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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 N\textsubscript{2} in a MBraun glovebox. Glasware was oven dried and flame dried prior to use. All chemicals were purchased from Fluka or Aldrich. CH\textsubscript{2}Cl\textsubscript{2} was dried over CaH\textsubscript{2} 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. \textsuperscript{1}H-, \textsuperscript{13}C-, \textsuperscript{19}F- and \textsuperscript{31}P-NMR spectra were recorded in CD\textsubscript{2}Cl\textsubscript{2} or CDCl\textsubscript{3} 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 theaverage 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 x 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 CH\textsubscript{2}Cl\textsubscript{2} (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 MgSO\textsubscript{4}, 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. Rf = 0.30 (hexanes/AcOEt = 4:1).

$^1$H-NMR (400.1 MHz, CDCl3, 295 K): δ = 1.28 (s, 20 H, CH$_2$), 1.35 (m, 4 H, CH$_2$), 1.64 (m, J = 7.4 Hz, 8 H, CH$_2$CH$_2$CO$_2$H + SCHRCH$_2$), 2.34 (t, J = 7.4 Hz, 4 H, CH$_2$CO$_2$H), 2.68 (t, J = 7.4 Hz, 4 H, SCHRCH$_2$), 10.98 (s, 2 H, CO$_2$H).

$^{13}$C-$^1$H-NMR (100.6 MHz, CDCl$_3$, 295 K): δ = 25.0 (CH$_2$), 28.9 (CH$_2$), 29.4 (CH$_2$), 29.5 (CH$_2$), 29.6 (CH$_2$), 29.7 (CH$_2$), 29.8 (CH$_2$), 34.4 (CH$_2$), 39.6 (SCHRCH$_2$), 180.7 (CO$_2$H).

IR (KBr): ν (cm$^{-1}$) = 2918s, 2849s, 2813s, 1696s, 1513s, 1479ms, 1435s, 1311ms, 1233w, 1158ms, 1099s, 998m, 958s, 927ms, 876s, 846s, 833ms, 800ms, 746w, 693s, 646s, 605s, 566s, 521s, 503s, 489s.

MS (FAB): m/z (rel int %) = 434 (M$^+$, 30), 417 (20), 344 (34), 328 (15), 232 (13), 171 (14), 111 (27), 101 (25), 87 (57), 81 (32), 69 (49), 55 (100), 43 (47).

Elemental analysis for C$_{22}$H$_{32}$O$_4$S$_2$: 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]$_D^{20}$ = +12.3 (c = 0.80, CHCl$_3$). Rf = 0.50 (diethyl ether).

$^1$H-NMR (400.1 MHz, CDCl$_3$, 295 K): δ = 2.59 (s, 1 H, NH), 3.12 (m, 2 H, NCHR), 3.27 (m, 2 H, NCHR), 4.01 (m, 2 H, PCH), 7.00 (m, 4 H, CH$_{Ph}$), 7.17 (m, 2 H, CH$_{Ph}$), 7.42 (m, 6 H, CH$_{Ph}$), 7.60 (m, 4 H, CH$_{Ph}$), 7.88 (m, 4 H, CH$_{Ph}$).

$^{13}$C-$^1$H-NMR (100.6 MHz, CDCl$_3$, 295 K): δ = 39.3 - 40.1 (dd, PCH), 53.1 (NCHR), 128.3 - 128.8 (m, CH$_{Ph}$-meta), 130.0 - 132.9 (m, C$_{Ph}$-ipso), 130.9 - 131.6 (m, CH$_{Ph}$-ortho and para).

$^{31}$P-$^1$H-NMR (162.0 MHz, CDCl$_3$, 295 K): δ = 51.2 (s).

IR (KBr): ν (cm$^{-1}$) = 3300m, 3048m, 2898m, 1749m, 1455s, 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 C$_{22}$H$_{27}$NP$_2$S$_2$: 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

\[ \text{Br} \]

\[ \text{C}{^1}\text{H}-\text{NMR} \ (400.1 \text{ MHz, CDCl}_3, 295 \text{ K}) : \delta = 1.51 (m_c, J = 2.5 \text{ Hz, 6 H, CCH}_2-\text{Ad}), 1.61 - 1.70 (m, 6 H, CCH}_2-\text{Ad}), 1.72 (m_c, 2 H, BrCH}_2CH}_2), 1.96 (m_c, 3 H, CCH}_2-\text{Ad}), 3.40 (m_c, 2 H, BrCH}_2).

\[ \text{C}{^13}\text{C}-\text{NMR} \ (100.6 \text{ MHz, CDCl}_3, 295 \text{ K}) : \delta = 28.6 (\text{CH}_2-\text{Ad}), 39.2 (\text{BrCH}_2), 34.1 (\text{C}_\text{Ad}), 37.1 (\text{CH}_2-\text{Ad}), 42.2 (\text{CCH}_2-\text{Ad}), 48.2 (\text{BrCH}_2\text{CH}_2).

IR (KBr): \nu \ (\text{cm}^{-1}) = 2896s, 2843s, 1452s, 1442m, 1344m, 1329m, 1312m, 1256m, 1215m, 1094m, 973m, 810m, 746w, 719m, 658m, 606s.

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

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

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

\[ \text{HCH} \]

3-Butenylmagnesium bromide solution (0.5 M in THF, 94 mL, 47.0 mmol) was added tropwise at 78 °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 °C and slowly warmed up to 23 °C over 12 hours. The resulting solution was washed with a saturated NH4Cl solution (100 mL) and water (100 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 \text{n}-pentane, gave 92% yield of 1-(hex-5'-enyl)adamantane (4.13 g).

R\text{f} = 0.86 (hexanes).

\[ \text{H-NMR} \ (400.1 \text{ MHz, CDCl}_3, 295 \text{ 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 (m_c, J = 2.2 \text{ Hz, 6 H, CCH}_2-\text{Ad}), 1.66
(m_c, 6 H, CH_{2-Ad}), 1.93 (m_c, 3 H, CH_{Ad}), 2.05 (m_c, 2 H, CCH_2CH_2CH_2CH_2) 4.96 (m_c, 2 H, CH_{2-vinyl}), 5.81 (m_c, 1 H, CH_{vinyl}).

^{13}C\{^{1}H\}-NMR (100.6 MHz, CDCl_3, 295 K): \delta = 22.0 (CH_2), 28.9 (CH_{Ad}), 30.0 (CH_2), 32.4 (C_{Ad}), 34.0 (CH_2), 37.4 (CH_{2-Ad}), 42.7 (CCH_2-Ad), 44.7 (CH_2), 114.2 (CH_{2-vinyl}), 139.4 (CH_{vinyl}).

IR (NaCl): \nu (cm\(^{-1}\)) = 3076w, 2898s, 2845s, 2656w, 1820w, 1640m, 1450m, 1098w, 991m, 908m.

MS (EI): \textit{m/z} (rel int %) = 218 (M\(^{+}\), 3), 135 (100), 107 (4), 93 (8), 79 (9), 67 (5), 55 (4), 41 (5).

Elemental analysis for C_{18}H_{36}O calc.: C 88.00%, H 12.00%; found: C 88.07%, H 12.01%.

\textbf{Synthesis of thioacetic acid (S)-6-(adamant-1'-yl)hexyl ester}

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: H_2O/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 Na_2CO_3 solution (100 mL) and water (100 mL). The organic phase was dried over MgSO_4, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with 5% diethyl ether in \textit{n}-pentane, gave 82% yield of thioacetic acid (S)-6-(adamant-1'-yl)hexyl ester (5.50 g).  

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

\textit{^1}H-NMR (400.1 MHz, CDCl_3, 295 K): \delta = 1.00 (t, J = 7.3 Hz, 2 H, CCH_2), 1.22 (m_c, 4 H, CH_2), 1.35 (quin, J = 7.3 Hz, 2 H, CCH_2CH_2), 1.43 (m_c, J = 2.3 Hz, 6 H, CCH_2-Ad), 1.55 (quin, J = 7.3 Hz, 2 H, CH_2CH_2S), 1.64 (m_c, 6 H, CH_2-Ad), 1.92 (m_c, 3 H, CH_{Ad}), 2.31 (s, 3 H, SC_{OCH_3}), 2.85 (t, J = 7.3 Hz, 2 H, CH_2S).

\textit{^{13}C\{^{1}H\}-NMR (100.6 MHz, CDCl_3, 295 K): \delta = 22.3 (CH_2), 28.8 (CH_{Ad}), 29.0 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 30.2 (CH_2), 30.7 (CH_3), 32.3 (C_{Ad}), 37.4 (CH_{2-Ad}), 42.6 (CCH_2-Ad), 44.7 (CH_2), 196.1 (CO).

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

MS (EI): \textit{m/z} (rel int %) = 294 (M\(^{+}\), 4), 251 (5), 135 (100), 107 (5), 93 (9), 79 (10), 43 (15).

Elemental analysis for C_{18}H_{36}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).

Rₛ = 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, CCH₂Ad), 1.60 (quin, J = 7.4 Hz, 2 H, CH₂CH₂SH), 1.64 (m, 6 H, CH₂-Ad), 1.92 (m, 3 H, CH₃Ad), 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 (CH₃Ad), 30.1 (CH₂), 32.3 (C₆Ad), 34.2 (CH₂), 37.4 (CH₂), 42.6 (CH₃Ad), 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 (s, 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 quintet 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, 3086m₁, 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 C₁₁H₂₅NO 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**

![Image of tert-butyl 11-hydroxyundecylcarbamate](image)

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-aminoundecanol (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. Rₚ = 0.38 (hexanes/AcOEt = 2:1).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.25 (sₙ, 10 H, CH₂), 1.30 (mₙ, 4 H, CH₂), 1.42 (sₙ, 11 H, C(CH₃)₃ + CH₂CH₂NH), 1.54 (mₙ, 3 H, OH + CH₂CH₂OH), 3.08 (mₙ, J = 6.3 Hz, 6.6 Hz, 2 H, CH₂NH), 3.61 (mₙ, J = 5.6 Hz, 6.3 Hz, 2 H, CH₂OH), 4.54 (sₙ, 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 (CH₂OH), 63.1 (CH₂OH), 79.1 (C(CH₃)₃), 156.1 (CO).

IR (NaCl): ν (cm⁻¹) = 3353m₁, 2926s, 2854m, 1693s, 1526m, 1348m, 1077m. 

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 C₁₆H₃₃NO₃ 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**

![Image of tert-butyl 11-bromoundecylcarbamate](image)

N-Bromosuccinimide (10.0 g, 56.2 mmol) and triphenylphosphine (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<sub>f</sub> = 0.37 (hexanes/AcOEt = 10:1).

<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>, 295 K): δ = 1.25 (s<sub>b</sub>, 12 H, CH<sub>2</sub>), 1.42 (s<sub>b</sub>, 13 H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br + C(CH<sub>3</sub>)<sub>3</sub> + CH<sub>2</sub>CH<sub>2</sub>NH), 1.83 (m<sub>c</sub>, J = 6.9 Hz, 7.2 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>Br), 3.08 (t, J = 6.6 Hz, 2 H, CH<sub>2</sub>NH), 3.38 (t, J = 6.9 Hz, 2 H, CH<sub>2</sub>Br), 4.53 (s<sub>b</sub>, 1 H, NH).

<sup>13</sup>C<sup>{1}H</sup>-NMR (100.6 MHz, CDCl<sub>3</sub>, 295 K): δ = 26.8 (CH<sub>2</sub>), 28.2 (CH<sub>2</sub>), 28.5 (C(CH<sub>3</sub>)<sub>3</sub>), 28.8 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>CH<sub>2</sub>NH), 32.9 (CH<sub>2</sub>CH<sub>2</sub>Br), 34.1 (CH<sub>2</sub>Br), 40.7 (CH<sub>2</sub>NH), 79.0 (C(CH<sub>3</sub>)<sub>3</sub>), 156.0 (CO).

IR (KBr): ν (cm<sup>-1</sup>) = 3377s, 2918s, 2851s, 1687s<sub>b</sub>, 1522s<sub>b</sub>, 1469m, 1374m, 1280m, 1237m, 1170m<sub>b</sub>, 1026w, 976w, 870m, 720m, 643m.

MS (FAB): m/z (rel int %) = 350 (M<sup>+</sup>, 4, <sup>79</sup>Br), 294 (96, <sup>79</sup>Br), 250 (13, <sup>79</sup>Br), 214 (8), 137 (8), 74 (41), 57 (100), 41 (20).

Elemental analysis for C<sub>16</sub>H<sub>32</sub>BrNO<sub>2</sub> 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-bromoundecycarbamate (14.5 g, 41.4 mmol) in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na<sub>2</sub>CO<sub>3</sub> solution (200 mL) and water (200 mL). The organic phase was dried over MgSO<sub>4</sub>, 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<sub>f</sub> = 0.25 (hexanes/AcOEt = 10:1).

<sup>1</sup>H-NMR (400.1 MHz, CDCl<sub>3</sub>, 295 K): δ = 1.22 (s<sub>b</sub>, 10 H, CH<sub>2</sub>), 1.25 (m<sub>c</sub>, 2 H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.30 (m<sub>c</sub>, 2 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>S), 1.41 (s<sub>b</sub>, 11 H, C(CH<sub>3</sub>)<sub>3</sub> + NCH<sub>2</sub>CH<sub>2</sub>), 1.52 (m<sub>c</sub>, J = 6.8 Hz, 7.4 Hz, 2 H, CH<sub>2</sub>CH<sub>2</sub>S), 2.29 (s, 3 H, SCOCH<sub>3</sub>), 2.83 (t, J = 7.4 Hz, 2 H, CH<sub>2</sub>S), 3.07 (t, J = 6.6 Hz, 2 H, NCH<sub>2</sub>), 4.55 (s<sub>b</sub>, 1 H, NH).

<sup>13</sup>C<sup>{1}H</sup>-NMR (100.6 MHz, CDCl<sub>3</sub>, 295 K): δ = 26.8 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.5 (C(CH<sub>3</sub>)<sub>3</sub>), 28.8 (CH<sub>2</sub>S), 29.1 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>CH<sub>2</sub>S), 29.4 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 29.5 (CH<sub>2</sub>), 30.1 (NCH<sub>2</sub>CH<sub>2</sub>), 30.7 (SCOCH<sub>3</sub>), 40.6 (NCH<sub>2</sub>), 78.9 (C(CH<sub>3</sub>)<sub>3</sub>), 156.0 (CO), 196.0 (SCO).

IR (KBr): ν (cm<sup>-1</sup>) = 3380m, 2918m, 2851m, 1687s<sub>b</sub>, 1522s<sub>b</sub>, 1469m, 1364m, 1282m, 1238m, 1172m, 1138m, 1116m, 1000w, 959m, 870m, 720w, 639m.

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

Elemental analysis for C<sub>18</sub>H<sub>35</sub>NO<sub>2</sub>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-mercaptopoundecylcarbamate

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-mercaptopoundecylcarbamate (0.86 g).

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

¹H-NMR (400.1 MHz, CDC1₃, 295 K): δ = 1.25 (sₖ, 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 = 7.7 Hz, 7.6 Hz, 2 H, CH₂SH), 3.09 (t, J = 6.6 Hz, 2 H, NCH₃), 4.50 (sₖ, 1 H, NH₃).

¹³C {¹H}-NMR (100.6 MHz, CDC1₃, 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, 1682sₖ, 1513sₗ, 1464m, 1367m, 1284m, 1241m, 1166sₖ, 1044w, 1001m, 977m, 864m, 783w, 723m, 580mₖ.

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

Elemental analysis for C₁₆H₃₃NO₂S calc.: C 63.32%, H 10.96%, N 4.62%, S 10.54%; found: C 63.41%, H 10.90%, N 4.62%, S 10.46%.

Synthesis of 11-aminoundecane-1-thiol hydrochloride

Tert-butyl 11-mercaptopoundecylcarbamate (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 (sₖ, 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 (sₖ, J = 7.4 Hz, 2 H, NCH₂), 7.78 (sₖ, 3 H, NH₃Cl).
$^{13}$C-$^{1}$H-NMR (100.6 MHz, (CD$_3$)$_2$SO, 295 K): \(\delta = 23.7 \text{ (CH}_2\text{SH)}, 25.8 \text{ (CH}_2\text{)}, 26.9 \text{ (NCH}_2\text{CH}_2\text{)}, 27.7 \text{ (NCH}_2\text{CH}_2\text{CH}_2\text{)}, 28.5 \text{ (CH}_2\text{)}, 28.5 \text{ (CH}_2\text{)}, 28.8 \text{ (CH}_2\text{)}, 28.9 \text{ (CH}_2\text{)}, 28.9 \text{ (CH}_2\text{)}, 33.4 \text{ (CH}_2\text{CH}_2\text{SH)}, 38.7 \text{ (NCH}_2\text{)}\).

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

MS (FAB): \(m/z \text{ (rel int \%)} = 204 \text{ ([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: