and to discuss the requirements for achieving metallic states in crystals consisting of single-component molecules (*6*).

Here, we report the synthesis, crystal structure, resistivity, and magnetic susceptibility of a single-component molecular metal, [Ni(tmdt)$_2$] (tmdt, trimethylenetetrathiafulvalenedithiolate) (Scheme 1) (*7*).

[Ni(tmdt)$_2$]

Scheme 1.

The typical route in the design of a molecular metal is to create an electron band and generate charge carriers in molecules "A" by charge transfer to another chemical species "B." In some cases, both molecules A and B come to form conduction bands when electron and hole carriers are generated by the charge transfer between A and B. For example, organic superconductor (TMTSF)$_2$PF$_6$ is composed of π-donor molecules and inorganic anions, and molecular superconductors based on transition metal complex (TTF)[Ni(dmit)$_2$]$_2$ (TTF, tetrathiafulvalene; dmit, 4,5-dimercapto-1,3-dithiole-2-thione) contain π-donor molecules and π-acceptor transition metal complex molecules (*8*).

The design of a single-component molecular metal is difficult because most molecules have an even number of electrons and their highest occupied molecular orbital (HOMO) is usually doubly occupied. Therefore, even if a conduction band is formed, it is usually fully occupied or completely vacant. Furthermore, the compact molecular arrangement needed for orbital overlapping and band formation that comes at the cost of a large intermolecular repulsion energy is not compensated by any energy stabilization upon the formation of the band. One approach for overcoming this problem is to use stable organic radical molecules with singly occupied molecular orbitals (*9*). These molecules, however, will tend to produce a narrow half-filled band, in which electron correlation will localize the electrons, even if an electronic band is formed. Another approach is to use single-component molecules that meet the
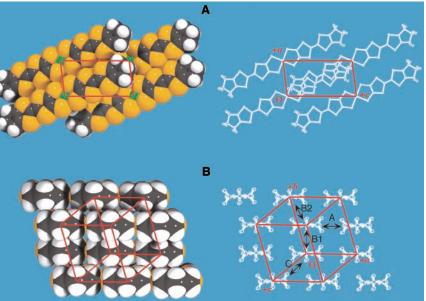
[1]Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan. [2]Research Centre for Spectrochemistry, Graduate School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

*To whom correspondence should be addressed. E-mail: akiko@chem.s.u-tokyo.ac.jp

Fig. 1. Crystal structure of [Ni(tmdt)$_2$]. Views along (**A**) the *b* axis and (**B**) the molecular long axis. The atoms are distinguished as Ni, green; S, yellow; C, dark gray; and H, white. The red lines show the frameworks of unit cells. As can be seen from (A) and (B), the "right half of the planar molecule" on (0, 0, 0) overlaps the left half of the molecule on (*a*, 0, *c*) (intermolecular interaction B2) and that on (*a*, *b*, *c*) (B1). The molecule on (0, 0, 0) has short S...S contacts with the right half of the molecule on (*a*, 0, 0) (A) and the left half of the molecule on (0, 0, *c*) (C). The intermolecular overlap integrals ($\times 10^{-3}$) of the HOMO and the LUMO calculated with an extended Hückel approximation are as follows: (i) HOMO...HOMO, A = 3.3, B1 = 6.5, B2 = 2.3, and C = 4.4; (ii) LUMO...LUMO, A = 3.6, B1 = −7.5, B2 = −3.4, and C = −5.1; and (iii) HOMO...LUMO, A = 0, B1 = −7.1, B2 = −2.8, and C = −4.8. These intermolecular overlap integrals are of the same order of magnitude as those of usual organic π molecular metals and show the 3D nature of the band structure.

following fundamental requirement to generate a metallic or semimetallic band: The energy separation between HOMO and the lowest unoccupied molecular orbital (LUMO) should be small enough to make the HOMO and LUMO bands overlap each other by two-dimensional or three-dimensional (3D) intermolecular interactions and to form partially filled bands.

The synthesis of tmdt ligand moiety with the cyanoethyl protecting group was performed according to the reported methods (*10, 11*). All of the synthetic procedures were carried out under a strictly inert atmosphere with the Schlenk technique because the anionic states of metal complexes are very sensitive to oxygen. The coordination of the ligands to the metal was also performed according to the reported method (*10*). Black plate crystals were obtained electrochemically from acetonitrile solution containing (Me$_4$N)$_2$[Ni(tmdt)$_2$] in H-shaped glass cells with Pt electrodes by applying a 0.2-μA current for 20 days. The crystals were insoluble in conventional organic solvents and stable in air. The composition was determined by electron probe x-ray microanalysis and elemental analysis (*12*).

Neutral [Ni(tmdt)$_2$] molecules crystallize into a very simple and closely packed structure with triclinic unit cell (Fig. 1) (*13*). A unit cell contains only one molecule

located on the lattice point. The molecule is ideally planar even in the terminal trimethylene groups. The deviations of carbon atoms from the least squares plane of NiC$_{12}$S$_{12}$ are less than 0.04 Å. There are many short S...S contacts between neighboring molecules in the *ac* plane and also along the [111] direction. These structural features suggest that the system has 3D intermolecular interactions.

A single-crystal resistivity measurement was made nearly along the *a* axis down to 0.6 K with the four-probe method. The room-temperature (RT) conductivity σ(RT) was 400 S cm^{-1}, which is almost one order of magnitude greater than those of typical BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] organic superconductors (*14*). The neutral [Ni(tmdt)$_2$] crystal was metallic down to 0.6 K (Fig. 2) and thus can be described as a single-component molecular metal (*15*). The crystal structure and resistivity show that this system has removed the boundary between molecular crystals and metallic crystals. A compacted powder sample also gave a very high conductivity [σ(RT) = 200 S cm^{-1}] and exhibited metallic behavior suggesting the small anisotropy of the resistivity, which is consistent with the 3D nature of the system. The susceptibility measured on a polycrystalline sample with a superconducting quantum interference device (SQUID) magnetometer
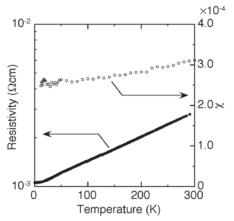
Fig. 2. Temperature dependence of the resistivity (●) and magnetic susceptibility χ (○) of $[Ni(tmdt)_2]$ crystals. The resistivity was measured on single crystals down to 0.6 K. The susceptibility was measured with a SQUID magnetometer. The contributions from paramagnetic impurities and diamagnetic susceptibilities were corrected $[\chi_{para}(RT) = 3.1 \times 10^{-4}$ emu mol^{-1} at 300 K].

exhibited an approximately temperature-independent paramagnetic susceptibility (2.6 to 3.1×10^{-4} emu mol^{-1}) consistent with the metallic nature of the system.

We have reported ab initio molecular orbital (MO) calculations on analogous molecule $[Ni(ptdt)_2]$ with extended TTF ligand (ptdt, propylenedithiotetrathiafulvalenedithiolate) at the Hartree-Fock level and by Becke's three-parameter hybrid density functional method using the Lee-Yang-Parr correlation functional (B3LYP), which shows that the HOMO and LUMO are π-like molecular orbitals with b_{2g} and b_{1u} symmetries, respectively, with the HOMO-LUMO energy separation (ΔE) being very small (6). As shown in Fig. 3A, almost the same wave functions with a π character were obtained for HOMO and LUMO of $[Ni(tmdt)_2]$. These molecular orbitals can be roughly considered to be constructed from bonding and antibonding combinations of the "wave function" on the left TTF-like ligand (ϕ_1) and that on the right TTF-like ligand (ϕ_2) (ϕ_1 and ϕ_2 closely resemble HOMO of a TTF-like π-donor molecule having the same sign on every S atom but the opposite sign on carbon atoms): $\phi(HOMO) = \phi_1 + \phi_2$, $\phi(LUMO) = \phi_1 - \phi_2$. Therefore, the $[Ni(tmdt)_2]$ molecule has not only a structurally but also an electronically close relation with TTF-like π-donor molecules. The small HOMO-LUMO energy separation (ΔE) suggested from the ab initio MO calculations is consistent with the small overlap integral between ϕ_1 and ϕ_2. We used these results to perform tight-binding band structure calculations of $[Ni(tmdt)_2]$ crystals. To simplify the calculations, we used the HOMO and LUMO obtained by a simple extended Hückel approximation, which were
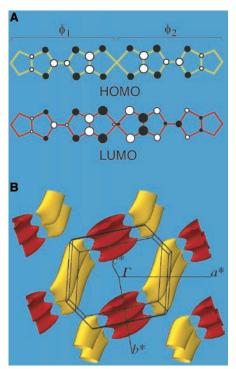

Fig. 3. (**A**) Schematic drawings of HOMO and LUMO of $[Ni(tmdt)_2]$ obtained by ab initio calculations. The open and solid circles indicate the plus and minus signs of the wave function on each atom, and the size of the circle indicates the amplitude. Roughly speaking, HOMO and LUMO are constructed from bonding and antibonding combinations of "wave functions" ϕ_1 and ϕ_2. (**B**) Calculated Fermi surfaces. The red and yellow Fermi surfaces denote electron and hole surfaces, respectively. ΔE is assumed to be 0.1 eV (see text). The intermolecular overlap integrals are given in the caption of Fig. 1.

almost the same as those obtained by the ab initio calculations.

The intermolecular overlap integrals given in Fig. 1 show that the system has a 3D π band. As suggested previously (6), 3D intermolecular interaction is considered to produce sufficiently large Fermi surfaces even when the HOMO and LUMO form "crossing bands." Extended Hückel MO calculations suggested that ΔE is 0.10 eV for $[Ni(tmdt)_2]$ and 0.12 eV for $[Ni(ptdt)_2]$, which is consistent with the result of ab initio calculations suggesting a small ΔE value. Because it is difficult to estimate ΔE precisely, the band calculations were performed while varying ΔE; the system had a 3D Fermi surface for $\Delta E < 0.6$ eV. The calculated Fermi surfaces are shown in Fig. 3B. Electron and hole Fermi surfaces are arranged alternately in the plane approximately parallel to the a^*-b^* and c^* axes (16).

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12. The results of an elemental analysis are as follows: found value% (calculated value%) C, 32.33 (32.18); H, 1.83 (1.80); N, 0.00 (0.00); S, 57.02 (57.28). The calculated value% is calculated as neutral $[Ni(tmdt)_2]$, $C_{18}H_{12}NiS_{12}$.
13. The crystal structure determination was made with a crystal with a size of 0.1 mm by 0.05 mm by 0.03 mm. Considering the small size of the crystal, a diffraction experiment was made on a Rigaku MERCURY charge-coupled device system at 123 K to collect a sufficient number of reflections. The lattice constants are $a = 6.376 \pm 0.003$ Å, $b = 7.359 \pm 0.001$, $c = 12.012 \pm 0.007$, $\alpha = 90.384° \pm 0.007°$, $\beta = 96.688 \pm 0.004$, $\gamma = 103.587 \pm 0.004$, and $V = 543.7 \pm 0.004$ Å^3 with space group $P\bar{1}$. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R value based on the 5905 reflections $[I > 2.0\sigma(I)]$ was 0.069. Crystallographic data in CIF format for $[Ni(tmdt)_2]$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC). The coordinates can be obtained, on request, from CCDC (12 Union Road, Cambridge CB2 1EZ, UK; fax: 011-44-1223-336-033; www.ccdc.cam.ac.uk/conts/).
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15. The possibility of metallic conduction has been suggested in the crystal of the neutral $[Ni(C_{10}H_{10}S_8)_2]$ complex in the small temperature region of 300 to 275 K $[\sigma(RT) = 10^{-1}$ S cm$^{-1}]$ [N. L. Narvor *et al.*, *J. Chem. Soc. Chem. Commun.* **1996**, 1363 (1996)]. Very recently, the possibility of a metallic state in the crystal of the neutral gold dithiolene complex $[\sigma(RT) = 6$ S cm$^{-1}]$ has also been suggested [D. Belo *et al.*, *Chem. Eur. J.* **7**, 511 (2001). To our knowledge, there has been no well-defined single-component molecular conductor showing a clear metallic behavior or conductivity comparable to those of usual molecular metals (>20 S cm^{-1}) in the wide temperature range (e.g., down to 100 K). In this light, it may be noteworthy that superconductivity has been found in such crystals as pentacene, tetracene, and anthracene, constructing field effect transistors [J. H. Schön, Ch. Kloc, B. Batlogg, *Nature* **406**, 702 (2000)].
16. To our knowledge, there is no 3D molecular metal with an experimentally confirmed band structure. We are planning to perform magnetoresistance experiments in the near future to obtain detailed information on the Fermi surfaces of the $[Ni(tmdt)_2]$ crystal.
17. We thank K. Sugimoto for the x-ray experiment and N. Inamoto for IUPAC nomenclature. H.K. and A.K. wish to dedicate this report to A. E. Underhill, who has made pioneering works on highly conducting transition metal complexes including systems with extended TTF ligands and who recently retired from the University of Wales, UK. This work was supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan.