Supporting Information

INTRODUCTION OF HETEROARENE FUNCTIONALITY ON THE BIPEDAL-THIOL-CAPPED GOLD NANOPARTICLE BY DEPROTONATIVE C-H COUPLING WITH PALLADIUM COMPLEX

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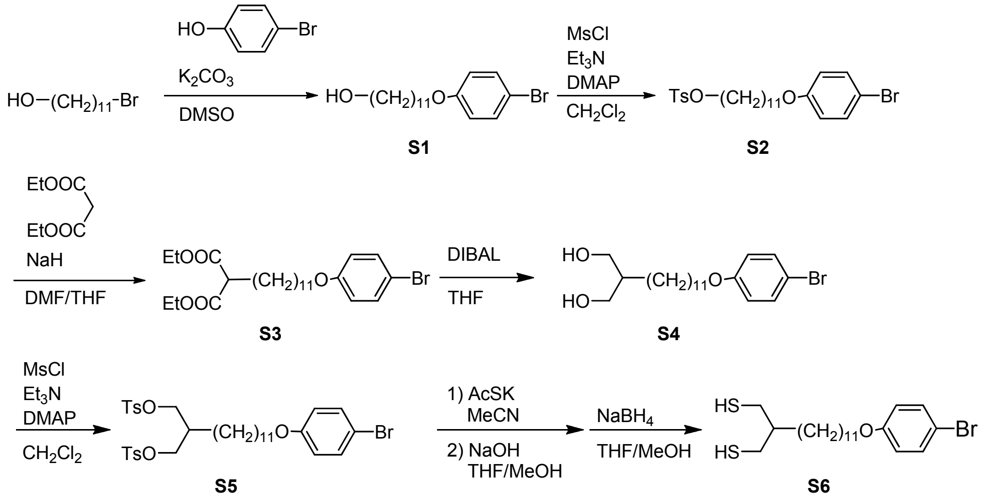
Experimental Section

Synthetic procedure for dithiol S6[1]



Synthesis of 11-(4-bromophenoxy)undecanol (S1): To a Schlenk tube equipped with a magnetic stirring bar were added 11-bromo-1-undecanol (12.6 g, 50 mmol), K_2CO_3 (20.7 g, 150 mmol), *p*-bromophenol (10.8 g, 62.5 mmol) and DMSO (50 mL). After stirring for 22 h, the reaction mixture was poured into water. The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel to afford 15.0 g of **S1** as white solid (87%). ^{1}H NMR : δ 7.34-7.37 (m, 2H), 6.75-6.78 (m, 2H), 3.91 (t, J = 6.6 Hz, 2H), 3.64 (t, J = 6.4, Hz, 2H), 1.71-1.81 (m, 3H), 1.22-1.46 (m, 17H). ^{13}C NMR: δ 158.18, 132.13, 116.23, 112.49, 68.19, 63.04, 32.74, 29.54, 29.50, 29.46, 29.38, 29.31, 29.11, 25.94, 25.70. IR: 2920, 2850, 1490, 1286, 1245, 1173, 1005, 815, 642 cm^{-1}. HRMS (EI) Calcd for $C_{17}H_{27}BrO_2$ $[M]^+$: 342.1194, found: m/z 342.1192.

Synthesis of 1-(4-bromophenoxy)-11-(toluenesulfonyl)undecane (S2): To a Schlenk tube were added **S1** (15.0 g, 43.7 mmol), triethylamine (7.3 mL, 52.5 mmol), DMAP (0.214 g, 1.75 mmol) and 150 mL of CH_2Cl_2. To the mixture was added 4-toluenesulfonyl chloride (10.0 g, 52.5 mmol) at 0 °C. After stirring for 40 h at room temperature, the resulting mixture was poured into water. The aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel to afford 17.4 g of **S2** as white solid (80%). The product was subjected to the following reaction without further purification.

Synthesis of diethyl-2-[11-(4-bromophenoxy)undecyl]malonate (S3): To a Schlenk tube equipped with a magnetic stirring bar were added NaH (2.94 g, 122.7 mmol), DMF (50 mL), and THF (150 mL) at 0 °C under N_2 atmosphere. Diethyl malonate (105.2 mL, 16.0 mmol) was added slowly to the resulting solution. The mixture was then stirred at room temperature for 15 min and **S2** (17.4 g, 35.1 mmol) thus obtained in the previous protocol was added. Stirring was continued for 17 h under reflux. The resulting mixture was concentrated under reduced pressure and then poured into water. The aqueous layer was extracted with Et_2O twice and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude oil, which was purified by column chromatography on silica gel to afford 13.9 g of **5** as white solid (82%).^{1}H NMR: δ 7.32-7.35 (m, 2H), 6.73-6.77 (m, 2H), 4.14-4.21 (m, 4H), 3.89 (t, *J*=6.6 Hz, 2H), 3.30 (t, *J*=7.5 Hz, 1H), 1.83-1.91 (m, 2H), 1.74 (tt, *J*=6.7, 7.9 Hz, 2H), 1.35-1.46 (m, 2H), 1.18-1.29 (m, 20H). ^{13}C NMR: δ 196.53, 158.18, 132.09, 116.22, 112.45, 68.17, 61.17, 52.01, 29.44, 29.42, 29.40, 29.28, 29.22, 29.14, 29.09, 28.67, 27.25, 25.91, 14.03. IR: 2926, 2848, 1732, 1489, 1243, 1181, 1031, 822, 45 cm^{-1}. HRMS (EI) Calcd for $C_{24}H_{37}BrO_5$ $[M]^+$: 484.1824; found: m/z 484.1826.

Synthesis of 1,3-dihydroxy-2-[11-(4-bromophenoxy)undecyl]propane (S4): To a Schlenk tube equipped with a magnetic stirring bar were added **S3** (13.9 g, 28.6 mmol) and 180 mL of THF. The resulting solution was cooled to -15 °C and hexane solution of DIBAL-H (1.02 M, 117 mL, 120 mmol) was added dropwise. Stirring was continued at -15 °C for 26 h. The reaction was quenched by the addition of methanol and HCl. The resulting mixture was concentrated under reduced pressure and then poured into water. The aqueous layer was extracted with Et_2O repeatedly and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude solid, which was washed repeatedly with hexane to afford 10.3 g of **S4** as white solid (89%).^{1}H NMR: δ 7.33-7.38 (m, 2H), 6.74-6.79 (m, 2H), 3.91 (t, *J*=6.5 Hz), 3.82 (dd, J=10.6, 3.5 Hz), 3.65 (dd, *J*=10.5, 7.6 Hz), 1.76 (tt, *J*=6.8, 6.5 Hz), 1.63 (s, 2H), 1.38-1.492 (m, 1H), 1.16-1.37 (m, 19H). ^{13}C NMR: δ 132.17, 116.28, 112.53, 68.25, 66.76, 41.97, 29.85, 29.56, 29.52, 29.50, 29.43, 29.33, 29.14, 27.67, 27.20, 25.96. IR: 2920, 2851, 1489, 1240, 1034, 820, 642 cm^{-1}. HRMS (EI) Calcd for $C_{20}H_{33}BrO_3$ $[M]^+$: 400.1613; found: m/z 400.1607,

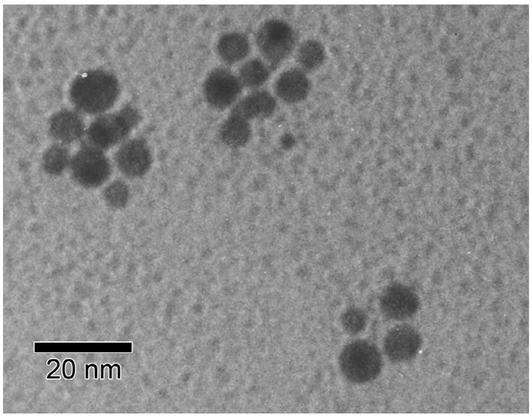
Synthesis of the 2-[11-(4-bromophenoxy)undecyl]-1,3-di(toluenesulfonyl)propane

(S5): To a Schlenk tube equipped with a magnetic stirring bar were added **S4** (10.29 g, 25.7 mmol), triethylamine (8.93 mL, 64.1 mmol), DMAP (0.25 g, 2.1 mmol), and 200 mL of CH_2Cl_2. To a resulting solution was added 4-toluenesulfonyl chloride (12.2 g, 64.1 mmol) at 0 °C. After stirring for 40 h at room temperature, the mixture was poured into water. The aqueous layer was extracted with CH_2Cl_2 twice and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude solid, which was purified by column chromatography on silica gel to afford 10.7 g of **S5** (74%). The product was subjected to the following reaction without further purification.

Synthesis of 2-[11-(4-bromophenoxy)undecyl]-1,3-dimercaptopropane (S6): To a Schlenk tube equipped with a magnetic stirring bar were added **S5** (10.7 g, 15.1 mmol), potassium thioacetate (4.15 g, 36.3 mmol), and 150 mL of MeCN and the resulting mixture was stirred at 70 °C for 3 h. The reaction mixture was poured into water and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layer was dried over anhydrous sodium sulfate and the solvent was concentrated under reduced pressure to leave a crude solid. THF(50 mL) and MeOH (100 mL) were added to form a solution. NaOH (1.81 g, 45.4 mmol) was added to the solution and stirring was continued for 4 h. The reaction was quenched by the addition of HCl. The resulting mixture was concentrated under reduced pressure and then poured into water. The aqueous layer was extracted with CH_2Cl_2 twice and combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude solid, which was purified by column chromatography on silica gel to afford a yellow solid.

To a flask equipped with a magnetic stirring bar were added the yellow solid, MeOH (40 mL), and THF (40 mL) to form a solution. $NaBH_4$ (0.50 g, 13.2 mmol) was added to the solution at 0 °C and the stirring was continued for 2 h. The reaction was quenched by the addition of HCl. The resulting mixture was concentrated under reduced pressure and then poured into water. The aqueous layer was extracted with CH_2Cl_2 twice and the combined organic layer was dried over anhydrous sodium sulfate. Concentration of the solvent under reduced pressure left a crude solid, which was purified by column chromatography on silica gel to afford 5.12 g of **S6** as yellow solid (90%).^{1}H NMR: δ 7.32-7.37 (m, 2H), 6.73-6.78 (m, 2H), 3.90 (t, J=6.6 Hz, 2H), 2.56-2.81 (m, 4H), 1.62-1.80 (m, 2H), 1.34-1.47 (m, 1H), 1.24-1.47 (m, 18H), 1.12 (t, J=8.4 Hz). ^{13}C NMR: δ 158.20, 132.12, 116.28, 116.25, 112.50, 68.21, 42.59, 31.63, 31.40, 29.66, 29.51, 29.48, 29.30, 29.12, 26.84, 26.70, 25.94. IR: 2923, 2852, 1488, 1243, 1171, 1002, 821, 640 cm^{-1}. HRMS (ESI-) Calcd for $C_{20}H_{32}BrOS_2$ [M-H]$^-$: 431.1078; found m/z 431.1079

TEM images of gold nanoparticles

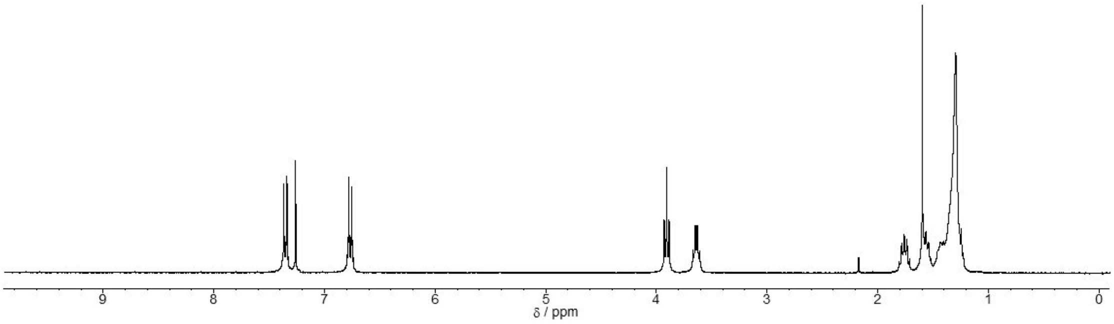


AuNP **3a** (7.6±1.6 nm)

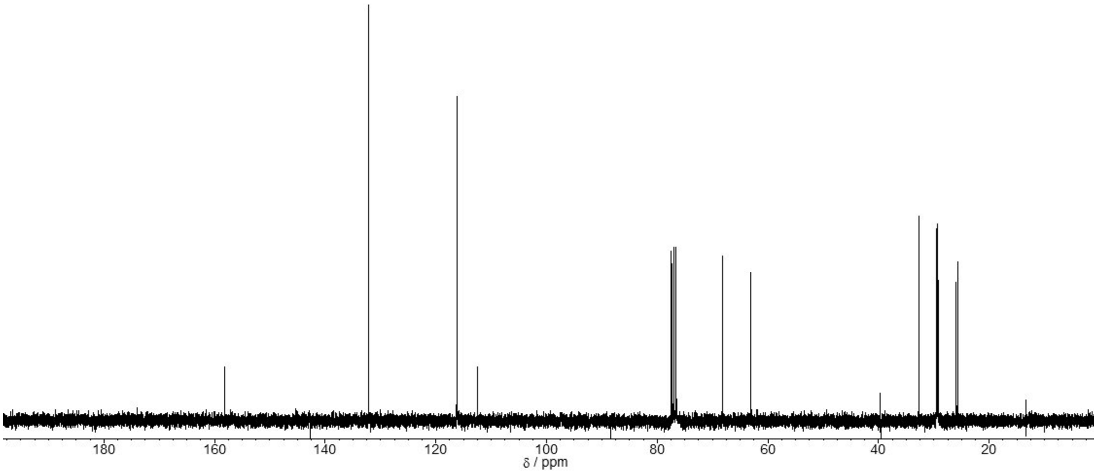
^{1}H NMR spectra

NMR spectra of 11-(4-bromophenoxy)undecanol (S1)

^{1}H NMR

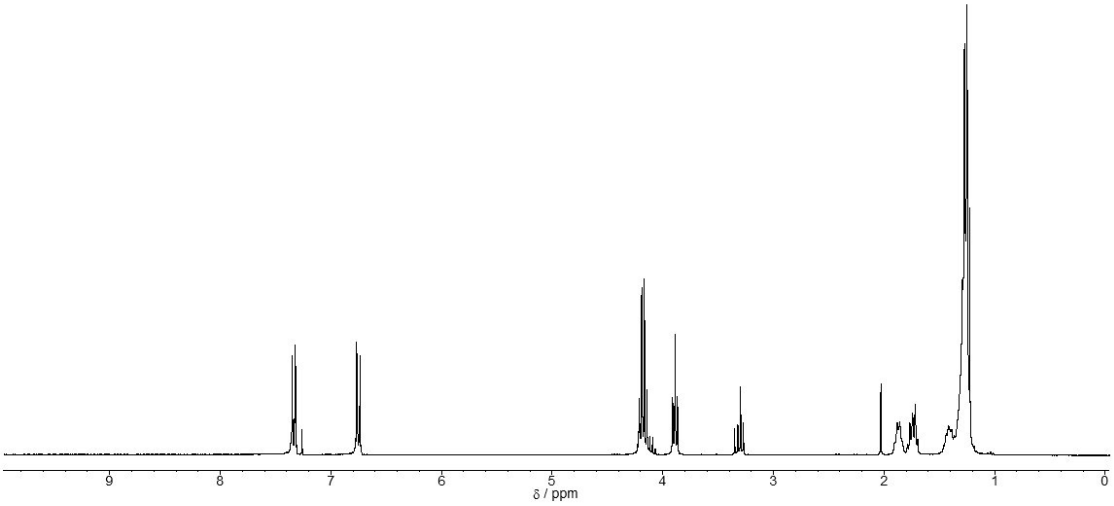


^{13}C NMR



NMR spectra of diethyl-2-[11-(4-bromophenoxy)undecyl]malonate (S3)

^{1}H NMR



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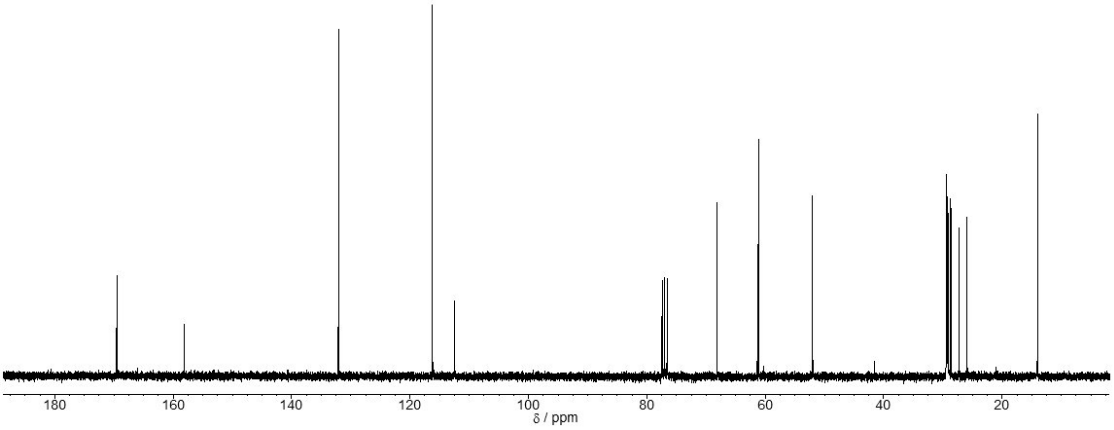
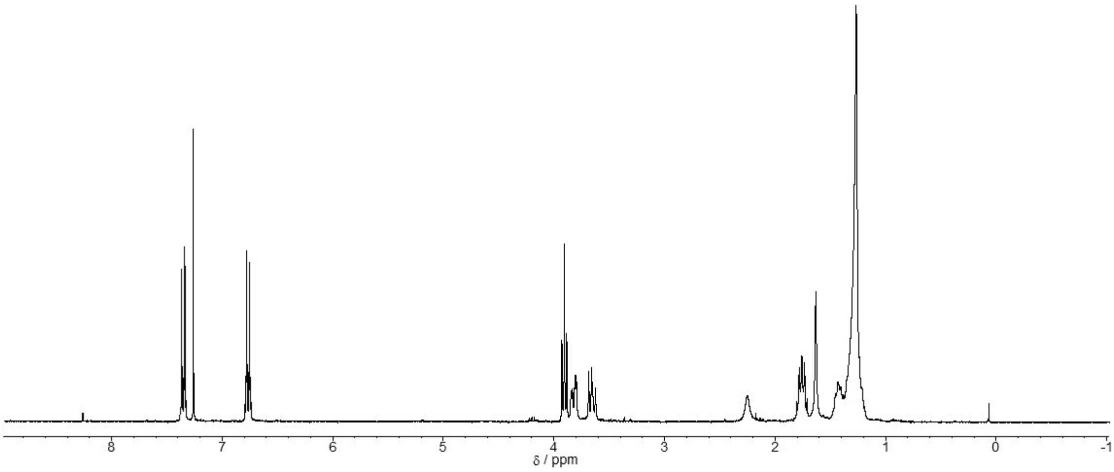
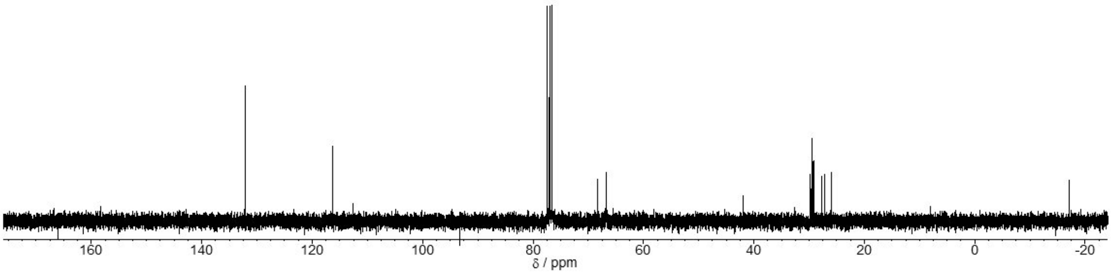


NMR spectra of 1,3-dihydroxy-2-[11-(4-bromophenoxy)undecyl]propane (S4)

^{1}H NMR

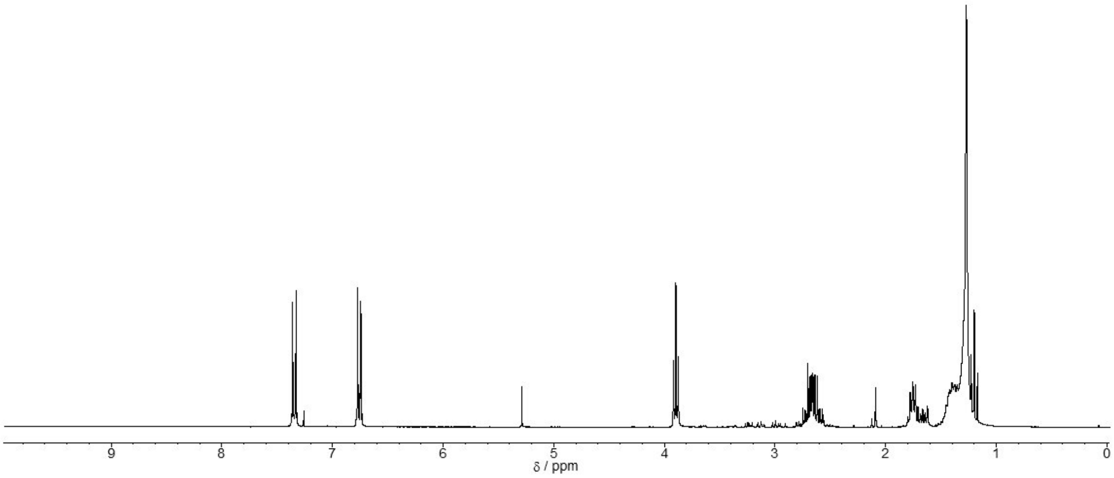


^{13}C NMR

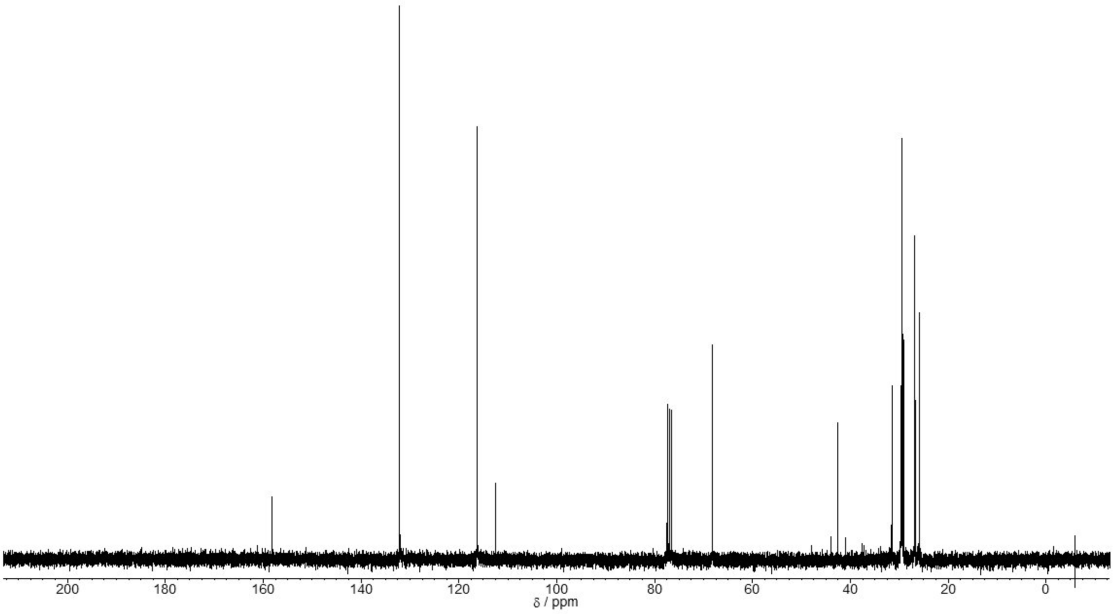


NMR spectra of 2-[11-(4-bromophenoxy)undecyl]-1,3-dimercaptopropane (S6)

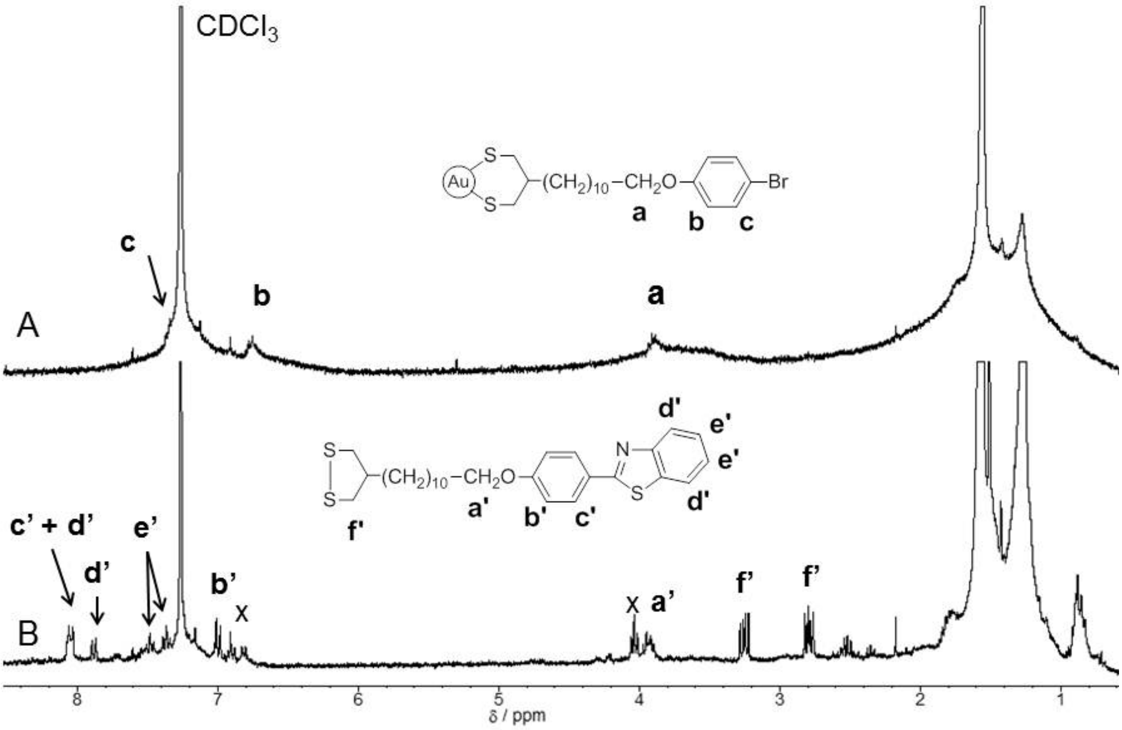
^{1}H NMR



^{13}C NMR



^{1}H NMR spectrum of AuNP 1 (A) and dithiorane 2 (B) in $CDCl_3$



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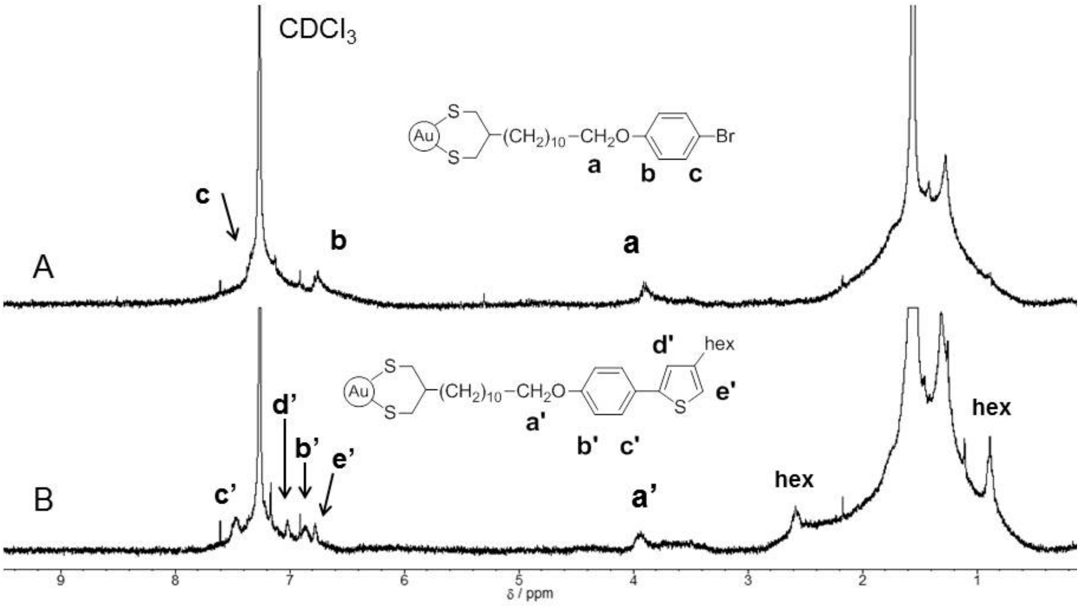

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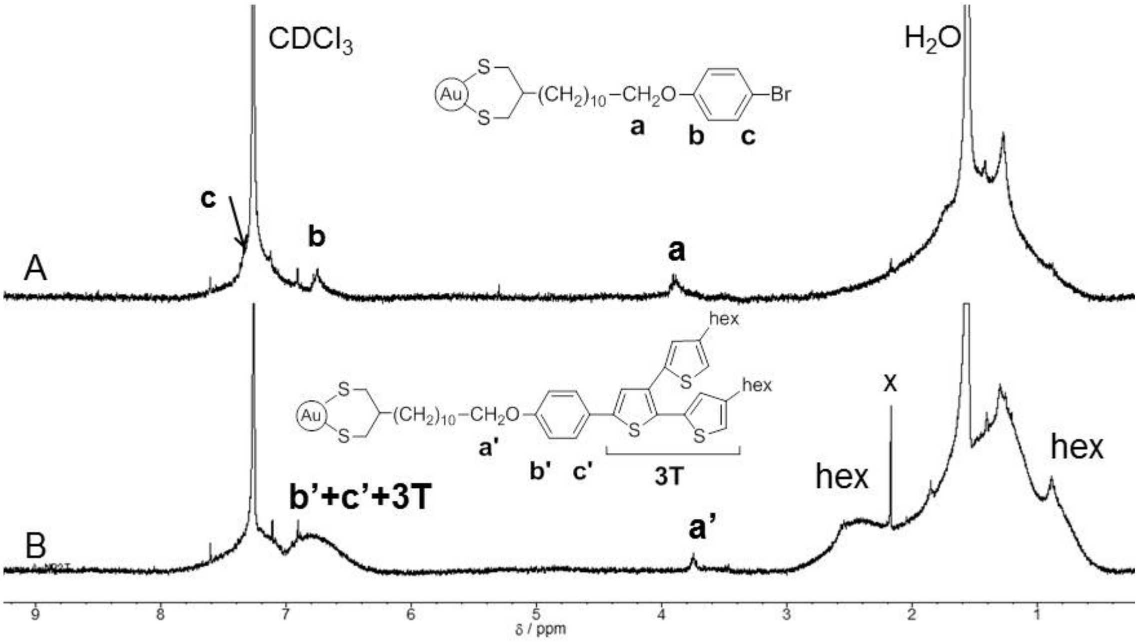

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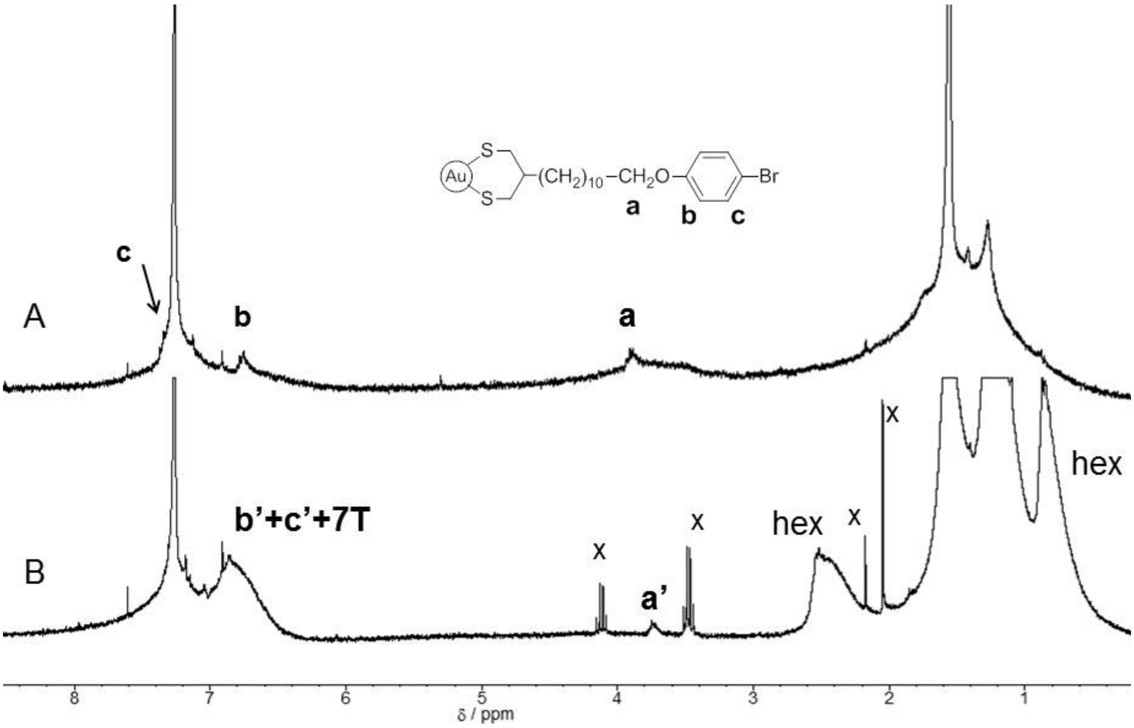

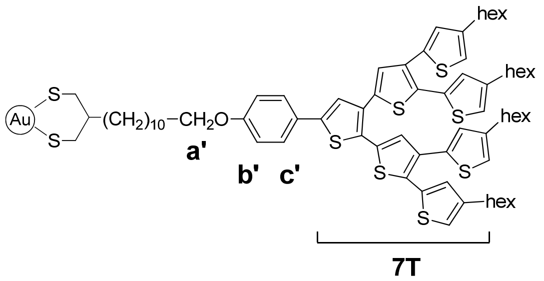

References

1 Sugie, A.; Kumazawa, K.; Hatta, T.; Kanie, K.; Muramatsu, A.; Mori, A. *Chem. Lett.* **2011**, *40*, 1450.