Supplementary Information for

Photoswitching of Conductance of Diarylethene-Gold Nanoparticles Network

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1. Experimental Details

^{1}H NMR spectra were recorded on a Bruker AVANCE 400 instrument. Mass spectra were obtained on a Shimadzu GCMS-QP5050A and a JEOL JMS-GCmate II. Melting points were measured on a Yanaco MP-500D instrument and were not corrected. All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto, 63-210 mesh). Recycling Preparative HPLC (Japan Analytical Industry, LC-908 with JAIGEL-1H + 2H) was used for the GPC purification with $CHCl_3$ as the eluent. Ultrapure water (> 18 MΩ·cm) was obtained by a Millipore Simpli Lab.

Absorption spectra were measured on a Hitachi U-3500 spectrophotometer. IR spectra were measured on a Perkin-Elmer Spectrum One instrument by ATR method. Photoirradiation was carried out by using a USHIO 500 W super high-pressure mercury lamp or a Hamamatsu 200 W mercury-Xenon lamp with a combination of optical filter and a monochromater (Ritsu MC-10N).

TEM measurement was performed on a Hitachi H-7500 instrument. The measurement was performed at 100 kV. TEM samples were prepared by placing a drop of ethyl acetate solution onto carbon-coated copper grid.

SEM measurement was performed on a Shimadzu SS-550 instrument. The measurement was performed at 15 kV. SEM samples were prepared by gold coating using a Sanyu SC-701 quick coater.

2. Preparation of Materials (Scheme S1).

3-Bromo-2,4-dimethyl-5-(4-methylthio-phenyl)thiophene (8). To a solution of 2,4-dibromo-3,5-dimethylthiophene (**7**)[1] (1.62 g, 6.0 mmol) and 4-methylthiophenylboronic acid (0.96 g, 5.7 mmol) in THF (48 mL) were added $Pd(PPh_3)_4$ (0.35g, 0.3 mmol) and aqueous Na_2CO_3 (20 wt%, 54 mL). The mixture was warmed at 80 °C overnight and extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-2,4-dimethyl-5-(4-methylthiophenyl)thiophene (**8**) (0.89 g, 50%, white powder): mp = 71-73 °C; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 18 H), 2.42 (s, 3 H), 2.51 (s, 3 H), 7.28 (d, J = 9 Hz, 2 H), 7.32 (d, J = 9 Hz, 2 H); Anal. Calcd for $C_{13}H_{13}BrS_2$: C, 49.75; H, 4.19; Found: C, 49.84; H, 4.18.

3-Bromo-2,4-dimethyl-5-(4-mercaptophenyl)thiophene (9). A solution of 3-bromo-2,4-dimethyl-5-(4-methylthiophenyl)thiophene (**8**) (0.62 g, 2 mmol) and sodium *t*-butylthiolate (0.34 g, 3 mmol) in dry DMF (24 mL) was refluxed for 6 h under Ar atmosphere. After the reaction mixture was cooled to room temperature, 10% hydrochloric aced was added slowly. The mixture was extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-2,4-dimethyl-5-(4-mercaptophenyl)thiophene (**9**) (0.38 g, 63%, white powder): mp = 68-70 °C; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 2.42 (s, 3 H), 3.50 (s, 1 H), 7.26 (d, *J* = 8 Hz, 2 H), 7.30 (d, *J* = 8 Hz, 2 H); Anal. Calcd for $C_{12}H_{11}BrS_2$: C, 48.19; H, 3.73; Found: C, 48.16; H, 3.71.

3-Bromo-2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)thiophene (10). To a solution of 3-bromo-2,4-dimethyl-5-(4-mercaptophenyl)thiophene (**9**) (0.5 g, 1.7 mmol) in dry DMF (11 mL) was added sodium hydride (52 mg, 2.17 mmol). After the reaction mixture was stirred for 1h at room temperature, (2-bromoethyl)trimethylsilane (0.45 g, 2.51 mmol) was added. The stirring was continued overnight and then water was poured into the reaction mixture. The mixture was extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane) gave 3-bromo-2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)thiophene (**10**) (0.56 g, 83%, white powder): mp = 54-56 °C; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 0.92-1.01 (m, 2 H), 2.25 (s, 3 H), 2.43(s, 3 H), 2.95-3.04 (m, 2 H), 7.29-7.33 (m, 4 H); MS (*m*/*z*) $[M]^+$ 398; Anal. Calcd for $C_{17}H_{23}BrS_2Si$: C, 51.11; H, 5.80; Found: C, 51.16; H, 5.64.

1,2-bis(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)hexafluorocyclopentene (4). To a solution of 3-bromo-2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)thiophene (**10**) (0.62 g, 1.6 mmol) in dry THF (7.8 mL) was added *n*-butyllithium (1.6 M, 1.2 mL, 1.9 mmol) at -78 °C under Ar atmosphere. The reaction mixture was stirred below -70 °C for 30 min, perfluorocyclopentene (92 μL, 0.70 mmol) was added slowly. The stirring was continued below -70 °C for 1 h and then the reaction mixture was allowed to warm up to room temperature. The reaction was quenched by adding water and then the reaction mixture was extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane:$CHCl_3$ = 10:1) and purification by GPC ($CHCl_3$) gave 1,2-bis(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)hexafluoro-

cyclopentene (**4**) (0.14 g, 22%, colorless viscous oil): ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 18 H), 0.94-0.99 (m, 4 H), 2.24-2.26 (m, 6 H), 2.42-2.44 (m, 6 H), 2.97-3.01 (m, 4 H), 7.30-7.33 (m, 8 H); MS (*m*/*z*) $[M]^+$ 812; Anal. Calcd for $C_{39}H_{46}F_6S_4Si_2$: C, 57.69; H, 5.68; Found: C, 57.60; H, 5.70.

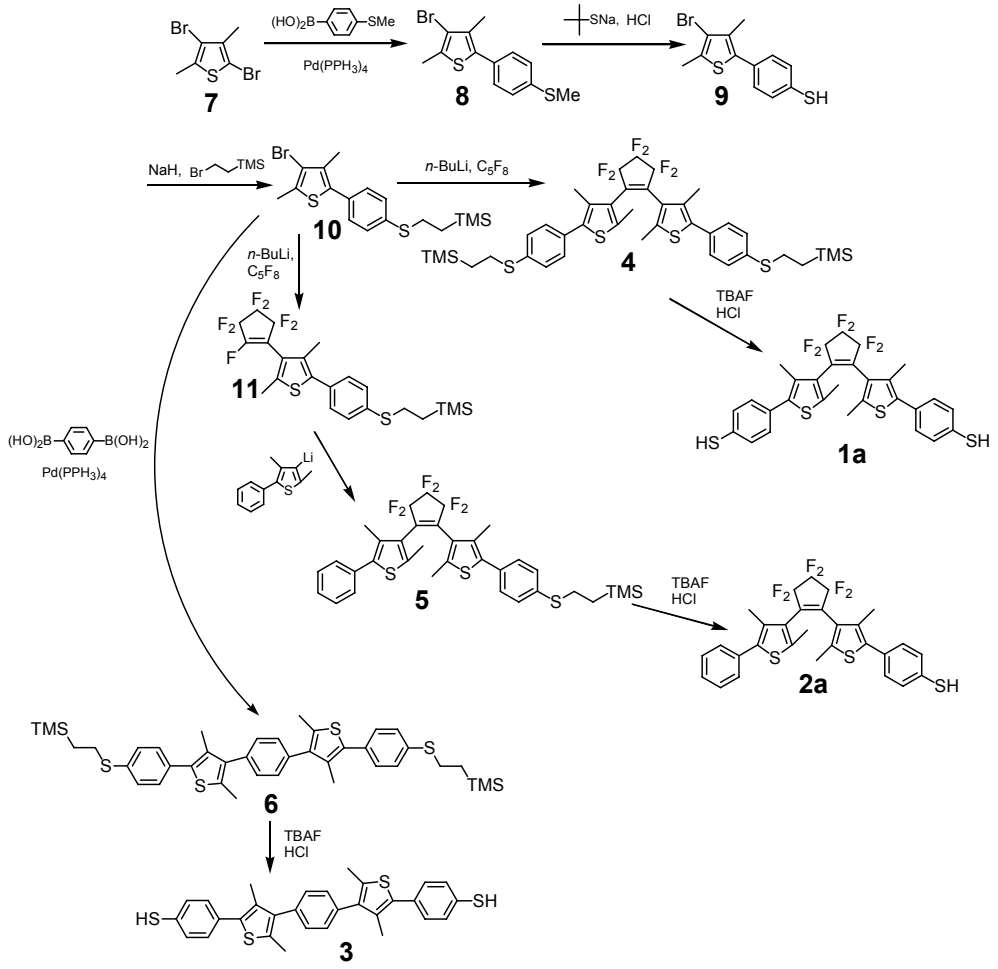
Separation of the closed-ring isomer was performed using normal phase HPLC with Mightysil Si60 (Kanto Chemical, 250-20 mm, Eluent: hexane/EtOAc = 98:2).

1-(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (5). To a solution of 3-bromo-2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)thiophene (**10**) (0.67 g, 1.7 mmol) in dry THF (23 mL) was added *n*-butyllithium (1.6 M, 1.1 mL, 1.8 mmol) at -78 °C under Ar atmosphere. The reaction mixture was stirred below -70 °C for 1 h, perfluorocyclopentene (0.75 mL, 1.8 mmol) was added in one portion at -90 °C. The stirring was continued below -70 °C for 1 h and then the reaction mixture was allowed to warm up to room temperature. The reaction was quenched by adding water and then the reaction mixture was extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane:$CHCl_3$ = 10:1) gave 1-(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)heptafluorocyclopentene **11** (0.47 g, 55%, pale yellow solid). This compound was used without characterization.

To a solution of 2,4-dimethyl-5-phenyl-3-bromothiophene[2] (0.26 g, 0.97 mmol) in dry THF (5.1 mL) was added *n*-butyllithium (1.6 M, 0.61 mL, 0.98 mmol) at -78 °C under Ar atmosphere. The reaction mixture was stirred below -70 °C for 1 h, (0.75 mL, 1.8 mmol) was added 1-(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)heptafluorocyclopentene (**11**) slowly. The stirring was continued below -70 °C for 30 min and then the reaction mixture was allowed to warm up to room temperature. The reaction was quenched by adding water and then the reaction mixture was extracted by Et_2O, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane:$CHCl_3$ = 4:1) gave 1-(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (**5**) (0.48 g, 77%, colorless viscous oil): ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 0.92-0.98 (m, 2 H), 2.07-2.10 (m, 6 H), 2.35-2.40 (m, 6 H), 2.96-3.01 (m, 2 H), 7.27-7.413 (m, 9 H); MS (*m*/*z*) $[M]^+$ 680; Anal. Calcd for $C_{34}H_{34}F_6S_3Si$: C, 60.26; H, 5.16; Found: C, 59.97; H, 5.03.

Separation of the closed-ring isomer was performed using normal phase HPLC with Mightysil Si60 (Kanto Chemical, 250-20 mm, Eluent: hexane/EtOAc = 98:2).

1,4-bis(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)benzene (6). To a solution of 3-bromo-2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)thiophene (**10**) (200 mg, 0.5 mmol) and 1,4-phenylenediboronic acid (33 mg, 0.2 mmol) in THF (20 mL) were added $Pd(PPh_3)_4$ (110 mg, 0.1 mmol) and aqueous Na_2CO_3 (20 wt%, 10 mL). The mixture was refluxed for 48 h and extracted by ethyl acetate, washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (silica, hexane:CH_2Cl_2 = 3:1) gave 1,4-bis(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)benzene **6** (25 mg, 12%, colorless solid): mp = 135.5-137.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 18 H), 0.94-1.01 (m, 4 H), 2.14 (s, 6 H), 2.39 (s, 6 H), 2.97-3.04 (m, 4 H), 7.30-7.37 (m, 8 H), 7.41 (d, J = 8 Hz, 4 H); HRMS (m/z) $[M]^+$ Calcd for $C_{40}H_{50}S_4Si_2$: 714.2334; Found: 714.2337.



Scheme S1.

3. Preparation of Au-1a Nanoparticle Network.

To a solution of 1,2-bis(2,4-dimethyl-5-(4-trimethylsilylethylthiophenyl)-3-thienyl)hexafluorocyclopentene **4** (10.5 mg, 12.9 μmol) in THF 1 mL was added tetrabutylammonium fluoride (1.0 M solution in THF, 1 mL) and then the mixture was stirred for 10 min. Hydrochloric acid (0.1 M, 1 mL) was added to the solution and then the mixture was stirred for 10 min. The mixture was extracted with Et_2O, washed with brine, dried with $MgSO_4$ and concentrated. Column chromatography (hexane:chloroform = 4:1) gave 1,2-bis(2,4-dimethyl-5-(4-mercaptophenyl)-3-thienyl)hexafluorocyclopentene **1a** (4.7 mg, 59%) as a viscous oil. Because the obtained thiol was not stable enough to store, the compound was immediately used in the following procedure.

1a: ^{1}H NMR ($CDCl_3$) δ 2.04-2.08 (m, 6 H), 2.33-2.36 (m, 6 H), 3.49 (s, 2 H), 7.22 (d, J = 8 Hz, 4 H), 7.28 (d, J = 8 Hz, 4 H); IR (GeATR) 2957, 2926, 2858, 1277, 1145, 1114, 1055, 988, 859, 818 cm^{-1}; UV-vis (EtOAc) λ_{max} 287 nm; MS (m/z) $[M]^+$ 612.

To a solution of tetrachloroaurate(III) hydrate in ultrapure water (30 mM, 0.64 mL, 19 μmol) was added tetraoctylammonium bromide (52.5 mg, 96 μmol) in toluene (1.9 mL) and then the reaction mixture was vigorously stirred for 10 min. After the water phase got colorless from yellow and the toluene phase got red from colorless, $NaBH_4$ (7.25 mg, 0.19 mmol) in ultrapure water (0.48 mL) was added to the reaction mixture and then the solution was stirred for 30 min. The color of the toluene phase turned black from red. 1,2-bis(2,4-dimethyl-5-(4-trimethylsilylethylthiophenyl)-3-thienyl)-hexafluorocyclopentene **1a** (2.35 mg, 3.84 μmol) in toluene (1 mL) was added to the reaction mixture and then the solution was stirred for 2 min. The color of the solution turned bluish purple from reddish purple due to the ligand exchange reaction from TOAB to compound **1a**.

The resultant reaction mixture (50 μL) was dropped onto the Au interdigitated electrode and left for 1 min. The electrode was washed with ethanol (× 3) and ultrapure water (× 3) and dried in the air.

Au-1b nanoparticle network was prepared using the closed-ring isomer **1b**, which is obtained from the closed-ring isomer of compound **4**.

4. Preparation of Au-2a Nanoparticles.

To a solution of 1-(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (**5**) (100 mg, 147 μmol) in THF 2 mL was added tetrabutylammonium fluoride (1.0 M solution in THF, 4 mL) and then the mixture was stirred for 8 min. Hydrochloric acid (0.1 M, 1 mL) was added to the solution and then the mixture was stirred for 10 min. The mixture was extracted with Et_2O, washed with brine, dried with $MgSO_4$ and concentrated. Column chromatography (hexane:chloroform = 4:1) gave 1-(2,4-dimethyl-5-(4-mercaptophenyl)-3-thienyl)-2-(2,4-dimethyl-5-phenyl-3-thienyl)hexafluorocyclopentene (**2a**) (83 mg, 97%) as a viscous oil. Because the obtained thiol was not stable enough to store, the compound was immediately used in the following procedure.

2a: ^{1}H NMR ($CDCl_3$) δ 2.05-2.10 (m, 6 H), 2.34-2.35(m, 6 H), 3.47 (s, 1 H), 7.20-7.39(m, 9H); IR (GeATR) 2958, 2922, 2851, 1275, 1143, 1112, 1054, 986, 859, 818 cm^{-1}; UV-vis (EtOAc) λ_{max} 278 nm; MS (*m*/*z*) $[M]^+$ 580.

To a solution of tetrachloroaurate(III) hydrate in ultrapure water (30 mM, 0.5 mL, 15 μmol) was added thiol **2a** (9 mg, 15 μmol) and tetraoctylammonium bromide (40.9 mg, 75 μmol) in toluene (1.5 mL) and then the reaction mixture was vigorously stirred for 40 min. $NaBH_4$ (6.2 mg, 0.16 mmol) in ultrapure water (0.38 mL) was added to the reaction mixture and then the solution was stirred overnight. The organic layer was separated and washed with brine, dried with $MgSO_4$, and then concentrated. The residue was dissolved by EtOAc, poured into hexane (10 mL), and then centrifuged (6000 rpm, 40 min). The black precipitates were collected, redissolved by EtOAc, and repeated the same cycle. Black viscous solid was obtained.

5. Preparation of Au-3 Nanoparticle Network.

To a solution of 1,4-bis(2,4-dimethyl-5-(4-trimethylsilylethylthio-phenyl)-3-thienyl)benzene **6** (0.766 mg, 1.07 μmol) in THF (1mL) was added tetrabutylammonium fluoride (1.0 M solution in THF, 1 mL) and then the mixture was stirred for 8 min. Hydrochloric acid (0.1 M, 1 mL) was added to the solution and then the mixture was stirred for 10 min. The mixture was extracted with Et_2O, washed with brine, and concentrated. Because the obtained thiol was not stable enough to store, the compound was immediately used in the following procedure.

To a solution of tetrachloroaurate(III) hydrate in ultrapure water (30 mM, 0.64 mL, 19 μmol) was added tetraoctylammonium bromide (52.5 mg, 96 μmol) in toluene (1.9 mL) and then the reaction mixture was vigorously stirred for 10 min. After the water phase got colorless from yellow and the toluene phase got red from colorless, $NaBH_4$ (7.25 mg, 0.19 mmol) in ultrapure water (0.48 mL) was added to the reaction mixture and then the solution was stirred for 30 min. The color of the toluene phase turned black from red. And then, 200 μL of the reaction mixture containing Au nanoparticle was collected and added to the solution of 1,4-bis(2,4-dimethyl-5-(4-mercaptophenyl)-3-thienyl) benzene **(3)** obtained from the preceding procedure in toluene (500 μL). The reaction mixture was stirred for 2 min. The color of the solution turned bluish purple from reddish purple due to the ligand exchange reaction from TOAB to compound **3**. The resultant reaction mixture (50 μL) was dropped onto the Au interdigitated electrode and left for 1 min. The electrode was washed with ethanol (× 3) and ultrapure water (× 3) and dried in the air.

6. Photochromic Spectral Change

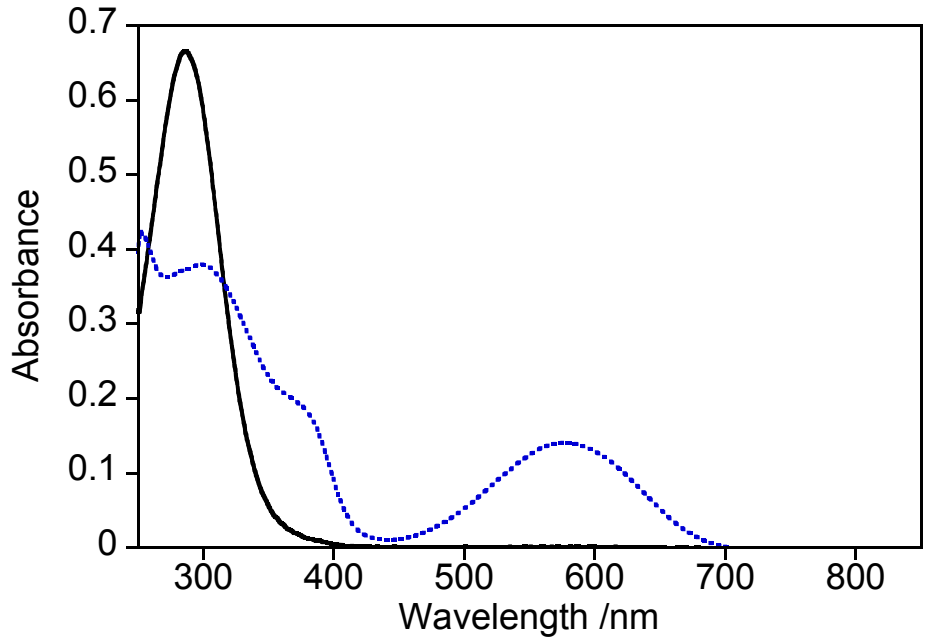


Figure S1. Photochromic spectral change of dithiophenol **1a** (in ethyl acetate). Black solid line: open-ring isomer; blue dotted line: in the photostationary state under irradiation with 313 nm light. Open-ring isomer: λ_{max} = 287 nm. Closed-ring isomer: λ_{max} = 577 nm.

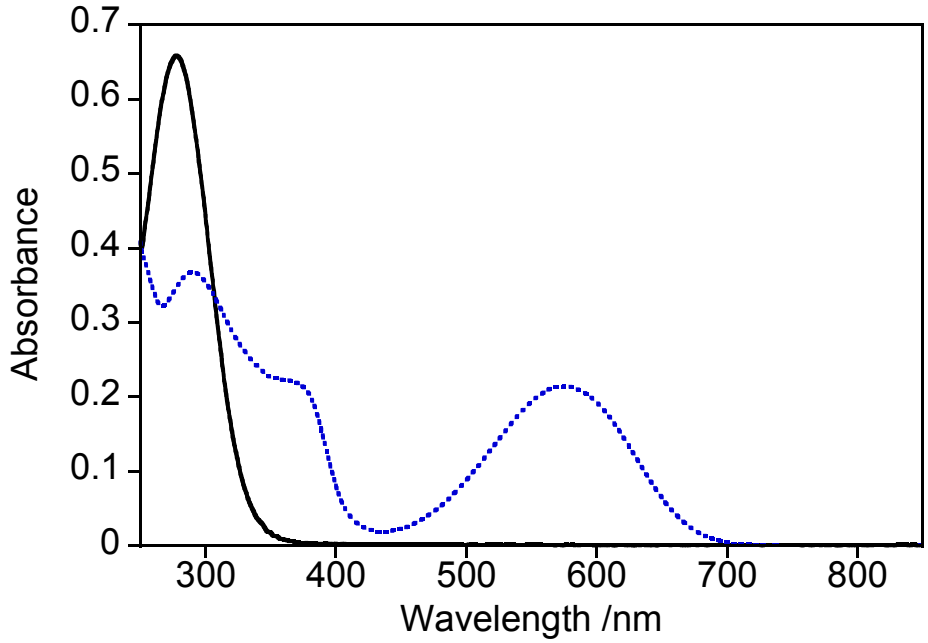


Figure S2. Photochromic spectral change of monothiophenol **2a** (in ethyl acetate). Black solid line: open-ring isomer; blue dotted line: in the photostationary state under irradiation with 313 nm light. Open-ring isomer: λ_{max} = 278 nm. Closed-ring isomer: λ_{max} = 577 nm.

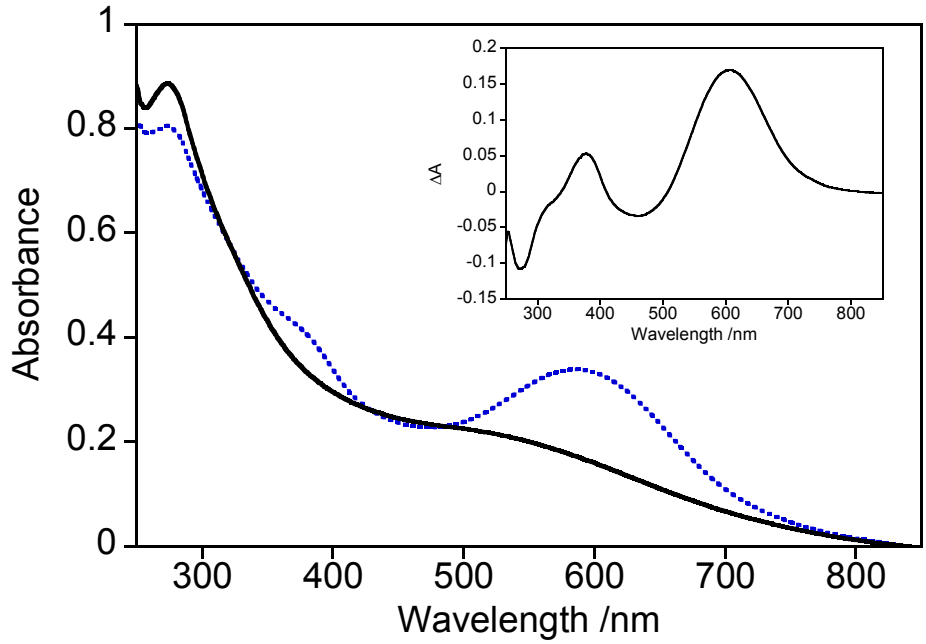


Figure S3. Photochromic spectral change of **Au-2a** nanoparticles (in ethyl acetate). Black line: open-ring isomer; blue dotted line: in the photostationary state under irradiation with 313 nm light. Inset: difference spectrum obtained by subtraction of the open-ring isomer.
Closed-ring isomer: λ_{max} = 609 nm.

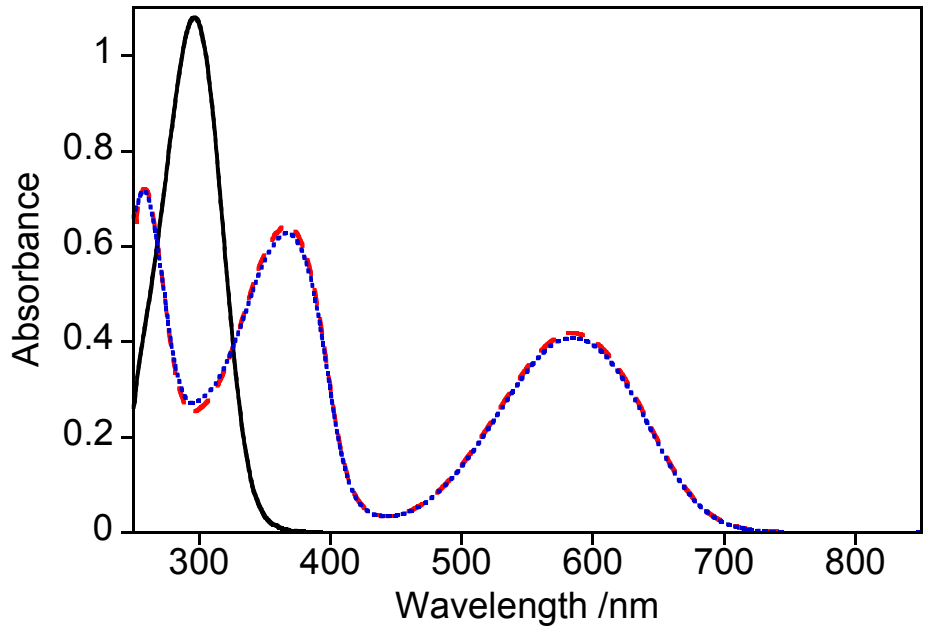


Figure S4. Trimethylsilylethyl-protected dithiophenol **4** (in ethyl acetate). Black solid line: open-ring isomer; red dashed line: closed-ring isomer; blue dotted line: in the photostationary state under irradiation with 313 nm light. The conversion from the open- to the closed-ring isomer was 98%. Open-ring isomer: λ_{max} = 297 nm. Closed-ring isomer: λ_{max} = 585 nm.

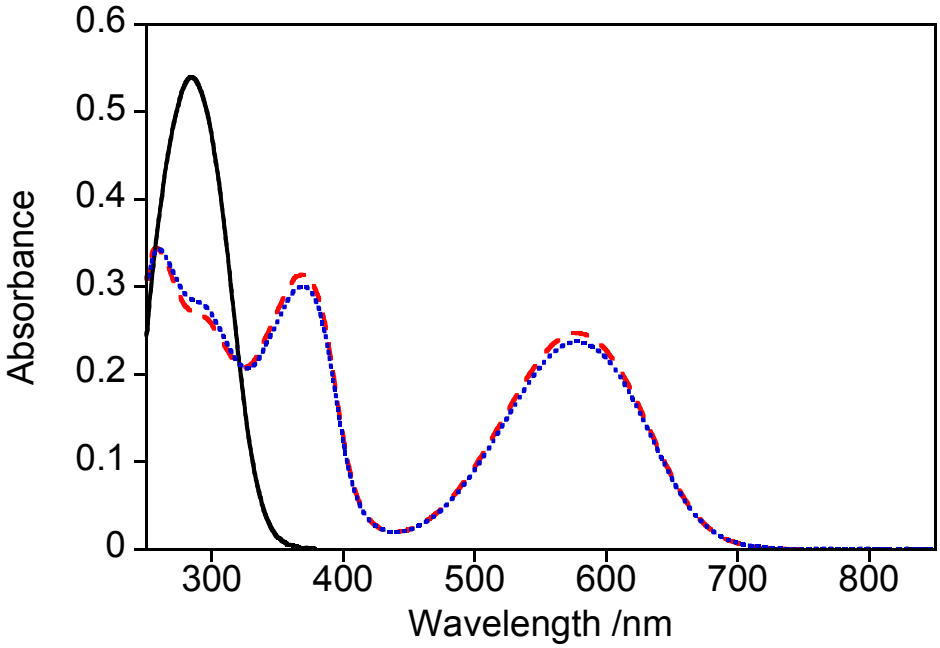


Figure S5. Trimethylsilylethyl-protected monothiophenol **5** (in ethyl acetate). Black solid line: open-ring isomer; red dashed line: closed-ring isomer; blue dotted line: in the photostationary state under irradiation with 313 nm light. The conversion from the open- to the closed-ring isomer was 96%. Open-ring isomer: λ_{max} = 284 nm. Closed-ring isomer: λ_{max} = 579 nm.

7. TEM image of Au-2a nanoparticles

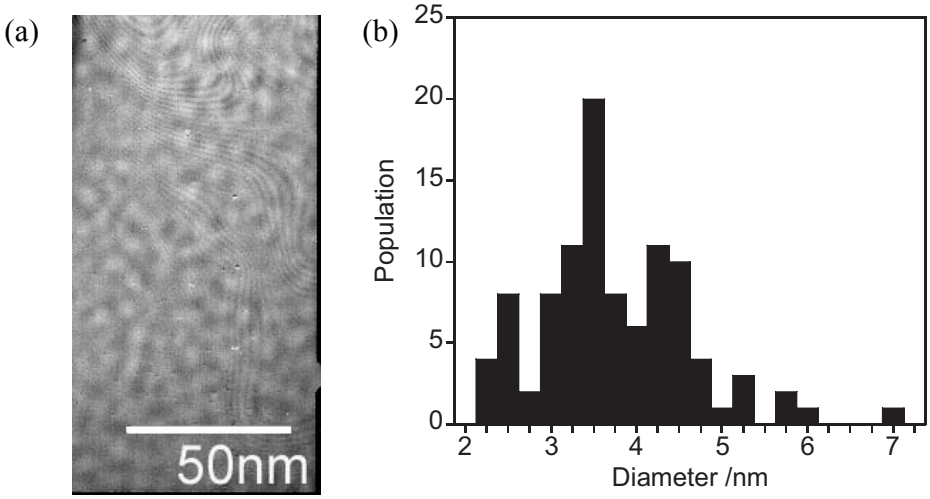


Figure S6. (a) TEM image of the **Au-2a** nanoparticles (100 kV, ×200000). (b) Histogram of the size of the nanoparticles in the **Au-2a** nanoparticles.

8. SEM image of Au-1a Networked Nanoparticle

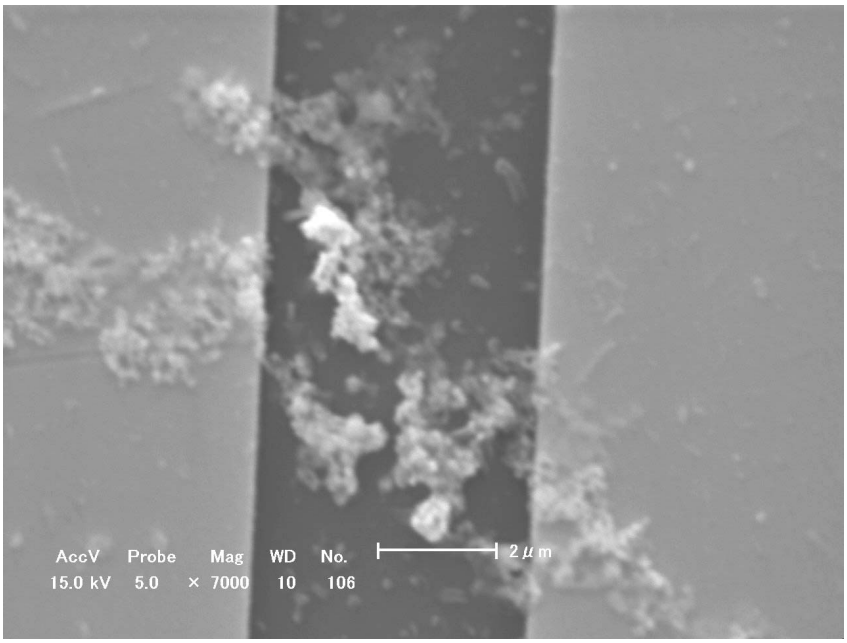


Figure S7. SEM image of the interdigitated Au electrode after depositing the **Au-1a** nanoparticle network (15 kV, × 7000). Samples are coated with Au.

9. Optical image of Au-1a Networked Nanoparticle

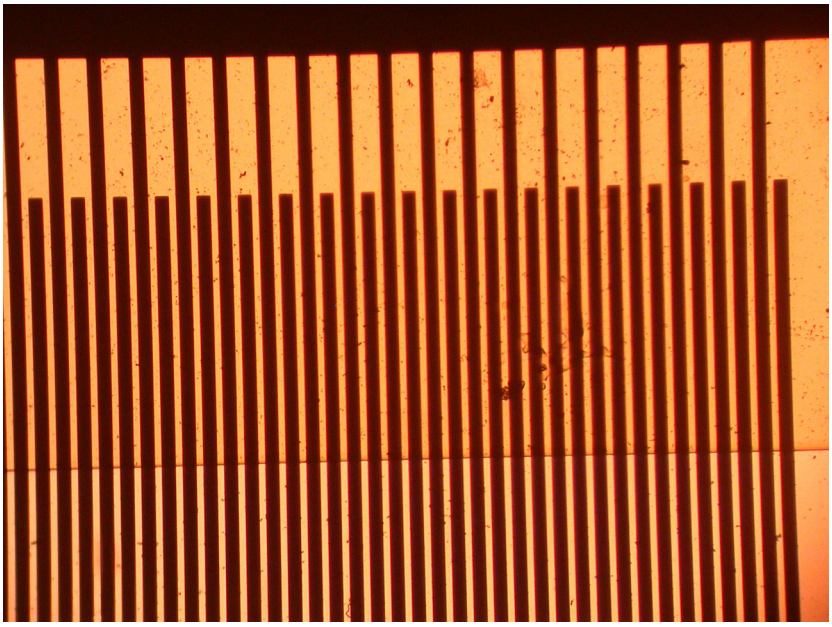


Figure S8. Optical image of the interdigitated Au electrode after depositing the **Au-1a** nanoparticle network. The upper half is coated with passivation film.

10. IR spectra

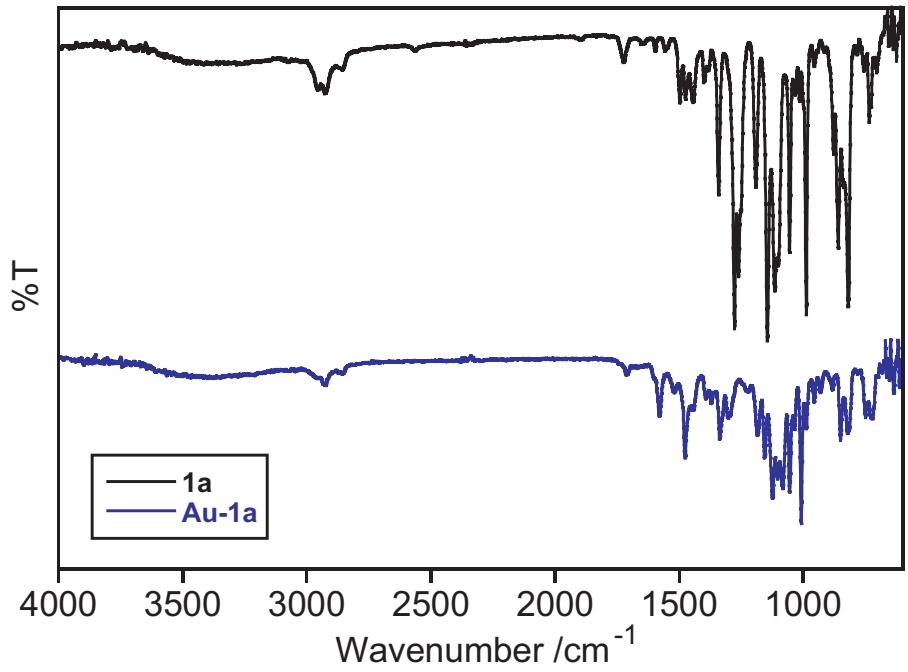


Figure S9. IR spectra of **1a** and **Au-1a** nanoparticle network.

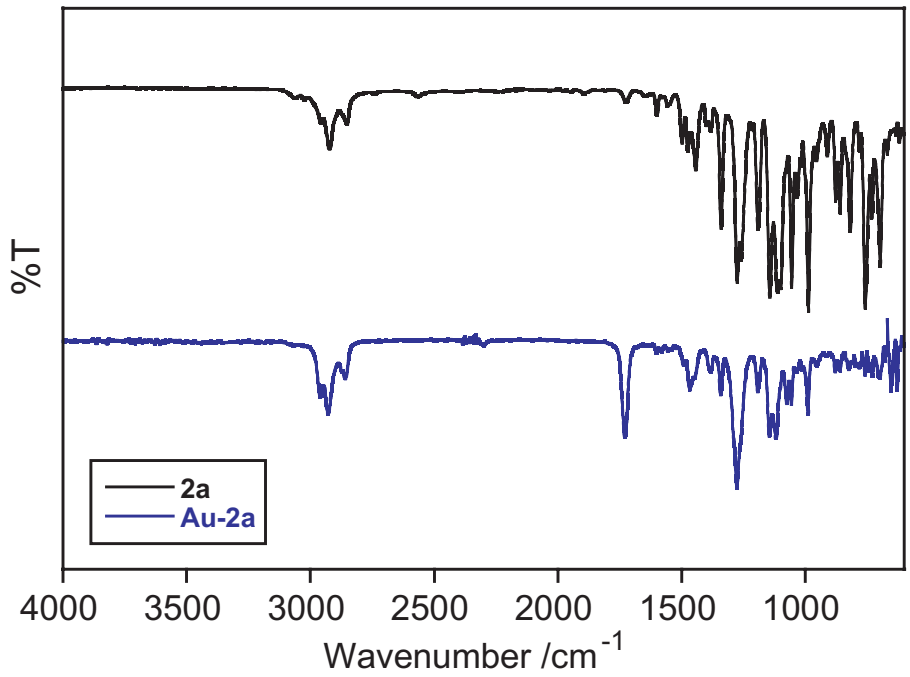


Figure S10. IR spectra of **2a** and **Au-2a** nanoparticles.

References

1 Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305-8309.

2 Kobatake, S.; Irie, M. *Tetrahedron* **2003**, *59*, 8359-8364.