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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-mercaptoundecanoic acid (2.00 g, 9.16 mmol) in methanol (50 mL) and the solution was stirred for 30 min. The brown reaction mixture was decolorized 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-decyldisulfanyl)undecanoic acid (1.25 g).

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

^1H -NMR (400.1 MHz, CDCl_3 , 295 K): δ = 1.28 (s_b , 20 H, CH_2), 1.35 (m_c , 4 H, CH_2), 1.64 (m_c , J = 7.4 Hz, 8 H, $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ + SCH_2CH_2), 2.34 (t, J = 7.4 Hz, 4 H, $\text{CH}_2\text{CO}_2\text{H}$), 2.68 (t, J = 7.4 Hz, 4 H, SCH_2), 10.98 (s_b , 2 H, CO_2H).

$^{13}\text{C}\{^1\text{H}\}$ -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), 29.5 (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_2H).

IR (KBr): ν (cm^{-1}) = 2918s, 2849s, 1696s_b, 1471m, 1427m, 1289m, 1261m, 1231m, 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 $\text{C}_{22}\text{H}_{42}\text{O}_4\text{S}_2$ calc.: C 60.79%, H 9.74%, O 14.72%; found: C 60.84%, H 9.68%, O 14.74%.

Synthesis of (3*R*,4*R*)-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. $[\alpha]_D^{20}$ = +12.3 (c = 0.80, CHCl_3). R_f = 0.50 (diethyl ether).

^1H -NMR (400.1 MHz, CDCl_3 , 295 K): δ = 2.59 (s_b , 1 H, NH), 3.12 (m_c , 2 H, NCH_2), 3.27 (m_c , 2 H, NCH_2), 4.01 (m_c , 2 H, PCH), 7.00 (m_c , 4 H, CH_{Ph}), 7.17 (m_c , 2 H, CH_{Ph}), 7.42 (m_c , 6 H, CH_{Ph}), 7.60 (m_c , 4 H, CH_{Ph}), 7.88 (m_c , 4 H, CH_{Ph}).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 295 K): δ = 39.3 - 40.1 (dd, PCH), 53.1 (NCH_2), 128.3 - 128.8 (m, $\text{CH}_{\text{Ph-meta}}$), 130.0 - 132.9 (m, $\text{C}_{\text{Ph-ipso}}$), 130.9 - 131.6 (m, $\text{CH}_{\text{Ph-ortho and para}}$).

$^{31}\text{P}\{^1\text{H}\}$ -NMR (162.0 MHz, CDCl_3 , 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 ($[\text{M} + \text{H}]^+$, 30), 286 (9), 217 (15), 185 (6), 77 (5), 68 (100), 39 (5).

Elemental analysis for $\text{C}_{28}\text{H}_{27}\text{NP}_2\text{S}_2$ 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

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 MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with *n*-pentane, gave 92% yield of 1-(2'-bromo-ethyl)adamantane (1.24 g).

m.p.: 66 - 68 °C. *R*_f = 0.78 (*n*-pentane).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.51 (m_c, *J* = 2.5 Hz, 6 H, CCH_{2-Ad}), 1.61 - 1.70 (m, 6 H, CH_{2-Ad}), 1.72 (m_c, 2 H, BrCH₂CH₂), 1.96 (m_c, 3 H, CH_{Ad}), 3.40 (m_c, 2 H, BrCH₂).

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 28.6 (CH_{Ad}), 29.2 (BrCH₂), 34.1 (C_{Ad}), 37.1 (CH_{2-Ad}), 42.2 (CCH_{2-Ad}), 48.2 (BrCH₂CH₂).

IR (KBr): ν (cm⁻¹) = 2896s, 2843s, 2652w, 1452s, 1442m, 1344m, 1329m, 1312m, 1256m, 1215m, 1094m, 973m, 810m, 746w, 719m, 658m, 560s.

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

Elemental analysis for C₁₂H₁₉Br calc.: C 59.27%, H 7.88%; found: C 59.22%, H 7.79%.

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

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 MgSO₄, filtered and concentrated under reduced pressure. Purification of the crude material by flash chromatography, eluting with *n*-pentane, gave 92% yield of 1-(hex-5'-enyl)adamantane (4.13 g).

*R*_f = 0.86 (hexanes).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.03 (t, *J* = 7.1 Hz, 2 H, CCH₂), 1.24 (quin, *J* = 7.1 Hz, 2 H, CCH₂CH₂), 1.33 (quin, *J* = 7.1 Hz, 2 H, CCH₂CH₂CH₂), 1.45 (m_c, *J* = 2.2 Hz, 6 H, CCH_{2-Ad}), 1.66

(m_c, 6 H, CH_{2-Ad}), 1.93 (m_c, 3 H, CH_{Ad}), 2.05 (m_c, 2 H, CCH₂CH₂CH₂CH₂) 4.96 (m_c, 2 H, CH_{2-vinyl}), 5.81 (m_c, 1 H, CH_{vinyl}).

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 22.0 (CH₂), 28.9 (CH_{Ad}), 30.0 (CH₂), 32.4 (C_{Ad}), 34.0 (CH₂), 37.4 (CH_{2-Ad}), 42.7 (CCH_{2-Ad}), 44.7 (CH₂), 114.2 (CH_{2-vinyl}), 139.4 (CH_{vinyl}).

IR (NaCl): ν (cm⁻¹) = 3076w, 2898s, 2845s, 2656w, 1820w, 1640m, 1450m, 1098w, 991m, 908m.

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 C₁₆H₂₆ 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: 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 (*n*-pentane/diethyl ether = 20:1).

¹H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.00 (t, *J* = 7.3 Hz, 2 H, CCH₂), 1.22 (m_c, 4 H, CH₂), 1.35 (quin, *J* = 7.3 Hz, 2 H, CCH₂CH₂), 1.43 (m_c, *J* = 2.3 Hz, 6 H, CCH_{2-Ad}), 1.55 (quin, *J* = 7.3 Hz, 2 H, CH₂CH₂S), 1.64 (m_c, 6 H, CH_{2-Ad}), 1.92 (m_c, 3 H, CH_{Ad}), 2.31 (s, 3 H, SCOCH₃), 2.85 (t, *J* = 7.3 Hz, 2 H, CH₂S).

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 295 K): δ = 22.3 (CH₂), 28.8 (CH_{Ad}), 29.0 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 30.2 (CH₂), 30.7 (CH₃), 32.3 (C_{Ad}), 37.4 (CH_{2-Ad}), 42.6 (CCH_{2-Ad}), 44.7 (CH₂), 196.1 (SCO).

IR (NaCl): ν (cm⁻¹) = 2902s, 2847s, 2661w, 1694s, 1450m, 1352m, 1132m, 954m, 864w, 624w.

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

Elemental analysis for C₁₈H₃₀OS 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 μ mol) 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 MgSO_4 , 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).

$R_f = 0.65$ (*n*-pentane).

^1H -NMR (400.1 MHz, CDCl_3 , 295 K): $\delta = 1.01$ (t, $J = 7.4$ Hz, 2 H, CCH_2), 1.22 (m_c , 4 H, CH_2), 1.32 (t, $J = 7.7$ Hz, 1 H, SH), 1.38 (quin, $J = 7.4$ Hz, 2 H, CCH_2CH_2), 1.44 (m_c , $J = 2.5$ Hz, 6 H, $\text{CCH}_2\text{-Ad}$), 1.60 (quin, $J = 7.4$ Hz, 2 H, $\text{CH}_2\text{CH}_2\text{SH}$), 1.64 (m_c , 6 H, $\text{CH}_2\text{-Ad}$), 1.92 (m_c , 3 H, CH_{Ad}), 2.51 (q, $J = 7.4$ Hz, 2 H, CH_2SH).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 295 K): $\delta = 22.3$ (CH_2), 24.8 (CH_2), 28.5 (CH_2), 28.9 (CH_{Ad}), 30.1 (CH_2), 32.3 (C_{Ad}), 34.2 (CH_2), 37.4 (CH_2), 42.6 (CH_{Ad}), 44.8 (CH_2).

IR (NaCl): $\nu(\text{cm}^{-1}) = 2902s, 2846s, 2663w, 1450m, 1347w, 1101w$.

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

Elemental analysis for $\text{C}_{16}\text{H}_{28}\text{S}$ 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 LiAlH_4 (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 H_2O (20 mL) and stirred for 30 min at 23 °C. The reaction mixture was dried over MgSO_4 , 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, CD_2Cl_2 , 295 K): $\delta = 1.27$ (s_b , 14 H, CH_2), 1.39 (quin, $J = 7.0$ Hz, 2 H, $\text{CH}_2\text{CH}_2\text{NH}_2$), 1.50 (quin, $J = 6.5$ Hz, 2 H, $\text{CH}_2\text{CH}_2\text{OH}$), 2.61 (t, $J = 7.0$ Hz, 2 H, CH_2NH_2), 3.54 (t, $J = 6.5$ Hz, 2 H, CH_2OH) $\Rightarrow$ OH und NH_2 signals lies under the quintetts between 1.36 - 1.54 Hz.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CD_2Cl_2 , 295 K): $\delta = 25.9$ (CH_2), 27.0 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 33.0 ($\text{CH}_2\text{CH}_2\text{OH}$), 34.1 ($\text{CH}_2\text{CH}_2\text{NH}_2$), 42.3 (CH_2NH_2), 62.7 (CH_2OH).

IR (KBr): ν (cm⁻¹) = 3338m, 3086m_b, 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

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. R_f = 0.38 (hexanes/AcOEt = 2:1).

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

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_f = 0.37 (hexanes/AcOEt = 10:1).

^1H -NMR (400.1 MHz, CDCl_3 , 295 K): δ = 1.25 (s_b , 12 H, CH_2), 1.42 (s_b , 13 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$ + $\text{C}(\text{CH}_3)_3$ + $\text{CH}_2\text{CH}_2\text{NH}$), 1.83 (m_c , J = 6.9 Hz, 7.2 Hz, 2 H, $\text{CH}_2\text{CH}_2\text{Br}$), 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_b , 1 H, NH).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 295 K): δ = 26.8 (CH_2), 28.2 (CH_2), 28.5 ($\text{C}(\text{CH}_3)_3$), 28.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 30.1 ($\text{CH}_2\text{CH}_2\text{NH}$), 32.9 ($\text{CH}_2\text{CH}_2\text{Br}$), 34.1 (CH_2Br), 40.7 (CH_2NH), 79.0 ($\text{C}(\text{CH}_3)_3$), 156.0 (CO).

IR (KBr): ν (cm^{-1}) = 3377 s , 2918 s , 2851 s , 1687 s_b , 1522 s_b , 1469 m , 1374 m , 1280 m , 1237 m , 1170 m_b , 1026 w , 976 w , 870 m , 720 m , 643 m .

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 $\text{C}_{16}\text{H}_{32}\text{BrNO}_2$ 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_2Cl_2 (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na_2CO_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. R_f = 0.25 (hexanes/AcOEt = 10:1).

^1H -NMR (400.1 MHz, CDCl_3 , 295 K): δ = 1.22 (s_b , 10 H, CH_2), 1.25 (m_c , 2 H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.30 (m_c , 2 H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{S}$), 1.41 (s_b , 11 H, $\text{C}(\text{CH}_3)_3$ + NCH_2CH_2), 1.52 (m_c , J = 6.8 Hz, 7.4 Hz, 2 H, $\text{CH}_2\text{CH}_2\text{S}$), 2.29 (s, 3 H, SCOCH_3), 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_b , 1 H, NH).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, CDCl_3 , 295 K): δ = 26.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 28.5 ($\text{C}(\text{CH}_3)_3$), 28.8 (CH_2S), 29.1 (CH_2), 29.2 (CH_2), 29.3 ($\text{CH}_2\text{CH}_2\text{S}$), 29.4 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 30.1 (NCH_2CH_2), 30.7 (SCOCH_3), 40.6 (NCH_2), 78.9 ($\text{C}(\text{CH}_3)_3$), 156.0 (CO), 196.0 (SCO).

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

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

Elemental analysis for $\text{C}_{18}\text{H}_{35}\text{NO}_3\text{S}$ 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. R_f = 0.36 (hexanes/AcOEt = 10:1).

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

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_b, 1513s_b, 1464m, 1367m, 1284m, 1241m, 1166s_b, 1044w, 1001m, 977m, 864m, 783w, 723m, 580m_b.

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, (CD₃)₂SO, 295 K): δ = 1.25 (s_b, 12 H, CH₂), 1.32 (m_c, 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_c, J = 6.8 Hz, 7.6 Hz, 2 H, CH₂SH), 2.75 (t_b, J = 7.4 Hz, 2 H, NCH₂), 7.78 (s_b, 3 H, NH₃Cl).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (100.6 MHz, $(\text{CD}_3)_2\text{SO}$, 295 K): δ = 23.7 (CH_2SH), 25.8 (CH_2), 26.9 (NCH_2CH_2), 27.7 ($\text{NCH}_2\text{CH}_2\text{CH}_2$), 28.5 (CH_2), 28.5 (CH_2), 28.8 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 33.4 ($\text{CH}_2\text{CH}_2\text{SH}$), 38.7 (NCH_2).

IR (KBr): ν (cm^{-1}) = 2918_s, 2657_m, 2547_m, 2021_w, 1625_m, 1511_m, 1473_m, 1398_w, 1308_w, 1196_w.

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

Elemental analysis for $\text{C}_{11}\text{H}_{26}\text{ClNS}$ 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

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

TEM-image of colloid 7

Complete Reference 13:

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