Supplementary Material (ESI) for *PCCP*

Supporting Information

Synthesis of Tripodal Anchor Units Bearing Selenium Functional Groups and Their Adsorption Behavior on Gold

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General Information. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm), or on aluminium oxide, MERCK aluminium oxide 90 standardized. TLC plates were visualized with UV light. Preparative gel-permeation chromatography (GPC) was performed on Japan Analytical Industry LC-908 equipped with JAI-GEL 1H/2H columns.

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JMN-400 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Mass spectra were obtained on Shimadzu

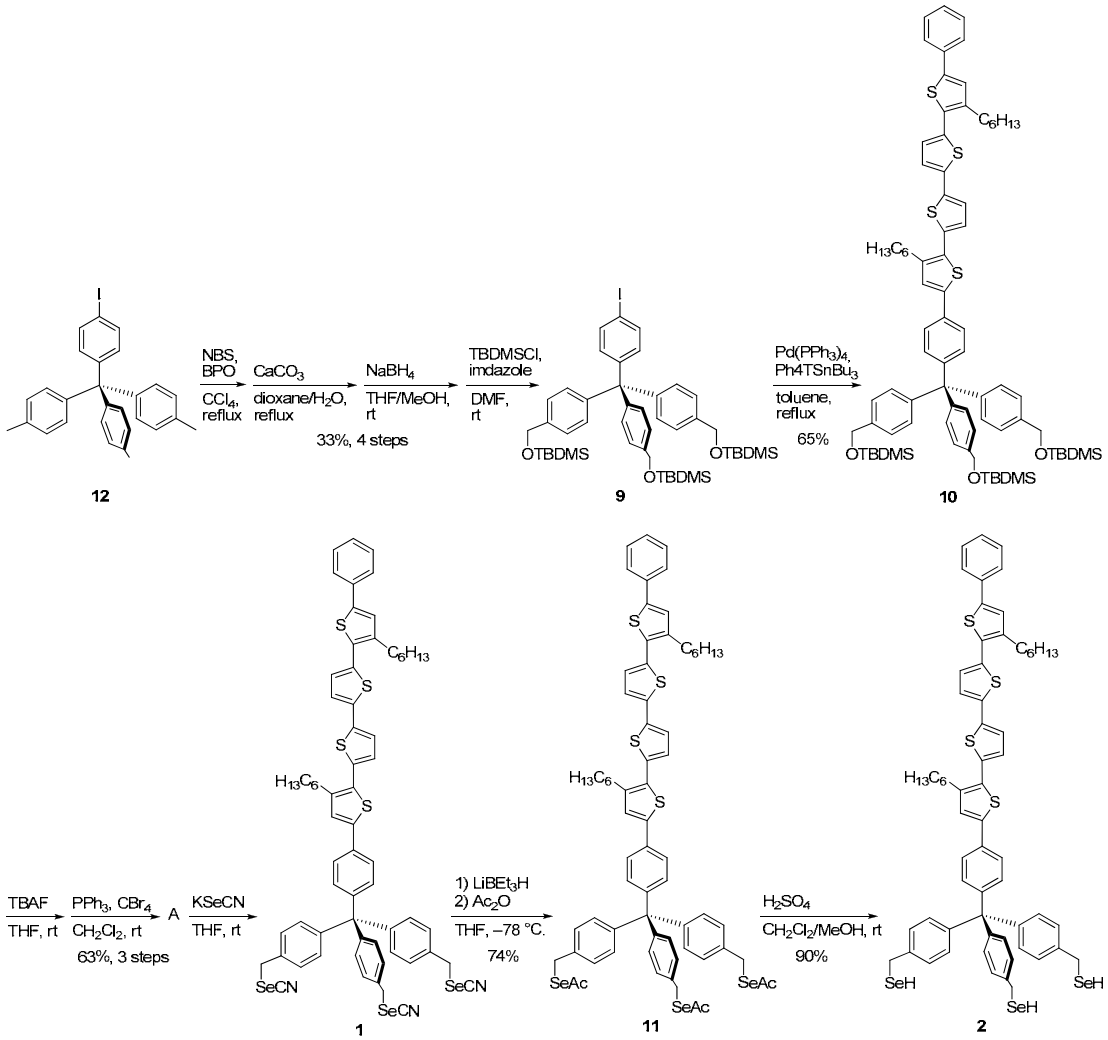
AXIMA-TOF. Cyclic voltammetry was carried out on a BAS ALC 620C voltammetric analyzer with a scan rate of 100 mV/s. A platinum wire and a $Ag/AgNO_3$ electrode were used as the counter and the reference electrodes, respectively. Monolayer-modified gold substrates on mica were used as a working electrode. The electrolyte solution was 0.1 M $n Bu_4NPF_6$ in CH_2Cl_2 for anodic scans and 0.5 M KOH in H_2O for cathodic scans. The X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopic (UPS) measurements were performed in an ultrahigh vacuum chamber (base pressure of 2×10^{-9} Pa) which is equipped with a hemisherical electrostatic electron energy analyzer (EA125, Omicron), an X-ray gun, and a He discharge lamp. In the XPS measurement, Al K_α (1486.6 eV) and Mg K_α (1253.6 eV) were used as X-ray source. The calibration of binding energy was carried out with the peak of Au $4f_{7/2}$ at 84.0 eV as an energy reference. For the UPS measurement, we used He I (21.2 eV), and photoelectrons emitted normal to the sample surface were detected by the energy analyzer. All the measurements were done in a vacuum condition below 5×10^{-7} Pa.

Elemental analyses were performed on Perkin Elmer LS-50B by the Elemental Analysis Section of Materials Analysis Center, ISIR, Osaka University.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 1,1',1''-[(4-Iodophenyl)methylidyne]tris[4-methyl-benzene] (**12**)[1] and 1-bromo4-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]methyl]benzene (**14**)[2] were prepared by reported procedures, and ^{1}H NMR data of these compounds were in agreement with those previously reported.

Experimental Procedures

Scheme S1. Synthesis of **1** and **2**



Compound **9**.

Compound **12** (3.91 g, 8.00 mmol) was placed in a 200 mL three-necked round-bottomed flask, dissolved with CCl_4 (80 mL), and degassed with nitrogen. To the solution were added NBS (4.84 g, 27.2 mmol) and BPO (97 mg, 0.40 mmol). After stirring at 90 °C for 12 h, the reaction mixture was filtered through celite, which was washed with $CHCl_3$. After removal of the solvent from the combined filtrate under reduced pressure, the residue was used for the next reaction without further purification.

The residue and $CaCO_3$ (7.21 g, 72.0 mmol) were placed in a 500 mL three-necked round-bottom

flask and dissolved with dioxane (150 mL) and water (150 mL). After stirring at 110 °C for 12 h, the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with 2M HCl and sat. $NaHCO_3$ aq and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

$NaBH_4$ (701 mg, 18.5 mmol) was placed in a 500 mL three-necked round-bottomed flask and dissolved with THF (200 mL). To the mixture was added a THF (30 mL) and MeOH (60 mL) solution of the residue. After stirring for 12 h at room temperature, 6M HCl (100 mL) was added, and the mixture was stirred for 1 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

The residual solid was placed in a 300 mL round-bottomed flask and dissolved with DMF (150 mL). To the mixture was added imidazole (3.31 g, 48.5 mmol) and *t*BuMe$_2$SiCl (TBDMSCl) (3.66 g, 24.3 mmol), and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of sat. Na_2CO_3 aq. After stirring for 20 min, the organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (3:1 hexane/CH_2Cl_2) to give **9** (2.36 g, 33% in 4 steps).

Colorless solid; Mp 164–165 °C; ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18H), 0.93 (s, 27H), 4.72 (s, 6H), 6.95 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.5 Hz, 6H), 7.19 (d, J = 8.7 Hz, 6H), 7.54 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.3, 18.4, 26.0, 64.1, 64.6, 91.6, 125.2, 130.9, 133.2, 136.5, 139.1, 145.0, 147.0; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 877.59 (M^+, calcd 878.34); Anal. Calcd for $C_{46}H_{67}IO_3Si_3$: C, 62.84; H, 7.68; N, 0.00; Found: C, 63.21; H, 7.79; N, 0.00.

Compound **10**.

Compound **9** (747 mg, 0.850 mmol), **Ph4TSnBu$_3$** (881 mg, 1.02 mmol), and tetrakis(triphenylphosphine)palladium(0) (98 mg, 0.085 mmol) were placed in a test tube and dissolved with toluene (10 mL). The reaction mixture was stirred at 120 °C for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (2:1 hexane/CH_2Cl_2) to give **10** (734 mg, 65%).

Yellow solid; Mp 170–171 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H), 0.87–0.94 (m, 33H), 1.30–1.45

(m, 12H), 1.65–1.72 (m, 4H), 2.70–2.85 (m, 4H), 4.73 (s, 6H), 7.05–7.07 (m, 2H), 7.13–7.15 (m, 3H), 7.17–7.23 (m, 15H), 7.25–7.30 (m, 1H), 7.34–7.40 (m, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.59–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –5.2, 14.1, 18.4, 22.6, 26.0, 29.2, 29.3, 29.6, 29.6, 30.5, 30.5, 31.7, 64.2, 64.7, 123.9, 123.9, 124.5, 125.1, 125.5, 126.0, 126.1, 126.2, 126.3, 127.5, 128.9, 129.7, 129.9, 130.9, 131.4, 131.6, 134.0, 135.3, 135.4, 136.6, 136.7, 139.0, 140.7, 140.7, 141.7, 142.0, 145.4, 146.6; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1325.12 (M^+, calcd 1325.62); Anal. Calcd for $C_{80}H_{104}O_3S_4Si_3$: C, 72.45; H, 7.90; N, 0.00; Found: C, 72.11; H, 7.87; N, 0.00.

Compound **1**.

Compound **10** (734 mg, 0.553 mmol) was placed in a 100 mL round-bottomed flask and dissolved with THF (20 mL). To the mixture was added nBu$_4$NF (1.0 M THF solution, 3.32 mL, 3.32 mmol), and the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of sat. $NaHCO_3$ aq, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

The residue was placed in a 50 mL round-bottom flask and dissolved with CH_2Cl_2 (35 mL). To the mixture was added PPh_3 (871 mg, 3.32 mmol) and CBr_4 (825 mg, 2.49 mmol) at 0 °C. The stirring mixture was gradually warmed up to room temperature and stirred for 1 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give tribromo compound **A** (431 mg, 67%).

Tribromo compound **A** (188 mg, 0.160 mmol) was placed in a 50 mL round-bottom flask and dissolved with THF (10 mL) and EtOH (10 mL). To the mixture was added KSeCN (692 mg, 4.80 mmol), and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give **1** (187 mg, 94%).

Yellow solid; Mp 72–74 °C; ^{1}H NMR ($CDCl_3$) δ 0.87–0.92 (m, 6H), 1.25–1.44 (m, 12H), 1.64–1.74 (m, 4H), 2.77–2.82 (m, 4H), 4.29 (s, 6H), 7.05–7.07 (m, 2H), 7.13–7.17 (m, 6H), 7.21 (d, J = 8.6 Hz, 6H), 7.26–7.29 (m, 7H), 7.36–7.39 (m, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.58–7.60 (m, 2H); ^{13}C

NMR ($CDCl_3$) δ 14.1, 22.6, 29.2, 29.2, 29.5, 29.6, 30.4, 30.5, 31.6, 32.2, 64.3, 101.8, 123.8, 123.9, 124.8, 125.5, 126.1, 126.3, 126.3, 126.3, 127.5, 128.5, 128.9, 129.8, 130.1, 131.3, 131.5, 132.0, 133.5, 133.9, 135.2, 135.3, 136.5, 136.7, 140.7, 141.1, 142.0, 144.9, 146.5; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1247.76 (M^+, calcd 1247.11); Anal. Calcd for $C_{65}H_{59}N_3S_4Se_3$: C, 62.59; H, 4.77; N, 3.37; Found: C, 62.31; H, 4.61; N, 3.20.

Compound **11**.

Compound **1** (35 mg, 0.028 mmol) was placed in a 50 mL two-necked round-bottomed flask, dissolved with THF (10 mL), and degassed with nitrogen. To the mixture was added $LiBEt_3H$ (SUPER HYDRIDE) (1.0 M THF solution, 0.17 mL, 0.17 mmol) dropwise at –78 °C. After stirring for 15 min at –78 °C, Ac_2O (0.08 mL, 0.84 mmol) was added. The mixture was gradually warmed up to room temperature. After stirring for 2 h, the reaction mixture was poured into ice and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:1 hexane/CH_2Cl_2) to give **11** (27 mg, 74%).

Yellow solid; Mp 117–120 °C; ^{1}H NMR ($CDCl_3$) δ 0.89–0.92 (m, 6H), 1.31–1.42 (m, 12H), 1.68–1.71 (m, 4H), 2.43 (s, 9H), 2.76–2.82 (m, 4H), 4.12 (s, 6H), 7.04–7.17 (m, 20H), 7.27–7.29 (m, 1H), 7.35–7.39 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.58–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 28.8, 29.2, 29.2, 29.6, 29.6, 29.7, 30.5, 30.5, 31.7, 34.4, 64.0, 123.9, 124.6, 125.5, 126.1, 126.1, 126.3, 126.3, 127.5, 128.1, 128.9, 129.8, 129.9, 131.2, 131.4, 131.6, 134.0, 135.3, 135.4, 136.6, 136.7, 140.7, 141.6, 142.0, 145.2, 146.0, 197.4; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1298.82 (M^+, calcd 1298.16); Anal. Calcd for $C_{68}H_{68}O_3S_4Se_3$: C, 62.90; H, 5.28; N, 0.00; Found: C, 62.61; H, 5.27; N, 0.00.

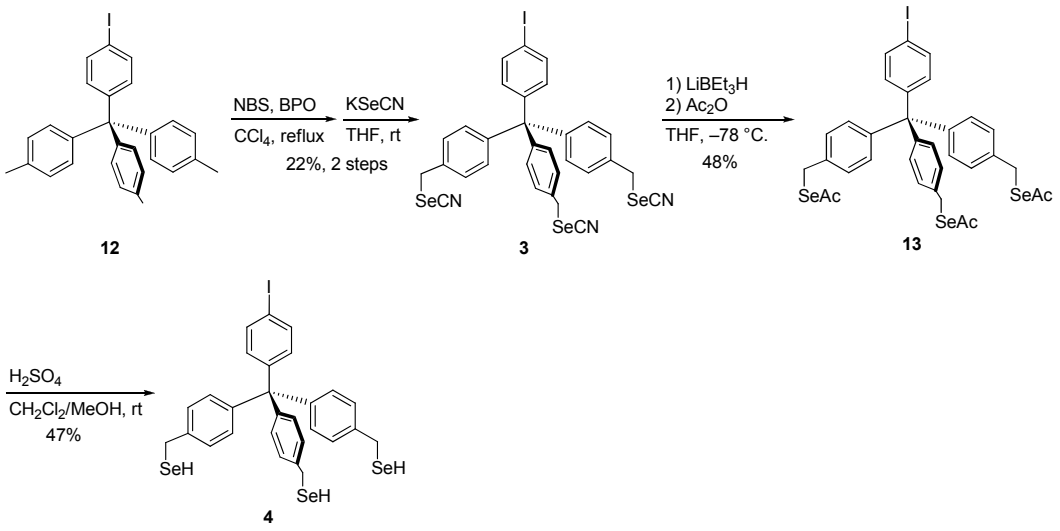
Compound **2**.

Compound **11** (24 mg, 0.019 mmol) was placed in a 100 mL two-necked round-bottomed flask and dissolved with degassed CH_2Cl_2 (37 mL) and degassed MeOH (19 mL). To the mixture was added conc. H_2SO_4 (3.7 mL) dropwise at 0 °C. The mixture was gradually warmed up to room temperature with stirring. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2)

to give **2** (20 mg, 90%).

White solid; ^{1}H NMR ($CDCl_3$) δ 0.02 (t, J = 6.1 Hz, 3H), 0.87–0.92 (m, 6H), 1.20–1.48 (m, 12H), 1.58–1.80 (m, 4H), 2.77–2.80 (m, 4H), 3.80 (d, J = 6.1 Hz, 6H), 7.03–7.08 (m, 2H), 7.10–7.22 (m, 18H), 7.28–7.31 (m, 1H), 7.35–7.42 (m, 2H), 7.45–7.48 (m, 2H), 7.56–7.62 (m, 2H).

Scheme S2. Synthesis of **3** and **4**



Compound **3**.

Compound **12** (1.21 g, 2.48 mmol) was placed in a 50 mL three-necked round-bottomed flask, dissolved with CCl_4 (25 mL), and degassed with nitrogen. To the mixture was added NBS (1.50 g, 8.44 mmol) and BPO (30 mg, 0.12 mmol). The reaction mixture was stirred at 90 °C for 12 h. The reaction mixture was filtered through celite, which was washed with $CHCl_3$. After removal of the solvent from the combined filtrate under reduced pressure, the residue was used for the next reaction without further purification.

The residue was placed in a 200 mL round-bottom flask and dissolved with THF (25 mL) and EtOH (25 mL). To the mixture was added KSeCN (10.73 g, 74.49 mmol), and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:1 hexane/EtOAc) to give **3** (438 mg, 22% in 2 steps).

Colorless solid; Mp 111–113 °C; ^{1}H NMR ($CDCl_3$) δ 4.28 (s, 6H), 6.91 (d, J = 8.7 Hz, 2H), 7.16 (d,

J = 8.5 Hz, 6H), 7.27 (d, *J* = 8.5 Hz, 6H), 7.59 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 32.2, 64.2, 92.3, 101.8, 128.5, 131.4, 132.8, 133.6, 136.9, 145.4, 146.1; Anal. Calcd for $C_{31}H_{22}IN_3Se_3$: C, 46.52; H, 2.77; N, 5.25; Found: C, 46.81; H, 3.17; N, 5.29.

Compound **13**.

Compound **3** (343 mg, 0.429 mmol) was placed in a 100 mL two-necked round-bottomed flask, dissolved with THF (60 mL), and degassed with nitrogen. To the mixture was added $LiBEt_3H$ (SUPER HYDRIDE) (1.0 M THF solution, 2.57 mL, 2.57 mmol) dropwise at –78 °C. After stirring for 15min at –78 °C, Ac_2O (1.22 mL, 12.9 mmol) was added. The mixture was gradually warmed up to room temperature. After stirring for 2 h, the reaction mixture was poured into ice and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:1 hexane/CH_2Cl_2) to give **13** (174 mg, 48%).

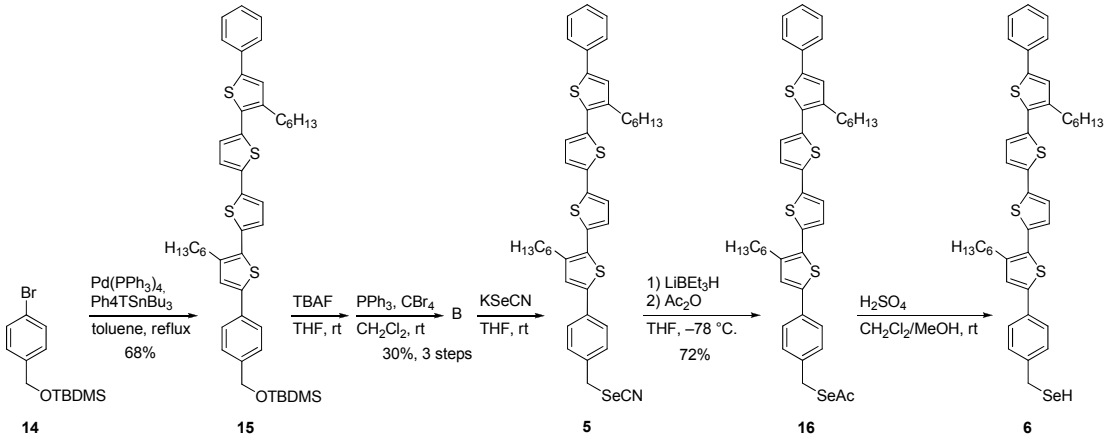
Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 9H), 4.11 (s, 6H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 6H), 7.13 (d, *J* = 8.6 Hz, 6H), 7.53 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 28.7, 34.5, 63.8, 91.8, 128.1, 131.0, 132.9, 136.5, 136.8, 144.7, 146.4, 197.5; Anal. Calcd for $C_{34}H_{31}IO_3Se_3$: C, 47.96; H, 3.67; N, 0.00; Found: C, 48.23; H, 3.71; N, 0.00.

Compound **4**.

Compound **13** (53 mg, 0.062 mmol) was placed in a 100 mL two-necked round-bottomed flask and dissolved with degassed CH_2Cl_2 (25 mL) and degassed MeOH (13 mL). To the mixture was added conc. H_2SO_4 (2.5 mL) dropwise at 0 °C. The mixture was gradually warmed up to room temperature with stirring. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give **4** (29 mg, 47%).

Colorless solid; ^{1}H NMR ($CDCl_3$) δ 0.02 (t, *J* = 6.6 Hz, 3H), 3.79 (d, *J* = 6.6 Hz, 6H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 6H), 7.17 (d, *J* = 8.8 Hz, 6H), 7.56 (d, *J* = 8.8 Hz, 2H).

Scheme S3. Synthesis of **5** and **6**



Compound **15**.

Compound **14** (1.15 g, 3.83 mmol), **Ph4TSnBu$_3$** (2.20 g, 2.55 mmol), and tetrakis(triphenylphosphine)palladium(0) (295 mg, 0.255 mmol) were placed in a test tube and dissolved with toluene (20 mL). The reaction mixture was stirred at 120 °C for 12 h. After removal of the solvent under reduced pressure, the residue was first isolated by column chromatography on silica gel (3:1 hexane/CH_2Cl_2), and then the fraction containing **15** was purified by crystallization from hexane/EtOH to give **15** (1.39 g, 68%).

Yellow solid; Mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 6H), 0.88–0.94 (m, 6H), 0.96 (s, 9H), 1.32–1.45 (m, 12H), 1.65–1.76 (m, 4H), 2.77–2.80 (m, 4H), 4.75 (s, 2H), 7.05–7.07 (m, 2H), 7.14–7.15 (m, 3H), 7.16 (s, 1H), 7.25–7.29 (m, 1H), 7.32–7.40 (m, 4H), 7.55–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –5.2, 14.1, 18.4, 22.6, 25.9, 29.3, 29.6, 30.5, 31.7, 64.7, 123.8, 123.8, 125.3, 125.5, 125.9, 126.1, 126.1, 126.2, 126.6, 127.5, 128.8, 129.6, 129.9, 132.6, 134.0, 135.2, 135.3, 136.5, 136.6, 140.6, 140.9, 141.9, 141.9; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 794.76 (M^+, calcd 794.31); Anal. Calcd for $C_{47}H_{58}OS_4Si$: C, 70.98; H, 7.35; N, 0.00; Found: C, 70.96; H, 7.29; N, 0.00.

Compound **5**.

Compound **15** (261 mg, 0.328 mmol) was placed in a 50 mL round-bottomed flask and dissolved with THF (10 mL). To the mixture was added TBAF (1.0 M THF solution, 0.66 mL, 0.66 mmol), and the mixture was stirred at room temperature for 30 min. The reaction was quenched by addition of sat. $NaHCO_3$ aq, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After

removal of the solvent under reduced pressure, the residue was used for the next reaction without further purification.

The residue was placed in a 50 mL round-bottom flask and dissolved with CH_2Cl_2 (20 mL). To the mixture was added PPh_3 (172 mg, 0.656 mmol) and CBr_4 (163 mg, 0.492 mmol) at 0 °C. The mixture was gradually warmed up to room temperature and stirred for 1 h. After removal of the solvent under reduced pressure, the residue was first isolated by column chromatography on silica gel (CH_2Cl_2), and then the fraction containing **B** was further purified by GPC ($CHCl_3$) to give monobromo compound **B** (114 mg, 47%).

Monobromo compound **B** (86 mg, 0.12 mmol) was placed in a 50 mL round-bottom flask and dissolved with THF (25 mL) and EtOH (25 mL). To the mixture was added KSeCN (167 mg, 1.16 mmol), and the mixture was stirred at room temperature for 12 h. The reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:1 hexane/CH_2Cl_2) to give **5** (56 mg, 63%).

Yellow solid; Mp 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 0.89–0.92 (m, 6H), 1.25–1.48 (m, 12H), 1.65–1.75 (m, 4H), 2.78–2.82 (m, 4H), 4.33 (s, 2H), 7.07 (d, J = 3.9 Hz, 1H), 7.08 (d, J = 3.9 Hz, 1H), 7.15 (d, J = 3.9 Hz, 2H), 7.17 (s, 1H), 7.19 (s, 1H), 7.26–7.30 (m, 1H), 7.36–7.40 (m, 4H), 7.58–7.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.2, 29.6, 30.5, 30.5, 31.6, 32.6, 101.8, 123.9, 123.9, 125.5, 125.9, 126.1, 126.2, 126.4, 126.7, 127.5, 128.9, 129.5, 129.8, 130.6, 133.9, 134.3, 134.4, 135.0, 135.4, 136.5, 136.8, 140.7, 140.7, 141.9; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 769.46 (M^+, calcd 769.14); Anal. Calcd for $C_{42}H_{43}NS_4Se$: C, 65.60; H, 5.64; N, 1.82; Found: C, 65.31; H, 5.54; N, 1.95.

Compound **16**.

Compound **5** (50 mg, 0.065 mmol) was placed in a 50 mL two-necked round-bottomed flask, dissolved with THF (20 mL), and degassed with nitrogen. To the mixture was added Li[Et_3BH] (SUPER HYDRIDE) (1.0 M THF solution, 0.13 mL, 0.13 mmol) dropwise at –78 °C. After stirring for 15 min at –78 °C, Ac_2O (0.06 mL, 0.65 mmol) was added. The mixture was gradually warmed up to room temperature with stirring. After stirring for 2 h, the reaction mixture was poured into ice and extracted with EtOAc. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography

on silica gel (3:1 hexane/CH_2Cl_2) to give **16** (37 mg, 72%).

Yellow solid; Mp 85–86 °C; ^{1}H NMR ($CDCl_3$) δ 0.88–0.92 (m, 6H), 1.30–1.45 (m, 12H), 1.65–1.75 (m, 4H), 2.44 (s, 3H), 2.77–2.82 (m, 4H), 4.16 (s, 2H), 7.06–7.07 (m, 2H), 7.13 (s, 1H), 7.14–7.15 (m, 2H), 7.17 (s, 1H), 7.26–7.31 (m, 3H), 7.36–7.41 (m, 2H), 7.48–7.52 (m, 2H), 7.59–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.0, 29.3, 29.6, 30.5, 30.5, 31.7, 34.5, 123.9, 125.5, 125.7, 126.1, 126.3, 127.5, 128.9, 129.4, 129.9, 132.7, 134.0, 135.3, 135.3, 136.6, 138.6, 140.7, 141.6, 142.0, 197.4; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 786.48 (M^+, calcd 786.16); Anal. Calcd for $C_{43}H_{46}OS_4Se$: C, 65.70; H, 5.90; N, 0.00; Found: C, 65.42; H, 5.87; N, 0.00.

Compound **6**.

Compound **16** (5.0 mg, 0.006 mmol) was placed in a 50 mL two-necked round-bottomed flask and dissolved with degassed CH_2Cl_2 (12 mL) and degassed MeOH (3 mL). To the mixture was added conc. H_2SO_4 (0.3 mL) dropwise at 0 °C. The mixture was gradually warmed up to room temperature with stirring. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The organic layer was washed with brine and dried over Na_2SO_4. This organic solution was used for preparation of monolayers as a 0.5 mM dichloromethane solution of **6**.

Compound **7**.

Tribromo compound **A** (131 mg, 0.112 mmol) and KSAc (128 mg, 1.12 mmol) were placed in a test tube and dissolved with THF (5 mL). The reaction mixture was stirred at 80 °C for 12 h. The reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (1:2 hexane/CH_2Cl_2) to give S-acetyl compound (117 mg, 90%).

Yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.88–0.91 (m, 6H), 1.31–1.42 (m, 12H), 1.65–1.71 (m, 4H), 2.35 (s, 9H), 2.76–2.81 (m, 4H), 4.09 (s, 6H), 7.04–7.06 (m, 2H), 7.11–7.17 (m, 18H), 7.27–7.29 (m, 1H), 7.35–7.39 (m, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.58–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 29.2, 29.2, 29.5, 29.6, 30.3, 30.5, 30.5, 31.7, 32.9, 64.0, 123.9, 124.6, 125.5, 126.1, 126.3, 127.5, 128.0, 128.9, 129.8, 129.9, 131.1, 131.4, 131.6, 134.0, 135.2, 135.3, 135.3, 136.6, 140.7, 140.7, 141.5, 142.0, 145.4, 145.9, 195.1; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z*

1157.23 (M^+, calcd 1156.32).

S-acetyl compound (7 mg, 0.006 mmol) was placed in a 50 mL two-necked round-bottomed flask and dissolved with degassed CH_2Cl_2 (12 mL) and degassed MeOH (6 mL). To the mixture was added conc. H_2SO_4 (1.2 mL) dropwise at 0 °C. The mixture was gradually warmed up to 60 °C with stirring. After stirring for 12 h, the reaction was quenched by addition of water, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to give **7** (3 mg, 48%). Yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.87–0.92 (m, 6H), 1.24–1.33 (m, 12H), 1.64–1.72 (m, 4H), 1.78 (t, J = 7.6 Hz, 3H), 2.78–2.84 (m, 4H), 3.73 (d, J = 7.6 Hz, 6H), 7.03–7.07 (m, 2H), 7.13–7.23 (m, 18H), 7.28–7.31 (m, 1H), 7.35–7.41 (m, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.58–7.62 (m, 2H).

Preparation of Monolayers

The Au(111) (1500 Å) on mica was purchased from Agilent Technologies. Gold substrates (200 Å) used for obtaining the data in Figures 3 and S2 were prepared by thermal evaporation onto freshly cleaved mica at a deposition rate of 1.0 Å s^{-1}. Monolayers were formed by immersion of the gold substrates into a 0.5 mM solution in CH_2Cl_2 (99.9%, HPLC grade, Aldrich) for CV measurements and a 5 mM solution in $CHCl_3$ (99.9%, HPLC grade, Aldrich) for XPS and UPS measurements. After immersion, the samples were rinsed with the same solvent repeatedly and dried under a stream of nitrogen.

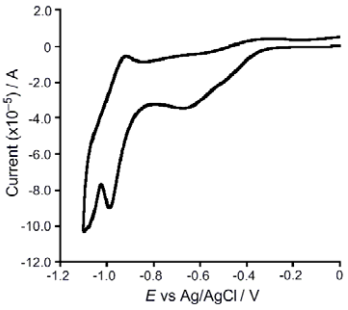
The surface coverage of monolayers was estimated by the following equation.

$$\Gamma(\text{mol cm}^{-2}) = \frac{A_p \times Es \times i_s}{e \times N_A \times S_E \times Ss \times As}$$

Γ (mol cm^{-2}) : surface coverage
A_p (cm^2) : peak area
e (C) : elementary electric charge (1.6022×10^{-19})
N_A (mol^{-1}) : Avogadro constant (6.022×10^{23})
S_E (cm^2) : area of gold electrode (0.50)
Es (V) × i_s (A) : integrated charge of standard area
Ss (V s^{-1}) : scan rate (100×10^{-3})
As (cm^2) : standard area

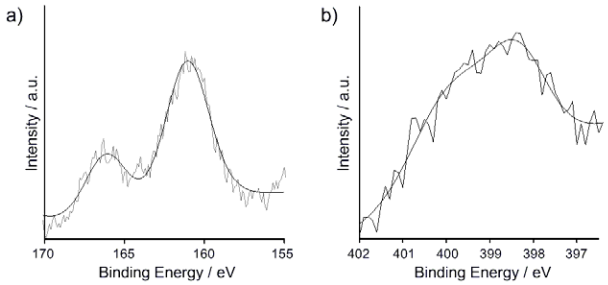
Cyclic Voltammetry of Monolayers

Fig. S1 Cyclic voltammogram of reductive desorption of **2** on Au(111) in 0.5 M KOH.



XPS Spectra of 3

Fig. S2 Normalized Se 3p (a) and N 1s (b) XPS spectra of **3** on Au.



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