Supporting Information

Coherent Resonant Electron Tunneling at 9 K and 300 K through a 4.5 nm Long, Rigid, Planar Organic Molecular Wire

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1. Supporting Figures

S1.1. SEM Image for Initial Au/Ti Nanogap Electrodes

Figure S1.1. A SEM image of a Au/Ti nanogap electrodes on thermally oxidized SiO₂/Si substrate used for ELGP processing, having source, drain and two side gates (not used in the present study) with a gap separation of ca. 20 nm.
S1.2. SEM Image for Electroless Au-plated (ELGP) Nanogap Electrodes

Figure S1.2. Nanogap electrodes after ELGP process. Typical SEM image of initial nanogap electrodes with gap separation of ca. 4 nm after self-terminating ELGP process.
S1.3. $I_d$–$V_d$ Characteristics of ELGP Nanogaps Before and After Immersion into COPV6(SH)$_2$ Solution

Figure S1.3. Typical the $I_d$–$V_d$ characteristics the nanogaps before (left) and after (right) COPV6(SH)$_2$ impregnation into COPV6(SH)$_2$ solution (device numbers refer to those used in the experiments). All the 80 ELGP nanogap electrodes on one substrate made in one operation showed no current flow before the immersion including the ELGP nanogap electrodes used for fabricate devices #1–5. We found no current flow after the COPV6(SH)$_2$ impregnation of the nanogaps except devices #1–5.
S1.4. Back Current Simultaneously Measured at the Same Time on COPV6 Device #1

Figure S1.4. Back gate current-drain bias voltage characteristic simultaneously measured on device #1 in Figure 2 at 9 K showing no leakage current.
2. Supporting Notes

2.1. Single COPV6(SH)$_2$ Molecular Wire Device Fabrication

2.1.1. General

Unless otherwise noted, all the reagents including acetone, ethanol, and toluene were purchased from Wako pure Chemical. Scanning electron microscopy (SEM) was carried out on a SU8000. Secondary electron resolution for SU8000 is 1.0 nm ($V_{\text{acc}} = 15$ kV) and 1.4 nm (Landing voltage: 1 kV). Accelerating voltage range is 0.5 - 30 kV and landing voltage is 0.1 – 2 kV. Magnification specified based on a display size of 127 mm × 95 mm is 20 – 1,000,000.

2.1.2. Fabrication of Initial Nanogap Electrodes by EBL and Pad Electrodes by Photolithography

We fabricate 4-nm nanogap electrodes by two steps; ca. 30 nm nanogap electrodes made of Au/Ti are initially fabricated by Electron Beam Lithography (EBL), which are fabricated on silicon dioxide (SiO$_2$)/silicon (Si, heavy doped Sb) substrate. The thickness of SiO$_2$ is 50 nm. Then, electroless Au-plating process is adopted to narrow the initial gap separation up to ca. 4 nm. Details of fabrication process of each step are described as follows.

A Si wafer was cut into many pieces of 15 nm square, photolithography pattern used in this experiment is 9 nm in square. It was cleaned by ultrasonic agitation in acetone for 1 min × 3 and in ethanol for 1 min × 3 to remove organic contamination and dust, which was followed by ultraviolet/ozone (UV/O$_3$) cleaning. The setting for UV/O$_3$ cleaning was 3 min for O$_2$ introduction, 12 min for ultraviolet irradiation, and 3 min for N$_2$ introduction.

ZEP-520A resist (ZEP-520A: ZEP-A = 1:5) was used. It was spread onto the substrate at 500 rpm × 5 sec to 4000 rpm × 2 min. Then, the substrate was baked at 180 °C for 2 min to dry the resist, followed by cooling down onto aluminum petri dish for 30 sec. The thickness of resist is ca. 100 nm.

An ELS7500EX (ELIONIX) lithography equipment was used for fabrication of initial nanogap electrodes. The drawing current intensity was set to 100 pA. After development, Ti was used as adhesion layer for Au electrodes. The thickness of Ti and Au were 3 and 30 nm, respectively.

ZDMAC is the remover of ZEP-520A resist. The substrate was immersed into ZDMAC for more than 60 min at room temperature. Ultrasonic agitation was required to remove residue of resist completely, followed by rinsing with IPA for a few seconds and dried by pure N$_2$ gas.

The S1813 positive photoresist was coated on the substrate after cleaning by in boiling acetone for 1 min and in ethanol for 1 min. It was spread onto the substrate at 1000 rpm × 5 sec to 4000 rpm × 60 sec. After that, the substrate was baked at 110°C for 1 min. MA-20 mask aligner (MIKASA) was used with ultraviolet light. Ti was used as adhesion layer for Au electrodes. The thickness of Ti and Au were 5 nm and 40 nm, respectively. Acetone was used as a remover for S1813 resist. The substrate
was immersed into acetone for more than 12 h at room temperature. Ultrasonic agitation was carried out to fully remove residue resist.

2.1.3. Self-Terminating ELGP Fabrication of Electrodes

The substrates in this paper are thermally oxidized SiO$_2$/Si(100) wafer with the SiO$_2$ thickness of 50 nm.

Eighty ELGP nanogap electrodes are simultaneously mass-produced by self-terminating ELGP of in the titanium electrodes. The self-termination property of the ELGP method, which enable us to obtain the devices in high yield without physisorption of Au clusters onto the sample during gold deposition. It means that an introduction of impurities such as metallic nanoparticles between nanogaps are not available for our devices.

Before electroless-Au-plating process, the thermally oxidized SiO$_2$/Si substrate was cleaned in boiling acetone and ethanol. O$_2$ plasma ashing was carried out to remove any organic contamination during previous EBL and photolithography processes and the amorphous carbon residuals generated during observation through SEM. 90% yield of 4-nm nanogap electrodes were achieved by established electroless-Au-plating process,$^{1,2}$ described as follows.

1. Preparation of electroless-Au-plating solution by mixing Au sheets (99.99%) and iodine tincture (Kozakai Seiyaku Co. Ltd.) in clean vials.
2. Ascorbic acid was added into the solution to reduce the Au ions. Repeating immersing the nanogap electrodes into the plating solution for certain times. The repetitive immersion was terminated when a desired width (4 nm) of the nanogap was achieved as examined electron microscope.

3. 2.1.4. Chemisorption of COPV6(SH)$_2$ between Nanogap Electrodes

The COPV6(SH)$_2$ compound was dissolved into toluene solvent to make 0.5 mM solution. The newly fabricated electroless-Au-plated nanogap electrodes on Si substrate was directly immersed into COPV6(SH)$_2$ solution for 3 h, which was kept at 80 °C. After the COPV6(SH)$_2$ impregnation, we rinse the substrate two times by using acetone and ethanol to remove any weakly adsorbed COPV6(SH)$_2$ molecules.

2.1.5. Electrical Characterization of the COPV6(SH)$_2$ Nanogap Devices

The electrical properties of the devices were characterized at 9 K and room temperature of 300 K by using a mechanical helium refrigerator-type prober station (GRAIL 10-LOGOS01S, Nagase, Japan) and a semiconductor parameter analyzer (B1500, Agilent, USA). The differential conductance as a function of the drain voltage ($dI_d/dV_d$) was calculated by the numerical differential of the drain current. The electrical simulator of the sequential single-electron tunneling based on the orthodox model was programmed by using C++ language.$^{3,4}$

All the ELGP nanogap electrodes within the samples in this paper measured the $I_d$-$V_d$ characteristics before immersing substrate into COPV6 solution as shown in Figure S1.3, and showed no current flow.

All of the COPV6(SH)$_2$ immersed nanogaps were measured for their $I_d$-$V_d$, $I_{bg}$-$V_d$ and back gate current ($I_{bg}$)-$V_d$ characteristics simultaneously by using the source
measure units (SMUs). The typical $I_d-V_d$ characteristics which showed no current flow are shown in Figure 2a. Such no current flow ensures the absence of functioning molecule. We found only five functioning devices #1–5, and all other nanogaps were entirely non-functioning.

The $I_{bg}-V_d$ characteristic simultaneously measured on the device in Figures 2 at 9 K is shown in Figure S1.4. No observable leakage current ensured perfect insulating property of the thermally oxidized SiO$_2$ layer on which the electrodes were placed.

Consequently, we can conclude that the $I_d-V_d$ characteristics in this work reflects the electron transporting properties of the devices, which showed clearly defined $dI/dV$ signals in the $I_d-V_d$ data.

### 2.2. Orthodox Model for Sequential Single-Electron Transportation

For a double barrier tunneling junction system, equivalent circuit shown in Figure S1.8, electrons tunneling rate for barrier 1 and 2 is present by $\Gamma_{1,2}^{\pm}(n)$, which can be obtained from a basic golden-rule calculation by

$$\Gamma_{1,2}^{\pm}(n) = \frac{1}{R_{1,2}e^2} \left( \frac{-\Delta E_{1,2}^{\pm}}{1 - \exp(\Delta E_{1,2}^{\pm}/k_BT)} \right)$$

where $\Delta E_{1,2}^{\pm}$ and $\Delta E_{1,2}^{\pm}$ are the energy changes of the system when one electron tunnels across tunneling barrier 1 and 2, $R_{1,2}$ is the corresponding resistance of barrier 1 or 2, $k_B$ is the Boltzmann constant, $T$ is the temperature. After application of positive bias $V = e/C$ (down plot), one electron tunnels through tunneling barrier 1. The energy changes of the system $\Delta E_{1}^{\pm}$ can be expressed as:

$$\Delta E_{1}^{\pm} = \frac{e}{C} \left( \frac{e + (ne + Q_0) \mp C_2 V}{2} \right)$$

Similarly, $\Delta E_{2}^{\pm}$ can be expressed as:

$$\Delta E_{2}^{\pm} = \frac{e}{C} \left( \frac{e + (ne + Q_0) \mp C_1 V}{2} \right)$$

where $n$ is the number of electrons staying the island, $C = C_1 + C_2$ is the total capacitance of double tunneling barrier junctions, $Q_0$ is the fraction residual charge surrounding island region. The +/- refers to electrons tunneling on/off the island region. By combining five parameters of $R_{1,2}$ and $C_{1,2}$ and fractional charge $Q_0$ in Coulomb island, we calculated theoretical $I-V$ characteristics. The charging energy can be simply calculated as $E_c = e^2/2C$.

### 2.3. Organic Synthesis
The starting materials have been prepared according to reported procedures. A mixture of compound 1 (500 mg, 0.93 mmol), COPV4(Bpin)2 (770 mg, 0.31 mmol), and potassium carbonate (300 mg, 2.1 mmol) in a mixed solvent of toluene (12 mL) and water (6 mL) was degassed by freeze degassing. A catalytic amount of Pd(PPh3)4 (100 mg, 0.11 mmol) was added to the solution and the mixture was stirred at 100 ºC for 19 h. The organic layer was concentrated in vacuo and obtained crude product was dissolved in CCl4 (20 mL). To the solution was added BF3•Et2O (1.0 g, 5.4 mmol) at room temperature. After stirring for 2 h, the reaction was quenched by addition of MeOH (10 mL). The mixture was concentrated in vacuo and crude mixture was purified by flash column chromatography on silica gel to give COPV6(SEHP)2 (400 mg, 32% in 2 steps) as orange solid. 1H NMR (400 MHz, CDCl3) δ 0.85–0.92 (m, 24H), 1.20–1.50 (m, 72H), 1.51–1.57 (m, 18H), 2.48 (t, J = 7.8 Hz, 8H), 2.63 (t, J = 7.5 Hz, 4H), 3.15 (t, J = 7.5 Hz, 4H), 4.00 (t, J = 4.8 Hz, 4H), 6.87 (d, J = 8.0 Hz, 8H), 6.99 (d, J = 8.0 Hz, 8H), 7.05–7.22 (m, 48H), 7.24–7.29 (m, 20H), 7.7.33–7.39 (m, 8H; 13C NMR (100 MHz, CDCl3) δ 10.93, 10.97, 14.04, 14.14, 22.69, 22.94, 23.71, 24.36, 24.44, 28.87, 29.26, 29.58, 29.70, 30.28, 30.33, 31.35, 31.94, 34.57, 35.59, 38.65, 44.52, 44.83, 62.13, 62.71, 67.10, 67.54, 117.61, 117.78, 126.52, 126.68, 128.01, 128.05, 128.12, 128.26, 128.31, 128.51, 128.55, 128.64, 140.55, 141.02, 143.47, 143.56, 155.60, 155.86, 155.95, 156.21, 156.23, 158.30, 159.58, 171.49, 172.06. (some peaks were overlapped); TOF MS (APCI+): 3043.6. (M); HRMS (APCI+) Calcd for C224H226O4S2 (M): 3043.6917; Found: 3043.5902.

Protecting group for thiol in COPV6(SEHP)2 was deprotected by sodium ethoxide (2.4 equivalent) at rt for 2 h, followed by the addition of aqueous HCl. After separation and removal of volatiles from the organic layer, reduction of disulfide by-product was performed with sodium borohydride (10 equivalent) at rt for 3 h to afford COPV6(SH)2. After short-path flash column chromatography, the obtained material was used for the device fabrication due to the lability toward oxidation of the compound under aerobic conditions.
Figure S2.1. $^1$H NMR chart of COPV6(SEHP)$_2$
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