

Crystals and Nanosticks of $(\text{EDO-TTFVO})_2 \cdot \text{FeCl}_4 \cdot (\text{DCE})_{0.5}$ ($X = \text{Cl}, \text{Br}$) Obtained by Electrochemical Oxidation of EDO-TTFVO with Native and Phospholipid-Modified Silicon Wafer Electrodes

Xiangfeng Shao¹, Sayo Yokota¹, Tadahiro Koike¹, Hideki Fujiwara¹, Toyonari Sugimoto¹,
Dominique de Caro², Lydie Valade²

¹ Department of Chemistry, Graduate School of Science, Osaka Prefecture University

² Laboratoire de Chimie de Coordination du CNRS, France

Current interest for the molecular conductors is directed to the coexistence of metallic conductivity and ferromagnetism by virtue of the interaction between the conducting π electrons and the localized spins on the counteranion. Electrocrystallization is an effective method to prepare magnetic molecular conductors, which are commonly obtained as the single crystals and hardly integrable to the devices. By fine tuning of the electrocrystallization conditions, i.e. the working electrode, the nanowires and nanosticks of the molecular conductors can also be obtained. We have reported the formation of the nanowires of $(\text{EDT-TTFVO})_4 \cdot (\text{FeCl}_4)_2$ by electrochemical oxidation of EDT-TTFVO using a phospholipid-modified silicon wafer as anode.^[1] However, the nanowires showed semiconducting behavior. To explore the metallic nanowires, a chemical modification of EDT-TTFVO was carried out by replacing the ethylenedithio (EDT) group with ethylenedioxy (EDO). Here, we report the syntheses and properties of the bulk crystals of the metallic $(\text{EDO-TTFVO})_2 \cdot \text{FeX}_4 \cdot (\text{DCE})_{0.5}$ ($X = \text{Cl}, \text{Br}$) salt and the corresponding nanosticks obtained by electrocrystallization using native and phospholipid-modified silicon wafers as anodes, respectively.

A piece of undoped (100)-oriented silicon wafer was used as anode in the electrochemical oxidation of EDO-TTFVO in 1,2-dichloroethane (DCE) containing a supporting electrolyte, $\text{NBu}_4 \cdot \text{FeX}_4$ ($X = \text{Cl}, \text{Br}$), with a constant current of $0.1 \mu\text{A}$ at room temperature. After several weeks, black-colored platelet crystals with a molecular formula of $(\text{EDO-TTFVO})_2 \cdot \text{FeX}_4 \cdot$

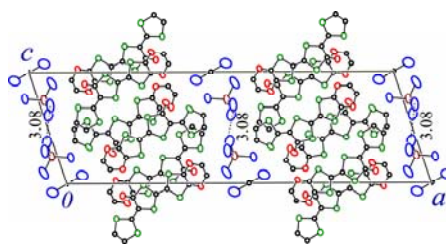
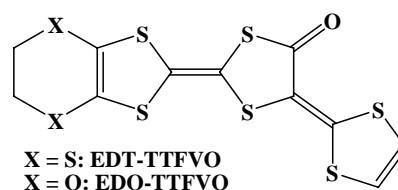


Fig. 1 Crystal structure of $(\text{EDO-TTFVO})_2 \cdot \text{FeCl}_4 \cdot (\text{DCE})_{0.5}$, projected along the b -axis.

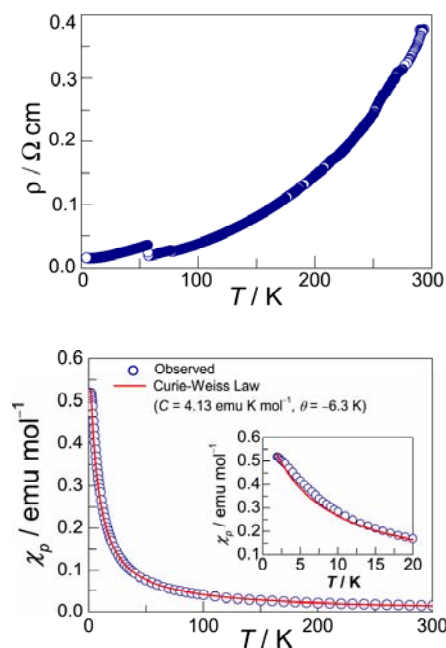


Fig. 2 Temperature-dependences of the resistivity ρ (top panel) and paramagnetic susceptibility χ_p (bottom panel) of $(\text{EDO-TTFVO})_2 \cdot \text{FeCl}_4 \cdot (\text{DCE})_{0.5}$.

(DCE)_{0.5} were obtained. The crystal structures of FeCl₄⁻ and FeBr₄⁻ salts are isostructural to each other. Fig. 1 shows the crystal structure of (EDO-TTFVO)₂•FeCl₄•(DCE)_{0.5} salt. The crystal is composed of alternating conducting layers of EDO-TTFVO molecules and insulating layers of FeCl₄⁻ ions and DCE molecules in a 2 : 1 ratio. Due to the disorder of the anion, the Cl...Cl short contacts between the neighboring two FeCl₄⁻ ions were observed along the *c*-axis (3.08 Å) and stacking axis (2.96 Å), which implies the relatively strong interaction between the anions. In the conducting layers, the donor molecules form β'-type packing pattern. In the diagonal and side-by-side arrays, there are multiple S...S, S...O, and O...O contacts shorter than the sum of the van der Waals radii, which favor the formation of the two-dimensional intermolecular interactions as observed in this salt. Based on the crystal structures, the tight-binding calculation provides two-dimensional Fermi surfaces for both salts. Consistent with the calculated band structures, both salts exhibit metallic behavior down to 5 K (Fig. 2), however, their room temperature resistivities are not so small (0.38 and 0.56 Ω cm for FeCl₄⁻ and FeBr₄⁻ salts, respectively). The paramagnetic susceptibilities (χ_p) for both salts obey a Curie–Weiss law with the following Curie constants (*C*) and Weiss temperatures (*θ*): *C* = 4.13 emu K mol⁻¹ and *θ* = -6.3 K for FeCl₄⁻ salt, and *C* = 4.24 emu K mol⁻¹ and *θ* = -19 K for FeBr₄⁻ salt.

On the other hand, a whole surface of the silicon wafer as above was soaked by adding several drops of MeOH/CHCl₃ solution of a polymerizable phospholipid. The thorough solvent evaporation and the subsequent irradiation with 254 nm UV light for 3 minutes brought about the formation of stable phospholipid-based multilamellas on the surface of the silicon wafer. This silicon wafer was used as anode in the electrochemical oxidation of EDO-TTFVO under the same conditions as described above. After several weeks, the nanosticks were obtained as shown in Fig. 3. Raman spectra indicate that the nanosticks should have the same structure to that of the bulk crystals of (EDO-TTFVO)₂•FeX₄•(DCE)_{0.5}. Further investigation of the transport properties for the nanosticks is in progress.

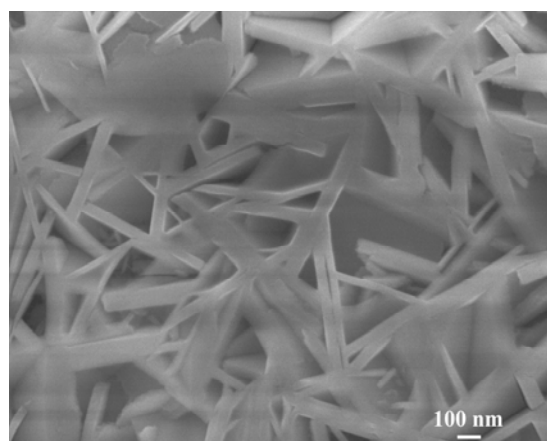


Fig. 3 TEM image for the nanosticks of (EDO-TTFVO)₂•FeBr₄•(DCE)_{0.5}.

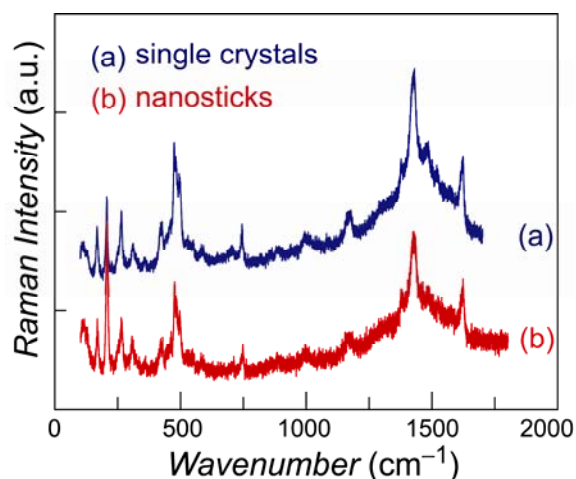


Fig. 4 Raman spectra of (EDO-TTFVO)₂•FeBr₄•(DCE)_{0.5}.

[1] J.-P. Savy, D. de Caro, C. Faulmann, L. Valade, M. Almeida, T. Koike, H. Fujiwara, T. Sugimoto, J. Fraxedas, T. Ondarçuhu, C. Pasquier, *New J. Chem.* **2007**, *31*, 519–527.