Direct formation of micro-/nano-crystalline 2,5-dimethyl-N,N'-dicyanoquinonediimine complexes on SiO₂/Si substrates and multi-probe measurement of conduction properties

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Supporting Information

Chemicals. DMe·DCNQI (Aumuller, A.; Hunig, S. Angew. Chem. Int. Ed. Engl. 1984, 23, 447) and DMe·DCNQI·d7 (Aonuma, S.; Sawa, H.; Kato, R. J. Chem. Soc., Perkin Trans. 2 1995, 1541) were synthesized according to literature procedures. (NEt₄)₂[CuBr₄] was obtained by mixing CuBr₂ and (NEt₄)Br in ethyl alcohol. HPLC-grade acetonitrile and silver perchlorate were purchased from Wako Pure Chemical Industries Ltd. and used without further purification.

Hazard Information. Solid silver perchlorate may explode upon stimuli, especially in complex form with aromatics.

Crystal Growth. The electrode was prepared as shown in Figure S1 (left), and chemical or electrochemical reaction was performed in acetonitrile solution. Among several dozens of the crystals (Figure S1: right) obtained, one single crystal in good geometry was selected for the measurement. Unnecessary electrodes and crystals were cut by laser ablation.

Two-Probe Measurements for (DMe·DCNQI·d7)₂Cu. The temperature dependence of the (DMe·DCNQI·d7)₂Cu resistance was measured by the two-probe method. More than ten samples were measured, and none of them exhibited a metal–insulator transition down to 4 K. A typical result is shown in Figure S2.

Rectifier Fabrication. For this experiment, relatively large samples were employed. The lengths of the samples were about 50-100 μm. Half of the crystal was shed by black resin fixed on the substrate while the other half of the crystal was irradiated by a halogen lamp.

Crystal Morphology. The nanocrystals are considered to have the same structures as the bulk for the following reasons. First, no other morphology is
known for the (DMe-DCNQI)\_2X (X = Ag or Cu) salts. And, the conduction properties of all the chemically or electrochemically grown nanocrystals examined were identical to one another, which suggests that the nanocrystals grow as a single phase. Finally, we grew the crystals by the electrochemical method until they were larger than 0.5 mm in length, and determined the cell parameters by X-ray diffraction. The cell parameters were identical to those for the previously reported bulk crystals within experimental errors.

**Resistivity of (DMe-DCNQI-\textit{d}7)\_2Cu.** We analyzed 4 samples with the four-probe method. The room temperature resistivity values were 6\times10^{-4}, 3.1\times10^{-3}, 3.5\times10^{-3}, and 7.3\times10^{-3} [\Omega \text{ cm}]. Because the resistivity of the bulk crystal is around 1\times10^{-3} [\Omega \text{ cm}], that of the nanocrystal is within the same order.

**Figure S1.** SEM images of a part of the substrate before (left) and after (right) crystal growth. There are seven such circuits in one substrate.

**Figure S2.** Temperature dependence of the resistance of (DMe-DCNQI-\textit{d}7)\_2Cu measured by the two-probe method.