Immobilization of Rhodium Complexes at Thiolate Monolayers on Gold Surfaces: Catalytic and Structural Studies

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SUPPORTING INFORMATION

General Methods: Reactions with air- or moisture-sensitive compounds were performed under argon using standard Schlenk techniques or under purified N₂ in a MBraun glovebox. Glassware was oven dried and flame dried prior to use. All chemicals were purchased from Fluka or Aldrich. CH₂Cl₂ was dried over CaH₂ and THF over Na/K and freshly distilled under a stream of nitrogen prior to use. Optical rotations were measured in a Perkin Elmer Polarimeter 341, sodium lamp, 1 dm cuvette length, c in g/100 mL. ¹H-, ¹³C-, ¹⁹F- and ³¹P-NMR spectra were recorded in CD₂Cl₂ or CDCl₃ on a Bruker Avance 400 MHz or 500 MHz spectrometer and coupling constants are reported in Hz. Chemical shifts are given in ppm relative to TMS. IR spectra: 1600 Perkin Elmer Series FT-IR spectrometer; FAB mass spectra: Finnigan MAT 312; EI mass spectra: VG 70 SE. Elemental analysis were carried out on a Leco CHN-900 and Leco RO-478. Chromatographic purifications were performed by flash chromatography using silica gel (Merck 0.040 - 0.063 mm). Yields for final products refer to isolated products and are the average of three runs. GC analyses: Carlo Erba HRGC Mega2 Series MFC 800 (column: Restek Rtx-1701; 0.25 m m, 30 m, 60 kPa He). HPLC analyses: Shimadzu VP-system (column: Daicel OD-H; 4.6 × 250 mm).

Synthesis of 11-(10'-carboxy-decyldisulfanyl)undecanoic acid

Sodium hydroxide (366 mg, 9.16 mmol), potassium iodide (50.0 mg, 0.30 mmol) and iodine (1.16 g, 4.58 mmol) were added to a solution of 11-mercaptopoundecanoic acid (2.00 g, 9.16 mmol) in methanol (50 mL) and the solution was stirred for 30 min. The brown reaction mixture was decolored with a saturated sodium sulfite solution, the solvents concentrated under reduced pressure, the precipitate dissolved in CH₂Cl₂ (50 mL) and the resulting solution washed with a HCl solution (1 M, 50 mL) and water (50 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced
pressure. Purification of the crude material by crystallization (hexanes/AcOEt) gave 63% yield of the desired 11-(10'-carboxy-decylsulfanyl)undecanoic acid (1.25 g).

m.p.: 68 - 70 °C. R_f = 0.30 (hexanes/AcOEt = 4:1).

_1^H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.28 (s, 20 H, CH₂), 1.35 (m, 4 H, CH₂), 1.64 (m, J = 7.4 Hz, 8 H, CH₂CH₂CO₂H + SCH₂CH₂), 2.34 (t, J = 7.4 Hz, 4 H, CH₂CO₂H), 2.68 (t, J = 7.4 Hz, 4 H, SCH₂), 10.98 (s, 2 H, CO₂H).

_1^3C-^1H-NMR (100.6 MHz, CDCl₃, 295 K): δ = 25.0 (CH₂), 28.9 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.8 (CH₂), 34.4 (CH₂), 39.6 (SCH₂), 180.7 (CO₂H).

IR (KBr): ν (cm⁻¹) = 2918s, 2849m, 1471m, 1427m, 1289m, 1261m, 1231m, 1206m, 2944m.

MS (FAB): m/z (rel int %) = 63 (M⁺, 30), 113 (20), 144 (34), 232 (13), 286 (28), 326 (15), 382 (13), 436 (14), 580 (27), 634 (25), 69 (57), 81 (32), 69 (49), 55 (100), 43 (47).

Elemental analysis for C₂₂H₄₂O₄S₂: calc.: C 60.79%, H 9.74%, O 14.72%; found: C 60.84%, H 9.68%, O 14.74%.

**Synthesis of (3R,4R)-3,4-bis(diphenylphosphorothioyl)pyrrolidine**

Sulfur (0.27 g, 8.40 mmol) was added to a solution of PYRPHOS (1.85 g, 4.20 mmol) in freshly distilled toluene (50 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with diethyl ether, gave 95% yield of the desired compound (2.01 g).

m.p.: 212 - 214 °C. [α]₂⁰⁺ = +12.3 (c = 0.80, CHCl₃). R_f = 0.50 (diethyl ether).

_1^H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 2.59 (s, 1 H, NH), 3.12 (m, 2 H, NCH₂), 3.27 (m, 2 H, NCH₂), 4.01 (m, 2 H, PCH), 7.00 (m, 4 H, CHPh), 7.17 (m, 2 H, CHPh), 7.42 (m, 6 H, CHPh), 7.60 (m, 4 H, CHPh), 7.88 (m, 4 H, CHPh).

_1^3C-^1H-NMR (100.6 MHz, CDCl₃, 295 K): δ = 39.3 - 40.1 (dd, PCH), 53.1 (NCH₂), 128.3 - 128.8 (m, CHPh-meta), 130.0 - 132.9 (m, CPh-ipsa), 130.9 - 131.6 (m, CHPh-ortho and para).

_3¹P-^1H-NMR (162.0 MHz, CDCl₃, 295 K): δ = 51.2 (s).

IR (KBr): ν (cm⁻¹) = 3300m, 3048m, 2898m, 1479m, 1435s, 1311m, 1233w, 1158m, 1099s, 998m, 861s, 745s, 718s, 693s, 646s, 605m, 566m, 521s, 503s, 489s.

MS (FAB): m/z (rel int %) = 504 ([M + H]⁺, 30), 286 (9), 217 (15), 185 (6), 77 (5), 68 (100), 39 (5).

Elemental analysis for C₂₈H₇₇NP₂S₂: calc.: C 66.78%, H 5.40%, N 2.78%; found: C 66.72%, H 5.32%, N 2.75%.
SYNTHESIS OF THE SPACERS FOR THE GOLD COLLOIDS

Synthesis of 1-(2'-bromo-ethyl)adamantane

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\text{N-Bromosuccinimide (987 mg, 5.55 mmol) and triphenylphosphine (1.46 g, 5.55 mmol) were added to a solution of 2-adamant-1-yl-ethanol (1.00 g, 5.55 mmol) in freshly distilled benzene (20 mL) and the reaction mixture was stirred for 12 hours at 23 }^\circ\text{C. The resulting solution was washed with a saturated NaCl solution (20 mL) and water (20 mL). The organic phase was dried over MgSO}_4, \text{ filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with \text{n}-pentane, gave 92\% yield of 1-(2'-bromo-ethyl)adamantane (1.24 g).}
\]

\[\text{m.p.: 66 - 68 }^\circ\text{C. } R_t = 0.78 (\text{\textit{n}-pentane).}\]

\[\text{^1H-NMR (400.1 MHz, CDCl}_3, 295 K): \delta = 1.51 (\text{m, } J = 2.5 \text{ Hz, 6 H, } CCH_{2-Ad}), 1.61 - 1.70 (\text{m, 6 H, } CH_{2-Ad}), 1.72 (\text{m, 2 H, BrCH}_2CH_2), 1.96 (\text{m, 3 H, } CH_{Ad}), 3.40 (\text{m, 2 H, BrCH}_2).\]

\[\text{^{13}C\{^1H\}-NMR (100.6 MHz, CDCl}_3, 295 K): \delta = 28.6 (CH_{Ad}), 39.2 (BrCH_2), 34.1 (C_{Ad}), 37.1 (CH_{2-Ad}), 42.2 (CCH_{2-Ad}), 48.2 (BrCH_2CH_2).\]

\[\text{IR (KBr): } \nu (\text{cm}^{-1}) = 2896s, 2843s, 2652w, 1452s, 1344m, 1239m, 1121m, 1256m, 1215m, 1294m, 973m, 810m, 746w, 719m, 658m, 560s.\]

\[\text{MS (EI): } m/z (\text{rel int } \%) = 242 (M^+, 1, 79\text{Br}), 135 (100), 107 (6), 93 (13), 79 (15), 67 (6), 55 (3), 41 (6).\]

\[\text{Elemental analysis for } C_{12}H_{19}Br \text{ calc.: C 59.27\%, H 7.88\%; found: C 59.22\%, H 7.79\%.}\]

Synthesis of 1-(hex-5'-eny)adamantane

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\text{3-Butenylmagnesium bromide solution (0.5 M in THF, 94 mL, 47.0 mmol) was added tropwise at -78 }^\circ\text{C to a solution of 1-(2'-bromo-ethyl)adamantane (5.00 g, 20.6 mmol) in freshly distilled THF (30 mL). After 10 min, a lithium tetrachlorocuprate(II) solution (0.1 M in THF, 2.10 mL, 0.21 mmol) was added and the reaction mixture was stirred for 2 hours at -78 }^\circ\text{C and slowly warmed up to 23 }^\circ\text{C over 12 hours. The resulting solution was washed with a saturated NH}_4\text{Cl solution (100 mL) and water (100 mL). The organic phase was dried over MgSO}_4, \text{ filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with } \text{n}-\text{pentane, gave 92\% yield of 1-(hex-5'-eny)adamantane (4.13 g).}
\]

\[R_t = 0.86 (\text{hexanes).}\]

\[\text{^1H-NMR (400.1 MHz, CDCl}_3, 295 K): \delta = 1.03 (t, J = 7.1 \text{ Hz, 2 H, } CCH_2), 1.24 (\text{quin, } J = 7.1 \text{ Hz, 2 H, } CCH_2CH_2), 1.33 (\text{quin, } J = 7.1 \text{ Hz, 2 H, } CCH_2CH_2CH_2), 1.45 (\text{m, } J = 2.2 \text{ Hz, 6 H, } CH_{2-Ad}), 1.66 \text{ Hz, } CCH_{2-Ad}).\]
Thioacetic acid (4.21 mL, 58.9 mmol) was added to a solution of 1-(hex-5'-enyl)adamantane (5.00 g, 22.9 mmol) in freshly distilled THF (250 mL) and cooled to 20 °C with a cryostate (cooling bath: H2O/EtOH = 80:20). The solution was irradiated during 7 hours with a 300 W lamp (Osram Ultra-Vitalux 300 W). During that time was added 2,2'-azobisisobutyronitrile (900 mg, 5.48 mmol) in freshly distilled THF (20 mL) with a syringe pump. Irradiation was continued for another 4 hours. The solvent was concentrated under reduced pressure and the residue dissolved in dichloromethane (100 mL). The resulting solution was washed with a saturated Na2CO3 solution (100 mL) and water (100 mL). The organic phase was dried over MgSO4, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 5% diethyl ether in n-pentane, gave 82% yield of thioacetic acid (S)-6-(adamant-1'-yl)hexyl ester (5.50 g).

\[ R_f = 0.67 \text{ (n-pentane/diethyl ether = 20:1).} \]

\[ \text{H-NMR (400.1 MHz, CDCl3, 295 K):} \delta = 1.00 \text{ (t,} J = 7.3 \text{ Hz,} 2 \text{ H,} CH_2) \text{,} 1.22 \text{ (m,} 4 \text{ H,} CH_2) \text{,} 1.35 \text{ (quin,} J = 7.3 \text{ Hz,} 2 \text{ H,} CCH_2CH_2) \text{,} 1.43 \text{ (m,} J = 2.3 \text{ Hz,} 6 \text{ H,} CCH_2Ad) \text{,} 1.55 \text{ (quin,} J = 7.3 \text{ Hz,} 2 \text{ H,} CH(CH_2)_2S) \text{,} 1.64 \text{ (m,} 6 \text{ H,} CH_2Ad) \text{,} 1.92 \text{ (m,} 3 \text{ H,} CHAd) \text{,} 2.31 \text{ (s,} 3 \text{ H,} SCOCH_3) \text{,} 2.85 \text{ (t,} J = 7.3 \text{ Hz,} 2 \text{ H,} CH_2S) \text{.} \]

\[ \text{13C{ }^1H}-\text{NMR (100.6 MHz, CDCl3, 295 K):} \delta = 22.3 \text{ (CH}_2) \text{,} 28.8 \text{ (CH}_Ad) \text{,} 29.0 \text{ (CH}_2) \text{,} 29.3 \text{ (CH}_2) \text{,} 29.6 \text{ (CH}_2) \text{,} 30.2 \text{ (CH}_2) \text{,} 30.7 \text{ (CH}_3) \text{,} 32.3 \text{ (C}_Ad) \text{,} 37.4 \text{ (CH}_2Ad) \text{,} 42.6 \text{ (CCH}_2Ad) \text{,} 44.7 \text{ (CH}_2) \text{,} 196.1 \text{ (SCO).} \]

IR (NaCl): \( v \text{ (cm}^{-1}) = 2902s, 2847s, 2661w, 1694s, 1450m, 1352m, 1132m, 954m, 864w, 624w. \]

MS (EI): \( m/z \text{ (rel int %)} = 294 \text{ (M}^+ 4), 251 \text{ (5),} 215 \text{ (100),} 107 \text{ (5),} 93 \text{ (9),} 79 \text{ (10),} 43 \text{ (15).} \]

Elemental analysis for \( C_{18}H_{30}OS \): calc.: C 73.41%, H 10.27%, O 5.43%; found: C 73.21%, H 10.14%, O 5.57%.
Synthesis of 6-(adamant-1'-yl)hexanethiol

Conc. HCl (37%, 425 mL, 5.18 mmol) was added to a solution of thioacetic acid (S)-6-(adamant-1'-yl)-hexyl ester (150 mg, 509 mmol) in methanol (5 mL) and the reaction mixture was stirred for 10 hours at 65 °C. The solvent was concentrated under reduced pressure and the residue dissolved in diethyl ether (20 mL). The resulting solution was washed with a HCl solution (1 M, 20 mL) and water (20 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with n-pentane, gave 86% yield of 6-(adamant-1'-yl)-hexanethiol (0.11 g).

Rₓ = 0.65 (n-pentane).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.01 (t, J = 7.4 Hz, 2 H, CH₂), 1.22 (m, 4 H, CH₂), 1.32 (t, J = 7.7 Hz, 1 H, SH), 1.38 (quin, J = 7.4 Hz, 2 H, CCH₂CH₂), 1.44 (m, J = 2.5 Hz, 6 H, CCH₂-Ad), 1.60 (quin, J = 7.4 Hz, 2 H, CH₂CH₂SH), 1.64 (m, 6 H, CH₂-Ad), 1.92 (m, 3 H, CH₂Ad), 2.51 (q, J = 7.4 Hz, 2 H, CH₂SH).

¹³C {¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 22.3 (CH₂), 24.8 (CH₂), 28.5 (CH₂), 28.9 (CH₂Ad), 30.1 (CH₂), 32.3 (CAd), 34.2 (CH₂), 37.4 (CH₂), 42.6 (CH₂Ad), 44.8 (CH₂).

IR (NaCl): ν (cm⁻¹) = 2920s, 2846s, 2663w, 1450m, 1347w, 1101w.

MS (EI): m/z (rel int %) = 252 (M⁺, 3), 135 (100), 93 (11), 79 (11), 67 (6), 41 (6).

Elemental analysis for C₁₆H₂₈S calc.: C 76.12%, H 11.18%; found: C 76.07%, H 11.08%.

Synthesis of 11-aminoundecanol

11-Aminoundecanoic acid (21.0 g, 102 mmol) was added slowly at -20 °C to a solution of LiAlH₄ (5.20 g, 137 mmol) in freshly distilled THF (200 mL) and the reaction mixture was stirred for 6 hours at 67 °C. The solution was cooled to 0 °C, treated with a NaOH solution (10%, 10 mL) and H₂O (20 mL) and stirred for 30 min at 23 °C. The reaction mixture was dried over MgSO₄, filtered and concentrated under reduced pressure to provide the desired 11-aminoundecanol (10.3 g) in 53% yield.

m.p.: 66 - 68 °C.

¹H-NMR (400.1 MHz, CD₂Cl₂, 295 K): δ = 1.27 (s₈, 14 H, CH₂), 1.39 (quin, J = 7.0 Hz, 2 H, CH₂CH₂NH₂), 1.50 (quin, J = 6.5 Hz, 2 H, CH₂CH₂OH), 2.61 (t, J = 7.0 Hz, 2 H, CH₂NH₂), 3.54 (t, J = 6.5 Hz, 2 H, CH₂OH) ⇒ OH und NH₂ signals lies under the quintetts between 1.36 - 1.54 Hz.

¹³C {¹H}-NMR (100.6 MHz, CD₂Cl₂, 295 K): δ = 25.9 (CH₂), 27.0 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.7 (CH₂), 29.7 (CH₂), 33.0 (CH₂CH₂OH), 34.1 (CH₂CH₂NH₂), 42.3 (CH₂NH₂), 62.7 (CH₂OH).
IR (KBr): ν (cm⁻¹) = 3338m, 3086m, 2923s, 2849s, 1614w, 1472m, 1348m, 1077m, 1031m, 991m.
MS (FAB): m/z (rel int %) = 188 ([M + H]+, 100), 69 (10), 55 (19), 44 (9), 41 (9).
Elemental analysis for C₅H₁₁NO calc.: C 70.53%, H 13.45%, N 7.48%; found: C 70.69%, H 13.43%, N 7.35%.

Synthesis of tert-butyl 11-hydroxyundecylcarbamate

Triethylamine (9.00 mL, 64.7 mmol) and di-tert-butyl dicarbonate (14.1 g, 64.6 mmol) were added at 0 °C to a solution of 11-aminoundecanole (12.0 g, 64.1 mmol) in freshly distilled CH₂Cl₂ (200 mL) and the reaction mixture was stirred for 2 hours at 0 °C and another 8 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (100 mL) and water (100 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 30% AcOEt in hexanes, gave 89% yield of tert-butyl 11-hydroxyundecylcarbamate (16.3 g).
m.p.: 34 – 36 °C. Rf = 0.38 (hexanes/AcOEt = 2:1).
¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.25 (s, 10 H, CH₂), 1.30 (m, 4 H, CH₂), 1.42 (s, 11 H, C(CH₃)₂, CH₂CH₂NH), 1.54 (m, 3 H, OH + CH₂CH₂OH), 3.08 (m, J = 6.3 Hz, 6.6 Hz, 2 H, CH₂NH), 3.61 (m, J = 5.6 Hz, 6.3 Hz, 2 H, CH₂OH), 4.54 (s, 1 H, NH).
¹³C {¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 25.8 (CH₂), 26.8 (CH₂), 28.5 (C(CH₃)₃), 29.3 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 30.1 (CH₂CH₂NH), 32.8 (CH₂CH₂OH), 40.7 (CH₂NH), 63.1 (CH₂OH), 79.1 (C(CH₃)₃) 156.1 (CO).
IR (NaCl): ν (cm⁻¹) = 3353m, 2926s, 2854m, 1693s, 1526m, 1387s.
MS (FAB): m/z (rel int %) = 288 ([M + H]+, 3), 232 (7), 188 (17), 74 (12), 69 (11), 57 (100), 41 (26).
Elemental analysis for C₁₃H₂₃NO₃ calc.: C 66.86%, H 11.57%, N 4.87%; found: C 66.95%, H 11.49%, N 4.79%.

Synthesis of tert-butyl 11-bromoundecylcarbamate

N-Bromosuccinimide (10.0 g, 56.2 mmol) and triphenylphospine (14.8 g, 56.4 mmol) were added to a solution of tert-butyl 11-hydroxyundecylcarbamate (16.0 g, 55.7 mmol) in freshly distilled benzene (200 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (200 mL) and water (200 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography, eluting with 10% AcOEt in hexanes, gave 74% yield of tert-butyl 11-bromoundecylcarbamate (14.5 g).
m.p.: 60 - 62 °C. R_\text{f} = 0.37 (hexanes/AcOEt = 10:1).

^1\text{H}-\text{NMR} (400.1 \text{ MHz, CDCl}_3, 295 \text{ K}): \delta = 1.25 (s_b, 12 \text{ H, } CH_2), 1.42 (s_b, 13 \text{ H, } CH_2CH_2CH_2Br + C(CH_3)_3 + CH_2CH_2NH), 1.83 (m_c, J = 6.9 \text{ Hz, } 7.2 \text{ Hz, } 2 \text{ H, } CH_2CH_2Br), 3.08 (t, J = 6.6 \text{ Hz, } 2 \text{ H, } CH_2NH), 3.38 (t, J = 6.9 \text{ Hz, } 2 \text{ H, } CH_2Br), 4.53 (s_b, 1 \text{ H, NH}).

^13\text{C}\{^1\text{H}\}-\text{NMR} (100.6 \text{ MHz, CDCl}_3, 295 \text{ K}): \delta = 26.8 (CH_2), 28.2 (CH_2), 28.5 (C(CH_3)_3), 28.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 30.1 (CH_2CH_2NH), 32.9 (CH_2CH_2Br), 34.1 (CH_2Br), 40.7 (CH_2NH), 79.0 (C(CH_3)_3), 156.0 (CO).

IR (KBr): v (cm\textsuperscript{-1}) = 3377s, 2918s, 2851s, 1687s\textsubscript{b}, 1522s\textsubscript{b}, 1469m, 1374m, 1280m, 1237m, 1170m\textsubscript{b}, 1026w, 976w, 870m, 720m, 643m.

MS (FAB): m/z (rel int \%) = 350 ([M\textsuperscript{+}, 4, ^79\text{Br}]), 294 (96, ^79\text{Br}), 250 (13, ^79\text{Br}), 214 (8), 137 (8), 74 (41), 57 (100), 41 (20).

Elemental analysis for C\textsubscript{16}H\textsubscript{32}BrNO\textsubscript{2} calc.: C 54.85\%, H 9.21\%, N 3.91\%; found: C 55.01\%, H 9.06\%, N 3.89\%.

**Synthesis of (S)-11-(tert-butoxycarbonyl)undecylethanethioate**

Thioacetic acid (4.00 mL, 56.0 mmol), triethylamine (8.00 mL, 57.5 mmol) and 4-DMAP (0.50 g, 4.10 mmol) were added to a solution of tert-butyl 11-bromoundecylcarbamate (14.5 g, 41.4 mmol) in freshly distilled CH\textsubscript{2}Cl\textsubscript{2} (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na\textsubscript{2}CO\textsubscript{3} solution (200 mL) and water (200 mL). The organic phase was dried over MgSO\textsubscript{4}, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 10\% AcOEt in hexanes and subsequent crystallization (n-pentane), gave 79\% yield of (S)-11-(tert-butoxycarbonyl)undecyl-ethanethioate (11.3 g).

m.p.: 64 - 66 °C. R_\text{f} = 0.25 (hexanes/AcOEt = 10:1).

^1\text{H}-\text{NMR} (400.1 MHz, CDCl\textsubscript{3}, 295 K): \delta = 1.22 (s\textsubscript{b}, 10 H, CH\textsubscript{2}), 1.25 (m\textsubscript{c}, 2 H, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 1.30 (m\textsubscript{c}, 2 H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}S), 1.41 (s\textsubscript{b}, 11 H, C(CH\textsubscript{3})\textsubscript{3} + NCH\textsubscript{2}CH\textsubscript{2}), 1.52 (m\textsubscript{c}, J = 6.8 Hz, 7.4 Hz, 2 H, CH\textsubscript{2}CH\textsubscript{2}S), 2.29 (s, 3 H, SCOCH\textsubscript{3}), 2.83 (t, J = 7.4 Hz, 2 H, CH\textsubscript{2}S), 3.07 (t, J = 6.6 Hz, 2 H, NCH\textsubscript{2}), 4.55 (s\textsubscript{b}, 1 H, NH).

^13\text{C}\{^1\text{H}\}-\text{NMR} (100.6 MHz, CDCl\textsubscript{3}, 295 K): \delta = 26.8 (NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}), 28.5 (C(CH\textsubscript{3})\textsubscript{3}), 28.8 (CH\textsubscript{2}S), 29.1 (CH\textsubscript{2}), 29.2 (CH\textsubscript{2}), 29.3 (CH\textsubscript{2}CH\textsubscript{2}S), 29.4 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 29.5 (CH\textsubscript{2}), 30.1 (NCH\textsubscript{2}CH\textsubscript{2}), 30.7 (SCOCH\textsubscript{3}), 40.6 (NCH\textsubscript{2}), 78.9 (C(CH\textsubscript{3})\textsubscript{3}), 156.0 (CO), 196.0 (SCO).

IR (KBr): v (cm\textsuperscript{-1}) = 3380m, 2918m, 2851m, 1687s\textsubscript{b}, 1522s\textsubscript{b}, 1469m, 1364m, 1282m, 1238m, 1172m, 1138m, 1116m, 1000w, 959m, 870w, 720w, 639m.

MS (FAB): m/z (rel int \%) = 346 ([M + H]\textsuperscript{+}, 24), 290 (26), 246 (100), 230 (9), 202 (9), 57 (55), 43 (31).

Elemental analysis for C\textsubscript{18}H\textsubscript{35}NO\textsubscript{2}S calc.: C 62.56\%, H 10.20\%, N 4.05\%; found: C 62.56\%, H 10.16\%, N 4.08\%.
Synthesis of tert-butyl 11-mercaptoundecylcarbamate

A hydrazine solution (1 M in THF, anhydrous, 30.0 mL, 30.0 mmol) was added at 0 °C to a solution of (S)-11-(tert-butoxycarbonyl)undecylethanethioate (1.00 g, 2.90 mmol) in freshly distilled CH₂Cl₂ (20 mL) and the reaction mixture was stirred for 4 hours at 23 °C. The solvent was concentrated under reduced pressure and the residue dissolved in CH₂Cl₂ (50 mL). The resulting solution was washed with a saturated NH₄Cl solution (50 mL) and water (50 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography, eluting with 10% AcOEt in hexanes, gave 98% yield of tert-butyl 11-mercaptoundecylcarbamate (0.86 g).

m.p.: 52 - 54 °C. Rₚ = 0.36 (hexanes/AcOEt = 10:1).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.25 (sₗ, 12 H, CH₂), 1.32 (t, J = 7.6 Hz, 1 H, SH), 1.36 (m, 2 H, CH₂CH₂CH₂SH), 1.43 (sₗ, 11 H, C(CH₃)₃ + NCH₂CH₂), 1.59 (quin, J = 7.2 Hz, 2 H, CH₂CH₂S), 2.51 (m, J = 7.2 Hz, 7.6 Hz, 2 H, CH₂SH), 3.09 (t, J = 6.6 Hz, 2 H, NCH₂), 4.50 (sₗ, 1 H, NH₂).

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 24.7 (CH₂SH), 26.9 (CH₂), 28.4 (CH₂CH₂CH₂SH), 28.5 (C(CH₃)₃), 29.1 (CH₂), 29.3 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 30.1 (NCH₂CH₂), 34.1 (CH₂CH₂SH), 40.7 (NCH₂), 79.0 (C(CH₃)₃), 156.0 (CO).

IR (KBr): ν (cm⁻¹) = 3373s, 2921s, 2848s, 1682s, 1513s, 1464m, 1367m, 1284m, 1241m, 1166s, 1044w, 1001m, 977m, 864m, 783w, 723m, 580m.

MS (FAB): m/z (rel int %) = 304 ([M + H]⁺, 10), 248 (41), 204 (100), 74 (13), 57 (77), 41 (14).

Elemental analysis for C₁₆H₃₃NO₄S calc.: C 63.32%, H 10.96%, N 4.62%, O 10.54%; found: C 63.41%, H 10.90%, N 4.62%, O 10.46%.

Synthesis of 11-aminoundecane-1-thiol hydrochloride

Tert-butyl 11-mercaptoundecylcarbamate (1.00 g, 3.30 mmol) was dissolved in a HCl solution in dioxane (4 M, 20.0 mL, 80 mmol) and the reaction mixture was stirred for 3 hours at 23 °C. The solvent was concentrated under reduced pressure and the solid washed with diethyl ether (50 mL) and n-pentane (50 mL) to provide the desired 11-aminoundecane-1-thiol hydrochloride (0.78 g) in 99% yield.

m.p.: 162 - 164 °C.

¹H-NMR (400.1 MHz, (CD₃)₂SO, 295 K): δ = 1.25 (sₗ, 12 H, CH₂), 1.32 (m, 2 H, NCH₂CH₂CH₂), 1.51 (quin, J = 6.8 Hz, 2 H, CH₂CH₂SH), 1.53 (quin, J = 7.4 Hz, 2 H, NCH₂CH₂), 2.23 (t, J = 7.6 Hz, 1 H, SH), 2.46 (m, J = 6.8 Hz, 7.6 Hz, 2 H, CH₂SH), 2.75 (t, J = 7.4 Hz, 2 H, NCH₂), 7.78 (sₗ, 3 H, NH₃Cl).
$^{13}$C-$^1$H\textsuperscript{-}NMR (100.6 MHz, (CD$_3$)$_2$SO, 295 K): $\delta = 23.7$ (CH$_2$SH), 25.8 (CH$_2$), 26.9 (NCH$_2$CH$_2$), 27.7 (NCH$_2$CH$_2$CH$_2$), 28.5 (CH$_2$), 28.5 (CH$_2$), 28.8 (CH$_2$), 28.9 (CH$_2$), 28.9 (CH$_2$), 33.4 (CH$_2$CH$_2$SH), 38.7 (NCH$_2$).

IR (KBr): $\nu$ (cm$^{-1}$) = 2918s, 2657m, 2547m, 2021w, 1625m, 1511m, 1473m, 1398w, 1308w, 1196w.

MS (FAB): $m/z$ (rel int %) = 204 ([M - Chlorid]$^+$, 100), 55 (6).

Elemental analysis for C$_{11}$H$_{26}$ClNS: calc.: C 55.09%, H 10.93%, N 5.84%; found: C 55.21%, H 10.89%, N 5.73%.

### Analyses of thiolate-protected gold colloids

<table>
<thead>
<tr>
<th>Colloid</th>
<th>d (TEM) [nm]</th>
<th>Elemental analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2.32 ± 0.46 nm</td>
<td>C 16.52%, S 2.29%, Au 79.5%</td>
</tr>
<tr>
<td>7</td>
<td>3.48 ± 0.61 nm</td>
<td>C 7.15%, S 2.38%, Au 90.1%</td>
</tr>
<tr>
<td>8</td>
<td>3.44 ± 0.59 nm</td>
<td>C 11.39%, S 2.22%, Au 76.8%</td>
</tr>
<tr>
<td>9</td>
<td>2.60 ± 0.43 nm</td>
<td>C 7.39%, N 0.71, S 1.40%, Au 81.5%</td>
</tr>
<tr>
<td>10</td>
<td>3.39 ± 0.73 nm</td>
<td>C 8.26%, O 0.83, S 1.79%, Au 79.3%</td>
</tr>
</tbody>
</table>

**TEM-image of colloid 7**
Complete Reference 13: