Supporting Information for

Rigid Bidentate Ligands Focus the Size of Gold Nanoparticles

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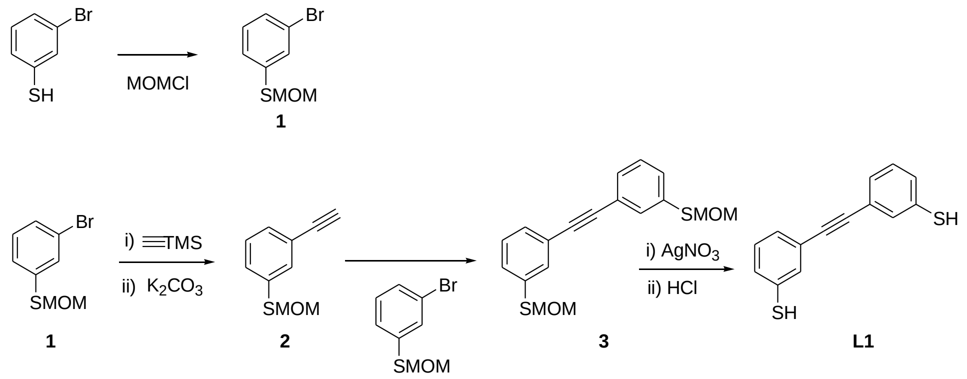
Synthesis of ligands, Ln

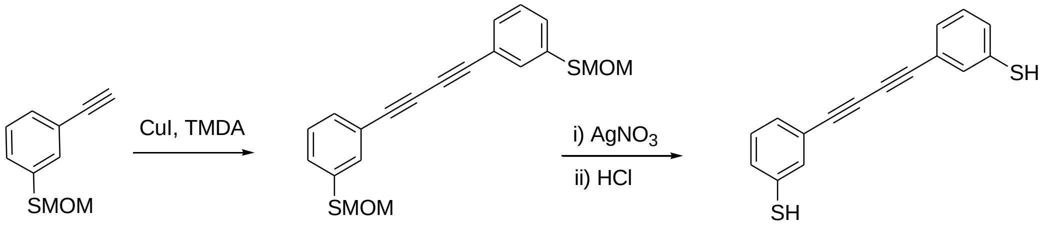
Materials. All materials were purchased from commercial suppliers and were used as received, unless otherwise stated.



Synthesis of L1. An acetonitrile solution (50 mL) of 3-bromobenzenethiol (10 g), diisopropyletylamine (11 mL), and 1-chloromethyl methyl ether (MOMCl) (6 ml) was stirred at 0°C for 3 h under ambient conditions. The solution was extracted using ethyl acetate, washed with brine, and evaporated to obtain a pale yellow oil (11.9 g, 96%) (**1**). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.43 (s, 3H), 4.96 (s, 2H), 7.14 (t, 2H), 7.35 (m, 4H), 7.61 (t, 2H). GC-MS (SEI): calcd for C_8H_9BrOS 231.96 found 232. A mixture of **1** (7.5 g), trimethylsilylacetylene (7.5 mL), CuI (0.5 mol%), Pd(PPh$_3$)$_2$Cl$_2$ (1 mol%), PPh (1 mol%), and triethylamine (TEA) (200 mL) was degassed under bubbling N$_2$ for 30 min. The solution was stirred overnight at 90°C under an N$_2$ atmosphere, and was extracted using ethyl acetate, washed with brine, dried by Na$_2$SO$_4$, and evaporated under reduced pressure. The residue was purified by silica column chromatography, using hexane/ethylacetate (99/1) as an eluent, to yield **2** as a pale yellow solution (8 g, 99%). **2** (8 g) was dissolved into a THF/methanol suspension (1/1) (20 mL) of K$_2$CO$_3$ (800 mg) and stirred overnight. The solution was washed with brine, dried with NaSO$_4$, and evaporated under reduced pressure to obtain **2** (5.6 g 100%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.09 (s, 1H), 3.43 (s, 3H), 4.95 (s, 2H), 7.11–7.59 (m, 8H). GC-MS (SEI): calcd for $C_{10}H_{10}OS$ 178.05 found 178.

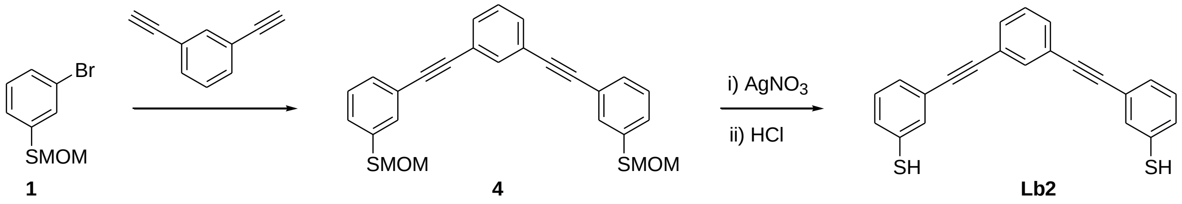
A TEA solution (200 mL) of **2** (1.4 g), **1** (2.7 g), CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol %) was degassed under bubbling N_2 for 30 min. The solution was stirred overnight at 90°C under an N_2 atmosphere, and was then extracted with ethyl acetate, washed with brine, dried by $NaSO_4$, and evaporated under reduced pressure. The residue was purified by silica column chromatography, using hexane/ethylacetate (9/1) as an eluent, to afford **3** as a pale yellow oil (800 mg, 30%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.46 (s, 6H), 4.99 (s, 3H), 7.23–7.64 (m, 8H). GC-MS (SEI): calcd for $C_{18}H_{18}O_2S_2$ 330.5 found 330.

The protected precursor **3** (60 mg) was suspended in a CH_2Cl_2/methanol (1/1) solution (80 mL) of $AgNO_3$ (65 mg) and stirred vigorously overnight. During this time, a yellow precipitate was formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL); this was followed by the addition of aqueous 6 M HCl (40 mL) and CH_2Cl_2 (40 mL). The resulting mixture was stirred vigorously in the dark for 3 h. The CH_2Cl_2 layer was separated, washed with water and brine, dried over Na_2SO_4, and evaporated to yield **L1** as a pale yellow solid (30 mg, 68% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.48 (s, 2H), 7.17–7.43 (m, 8H). GC-MS (SEI): calcd for $C_{14}H_{10}S_2$ 242.4 found 242.



Synthesis of L1.5. A CH_2Cl_2 solution (100 mL) of **2** (2.2 g), CuI (10 mol%), and tetramethylethylenediamine (10 mol%) was stirred overnight at r.t., and was then extracted using ethyl acetate, washed with brine, and the solvent was dried by $NaSO_4$ and evaporated under reduced pressure. The residue was corrected without further purification to give **4** as a yellow solid (2.2 g, 96 %). ^{1}H NMR (200 MHz, CDCl$_3$): δ 3.44 (s, 6H), 4.97 (s, 4H), 7.22–7.63 (m, 8H). GC-MS (SEI): calcd for $C_{20}H_{18}O_2S_2$ 354.07 found 354.

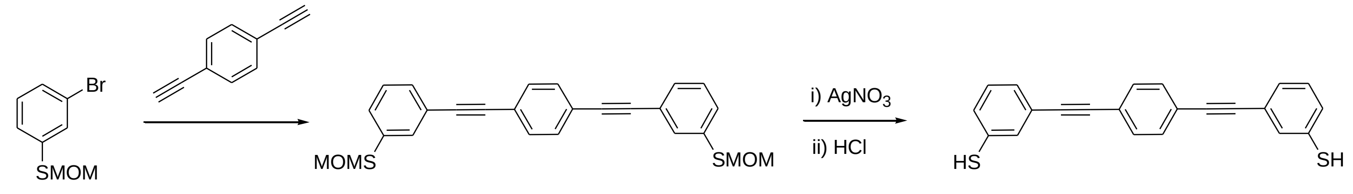
The protected precursor **4** (100 mg) was suspended in a CH_2Cl_2/EtOH (1/1) solution (100 mL) of $AgNO_3$ (120 mg), and was stirred vigorously overnight. During this time, a yellow precipitate was formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL), which was followed by the addition of aqueous 6 M HCl (50 mL) and CH_2Cl_2 (50 mL). The resulting mixture was stirred vigorously in the dark for 3 h. The CH_2Cl_2 layer was separated, washed with water and brine, dried over Na_2SO_4, and evaporated to yield **L1.5** as a pale yellow solid (55 mg, 73% yield). ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.49 (s, 2H), 7.16–7.43 (m, 8H). GC-MS (SEI): calcd for $C_{16}H_{10}S_2$ 266.02 found 266.



Synthesis of Lb2. A TEA solution (100 mL) of **1** (3.6 g), 1,3-diethynylbenzene, CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol%) was degassed under bubbling N_2 for 30 min. The solution was stirred overnight at 90°C under an N_2 atmosphere, and was then extracted using ethyl acetate and washed with brine, and the solvent was dried using $NaSO_4$ and evaporated under reduced pressure. The residue was purified by silica column chromatography, using hexane/CH_2Cl_2 (1/1) as an eluent, to afford **4** as a yellow oil (653 mg, 26%). ^{1}H NMR (200 MHz,

$CDCl_3$): δ 3.43 (s, 6H), 4.99 (s, 4H), 7.23–7.70 (m, 12H). GC-MS (SEI): calcd for $C_{26}H_{22}O_2S_2$ 430.11 found 430.

The protected precursor **4** (160 mg) was suspended in a CH_2Cl_2/EtOH (4/1) solution (40 mL) of $AgNO_3$ (140 mg) and stirred vigorously overnight. During this time, a yellow precipitate was formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL); this was followed by the addition of aqueous 6 M HCl (40 mL) and CH_2Cl_2 (40 mL). The resulting mixture was stirred vigorously in the dark for 3 h. The CH_2Cl_2 layer was separated, washed with water and brine, dried over Na_2SO_4, and evaporated to yield **Lb2** as a pale yellow solid (96 mg, 76% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.49 (s, 2H), 7.21–7.69 (m, 12H). GC-MS (SEI): calcd for $C_{22}H_{14}S_2$ 342.1 found 342.



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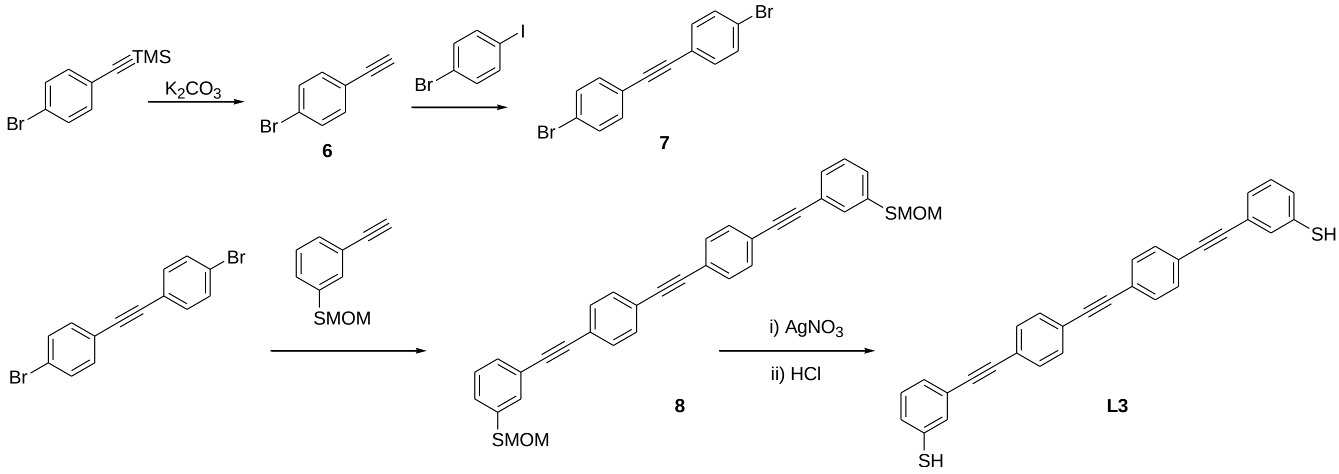
L2

Synthesis of L2. A diethylamine solution (140 mL) of **1** (3.6 g), 1,4-diethynylbenzene (750 mg), CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol%) was degassed under bubbling N_2 for 30 min. The solution was stirred overnight at 90°C under an N_2 atmosphere, and was extracted using ethyl acetate and washed with brine, and the solvent was dried by $NaSO_4$ and evaporated under reduced pressure. The residue was purified by silica column chromatography, using a hexane/CH_2Cl_2 (2/1) solution as an eluent, to afford **5** as a yellow solution (1.13 g, 44%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.46 (s, 6H), 5.00 (s, 4H), 7.24–7.64 (m, 12H). GC-MS (SEI): calcd for $C_{22}H_{14}S_2$ 430.11 found 430.

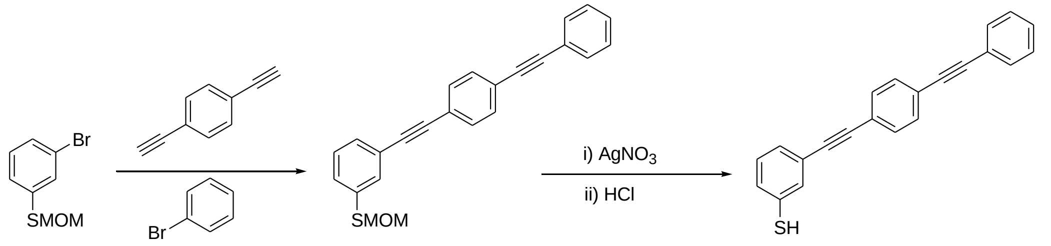
The protected precursor **5** (116 mg) was suspended in a CH_2Cl_2/EtOH (1/1) solution (80 mL) of $AgNO_3$ (101 mg) and stirred vigorously overnight. During this time, a yellow precipitate was formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL), which was followed by the addition of aqueous 6 M HCl (40 mL) and CH_2Cl_2 (40 mL). The resulting mixture was stirred vigorously in the dark for 3 h. The CH_2Cl_2 layer was separated, washed with water and brine, dried over $NaSO_4$, and evaporated to yield **L2** as a yellow solid (70 mg 76% yield). ^1H NMR (270 MHz, $CDCl_3$): δ 3.49 (s, 2H), 7.22–7.50 (m, 12H). GC-MS (SEI): calcd for $C_{22}H_{14}S_2$ 342.1 found 342.



Synthesis of L3. A THF/MeOH (1/1) suspension (20 mL) of 1-bromo-4-[2-(trimethylsilyl)ethynyl]-benzene (1 g) and K_2CO_3 (100 mg) was stirred overnight. The solution was washed with brine, dried by $NaSO_4$ and evaporated under reduced pressure to obtain **6** (0.71 g, 100%). A TEA solution (150 mL) of **6** (0.71 g), 1-bromo-4-iodobenzene (1.41 g), CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol %) was degassed under bubbling N_2 for 30 min. The solution was stirred overnight at 60°C under an N_2 atmosphere, and was extracted with CH_2Cl_2 and washed with brine, and the solvent was dried by $NaSO_4$ and evaporated under reduced pressure to afford **7** as a yellow solid (1.4 g, 99%). ^1H NMR (270 MHz, $CDCl_3$): δ 7.40 (d, 4H), 7.47 (d, 4H). GC-MS (SEI): calcd for $C_{14}H_8Br_2$ 336 found 336.

A *N*,*N'*-dimethylformamide (DMF)/TEA (1/1) solution (180 mL) of **2** (1.03 g), **7** (650 mg), CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol%) was degassed under bubbling N_2 for 30 min. The solution was stirred for 2 days at 60°C under an N_2 atmosphere, and was extracted with CH_2Cl_2 and washed with brine, and the solvent was dried by $NaSO_4$ and evaporated under reduced pressure. The residue was purified using silica column chromatography, using toluene as an eluent, to afford **8** as a yellow powder (530 mg, 51%). ^1H NMR (270 MHz, $CDCl_3$): δ 3.44 (d, 6H), 4.98 (d, 4H), 7.23–7.63 (m, 16H). GC-MS (SEI): calcd for $C_{14}H_8Br_2$ 530 found 530.

A DMF/EtOH (1/1) solution (80 mL) of **8** (600 mg) and $AgNO_3$ (1.24 g) was stirred vigorously overnight in the dark. During this time, a yellow precipitate formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL); this was followed by the addition of aqueous 6 M HCl (40 mL) and ether (40 mL). The resulting mixture was stirred vigorously in the dark for 1 h. The CH_2Cl_2 layer was separated, washed with brine, dried over Na_2SO_4, and evaporated to yield **L3** as a yellow solid with a 70% yield. ^1H NMR (270 MHz, DMSO-d_6): δ 5.74 (s, 2H), 7.38 (m, 4H), 7.57 (m, 2H), 7.66 (m, 10H). GC-MS (SEI): calcd for $C_{30}H_{18}S_2$ 442.08 found 442.



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3-(4-phenylethynyl-phenylethynyl) benzenethiol

Synthesis of 3-(4-phenylethynyl-phenylethynyl)benzenethiol. A diethylamine solution (40 mL) of **1** (1.86 g), 1,4-diethynylbenzene (1 g), bromobenzene (1.25 g), CuI (0.5 mol%), $Pd(PPh_3)_2Cl_2$ (1 mol%), and PPh (1 mol%) was degassed under bubbling N_2 for 30 min. The solution was stirred overnight at 90°C under an N_2 atmosphere, and was extracted using ethyl acetate and washed with brine, and the solvent was dried using $NaSO_4$ and evaporated under reduced pressure. The residue containing the protected precursor **10** (110 mg) was suspended in a solution of $AgNO_3$ (60 mg) in CH_2Cl_2/EtOH (1/1, 80 mL), and was stirred vigorously overnight. During this time, a yellow precipitate formed, which was isolated by filtration. The precipitate was then washed with CH_2Cl_2 (80 mL); this was followed by the addition of aqueous 6 M HCl (40 mL) and CH_2Cl_2 (40 mL). The resulting mixture was stirred vigorously in the dark for 3 h. The CH_2Cl_2 layer was separated, washed with water and brine, dried over $NaSO_4$, and evaporated to yield 3-(4-phenylethynyl-phenylethynyl) benzenethiol as a white solid (50 mg 58% yield). ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.49 (s, 1H), 7.22–7.50 (m, 13H). GC-MS (SEI): calcd for $C_{22}H_{14}S$ 310.4 found 310.

Synthesis of Ln-AuNPs

$HAuCl_4 \cdot 4H_2O$ (2.4 μmol), and ~0.01–8 equivalent of **Ln** dissolved in DMF (23 mL) and methanol (2 mL), were mixed in a glass vial. Since $NaBH_4$ does not show good solubility toward DMF, methanol was used to support the rapid and uniform reduction of the Au(III) ions by $NaBH_4$, leading to the formation of uniform Au seeds. The mixed solution was cooled to –55°C in a thermostated bath under an N_2 atmosphere. On reaching –55°C, a methanol solution (1 mL) of $NaBH_4$ (64 μmol, 20 equiv. of Au(III) ions) was quickly added to the solution. The reaction was allowed to proceed overnight. The color of the solution changed from pale yellow to dark brown (or vivid yellow). Monodispersed NPs were also formed at 0 °C or r.t. (See synthesis temperature dependence of size dispersing quality in S.I.), indicating that the low temperature is not necessary for the fabrication of monodispersed NPs. Excess **Ln** were removed using gel permeation chromatography (LH 20), using a DMF solution as an eluent. The obtained **Ln**-AuNP solution was concentrated to 5 mL by evaporation, and was purified again using gel permeation chromatography. The purified **Ln**-AuNPs were stored in a refrigerator. When the **Ln**-AuNPs were stored in air at r.t., the NPs tended to aggregate due to the formation of disulfide bonds.

Instruments

^{1}H NMR spectra were recorded on a 200 MHz Varian Gemini 200 NMR spectrometer. UV-vis-NIR spectral data were recorded on a Shimadzu U-3310. Gas chromatography mass spectrometry data were recorded on Shimadzu GCMS-QP5050. ICP-AES measurements were carried out using a PerkinElmer Optima 7300DV. UV-vis-NIR absorption spectra measurements were carried out using a Hitachi U-4100. Transmission electron microscope (TEM) images were recorded using a JEOL JEM-1011, at an acceleration voltage of 100 kV.

Synthesis temperature dependence of size dispersing quality

We investigated the synthesis temperature dependence of dispersing quality of **L2**-AuNPs. Although the dispersing quality was slightly degraded with increasing temperature, uniform and monodispersed spherical NPs were formed at 0 °C or r.t. This fact indicates that the low temperature is not necessary for the fabrication of monodispersed NPs. We consider that the present approach is convenient and versatile choice for the size focusing of NPs.

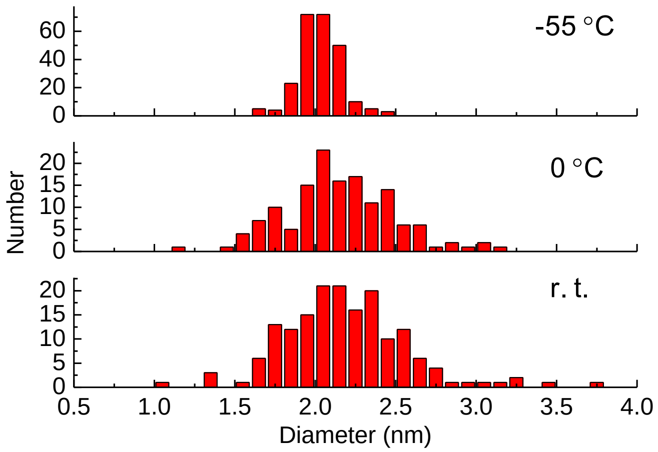

Figure S1. Size distribution of **Ln**-AuNPs fabricated at r. t., 0, and -55 °C.

TEM images of Ln-AuNPs

TEM images of **Ln**-AuNPs are shown in Figure S2. The diameter of the **Ln**-AuNPs increased with increasing *D*.

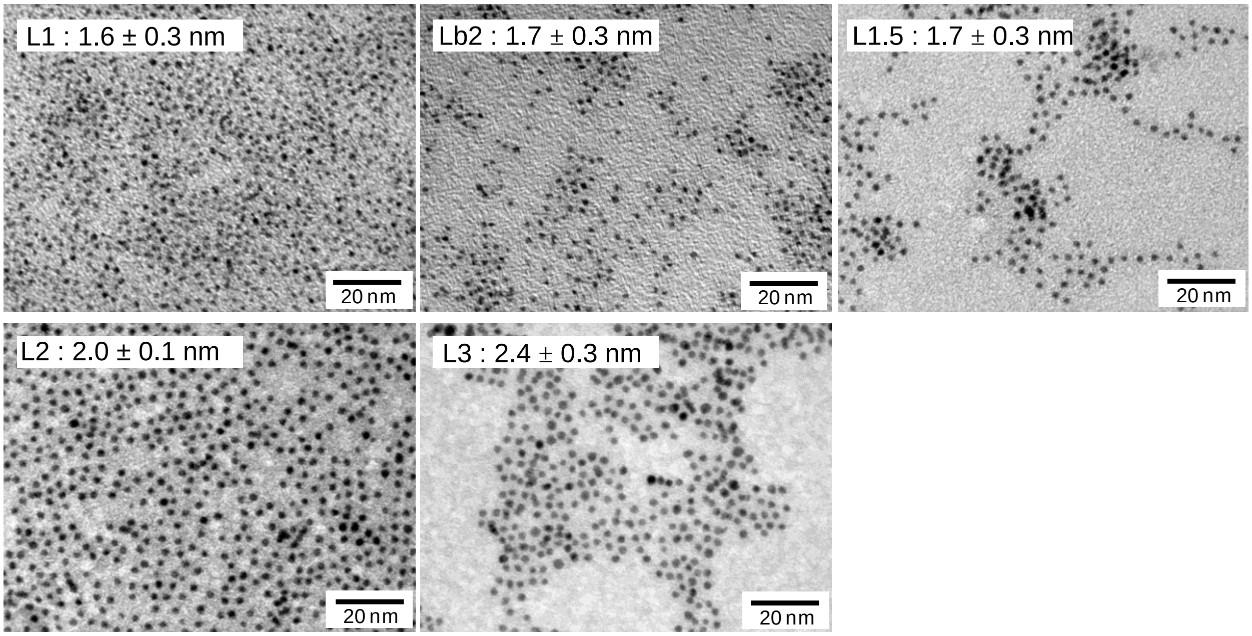

Figure S2. TEM images of **Ln**-AuNPs.

TEM images of monodentate ligand-protected AuNPs

When the AuNPs were synthesized using monodentate ligands such as dodecanethiol, 2-phenylethanethiol, thiophenol, and 3-(4-phenylethynyl-phenylethynyl)-benzenethiol, polydisperse and partly aggregated AuNPs were formed in the present condition. Since the DMF utilized as a solvent tends to attach on the surface of Au NPs, the attachment of DMF, which exist in excess amount in the system, on the surface of NPs would suppress the stabilization of AuNPs by the monodentate protecting ligands resulting in the aggregation.[1] On the contrary, the bidentate coordination of Ln was strong enough to stabilize the AuNPs even in the presence of excess DMF.

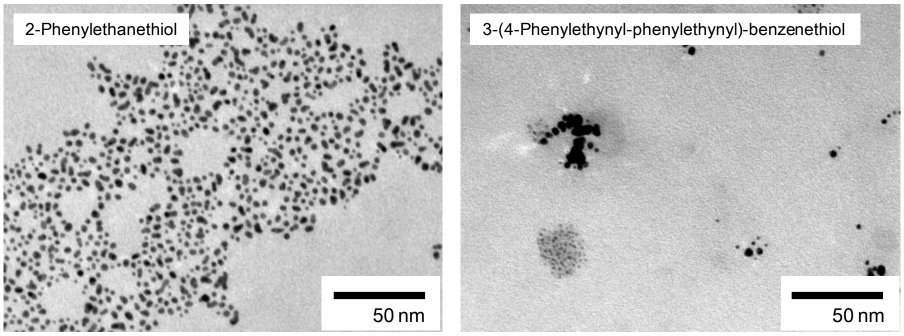

Figure S3. TEM images of 2-phenylethanethiol-protected AuNPs and 3-(4-phenylethynyl-phenylethynyl)-benzenethiol-protected AuNPs.

Absorption spectra of L1.5, Lb2, L1.5-AuNPs and Lb2-AuNPs

The absorption spectra of **L1.5**, **Lb2**, **L1.5**-AuNPs and **Lb2**-AuNPs are shown in Figure S4a and S4b. The **Ln** absorption spectra were also observed for the **Ln**-AuNPs, and indicated the attachment of **Ln** on the AuNPs. The broad shoulders extending to the near-infra red region were attributed to the small AuNPs. The absorption coefficient of **Ln** on the AuNPs increased with increasing χ.

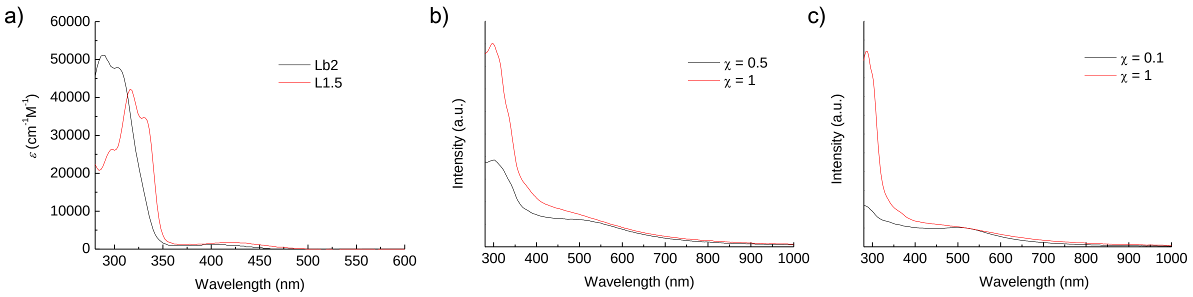

Figure S4. Absorption spectra of a) **L1.5** and **Lb2**, b) **L1.5**- and c) **Lb2**-AuNPs synthesized at various χ values in DMF solution. The spectra were normalized at 550 nm for clarity.

Loading ratio (χ = [Ln]/[Au(III)]) dependence for size focusing of L1- and L3-AuNPs

We fabricated the **L1** or **L3** protected AuNPs at χ = 0.5 ~ 2.0 and found that the size focusing by **L1** or **L3** occur at the similar region of **L2** protected AuNPs.

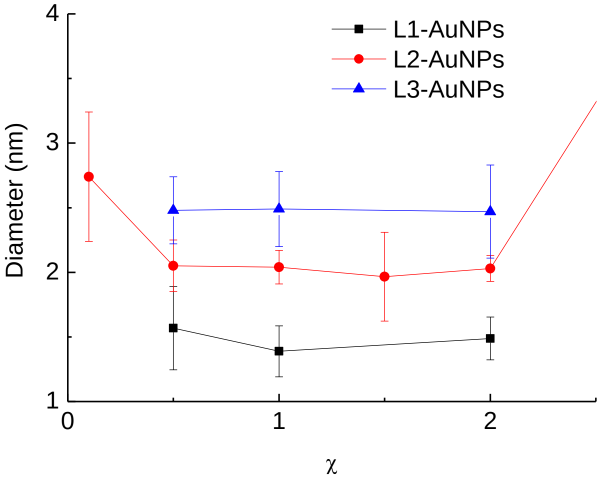

Figure S5. The relation between the diameter of **Ln**-AuNPs (n = 1, 2, 3) and χ at size focusing region.

Reference

(1) Kawasaki, H.; Yamamoto, H.; Fujimori, H.; Arakawa, R.; Iwasaki Y.; Inada, M. *Langmuir*, **2010**, *26*, 5926.