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

Thomas Belser†, Meike Stöhr‡,* and Andreas Pfaltz†,*

Contribution from the Department of Chemistry,† St. Johanns-Ring 19 and the Department of Physics,‡ Klingelbergstrasse 82, University of Basel, 4056 Basel (Switzerland).

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 x 250 mm).

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

\[
\begin{align*}
\text{HO} & \quad \text{O} \\
\text{S-S} & \quad \text{O} \\
\end{align*}
\]

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 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-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, CH_2CH_2CO_2H + SCH_2CH_2), 2.34 (t, J = 7.4 Hz, 4 H, CH_2CO_2H), 2.68 (t, J = 7.4 Hz, 4 H, SCH_2), 10.98 (s_b, 2 H, CO_2H).

^13C, ^1H-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 (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 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. [\(\alpha\)\(^D\)]\(_{b}\) = +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\(_{Ph}\)).

^13C\(^1\)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, CH\(_{Ph-meta}\)), 130.0 - 132.9 (m, C\(_{Ph-ipso}\)), 130.9 - 131.6 (m, CH\(_{Ph-ortho\ and\ para}\)).

^31P \(^1\)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 ([M + H]\(^+\), 30), 286 (9), 217 (15), 185 (6), 77 (5), 68 (100), 39 (5).

Elemental analysis for C\(_{28}\)H\(_{47}\)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

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

m.p.: 66 – 68 °C. \( R_f = 0.78 \) (\( n\)-pentane).

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\), 295 K): \( \delta = 1.51 \) (m, \( J = 2.5 \text{ Hz, } 6 \text{ H, } CCH_2\text{-Ad} \)), 1.61 – 1.70 (m, 6 H, \( CH_2\text{-Ad} \)), 1.72 (m, 2 H, BrCH\(_2\)CH\(_2\)), 1.96 (m, 3 H, \( CH_3\text{-Ad} \)), 3.40 (m, 2 H, BrCH\(_2\)).

\(^1\)C\({}^1\)H-NMR (100.6 MHz, CDCl\(_3\), 295 K): \( \delta = 28.6 \) (\( CH_3\text{-Ad} \)), 29.2 (BrCH\(_2\)), 34.1 (\( C_\text{Ad} \)), 37.1 (\( CH_2\text{-Ad} \)), 42.2 (\( CCH_2\text{-Ad} \)), 48.2 (BrCH\(_2\)CH\(_2\)).

IR (KBr): \( \nu \) (cm\(^{-1}\)) = 2896s, 2843s, 2652w, 1452s, 1344m, 1329m, 1312m, 1256m, 1215m, 1094m, 973m, 810m, 746w, 719m, 658m, 560s.

MS (EI): \( m/z \) (rel int \%) = 242 (M\(^+\), 1, \( 79\)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{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 NH\(_4\)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 } n\text{-pentane, gave 92\% yield of 1-(hex-5'-enyl)adamantane (4.13 g).}
\]

\( R_f = 0.86 \) (hexanes).

\(^1\)H-NMR (400.1 MHz, CDCl\(_3\), 295 K): \( \delta = 1.03 \) (t, \( J = 7.1 \text{ Hz, } 2 \text{ H, } CCH_2 \)), 1.24 (quin, \( J = 7.1 \text{ Hz, } 2 \text{ H, } CCH_2\text{-CH}_2 \)), 1.33 (quin, \( J = 7.1 \text{ Hz, } 2 \text{ H, } CCH_2\text{-CH}_2\text{-CH}_2 \)), 1.45 (m, \( J = 2.2 \text{ Hz, } 6 \text{ H, } CCH_2\text{-Ad} \)), 1.66
(m, 6 H, \(CH_{2-Ad}\)), 1.93 (m, 3 H, \(CH_{Ad}\)), 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 \({}^{1}\text{H}\)-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): \(m/z\) (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%.

**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'-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\(_2\)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\(_f\) = 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, \(CH_{Ad}\)), 2.31 (s, 3 H, \(SCOCH_{3}\)), 2.85 (t, \(J = 7.3\) Hz, 2 H, \(CH_{2}S\)).

\(^{13}\)C \({}^{1}\text{H}\)-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 (\(SCO\)).

IR (NaCl): \(\nu\) (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 \(C_{18}H_{30}O\): 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, CCH₂), 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, CH₂Ad), 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 (CH₃Ad), 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 C₁₆H₃₈S 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$_{25}$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**

![Chemical structure](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 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, 2926s, 2854m, 1693s, 1526m, 1348m, 1077m, 1031m, 991m, 791m, 723m, 691m, 647m, 557m, 487m.
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**

![Chemical structure](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 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).

1H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.25 (sₙ, 12 H, CH₂), 1.42 (sₙ, 13 H, CH₂CH₂CH₂Br + C(CH₃)₃ + CH₂CH₂NH), 1.83 (mₜ, J = 6.9 Hz, 7.2 Hz, 2 H, CH₂CH₂Br), 3.08 (t, J = 6.6 Hz, 2 H, CH₂NH), 3.38 (t, J = 6.9 Hz, 2 H, CH₂Br), 4.53 (sₙ, 1 H, NH).

13C NMR (100.6 MHz, CDCl₃, 295 K): δ = 26.8 (CH₂), 28.2 (CH₂), 28.5 (C(CH₃)₃), 28.8 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 30.1 (CH₂CH₂NH), 32.9 (CH₂CH₂Br), 34.1 (CH₂Br), 40.7 (CH₂NH), 79.0 (C(CH₃)₃), 156.0 (CO).

IR (KBr): ν (cm⁻¹) = 3377s, 2918s, 2851s, 1687s, 1560m, 1469m, 1374m, 1280m, 1237m, 1170m, 1026w, 976w, 870m, 720m, 643m.

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

Elemental analysis for C₁₆H₃₂BrNO₂ 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)undecylethanothioate**

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 CH₂Cl₂ (200 mL) and the reaction mixture was stirred for 24 hours at 23 °C. The solution was washed with a saturated Na₂CO₃ solution (200 mL) and water (200 mL). The organic phase was dried over MgSO₄, 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-ethanothioate (11.3 g).

m.p.: 64 - 66 °C. Rf = 0.25 (hexanes/AcOEt = 10:1).

1H-NMR (400.1 MHz, CDCl₃, 295 K): δ = 1.22 (sₙ, 10 H, CH₂), 1.25 (mₜ, 2 H, NCH₂CH₂CH₂), 1.30 (mₜ, 2 H, CH₂CH₂CH₂S), 1.41 (sₙ, 11 H, C(CH₃)₃ + NCH₂CH₂), 1.52 (mₜ, J = 6.8 Hz, 7.4 Hz, 2 H, CH₂CH₂S), 2.29 (s, 3 H, SCOH₃), 2.83 (t, J = 7.4 Hz, 2 H, CH₂S), 3.07 (t, J = 6.6 Hz, 2 H, NCH₂), 4.55 (sₙ, 1 H, NH).

13C NMR (100.6 MHz, CDCl₃, 295 K): δ = 26.8 (NCH₂CH₂CH₂), 28.5 (C(CH₃)₃), 28.8 (CH₂S), 29.1 (CH₂), 29.2 (CH₂), 29.3 (CH₂CH₂S), 29.4 (CH₂), 29.5 (CH₂), 29.5 (CH₂), 30.1 (NCH₂CH₂S), 30.7 (SCOH₃), 40.6 (NCH₂), 78.9 (C(CH₃)₃), 156.0 (CO), 196.0 (SCO).

IR (KBr): ν (cm⁻¹) = 3380m, 2918m, 2851m, 1687s, 1560m, 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 C₁₈H₃₅NO₂S 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 \((S)-11-(\text{tert-butoxycarbonyl})\text{undecylethanothioate (1.00 g, 2.90 mmol)}\) in freshly distilled \(\text{CH}_2\text{Cl}_2\) (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 \(\text{CH}_2\text{Cl}_2\) (50 mL). The resulting solution was washed with saturated \(\text{NH}_4\text{Cl}\) solution (50 mL) and water (50 mL). The organic phase was dried over \(\text{MgSO}_4\), filtered and concentrated under reduced pressure. Purification by flash chromatography, eluting with 10% \(\text{AcOEt}\) 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).

\(^1\text{H}-\text{NMR}\) (400.1 MHz, \(\text{CDCl}_3\), 295 K): \(\delta = 1.25\) (\(s_b\), 12 H, \(\text{CH}_2\)), 1.32 (t, \(J = 7.6\) Hz, 1 H, \(\text{SH}\)), 1.36 (\(m_c\), 2 H, \(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}\)), 1.43 (\(s_b\), 11 H, \(\text{C(CH}_3)_3 + \text{NCH}_2\text{CH}_2\)), 1.59 (quin, \(J = 7.2\) Hz, 2 H, \(\text{CH}_2\text{CH}_2\text{S}\)), 2.51 (\(m_c\), \(J = 7.2\) Hz, 7.6 Hz, 2 H, \(\text{CH}_2\text{SH}\)), 3.09 (t, \(J = 6.6\) Hz, 2 H, \(\text{NCH}_2\)), 4.50 (\(s_b\), 1 H, \(\text{NH}\)).

\(^{13}\text{C}\{^1\text{H}\}-\text{NMR}\) (100.6 MHz, \(\text{CDCl}_3\), 295 K): \(\delta = 24.7\) (\(\text{CH}_2\text{SH}\)), 26.9 (\(\text{CH}_2\)), 28.4 (\(\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}\)), 28.5 (\(\text{C(CH}_3)_3\)), 29.1 (\(\text{CH}_2\)), 29.3 (\(\text{CH}_2\)), 29.5 (\(\text{CH}_2\)), 29.6 (\(\text{CH}_2\)), 30.1 (\(\text{NCH}_2\text{CH}_2\)), 34.1 (\(\text{CH}_2\text{CH}_2\text{SH}\)), 40.7 (\(\text{NCH}_2\)), 79.0 (\(\text{C(CH}_3)_3\)), 156.0 (CO).

IR (KBr): \(\nu\) (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 \(\text{C}_{16}\text{H}_{33}\text{NO}_3\text{S}\) 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

\(\text{Tert-butyl 11-mercaptopundecylcarbamate (1.00 g, 3.30 mmol)}\) 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.

\(^1\text{H}-\text{NMR}\) (400.1 MHz, \(\text{CD}_2\text{SO}\), 295 K): \(\delta = 1.25\) (\(s_b\), 12 H, \(\text{CH}_2\)), 1.32 (\(m_c\), 2 H, \(\text{NCH}_2\text{CH}_2\text{CH}_2\)), 1.51 (quin, \(J = 6.8\) Hz, 2 H, \(\text{CH}_2\text{CH}_2\text{SH}\)), 1.53 (quin, \(J = 7.4\) Hz, 2 H, \(\text{NCH}_2\text{CH}_2\)), 2.23 (t, \(J = 7.6\) Hz, 1 H, \(\text{SH}\)), 2.46 (\(m_c\), \(J = 6.8\) Hz, 7.6 Hz, 2 H, \(\text{CH}_2\text{SH}\)), 2.75 (\(s_b\), \(J = 7.4\) Hz, 2 H, \(\text{NCH}_2\)), 7.78 (3 H, \(\text{NH}_3\text{Cl}\)).
$^{13}\text{C}\{^{1}\text{H}\}$-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: