Supplementary Material

Multivalent interaction and selectivities in selectin binding of functionalized gold colloids decorated with carbohydrate mimetics

Meike Roskamp[a], Sven Enders[b], Fabian Pfrengle[a], Shahla Yekta[a], Vjekoslav Dekaris[a], Jens Dernedde[b], Hans-Ulrich Reissig[a], Sabine Schlecht[a,#,*]

[a] Freie Universität Berlin, Institut für Chemie und Biochemie, Takustr. 3, 14195 Berlin, Germany

[b] Charité Universitätsmedizin Berlin, Zentralinstitut für Laboratoriumsmedizin und Pathobiochemie, Hindenburgdamm 30, 12203 Berlin, Germany

*# New address: Prof. Dr. Sabine Schlecht, Justus-Liebig-Universität Gießen, Institut für Anorganische und Analytische Chemie, Heinrich-Buff-Ring 58, 35392 Gießen, Tel.: +49 (0)641 99-34100; Fax: +49 (0)641 99-34109; E-mail: Sabine.Schlecht@anorg.chemie.uni-giessen.de

Synthetic procedures for sulfated functionalized colloids

Synthesis of gold nanoparticles bearing aminopyran 1 (NP-1). A solution of 4.2 mg **1** (0.02 mmol) in anhydrous DMF was added to 5 ml of a 0.2 µM solution of MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 20 µl of triethylamine (0.14 mmol) was added and the mixture stirred for another 24 h. The clear colloid solution was dialysed against 300 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-1 (NP-1-sulf). At 0 °C 15.3 mg SO_3·DMF complex (0.10 mmol), solved in 1 ml of anhydrous DMF, was slowly dropped to 10 ml of a 0.1 µM solution of AP-functionalized gold nanoparticles in anhydrous DMF. After 24 h of stirring at r.t. the clear solution was dialysed against 300 ml of DMF for one time and 300 ml of triple-distilled water for three times. For storage the colloid solution was diluted to a 0.03 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.30 (*bs*), 1.32 (*s*), 1.47 (*s*), 1.59 (*m*), 1.68 (*m*), 2.30 (*bt*), 2.39 (*q*), 2.76 (*bs*), 4.01 (*m*), 4.18 (*m*), 4.46 (*m*), 4.54 (*m*).
ATR-IR: ν = 3448 cm^{-1} (w, ν(N-H)), 3075 (w), 2923 and 2852 (s, ν(C-H)), 2484 (w), 1687 and 1647 (s, ν(C=O)), 1529 (s, δ(N-H)), 1467 and 1207 (s, R-O-SO_2-OR'), 1058 (s), 985 (s), 810 (s), 582 (s).

Synthesis of gold nanoparticles bearing aminopyran 2 (NP-2). A solution of 10.5 mg **2** (0.05 mmol) in 1.25 ml of anhydrous DMF was added to 6.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-2 (NP-2-sulf). At 0 °C 76.6 mg SO_3·DMF complex (0.50 mmol), dissolved in 0.2 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-2** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was dialysed against 500 ml of triple-distilled water for three times. For storage the colloid solution was set to a 0.2 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.27 (*bs*), 1.31 (*s*), 1.38 (*s*), 1.56 (*m*), 1.65 (*m*), 2.04 (*m*), 2.22 (*m*), 4.02 (*m*).
ATR-IR: ν = 3286 cm^{-1} (w, ν(N-H)), 2919 and 2855 (s, ν(C-H)), 1670 (s, ν(C=O)), 1635 (s, δ(N-H)), 1467 (s, R-O-SO_2-OR'), 1402 (w), 1224(w), 1165 (w), 1040 (s), 971 (s), 867 (s), 802 (s), 575 (s).

Synthesis of gold nanoparticles bearing aminopyran 3 (NP-3). A solution of 10.4 mg **3** (0.05 mmol) in 0.6 ml of anhydrous DMF was added to 6.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-3 (NP-3-sulf). At 0 °C 76.6 mg SO_3·DMF complex (0.50 mmol), dissolved in 0.2 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-3** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.2 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.2-1.4 (*m*), 1.57 (*m*), 1.66 (*m*), 2.28 (*bt*), 2.37 (*q*), 3.43 (*s*), 4.16 (*m*), 4.23 (*m*), 4.50 (*m*).
ATR-IR: ν = 2919 and 2850 (s, ν(C-H)), 2484 (w), 1701 and 1634 (s, ν(C=O)), 1518 (s, δ(N-H)), 1465 and 1151 (s, R-O-SO_2-OR'), 1041 (s), 860 (s), 575 (s).

Synthesis of gold nanoparticles bearing aminopyran 4 (NP-4). A solution of 10.4 mg **4** (0.05 mmol) in 0.6 ml of anhydrous DMF was added to 6.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-4 (NP-4-sulf). An amount of 76.6 mg SO_3·DMF complex (0.50 mmol), dissolved in 0.2 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-4** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.2 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.2-1.4 (*bs*), 1.57 (*bs*), 1.62 (*bs*), 2.29 (*bs*), 2.39 (*m*), 3.43 (*m*), 4.10 (*m*), 4.23 (*m*), 4.50 (*m*).
ATR-IR: ν **=** 2920 and 2845 (s, ν(C-H)), 1692 and 1650 (s, ν(C=O)), 1580 (s, δ(N-H)), 1469 and 1220 (s, R-O-SO_2-OR'), 1045 (s), 865 (s), 580 (s).

Synthesis gold nanoparticles bearing aminopyran 5 (NP-5). A solution of 9.6 mg **5** (0.05 mmol) in 1.3 ml of anhydrous DMF was added to 8.8 ml of a solution of 2.5 nmol MUDHSE

protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-5 (NP-5-sulf). An amount of 45.9 mg SO_3·DMF complex (0.30 mmol), dissolved in 10 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-5** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.14 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.32 (*m*), 1.41 (*m*), 1.55 (*m*), 1.69 (*m*), 2.18 (*t*), 2.37 (*m*), 2.78 (*t*), 3.98 (*m*), 4.14 (*m*), 4.24 (*m*), 4.51 (*m*).
ATR-IR: ν = 2914 and 2849 (s, ν(C-H)), 1601 and 1634 (w), 1561 (s, δ(N-H)), 1422 (s, R-O-SO_2-OR'), 1224 (w), 1145 (w), 956 (s), 877 (s).

Synthesis of gold nanoparticles bearing aminopyran 6 (NP-6). A solution of 8.8 mg **6** (0.05 mmol) in 1.3 ml of anhydrous DMF was added to 8.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-6 (NP-6-sulf). An amount of 30.6 mg SO_3·DMF complex (0.20 mmol), dissolved in 10 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-6** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.15 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.33 (*m*), 1.35 (*s*), 1.5-1.7 (*m*), 2.03 (*m*), 2.16 (*m*), 2.36 (*m*), 2.78 (*m*), 4.00 (*m*), 4.23 (*m*), 4.53 (*m*).
ATR-IR: ν = 3286 (w, ν(N-H)), 2914 and 2850 (s, ν(C-H)), 1640 (w), 1561 (s, δ(N-H)), 1412 (s, R-O-SO_2-OR'), 1256 (w), 1145 (w), 976 (s), 872 (s).

Synthesis of gold nanoparticles bearing aminofuran 7 (NP-7). A solution of 8.9 mg **7** (0.05 mmol) in 0.6 ml of anhydrous DMF was added to 6.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-7 (NP-7-sulf). An amount of 76.6 mg SO_3·DMF complex (0.5 mmol), dissolved in 0.2 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-7** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.2 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.30 (*m*), 1.41 (*s*), 1.55 (*m*), 1.63 (*m*), 1.70 (*m*), 2.18 (*t*), 2.31 (*m*), 2.78 (*t*), 3.48 (s), 4.10 (*m*), 4.1-4.3 (*m*), 4.42 (*m*), 4.80 (*m*).

ATR-IR: ν = 2923 and 2852 (s, ν(C-H)), 1701 and 1644 (s, ν(C=O)), 1546 (s, δ(N-H)), 1466 and 1200 (s, R-O-SO_2-OR'), 1136 (s), 1056 (s), 993 (s), 578 (s).

Synthesis of gold nanoparticles bearing aminofuran (NP-8). A solution of 11.0 mg **8** (0.05 mmol) in 1.3 ml of anhydrous DMF was added to 8.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.
Sulfation of NP-8 (NP-8-sulf). An amount of 30.6 mg SO_3·DMF complex (0.20 mmol), dissolved in 10 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-8** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.16 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.30-1.40 (*m*), 1.35 (*s*), 1.44 (*s*), 1.50-1.65 (*m*), 1.70 (*m*), 2.18 (*t*), 2.30 (*s*), 2.78 (*m*), 3.44 (*s*), 3.50 (*m*), 3.97 (*m*), 4.13 (*m*), 4.31 (*m*).
ATR-IR: ν = 3281 (w, ν(N-H)), 2914 and 2849 (s, ν(C-H)), 1626 (w), 1566 (s, δ(N-H)), 1417 (s, R-O-SO_2-OR'), 1259 (w), 1135 (w), 922 (s), 872 (s), 624 (w).

Synthesis of gold nanoparticles bearing ethanolamine 9 (NP-9). A solution of 9 µl ethanolamine **9** (0.15 mmol) in anhydrous DMF was added to 5 ml of a 0.2 µM solution of MUDHSE-protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 20 µl triethylamine (0.14 mmol) was added and the mixture stirred for another 24 h. The clear colloid solution was dialysed against 300 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-9 (NP-9-sulf). At 0 °C 300 mg SO_3·DMF-complex (1.96 mmol), dissolved in 1 ml of anhydrous DMF, was slowly dropped to 10 ml of a 0.1 µM solution of **NP-9** anhydrous DMF. After 24 h of stirring at r.t. the clear solution was dialysed against 300 ml of DMF for two times and 300 ml of triple-distilled water for three times. For storage the colloid solution was diluted to a 0.03 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.25 (*bs*), 1.56 (*bs*), 2.22 (*bs*), 2.69 (*bs*), 3.45 (*bs*), 4.06 (*bs*).
ATR-IR: ν = 3302 cm^{-1} (s, ν(N-H)), 2918 and 2850 (s, ν(C-H)), 1686 and 1639 (s, ν(C=O)), 1532 (s, δ(N-H)), 1465 - 1452 and 1211 (s, R-O-SO_2-OR'), 1066 (s), 1020 (s), 959 (w), 719 (s), 579 (s).

Synthesis of gold nanoparticles bearing serinol (NP-10). A solution of 9 mg serinol **10** (0.10 mmol) in anhydrous DMF was added to 5 ml of a 0.2 µM solution of MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 20 µl triethylamine (0.14 mmol) was added and the mixture stirred for another 24 h. The clear colloid solution was dialysed against 300 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-10 (NP-10-sulf). At 0 °C 154 mg SO_3·DMF complex (1.01 mmol), dissolved in 1 ml of anhydrous DMF, was slowly dropped to 10 ml of a 0.1 µM solution of **NP-10** in anhydrous DMF. After 24 h of stirring at r.t. the clear solution was dialysed against 300 ml of DMF for two times and 300 ml of triple-distilled water for three times. For storage the colloid solution was diluted to a 0.03 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.32 (*bs*), 1.62 (*bs*), 2.30 (*bs*), 2.89 (*bs*), 4.15 (*bs*), 4.43 (*bs*).
ATR-IR: ν = 3482 und 3294 cm^{-1} (s, ν(O-H)), 3039 (w), 2924 and 2853 (s, ν(C-H)), 1683 and 1653 (s, ν(C=O)), 1539 (s, δ(N-H)), 1490 (s), 1465 - 1453 and 1218 (s, RO-SO_2-OR'), 1004 (s), 950 (s), 788 (s), 577 (s).

Synthesis of gold nanoparticles bearing tromethamine 11 (NP-11). A solution of 18.2 mg tromethamine **11** (0.15 mmol) in anhydrous DMF was added to 5 ml of a 0.2 µM solution of MUDHSE-protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 80 µl triethylamine (0.56 mmol) was added and the mixture stirred for another 24 h. The clear colloid solution was dialysed against 300 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-11 (NP-11-sulf). At 0 °C 300 mg SO_3·DMF-complex (1.96 mmol), dissolved in 1 ml of anhydrous DMF, was slowly dropped to 10 ml of a 0.1 µM solution of **NP-11** in anhydrous DMF. After 24 h of stirring at r.t. the clear solution was dialysed against 300 ml of DMF for two times and 300 ml of triple-distilled water for three times. For storage the colloid solution was diluted to a 0.03 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.29 (*bs*), 1.59 (*bs*), 2.24 (*bs*), 2.90 (*bs*), 4.3 (*bs*).
ATR-IR: ν = 3291 cm^{-1} (w, ν(N-H)), 2920 and 2851 (s, ν(C-H)), 1682 and 1633 (s, ν(C=O)), 1528 (s, δ(N-H)), 1466 - 1453 and 1210 (s, R-O-SO_2-OR'), 1002 (s), 801 - 774 (s), 578 (s).

Synthesis of gold nanoparticles bearing aminodiol 12 (NP-12). A solution of 8.4 mg **12** (0.05 mmol) in 1.8 ml of anhydrous DMF was added to 8.8 ml of a solution of 2.5 nmol MUDHSE protected gold nanoparticles in DMF. After 30 minutes of stirring at r.t. 50 µl of triethylamine (0.35 mmol) was added and the mixture stirred for another 15 h. The clear colloid solution was dialysed against 400 ml of DMF for three times, dried under vacuum and resolved in 5 ml of anhydrous DMF.

Sulfation of NP-12 (NP-12-sulf). An amount of 30.6 mg SO_3·DMF complex (0.20 mmol), dissolved in 10 ml of anhydrous DMF, was slowly dropped to 5 ml of a solution of 2.5 nmol of **NP-12** in anhydrous DMF. After 1 h of stirring at r.t. the clear solution was reduced in its volume and dialysed against 500 ml of triple-distilled water for six times. For storage the colloid solution was set to a 0.27 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.20-1.50 (*m*), 1.62 (*m*), 1.74 (*m*), 2.25 (*m*), 2.81 (*m*), 4.02 (*m*), 4.25 (*m*), 4.57 (*m*), 5.47 (*bs*), 7.4-7.5 (*m*).
ATR-IR: ν = 3281 (w, ν(N-H)), 2914 and 2849 (s, ν(C-H)), 1626 (w), 1566 (s, δ(N-H)), 1417 (s, R-O-SO_2-OR'), 1259 (w), 1135 (w), 922 (s), 872 (s), 624 (w).

Synthesis of Au/MUDSulfate (NP-16-sulf). An amount of 29.8 mg 11-mercatoundecanyl sulfate (0.10 mmol) was dissolved in a solution of 5 ml triple-distilled water and 50 µl tetramethylammonium hydroxide (TMAH). 1 mL of a 3 µM solution of dodecanethiol-protected gold nanoparticles in chloroform was added and the mixture stirred at room temperature for 2 hours, which led to a complete phase transfer of the colloids from the organic into the water phase. The organic phase was removed and, in order to remove the excess of ligands and to reduce the pH to approximately 8, the water phase was dialysed against 300 ml triple-distilled water three times. For storage the solution was diluted to a 0.03 µM concentration of nanoparticles.

^{1}H NMR (D_2O, 400 MHz): δ = 1.34 (*bs*), 1.71 (*bs*), 2.73 (*bs*), 4.06 (*bs*).
ATR-IR: ν = 3602 cm^{-1} (w), 3040 (w), 2916 and 2849 (s, ν(C-H)), 1490 - 1468 and 1220 (s, R-O-SO_2-OR'), 1066 - 950 (s), 783 (s), 623 (s), 577 (s).

Synthesis of 6-acetylsulfanylhexanoic acid.[S1] An amount of 1.50 g (7.67 mmol) of 6-bromohexanoic acid was dissolved in 15 ml of anhydrous DMF. A solution of 1.32 g (11.48 mmol) of potassium thioacetate in 15 ml of DMF was added dropwise and the mixture was stirred for 1 h. The solvent was removed under vacuum and water was added to the residue. Then the product was extracted with CH_2Cl_2 repeatedly. The organic phases were collected and the solvent was removed under vacuum. The product was dried and 1.06 g (72% yield) of the product were obtained.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.35-1.45 (*m,* 2H), 1.57 (*quin,* 2H), 1.63 (*quin,* 2H), 2.30 (*s,* 3H) 2.33 (*t,* 2H), 2.85 (*t,* 2H).

Synthesis of N-hydroxysuccinimide-6-acetylsulfanylhexanoate.[S2] An amount of 1.06 g (5.58 mmol) of 6-acetylsulfanylhexanoic acid was added to a solution of 708 mg (6.16 mmol) of N-hydroxysuccinimide in 100 ml of CH_2Cl_2. A solution of 1.27 g (6.16 mmol) of dicyclohexylcarbodiimide (DCC) in 5 ml of CH_2Cl_2 was added dropwise and after a few minutes a white solid precipitated. The reaction mixture was stirred for 1 h. The solvent was removed under vacuum and the raw product was dissolved in little CH_2Cl_2 and filtered. The solvent was evaporated and 1.55 g of a brownish oil were obtained (98% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.46 (*m,* 2H), 1.61 (*quin,* 2H), 1.74 (*quin,* 2H), 2.30 (*s,* 3H), 2.59 *(t*, 2H), 2.82 (*s*, 4H), 2.86 (*t*, 2H).

Synthesis of [5-(2-hydroxy-1-hydroxymethyl-ethylcarbamoyl)-pentyl]-S-thioacetate.[S1] An amount of 765 mg (8.41 mmol) of serinol **10** was added to 20 ml of a solution of 1.62 g (5.64 mmol) of N-hydroxysuccinimide-6-acetylsulfanylhexanoate in DMF. After a few minutes the solution became cloudy and the mixture was stirred for 30 min. The solvent was removed under vacuum and the residue was suspended in 50 ml of water. The suspension was stored over night at 4-8 °C. The white precipitate was filtered off, washed with water, dried under high vacuum and purified by chromatography (CH_2Cl_2). A white solid was obtained (448 mg, 30% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.34 (*quin,* 2H), 1.55 (*quin,* 2H), 1.62 (*quin,* 2H), 2.19 (*t,* 2H), 2.29 (*s*, 3H), 2.82 (*t*, 2H), 3.72 (*ddd*, 4H), 3.92 (*quin*, 1H).

Synthesis of 17-sulf. [5-(2-Hydroxy-1-hydroxymethyl-ethylcarbamoyl)-pentyl]-S-thioacetate (52 mg, 0.20 mmol) was dissolved in 2 ml of DMF and 123 mg (0.80 mmol) of SO_3·DMF in 1 ml of DMF were added dropwise. The solution was stirred for 1 h. 3.2 ml of 1M NaOH were added and the reaction mixture was stirred for 5 h. The completeness of the reaction was monitored by TLC. The product was not isolated but directly reacted with the Au/citrate nanoparticles.

Synthesis of NP-17-sulf. A solution of 0.20 mmol **17-sulf** in 6 ml of DMF/NaOH was added to 50 ml of a 2.6 nM aqueous solution of Au/citrate and the mixture was stirred for 72 h. Then the particles were dialysed against 600 ml of water for three times. After concentration of the solution to 10 ml a 12.7 nM solution of **NP-17-sulf** was obtained.

^{1}H NMR (D_2O, 400 MHz): δ = 1.37 (*m*), 1.59 (*m*), 1.66 (*m*), 2.26 (*t*), 2.71 (*m*), 4.09 (*m*), 4.38 (*m*).

Synthesis of 8-acetylsulfanyloctanoic acid.[S3] An amount of 1.12 g (5.02 mmol) of 8-bromooctanoic acid was dissolved in 15 ml of anhydrous DMF. A solution of 0.86 g (7.48 mmol) of potassium thioacetate in 15 ml of DMF was added dropwise and the mixture was stirred for 1 h. The solvent was removed under vacuum and some water was added to the residue. The white solid was filtered and washed with water. Then the solid was dried and 0.66 g of the product were obtained (60% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.31 (*m,* 6H), 1.54 (*quin,* 2H), 1.60 (*quin,* 2H), 2.30 (*s,* 3H), 2.32 (*t,* 2H), 2.83 (*t,* 2H).

Synthesis of N-hydroxysuccinimide-8-acetylsulfanyloctanoate.[S4] An amount of 0.48 g (2.20 mmol) of 8-acetylsulfanyloctanoic acid was added to a solution of 279 mg (2.43 mmol) N-hydroxysuccinimide in 150 ml of CH_2Cl_2. A solution of 0.500 g (2.43 mmol) of dicyclohexylcarbodiimide (DCC) in 5 ml of CH_2Cl_2 was added dropwise and after a few minutes a white solid precipitated. The reaction mixture was stirred for 3 d. The solvent was removed under vacuum and the crude product was dissolved in little CH_2Cl_2 and filtered. The solvent was evaporated and 0.64 g of a light yellow oil were obtained (92% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30-1.45 (*m,* 6H), 1.53 (*quin,* 2H), 1.72 (*quin,* 2H), 2.30 (*s,* 3H), 2.58 (*t*, 2H), 2.80 (*s*, 4H), 2.84 (*t*, 2H).

Synthesis of [7-(2-hydroxy-1-hydroxymethyl-ethylcarbamoyl)heptyl]-S-thioacetate.[S1] An amount of 273 mg (3.00 mmol) of serinol **10** was added to 10 ml of a solution of 0.46 g (1.46 mmol) of N-hydroxysuccinimide-8-acetylsulfanyloctanoate in DMF. After a few minutes the solution became cloudy and the mixture was stirred for 30 min. The solvent was removed under vacuum and the residue was suspended in 50 ml of water. The white precipitate was filtered, washed with water and dried under high vacuum. A white solid was obtained (200 mg, 47% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.30 (*m,* 6H), 1.52 (*quin,* 2H), 1.62 (*quin,* 2H), 2.22 (*t,* 2H), 2.30 (*s*, 3H), 2.82 (*t*, 2H), 3.80 (*ddd*, 4H), 3.94 (*m*, 1H).

Synthesis of 18-sulf. [7-(2-Hydroxy-1-hydroxymethyl-ethylcarbamoyl)heptyl]-S-thioacetate (203 mg, 0.71 mmol) was dissolved in 5 ml of DMF and 429 mg (2.80 mmol) of SO_3·DMF in 5 ml of DMF were added dropwise. The solution was stirred for 1 h. 100 ml of 0.2 M NaOH were added and the reaction mixture was stirred for 3 h. The completeness of the reaction was monitored by TLC. The product was not isolated but directly reacted with the Au/citrate nanoparticles.

Synthesis of NP-18-sulf. A solution of 0.20 mmol **18-sulf** in 10 ml of water/NaOH was added to 50 ml of a 2.6 nM aqueous solution of Au/citrate and the mixture was stirred for 72 h. Then the particles were dialysed against 600 ml of water for three times. After concentration of the solution to 10 ml a 12.7 nM solution of **NP-18-sulf** was obtained.

^{1}H NMR (D_2O, 400 MHz): δ = 1.36 (*m*), 1.56 (*m*), 1.64 (*m*), 2.24 (*m*), 2.72 (*m*), 4.09 (*m*), 4.37 (*m*).

Synthesis of 11-acetylsulfanylundecanoic acid.[S5] An amount of 1.00 g (3.77 mmol) of 11-bromoundecanoic acid was dissolved in 150 ml of anhydrous DMF. A solution of 1.04 g (9.00

mmol) of potassium thioacetate in 15 ml of DMF was added dropwise and the mixture was stirred for 2 h. The solvent was removed under vacuum and some water was added to the residue. The white solid was filtered and washed with water. Then the solid was dried and 0.96 g of the product were obtained (86% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.54 (*quin,* 2H), 1.59 (*quin,* 2H), 2.31 (*s,* 3H), 2.33 (*t,* 2H), 2.83 (*t,* 2H).

Synthesis of N-hydroxysuccinimide-11-acetylsulfanylundecanoate.[S6] An amount of 0.75 g (2.88 mmol) of 11-acetylsulfanylundecanoic acid was added to a solution of 367 mg (3.19 mmol) of N-hydroxysuccinimide in 200 ml of CH_2Cl_2. A solution of 0.65 g (3.16 mmol) of dicyclohexylcarbodiimide (DCC) in 15 ml of CH_2Cl_2 was added dropwise and after 1 h a white solid started to precipitate. The reaction mixture was stirred for 18 h. The solvent was removed under vacuum and the crude product was dissolved in little CH_2Cl_2 and filtered. The solvent was evaporated and the product was washed with pentane. 1.02 g of a white solid were obtained (99% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.54 (*quin,* 2H), 1.72 (*quin,* 2H), 2.30 (*s,* 3H), 2.58 (*t*, 2H), 2.83 (*s*, 4H), 2.84 (*t*, 2H).

Synthesis of [10-(2-hydroxy-1-hydroxymethyl-ethylcarbamoyl)decyl]-S-thioacetate.[S1] An amount of 388 mg (4.26 mmol) of serinol **10** was added to 20 ml of a solution of 1.02 g (2.86 mmol) of N-hydroxysuccinimide-11-acetylsulfanylundecanoate in DMF. After 1 h the solution became cloudy and the mixture was stirred for 16 h. After addition of 100 ml of water a voluminous white precipitate was obtained. The white precipitate was filtered, washed with water and dried under high vacuum. A white solid was obtained (803 mg, 85% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.53 (*quin,* 2H), 1.61 (*quin,* 2H), 2.21 (*t,* 2H), 2.30 (*s*, 3H), 2.84 (*t*, 2H), 3.80 (*ddd*, 4H), 3.96 (*m*, 1H).

Synthesis of 14-sulf. [10-(2-Hydroxy-1-hydroxymethyl-ethylcarbamoyl)decyl]-S-thioacetate (334 mg, 1.00 mmol) was dissolved in 10 ml of DMF and 613 mg (4.01 mmol) of SO_3·DMF in 20 ml of DMF were added dropwise. The solution was stirred for 1 h. 100 ml of 0.2 M NaOH were added and the reaction mixture was stirred for 5 h. The solvent was removed under vacuum and the residue was diluted with some ethanol. The resulting precipitate was filtered and dried. 249 mg of a white solid were obtained (48% yield).

^{1}H NMR (D_2O, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.59 (*m,* 4H), 2.28 (*t,* 2H), 2.53 (*t,* 2H), 4.12 (*d,* 4H), 4.40 (*m,* 1H).

Synthesis of NP-14-sulf. A solution of 0.20 mmol **14-sulf** in 2 ml of water/NaOH was added to 50 ml of a 2.6 nM aqueous solution of Au/citrate and the mixture was stirred for 72 h. Then the particles were dialysed against 600 ml of water for three times. After concentration of the solution to 10 ml a 12.7 nM solution of **NP-14-sulf** was obtained.

^{1}H NMR (D_2O, 400 MHz): δ = 1.28 (*m*), 1.37 (*bs*), 1.58 (*m*), 1.66 (*m*), 2.26 (*t*), 2.67 (*t*), 4.11 (*d*), 4.44 (*m*).

Synthesis of [10-(2-hydroxy-ethylcarbamoyl)decyl]-S-thio-acetate.[S1] An amount of 292 µl (4.81 mmol) of ethanolamine was added to 25 ml of a solution of 1.00 g (2.80 mmol) of N-hydroxysuccinimide-11-acetylsulfanylundecanoate in DMF. After 5 min. the solution became

cloudy and the mixture was stirred for 30 min. After addition of 100 ml of water a voluminous white precipitate was obtained. The white precipitate was filtered off, washed with water and dried under high vacuum. A white solid was obtained (702 mg, 82% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.53 (*quin,* 2H), 1.60 (*quin,* 2H), 2.18 (*t,* 2H), 2.30 *(s*, 3H), 2.75 (*bs*, 1H), 2.81 (*t*, 2H), 3.40 (*qua*, 2H), 3.70 (*t*, 2H).

Synthesis of 13-sulf. 304 mg (1.00 mmol) of [10-(2-hydroxy-ethylcarbamoyl)decyl]-S-thioacetate were dissolved in 10 ml of DMF and 306 mg (2.00 mmol) of SO_3·DMF in 5 ml of DMF were added dropwise. The solution was stirred for 1 h. 100 ml of 0.2 M NaOH were added and the reaction mixture was stirred for 5 h. The solvent was removed under vacuum and the residue was diluted with some ethanol. The resulting precipitate was filtered off and dried. 200 mg of a white solid were obtained (55% yield).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.44 (*m*, 2H), 1.56 (*quin,* 2H), 2.02 (*t*, 2H), 2.66 (*t,* 2H), 3.17 (*qua*, 2H), 3.65 (*t*, 2H).

Synthesis of NP-13-sulf. A solution of 0.20 mmol **13-sulf** in 2 ml of water/NaOH was added to 50 ml of a 2.6 nM aqueous solution of Au/citrate and the mixture was stirred for 72 h. Then the particles were dialysed against 600 ml of water for three times. After reduction of the volume of the solution to 10 ml a 12.7 nM solution of **NP-13-sulf** was obtained.

^{1}H NMR (D_2O, 400 MHz): δ = 1.20-1.40 (*bs*), 1.53 (*bs*), 1.63 (*bs*), 2.20 (*bs*), 2.70 (*bs*), 3.43 (*bs*), 4.04 (*bs*).

Synthesis of [10-(2-hydroxy-1,1-bis-hydroxymethyl-ethylcarbamoyl)decyl]-S-thio-acetate.[S1] An amount of 509 mg (4.21 mmol) of tromethamine **11** dissolved in 20 ml of DMF/H_2O 20:1 was added to 20 ml of a solution of 1.00 g (2.80 mmol) of N-hydroxysuccinimide-11-acetylsulfanylundecanoate in DMF. The mixture was stirred for 18 h. After addition of 100 ml of water a voluminous white precipitate was obtained. The white precipitate was filtered off, washed with water and dried under high vacuum. A white solid was obtained (740 mg, 73% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.20-1.40 (*m,* 12H), 1.53 (*quin,* 2H), 1.60 (*quin,* 2H), 2.23 (*t,* 2H), 2.30 *(s*, 3H), 2.83 (*t*, 2H), 3.64 (*s*, 6H).

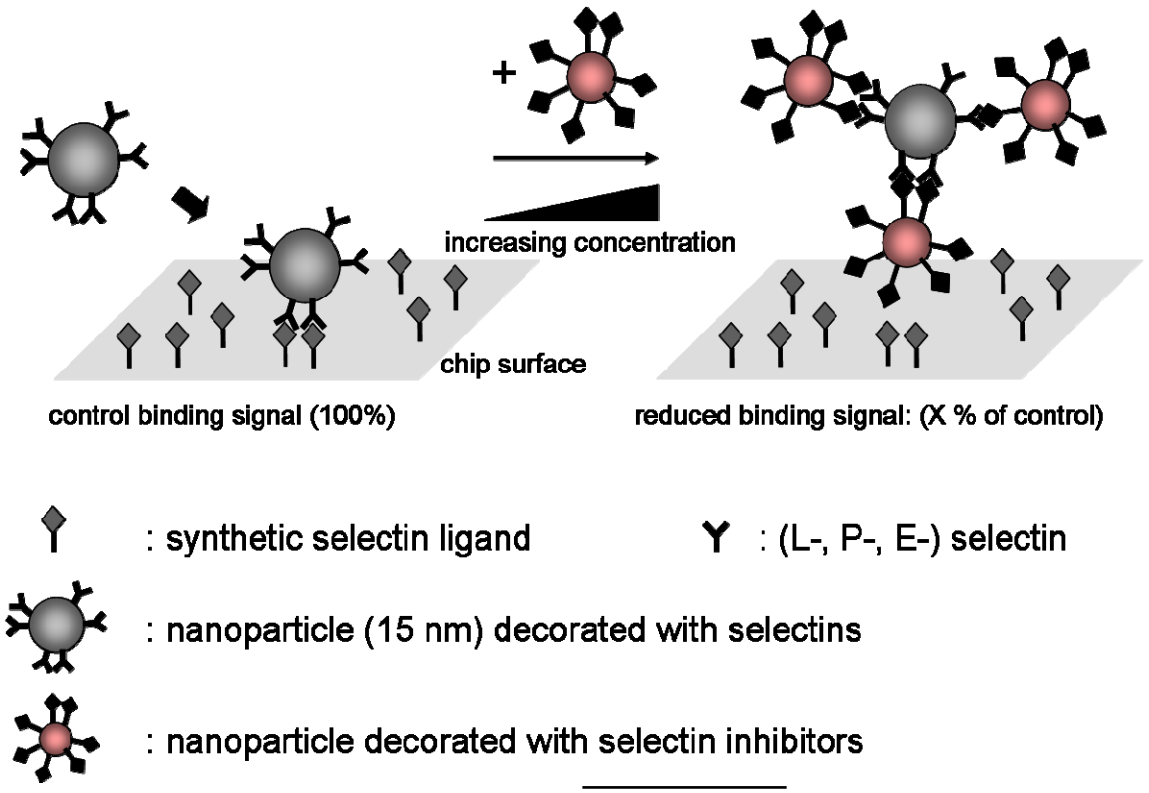
Synthesis of 15-sulf. 363 mg (1.00 mmol) of [10-(2-hydroxy-1,1-bis-hydroxymethyl-ethylcarbamoyl)decyl]-S-thioacetate were dissolved in 10 ml of DMF and 919 mg (6.01 mmol) of SO_3·DMF in 25 ml of DMF were added dropwise. The solution was stirred for 1 h. 100 ml of 0.2 M NaOH were added and the reaction mixture was stirred for 5 h. The solvent was removed under vacuum and the residue was diluted with some ethanol. The resulting precipitate was filtered off and dried. 344 mg of a white solid were obtained (53% yield).

^{1}H NMR (DMSO-d_6, 400 MHz): δ = 1.20-1.40 (*m,* 10H), 1.44 (*m*, 2H), 1.56 (*quin,* 2H), 2.02 (*t*, 2H), 2.66 (*t,* 2H), 3.17 (*qua*, 2H), 3.65 (*t*, 2H).

Synthesis of NP-15-sulf. A solution of 0.20 mmol **15-sulf** in 2 ml of water/NaOH was added to 50 ml of a 2.6 nM aqueous solution of Au/citrate and the mixture was stirred for 72 h. Then the particles were dialysed against 600 ml of water for three times. After reduction of the volume of the solution to 10 ml a 12.7 nM solution of **NP-15-sulf** was obtained.

^{1}H NMR (D_2O, 400 MHz): δ = 1.28 (*bs*), 1.37 (*bs*), 1.57 (*bs*), 1.68 (*bs*), 2.46 (*t*), 2.74 (*t*), 4.32 (*bs*).

Schematic representation of the SPR flow assay



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