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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 N₂ in a MBraun glovebox. Glasware 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 mm, 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. Rf = 0.30 (hexanes/AcOEt = 4:1).

$^1$H-NMR (400.1 MHz, CDCl$_3$, 295 K): $\delta = 1.28$ ($s_b$, 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 + SCH$_2$CH$_2$), 2.34 (t, J = 7.4 Hz, 4 H, CH$_2$CO$_2$H), 2.68 (t, J = 7.4 Hz, 4 H, S(CH$_2$), 10.98 (s, 2 H, CO$_2$H).

$^{13}$C ($^1$H)-NMR (100.6 MHz, CDCl$_3$, 295 K): $\delta = 25.0$ (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 (SCH$_2$), 180.7 (CO$_2$H).

IR (KBr): $\nu$ (cm$^{-1}$) = 2918s, 2849s, 1696m, 1427m, 1289m, 1261m, 1206m, 944m.

MS (FAB): m/z (rel int %) = 434 (M$^+$, 30), 417 (20), 344 (34), 328 (15), 232 (13), 171 (15), 127 (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. $[\alpha]_D^{23}$ = +12.3 (c = 0.80, CHCl$_3$). Rf = 0.50 (diethyl ether).

$^1$H-NMR (400.1 MHz, CDCl$_3$, 295 K): $\delta = 2.59$ ($s_b$, 1 H, NH), 3.12 (m, 2 H, NCH$_2$), 3.27 (m, 2 H, NCH$_2$), 4.01 (m, 2 H, PCH), 7.00 (m, 4 H, CH$_2$Ph), 7.17 (m, 2 H, CH$_2$Ph), 7.42 (m, 6 H, CH$_2$Ph), 7.60 (m, 4 H, CH$_2$Ph), 7.88 (m, 4 H, CH$_2$Ph).

$^{13}$C ($^1$H)-NMR (100.6 MHz, CDCl$_3$, 295 K): $\delta = 39.3$ - 40.1 (dd, PCH), 53.1 (NCH$_2$), 128.3 - 128.8 (m, CH$_{Ph-meta}$), 130.0 - 132.9 (m, C$_{Ph-isp}$), 130.9 - 131.6 (m, CH$_{Ph-ortho and para}$).

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

IR (KBr): $\nu$ (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 C$_{28}$H$_{37}$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

\[
\text{N-Bromosuccinimide (987 mg, 5.55 mmol) and triphenylphosphine (1.46 g, 5.55 mmol) were added to a solution of 2-adamant-1-yl-ethanol (1.00 g, 5.55 mmol) in freshly distilled benzene (20 mL) and the reaction mixture was stirred for 12 hours at 23 °C. The resulting solution was washed with a saturated NaCl solution (20 mL) and water (20 mL). The organic phase was dried over MgSO}_{4}, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with } n\text{-pentane, gave 92% yield of } 1-(2\text{-bromo-ethyl})\text{adamantane (1.24 g).}
\]
m.p.: 66 - 68 °C. \( R_f = 0.78 \) (n-pentane).

\(^1\)H-NMR (400.1 MHz, CDCl\textsubscript{3}, 295 K): \( \delta = 1.51 \) (m, \( J = 2.5 \) Hz, 6 H, C\textsubscript{CH\textsubscript{2-Ad}}), 1.61 - 1.70 (m, 6 H, C\textsubscript{CH\textsubscript{2-Ad}}), 1.72 (m, 2 H, BrC\textsubscript{2}CH\textsubscript{2}), 1.96 (m, 3 H, C\textsubscript{Ad}), 3.40 (m, 2 H, BrCH\textsubscript{2}).

\(^{13}\)C\{\(^1\)H\}\text{-NMR (100.6 MHz, CDCl\textsubscript{3}, 295 K): \( \delta = 28.6 \) (CH\textsubscript{Ad}), 29.2 (BrCH\textsubscript{2}), 34.1 (C\textsubscript{Ad}), 37.1 (CH\textsubscript{2-Ad}), 42.2 (C\textsubscript{CH\textsubscript{2-Ad}}), 48.2 (BrCH\textsubscript{2}CH\textsubscript{2}).

IR (KBr): \( \nu \) (cm\textsuperscript{-1}) = 2896s, 2843s, 1452w, 1442m, 1344m, 1329m, 1312m, 1256m, 1215m, 1094m, 973m, 810m, 746w, 719m, 658m, 560s.

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

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

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

\[
3\text{-Butenylmagnesium bromide solution (0.5 M in THF, 94 mL, 47.0 mmol) was added tropwise at } -78 \text{ °C to a solution of } 1-(2\text{-bromo-ethyl})\text{adamantane (5.00 g, 20.6 mmol) in freshly distilled THF (30 mL). After 10 min, a lithium tetrachlorocuprate(II) solution (0.1 M in THF, 2.10 mL, 0.21 mmol) was added and the reaction mixture was stirred for 2 hours at } -78 \text{ °C and slowly warmed up to } 23 \text{ °C over 12 hours. The resulting solution was washed with a saturated NH}_{4}Cl \text{ solution (100 mL) and water (100 mL). The organic phase was dried over MgSO}_{4}, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with } n\text{-pentane, gave 92% yield of } 1-(hex-5\text{-enyl})\text{adamantane (4.13 g).}
\]

\( R_f = 0.86 \) (hexanes).

\(^1\)H-NMR (400.1 MHz, CDCl\textsubscript{3}, 295 K): \( \delta = 1.03 \) (t, \( J = 7.1 \) Hz, 2 H, C\textsubscript{CH\textsubscript{2}}), 1.24 (quin, \( J = 7.1 \) Hz, 2 H, C\textsubscript{CH\textsubscript{2}CH\textsubscript{2}}), 1.33 (quin, \( J = 7.1 \) Hz, 2 H, C\textsubscript{CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}}), 1.45 (m, \( J = 2.2 \) Hz, 6 H, C\textsubscript{CH\textsubscript{2-Ad}}), 1.66
(m, 6 H, CH$_2$-Ad), 1.93 (m, 3 H, CH$_3$), 2.05 (m, 2 H, CCH$_2$CH$_2$CH$_2$CH$_2$) 4.96 (m, 2 H, CH$_2$-vinyl), 5.81 (m, 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$^{-1}$) = 3076 w, 2898 s, 2845 s, 2656 w, 1820 w, 1640 m, 1450 m, 1098 w, 991 m, 908 m.

MS (EI): 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$_{15}$H$_{26}$ calc.: C 88.00%, H 12.00%; found: C 88.07%, H 12.01%.

**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$_2$O/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'-azobis(isobutyronitrile (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$_2$CO$_3$ 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 n-pentane, gave 82% yield of thioacetic acid (S)-6-(adamant-1'-yl)hexyl ester (5.50 g).

R$_r$ = 0.67 (n-pentane/diethyl ether = 20:1).

$^1$H-NMR (400.1 MHz, CDCl$_3$, 295 K): $\delta$ = 1.00 (t, $J$ = 7.3 Hz, 2 H, CCH$_2$), 1.22 (m, 4 H, CH$_2$), 1.35 (quin, $J$ = 7.3 Hz, 2 H, CCH$_2$CH$_2$), 1.43 (m, $J$ = 2.3 Hz, 6 H, CCH$_2$-Ad), 1.55 (quin, $J$ = 7.3 Hz, 2 H, CH$_2$CH$_2$S), 1.64 (m, 6 H, CH$_2$-Ad), 1.92 (m, 3 H, CH$_3$-Ad), 2.31 (s, 3 H, SCOCH$_3$), 2.85 (t, $J$ = 7.3 Hz, 2 H, CH$_2$S).

$^{13}$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 (CCH$_2$-Ad), 42.6 (CCH$_2$-Ad), 44.7 (CH$_2$), 196.1 (SCO).

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

MS (EI): 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$_{30}$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).

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 (quint, J = 7.4 Hz, 2 H, CCH₂CH₂), 1.44 (m, J = 2.5 Hz, 6 H, CCH₂-Ad), 1.60 (quint, 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 (CAd), 34.2 (CH₂), 37.4 (CH₂), 42.6 (CH₃Ad), 44.8 (CH₂).

IR (NaCl): ν (cm⁻¹) = 2902s, 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 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): $\nu$ (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 $C_{11}H_{23}NO$ 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-aminoundecanol (12.0 g, 64.1 mmol) in freshly distilled CH$_2$Cl$_2$ (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 MgSO$_4$, 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. R$_f$ = 0.38 (hexanes/AcOEt = 2:1).

$^1$H-NMR (400.1 MHz, CDCl$_3$, 295 K): $\delta$ = 1.25 (s$_b$, 10 H, CH$_2$), 1.30 (m$_c$, 4 H, CH$_2$), 1.42 (s$_b$, 11 H, C(CH$_3$)$_3$ + CH$_2$CH$_2$NH), 1.54 (m$_c$, 3 H, OH + CH$_2$CH$_2$OH), 3.08 (m$_c$, J = 6.3 Hz, 6.6 Hz, 2 H, CH$_2$NH), 3.61 (m$_c$, J = 5.6 Hz, 6.3 Hz, 2 H, CH$_2$OH), 4.54 (s$_b$, 1 H, NH).

$^{13}$C{$^1$H}-NMR (100.6 MHz, CDCl$_3$, 295 K): $\delta$ = 25.8 (CH$_2$), 26.8 (CH$_2$), 28.5 (C(CH$_3$)$_3$), 29.3 (CH$_2$), 29.5 (CH$_2$), 29.5 (CH$_2$), 29.6 (CH$_2$), 29.6 (CH$_2$), 30.1 (CH$_2$CH$_2$NH), 32.8 (CH$_2$CH$_2$OH), 40.7 (CH$_2$NH), 63.1 (CH$_2$OH), 79.1 (C(CH$_3$)$_3$), 156.1 (CO).

IR (NaCl): $\nu$ (cm$^{-1}$) = 3353m$_b$, 2926s, 2854m, 1693s, 1526m$_b$, 1366m, 1275m, 1251m, 1173s.

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 $C_{16}H_{33}NO_3$ 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 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 MgSO$_4$, 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. Rf = 0.37 (hexanes/AcOEt = 10:1).

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

\(^13\)C\(^{1\text{H}}\)-NMR (100.6 MHz, CDCl\(_3\), 295 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): \(\nu\) (cm\(^{-1}\)) = 3377s, 2918s, 2851s, 1687s, 1522s, 1469m, 1374m, 1280m, 1237m, 1170m, 1026w, 976w, 870m, 720m, 643m.

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

Elemental analysis for \(C_{16}H_{32}BrNO_2\) 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\(_2\)Cl\(_2\) (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na\(_2\)CO\(_3\) solution (200 mL) and water (200 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 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. Rf = 0.25 (hexanes/AcOEt = 10:1).

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\), 295 K): \(\delta = 1.22\) (s, 10 H, \(CH_2\)), 1.25 (m, 2 H, NCH\(_2CH_2CH_2\)), 1.30 (m, 2 H, \(CH_2CH_2CH_2S\)), 1.41 (s, 11 H, C(CH\(_3\))\(_3\) + NCH\(_2CH_2\)), 1.52 (m, \(J = 6.8\) Hz, 7.4 Hz, 2 H, \(CH_2CH_2S\)), 2.29 (s, 3 H, SCONH\(_2\)), 2.83 (t, \(J = 7.4\) Hz, 2 H, \(CH_2S\)), 3.07 (t, \(J = 6.6\) Hz, 2 H, NCH\(_2\)), 4.55 (s, 1 H, NH).

\(^13\)C\(^{1\text{H}}\)-NMR (100.6 MHz, CDCl\(_3\), 295 K): \(\delta = 26.8\) (NCH\(_2CH_2CH_2\)), 28.5 (C(CH\(_3\))\(_3\)), 28.8 (CH\(_2\)), 29.1 (CH\(_2\)), 29.2 (CH\(_2\)), 29.3 (CH\(_2CH_2S\)), 29.4 (CH\(_2\)), 29.5 (CH\(_2\)), 29.6 (CH\(_2\)), 30.1 (NCH\(_2CH_2\)), 30.7 (SCOCONH\(_2\)), 40.6 (NCH\(_2\)), 78.9 (C(CH\(_3\))\(_3\)), 156.0 (CO), 196.0 (SCO).

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

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

Elemental analysis for \(C_{18}H_{35}NO_2S\) 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 (sₘ, 12 H, CH₂), 1.32 (t, J = 7.6 Hz, 1 H, SH), 1.36 (mₘ, 2 H, CH₂CH₂CH₂SH), 1.43 (sₘ, 11 H, C(CH₃)₃ + NCH₂CH₂), 1.59 (quin, J = 7.2 Hz, 2 H, CH₂CH₂S), 2.51 (mₘ, J = 7.2 Hz, 7.6 Hz, 2 H, CH₂SH), 3.09 (t, J = 6.6 Hz, 2 H, NCH₂), 4.50 (sₘ, 1 H, NH₃).

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), 29.6 (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 C₁₆H₃₃NO₂S; 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, (CD₂)SO, 295 K): δ = 1.25 (sₘ, 12 H, CH₂), 1.32 (mₘ, 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 (mₘ, J = 6.8 Hz, 7.6 Hz, 2 H, CH₂SH), 2.75 (tₘ, J = 7.4 Hz, 2 H, NCH₂), 7.78 (sₘ, 3 H, NH₃Cl).
$^{13}$C-$^1$H-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: