Supplementary Material (ESI) for Chemical Communications

Electronic supplementary information (ESI)

One-Phase Synthesis of Small Gold Nanoparticles Coated by a Horizontal Porphyrin Monolayer

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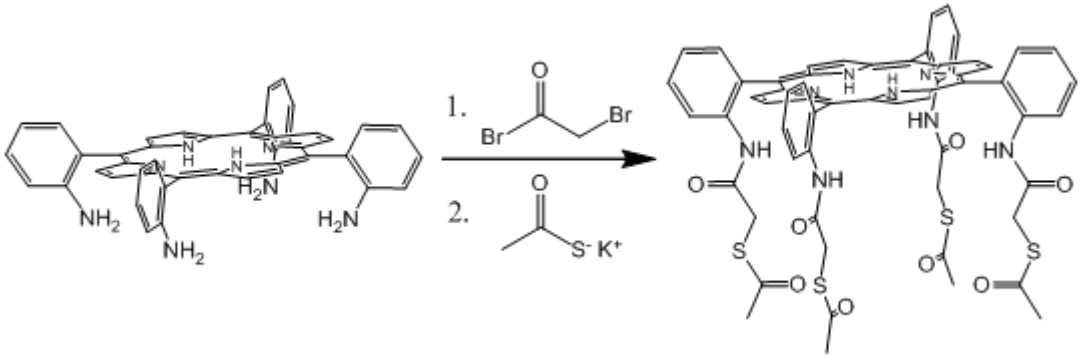
General methods. Electronic absorption spectra were measured on a HITACHI U-3500 UV-VIS-NIR spectrometer by using a quarts cell with a 1-cm path length. ^{1}H, ^{13}C, 2D (HMQC, HMBC) NMR spectra were measured in $CDCl_3$ on a JEOL JNM-ECX400 spectrometer. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-100SX operating at an accelerating voltage of 100 kV.TEM samples were prepared by depositing of drops of a methanol solution onto a carbon-coated copper grid (Okenshoji Co. LTD.) and dried to the solvent at room temperature. X-ray photoelectron spectra (XPS) were acquired using an ULVAC PHI 5500MT. XPS samples were mounted on an indium foil and the spectra were measured using Mg K_{α} radiation (15 kV, 400 W) in a chamber with the base pressure of ca. 1×10^{-8} Torr. The take-off angle was set at 45º. All binding energies were corrected for charge shifting by referencing to the C(ls) line from the adventitious carbon at 284.6 eV.

Materials. All solvents were purchased from Wako Pure Chemical Industry. 2-Nitrobenzaldehyde, pyrrole, and potassium thioacetate were purchased from Tokyo Chemical Industry, and the other chemicals were from Wako Pure Chemical Industry. 5,10,15,20-Tetrakis(*o*-nitrophenyl)-porphyrin and 5,10,15,20-tetrakis(*o*-aminophenyl)-

porphyrin were synthesized according to the literature,[1] and the latter was atropisomerized to the α,α,α,α−atoropisomer according to the Lindsey's procedure.[2]

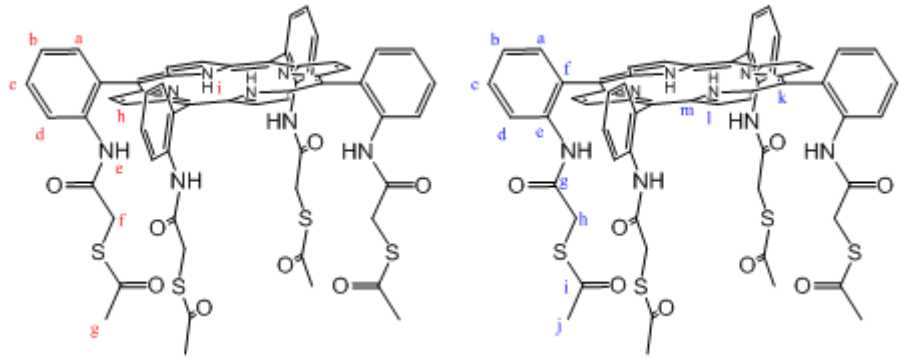
α,α,α,α-5,10,15,20-tetrakis(2-(S-acetyl-thioacetamido)phenyl)porphyrin (1).



To a solution of α,α,α,α−5,10,15,20-tetrakis(2-aminophenyl) porphyrin (0.498 g, 0.738 mmol) in dry THF (80 mL) was diethylaniline (1.6 mL, 10.3 mmol) added under N_2. Bromoacetyl bromide (641 μL, 7.34 mmol) in CH_2Cl_2 (11 mL) was added to the mixture dropwise over 5 min at 0ºC and stirred for 1 h at 0ºC. Then, potassium thioacetate (1.7 g, 14.9 mmol) in dry EtOH (80mL) was added to the mixture and stirred for 2 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluted with $CHCl_3$ and subsequent recrystalization from $CHCl_3$-MeOH. 0.240 g (0.211 mmol, 29%). TLC R_f = 0.62 ($CHCl_3$:MeOH 10:1); HRMS-FAB (m/z): $[M+H]^+$ calcd for $C_{60}H_{50}O_8N_8S_4$, 1138.26; found, 1138.2642; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.78 (s, 8H, H_h), 8.57 (d, 4H, H_a), 7.99 (d, 4H, H_d), 7.85

(dd, 4H, H_c), 7.64 (s, 4H, H_e), 7.54 (dd, 4H, H_b), 3.56 (s, 8H, H_f), 0.75 (s, 12H, H_g), -2.69 (s, 2H, H_i).; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 194.1 (C_i), 165.9 (C_g), 138.2 (C_e), 134.6 (C_d), 131.8 (C_f), 131.4 (C_l), 129.9 (C_c), 123.6 (C_b), 121.8 (C_a), 114.8 (C_k), 33.2 (C_h), 28.7 (C_j) (C_m could not be observed, presumably due to N-H tautomerism[3];

UV-Vis λ_{max} in DMF: 422, 516, 550, 591, 647 nm.



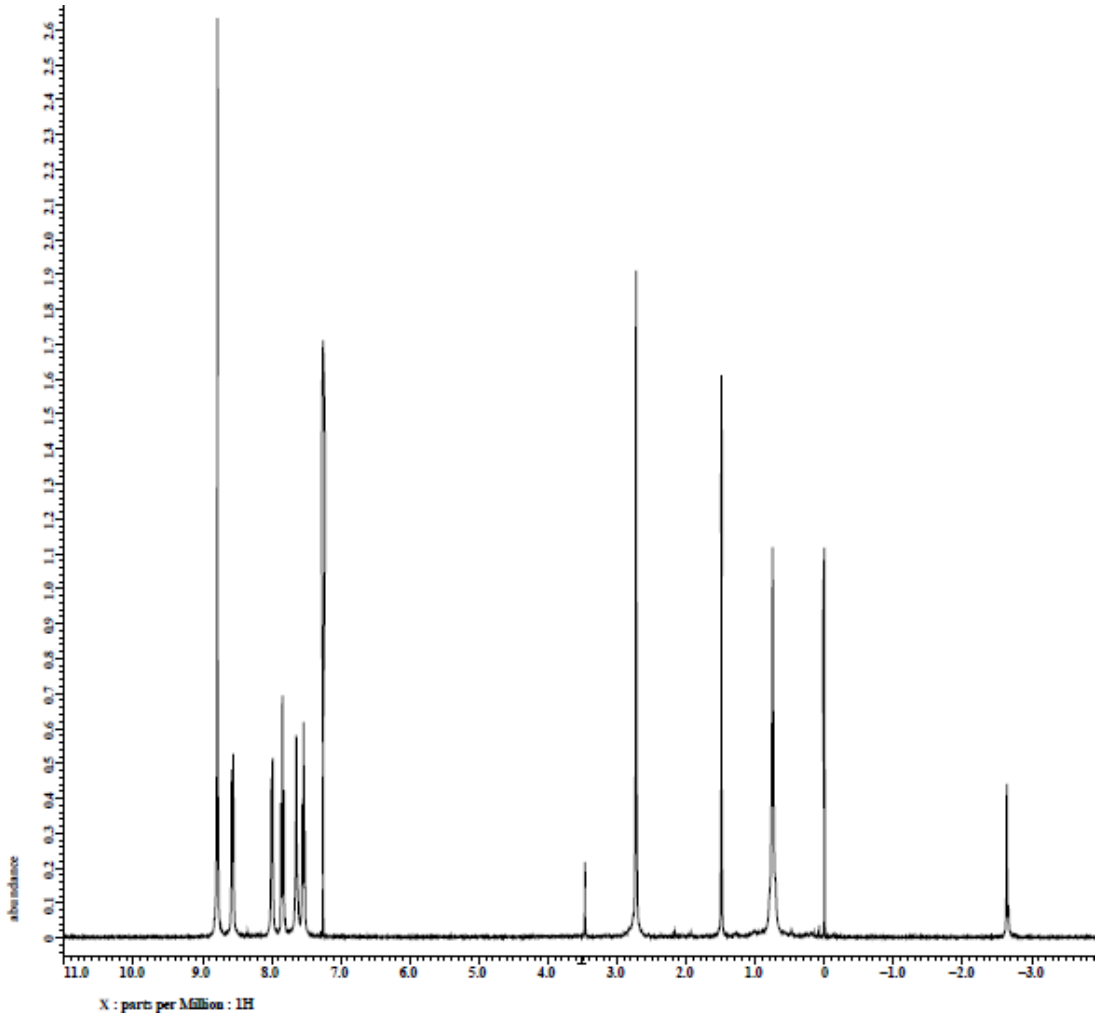


Fig. S1 ^{1}H-NMR chart of **1**.

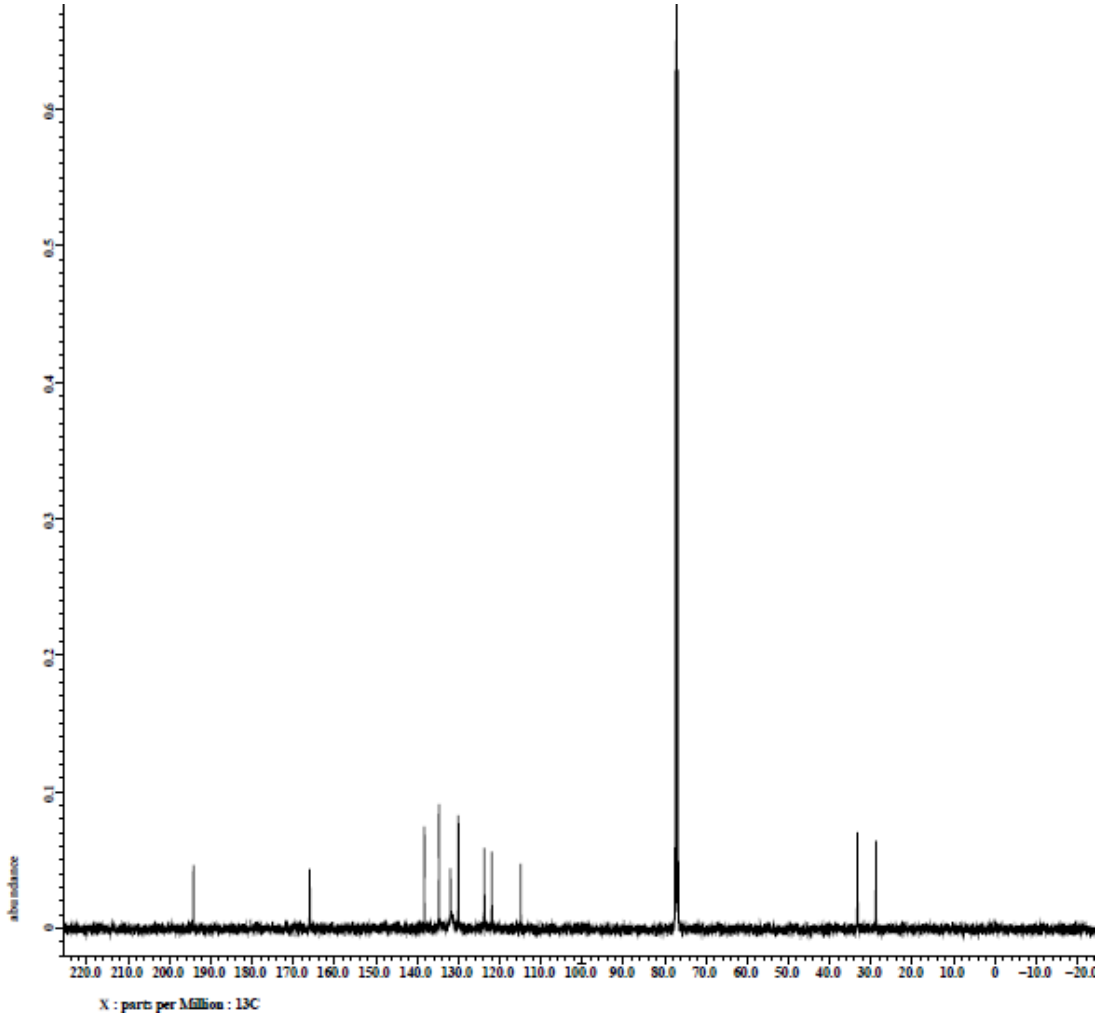


Fig. S2 ^{13}C-NMR chart of **1**.

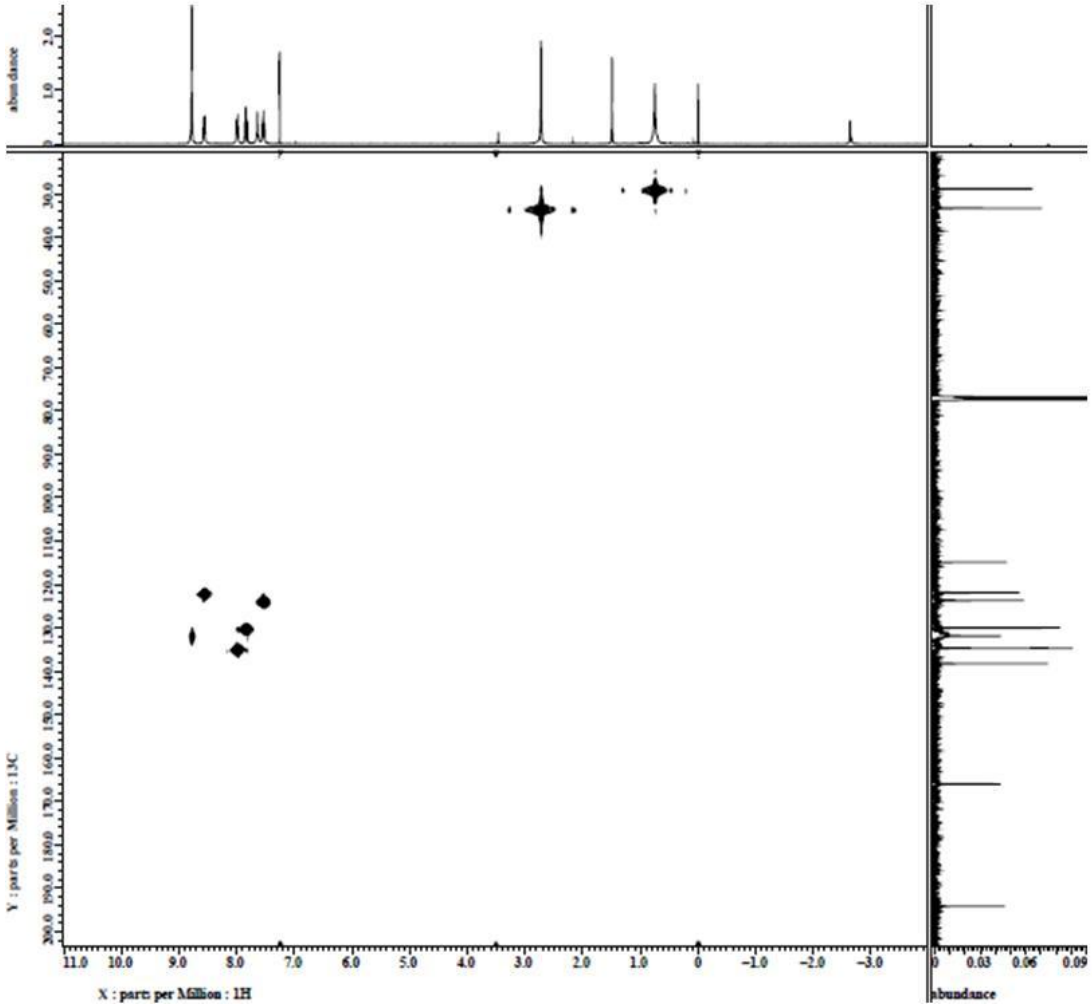


Fig. S3 HMQC chart of **1**.

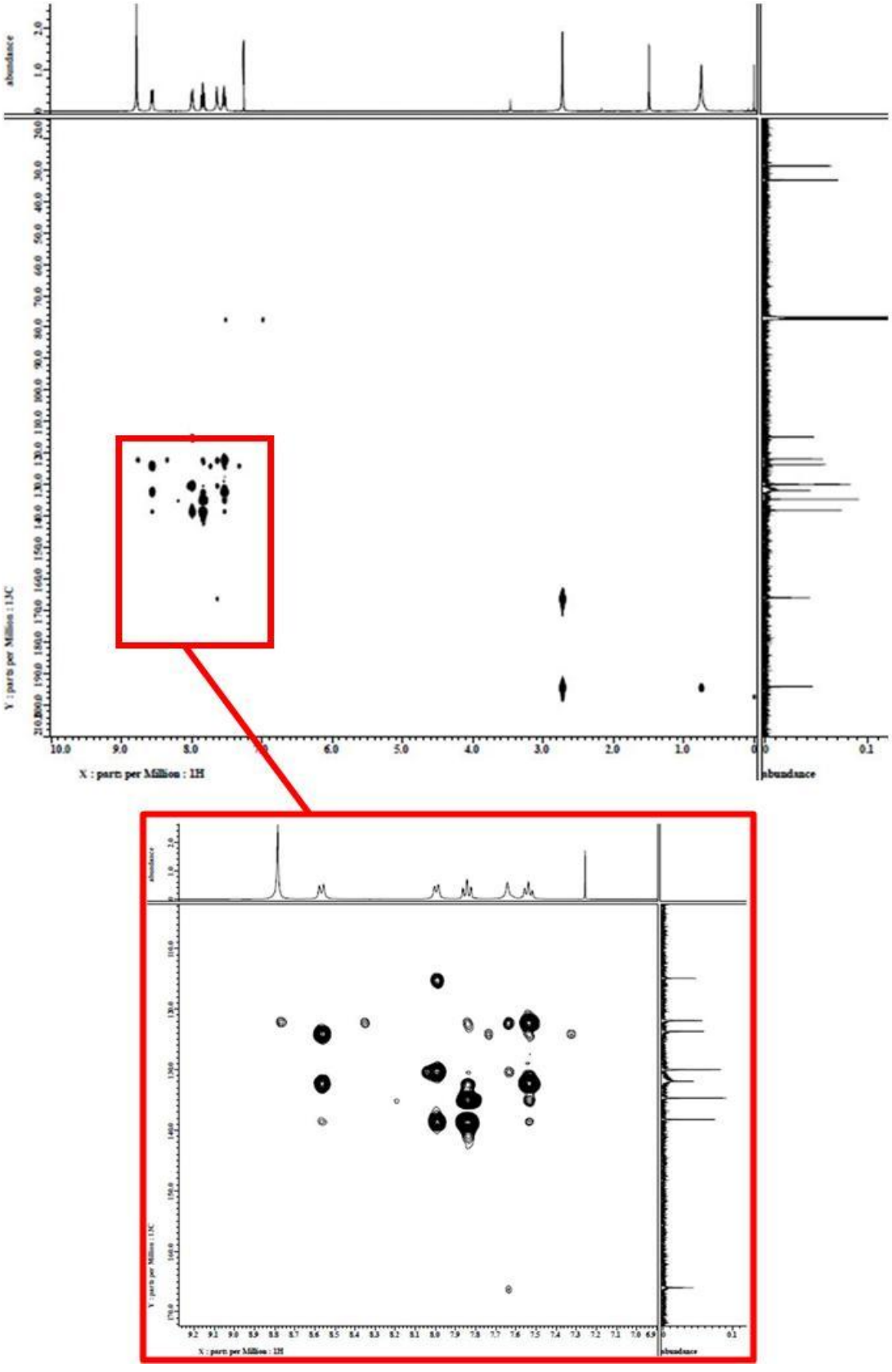
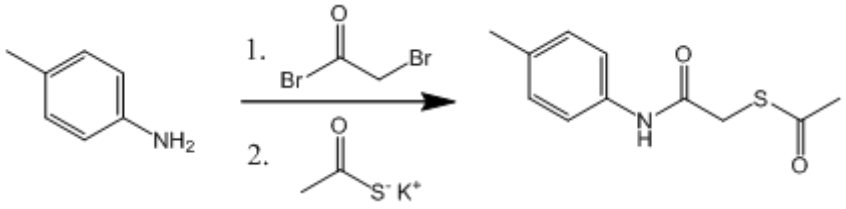
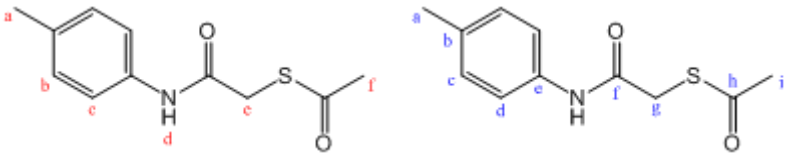


Fig. S4 HMBC chart of **1**.

4-(S-Acetyl-thioacetamido)-toluene (2).



Compound **2** was synthesized by the similar procedure to **1**. *p*-Toluidine (535.8 mg, 5.00 mmol) was reacted with bromoacetyl bromide (1.1 mL, 12.6 mmol) in the presence of diethylaniline (2.5 mL, 15.6 mmol) under N_2 and 0 ºC, followed by reaction with potassium thioacetate (2.83 g, 24.8 mmol) under N_2. The product was purified by column chromatography on silica gel with chloroform and 100:1 chloroform:methanol, and followed by recrystalization from hexane-AcOEt. 0.786 g (3.52 mmol, 70%). TLC R_f = 0.50 ($CHCl_3$:MeOH 100:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02 (s, 4H, H_d), 7.37 (d, 2H, H_c), 7.12 (d, 2H, H_b), 3.65 (s, 2H, H_e), 2.45 (s, 3H, H_a), 2.31 (s, 3H, H_f). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 197.0 (C_h), 166.2 (C_f), 135.0 (C_b), 134.2 (C_e), 129.5 (C_c), 120.0 (C_d), 34.2 (C_g), 30.3 (C_i), 20.9 (C_a).



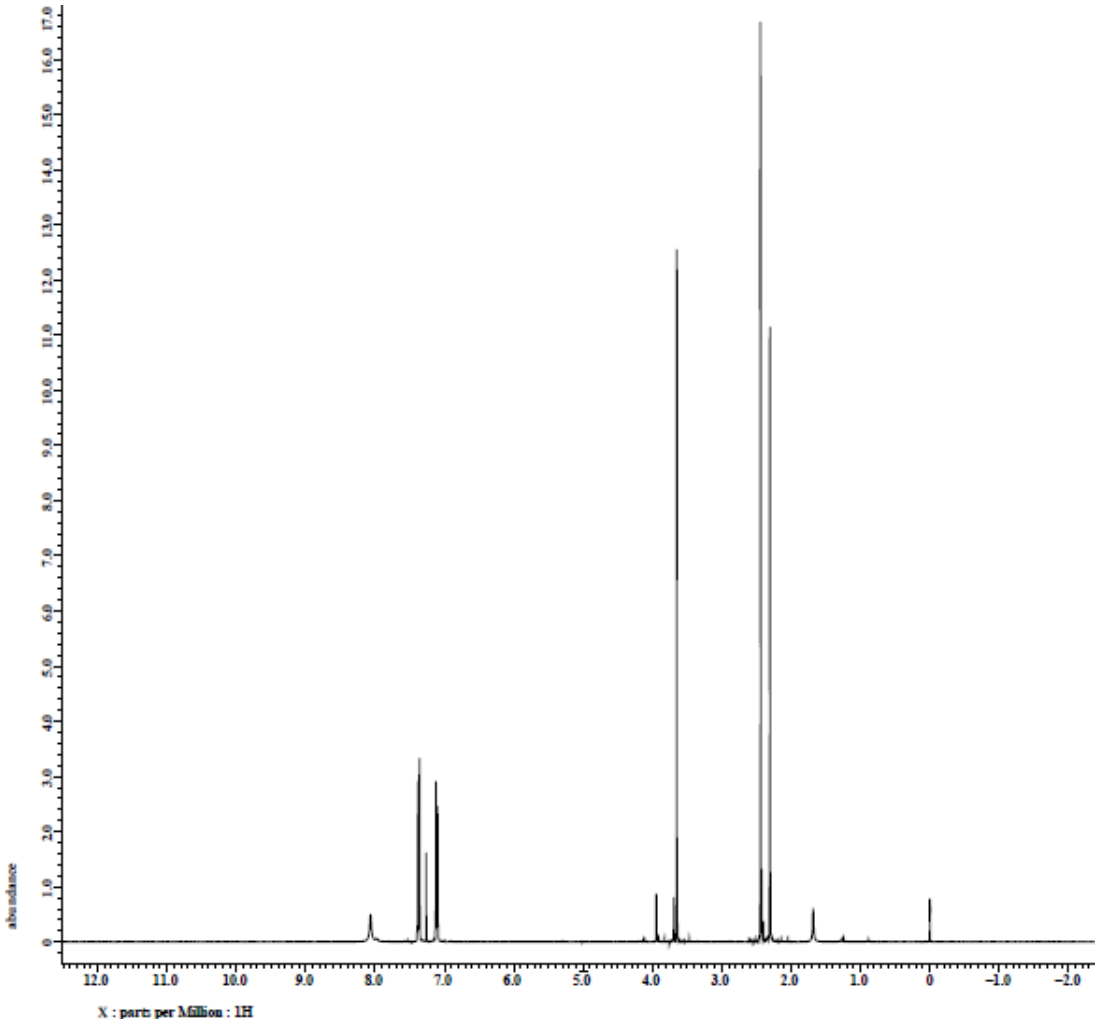


Fig. S5 ^{1}H-NMR chart of **2**.

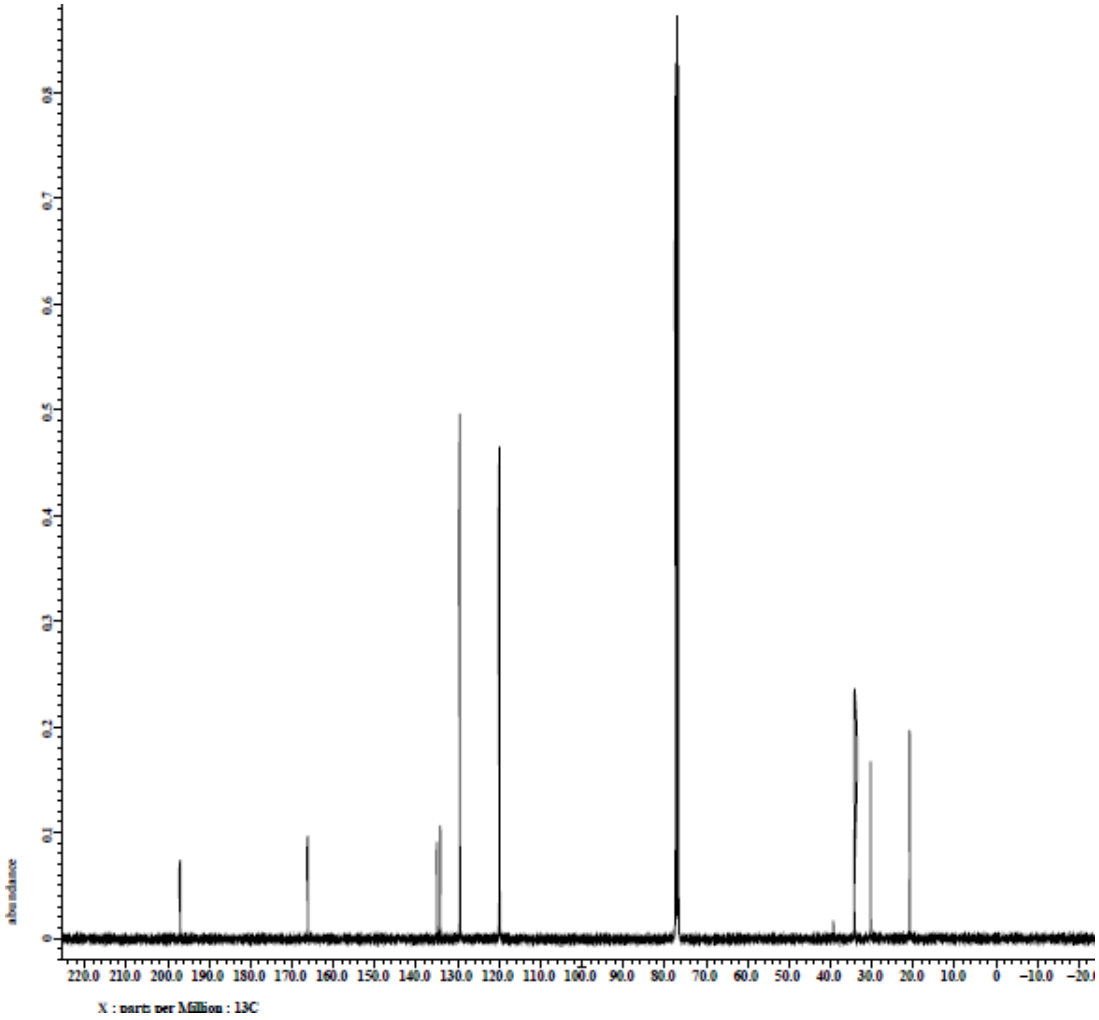


Fig. S6 ^{13}C-NMR chart of **2**.

Gold nanoparticles covered with 1 (GN@1).

A solution of **1** (11.4 mg, 10.0 μmol) in DMF (180 mL) was added to a 300 mL round-bottom flask which was cleaned with piranha solution. 40.0 μM $HAuCl_4$ solution in DMF (2 mL) was added and the mixture was reduced with $NaBH_4$ (18.25 mg, 772

μmol) dissolved in DMF. After 2 hour stirring, the reaction mixture was evaporated to ca. 3 mL and precipitated by 30 mL of methanol to remove excess amount of **1** and $NaBH_4$. The precipitate was dissolved in 2 mL of DMF and reprecipitated by 30 mL of $CHCl_3$. The reprecipitation process was repeated five times. Purified **GN@1** was characterized by TEM, UV-vis and XPS measurements.

Size controlled synthesis of gold nanoparticles. Gold nanoparticles were synthesized in the presence of **1**, **2**, and dodecanethiol under various molar ratios (S/Au = 0, 0.1, 0.2, 1, 4 and 16). All of glass vials for the syntheses of gold nanoparticles were cleaned with piranha solution. A typical method is as follows; 8 mL of 1.01 mM **1** solution of DMF (8.08 μmol), 93.5 μL of 21.4 mM hydrogen tetrachloroaurate trihydrate solution of DMF (2.00 μmol) and 1.8 mL of DMF were added to a reaction vessel. While the mixture was vigorously stirring, 100 μL of 0.248 M sodium borohydride (24.8 mmol) was swiftly added and then stirred for 1 hour. The solutions were evaporated and the residue was dispersed in MeOH. All samples were observed by TEM without purification.

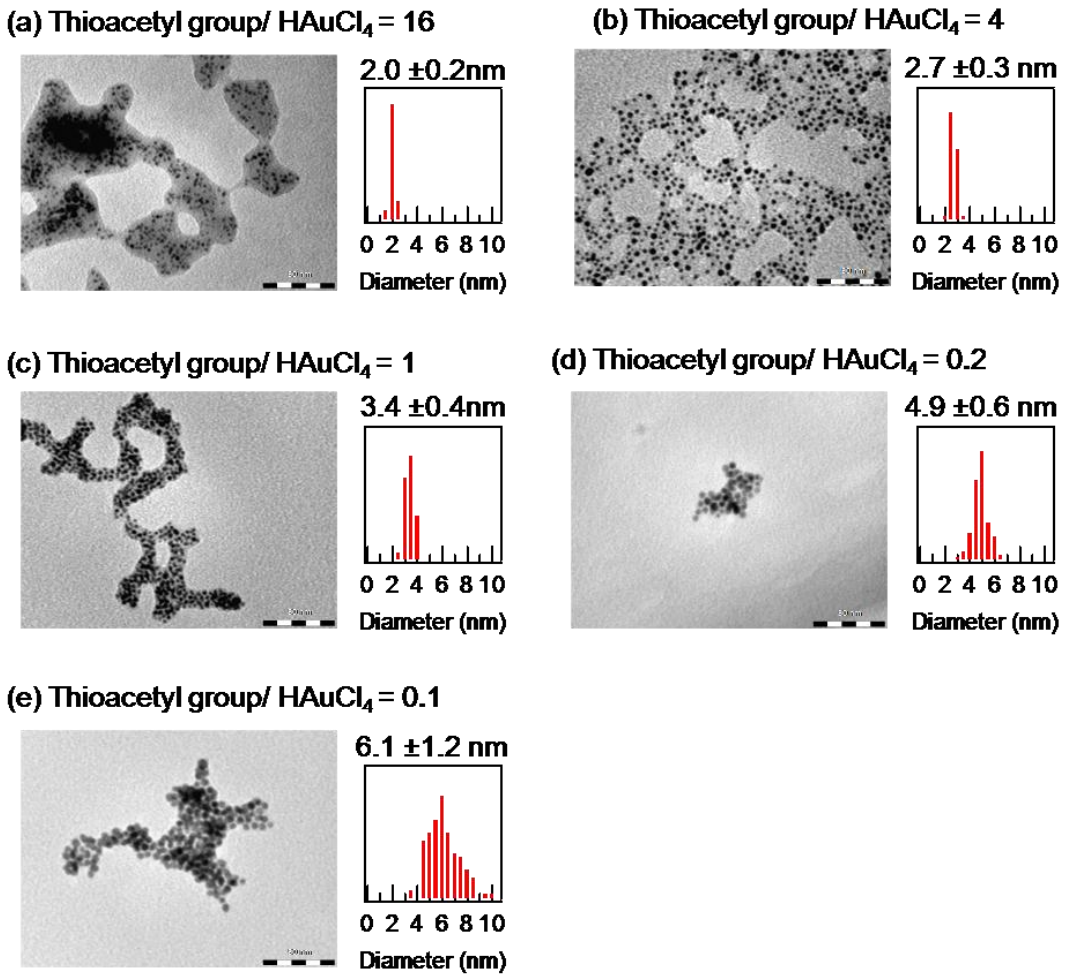


Fig. S7 TEM images and size distributions of as-synthesized **GN@1** synthesized at various values of ξ.

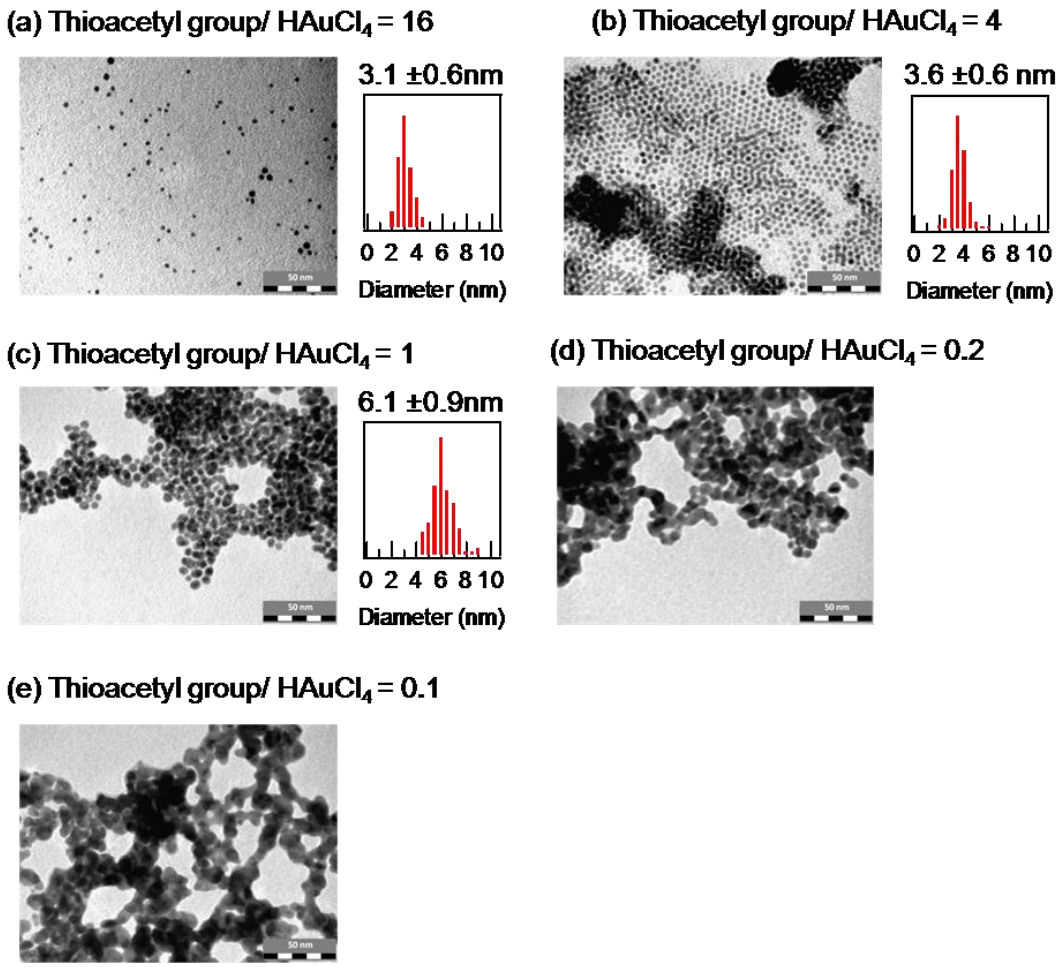


Fig. S8 TEM images and size distributions of as-synthesized **GN@2** synthesized at various values of ξ. The TEM images of (d) and (e) didn't show particle boundaries because of aggregation of particles.

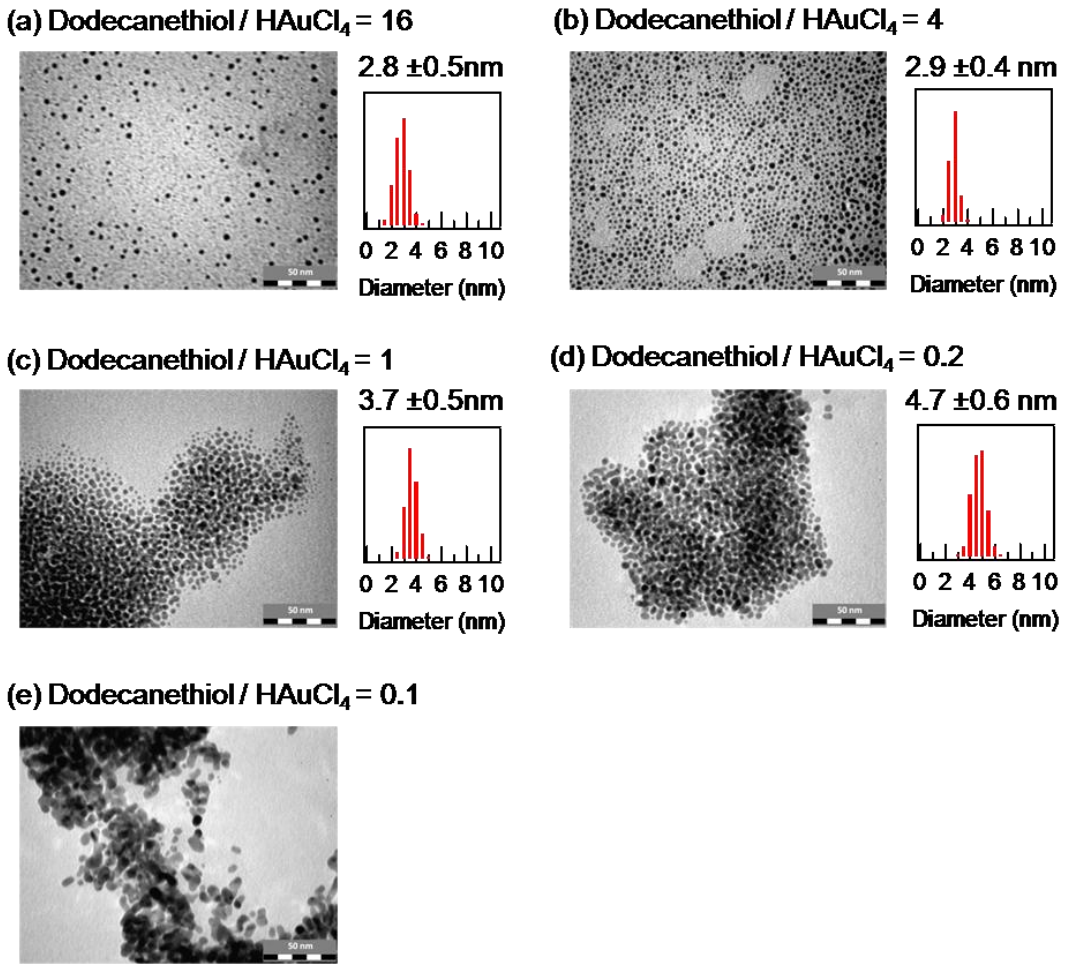


Fig. S9 TEM images and size distributions of as-synthesized gold nanoparticles covered with dodecanethiol synthesized at various values of ξ. The TEM image of (e) didn't show particle boundaries because of aggregation of particles.

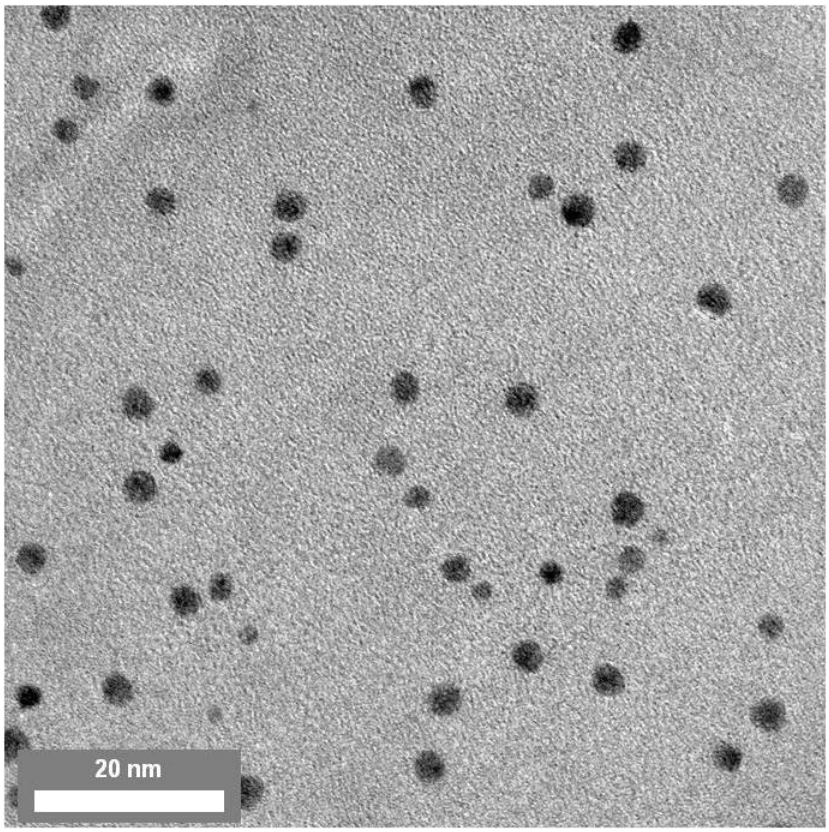


Fig. S10 TEM image of **GN@1**. The scale bar corresponds to 20 nm.

References

1. J. P. Collman, R. R. Gagne, C. Reed, T. R. Halbert, G. Lang and W. T. Robinson, *J. Am. Chem. Soc.*, 1975, **97**, 1427.
2. J. Lindsey, *J. Org. Chem.*, 1980, **45**, 5215.
3. R. J. Abraham, G. E. Hawkes, M. F. Hudson and K. M. Smith, *J. Chem. Soc. -Perkin Trans. 2*, 1975, 204.