"Tunable Complex Stability in Surface Molecular Recognition Mediated by Self-Complementary Quadruple Hydrogen Bonds"

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Supporting Information

Experimental Section

General Methods. The ^{1}H-NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz). ^{1}H-NMR chemical shifts are given relative to residual $CHCl_3$ (7.25 ppm). Fast-Atom-Bombardment Mass-Spectrometry (FAB-MS) was carried out on a Finnigan MAT 90 Spectrometer using NBA/NPOE as a matrix.

Synthesis. (6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone and bis-11,11' undecanol disulfide were synthesized according to published procedures. [1;2]

1. Synthesis of 2-(6-(2-ethyl-2'-hydroxyethyl dithio)hexylaminocarbonylamino) -6-methyl-4[1H]pyrimidinone **1.** (6-isocyanatohexylaminocarbonylamino)-6-methyl- 4[1H]pyrimidinone (293 mg, 1 mmol) was dissolved in 10 mL dry chloroform and added to bis-hydroxyethyl disulfide (0.7 ml, 3 mmol) in 3 mL dry chloroform. After addition of one drop of dibutyltindilaurate, the resulting solution was refluxed and stirred for 16 hours. The crude product was purified by column chromatography on silica using dichloromethane / methanol (95 / 5) as an eluent: isolated yield 10%; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 13.1 (s, 1H, CH_3-C-N$\underline{H}$), 11.9 (s, 1H, CH_2-NH-(C=O)-N$\underline{H}$), 10.1 (s, 1H, CH_2-N$\underline{H}$-(C=O)-NH), 5.8 (s, 1H, C$\underline{H}$=C-CH_3), 5.1 (s, 1H, N$\underline{H}$-(C=O)-O), 4.3 (t, 2H, C$\underline{H}_2$-O-(C=O)), 3.9 (t, 2H, CH_2-C$\underline{H}_2$-OH), 3.3 (m, 2H, C$\underline{H}_2$-NH-(C=O)-NH), 3.2 (m, 2H, C$\underline{H}_2$-NH(C=O)-O), 2.9 (m, 4H, (C$\underline{H}_2$-S)$_2$), 2.2 (s, 3H, C$\underline{H}_3$-C=CH), 1.6-1.4 (m, 8H, CH_2-C$\underline{H}_2$-CH_2); mass(FAB-MS), *m/z* = 448.6(M+H). Calculated for $C_{17}H_{29}N_5O_5S_2$: 447.6 g/mol.

2. Synthesis of 2-(6-(11-undecanyl-11'-hydroxy undecanyl dithio)hexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone **2.** (6-isocyanatohexylaminocarbonylamino)-6-methyl- 4[1H]pyrimidinone

(137 mg, 0.46 mmol) was dissolved in 5 mL dry chloroform and added to bis-11,11' undecanol disulfide (495 mg, 1.3 mmol) in 5 mL dry chloroform. After addition of one drop of dibutyltindilaurate, the resulting solution was refluxed and stirred for 20 hours. The crude product was purified by column chromatography on silica using dichloromethane / methanol (92 / 8) as an eluent: isolated yield 5%; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 13.1 (s, 1H, CH_3-C-N$\underline{H}$), 11.9 (s, 1H, CH_2-NH-(C=O)-N$\underline{H}$), 10.1 (s, 1H, CH_2-N$\underline{H}$-(C=O)-NH), 5.8 (s, 1H, C$\underline{H}$=C-CH_3), 4.9 (1 (s, 1H, N$\underline{H}$-(C=O)-O), 4.1 (t, 2H, $C\underline{H}_2$-O-(C=O)), 3.6 (t, 2H, CH_2-$C\underline{H}_2$-OH), 3.3 (m, 2H, $C\underline{H}_2$-NH-(C=O)-NH), 3.2 (m, 2H, $C\underline{H}_2$-NH(C=O)-O), 2.7 (m, 4H, $(C\underline{H}_2\text{-}S)_2$), 2.2 (s, 3H, $C\underline{H}_3$-C=CH), 1.6-1.4 (m, 44H, CH_2-$C\underline{H}_2$-CH_2); mass(FAB-MS), *m/z* = 700.4(M+H) and 698.3(M-H). Calculated for $C_{35}H_{65}N_5O_5S_2$: 699.4 g/mol.

3. Synthesis of 2-(6-trifluroethylhexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone **3.** (6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (845 mg, 2.88 mmol) was dissolved in 15 mL dry chloroform. Trifluoroethanol (0.5 mL, 6.86 mmol) was added and after addition of one drop of dibutyltindilaurate the resulting solution was refluxed and stirred for 15 hours. The crude product was purified by column chromatography on silica using dichloromethane as an eluent: isolated yield 65%; ^{1}H-NMR (250 MHz, $CDCl_3$): δ 13.1 (s, 1H, CH_3-C-N$\underline{H}$), 11.9 (s, 1H, CH_2-NH-(C=O)-N$\underline{H}$), 10.1 (s, 1H, CH_2-N$\underline{H}$-(C=O)-NH), 5.8 (s, 1H, C$\underline{H}$=C-CH_3), 5.5 (s, 1H, N$\underline{H}$-(C=O)-O), 4.5 (t, 2H, CF_3-$C\underline{H}_2$-O-(C=O)), 3.3 (m, 2H, $C\underline{H}_2$-NH-(C=O)-NH), 3.2 (m, 2H, $C\underline{H}_2$-NH(C=O)-O), 2.2 (s, 3H, $C\underline{H}_3$-C=CH), 1.6-1.4 (m, 8H, CH_2-$C\underline{H}_2$-CH_2); mass(FAB-MS), *m/z* = 394.3(M+H) and 392.4(M-H). Calculated for $C_{15}H_{22}N_5$O4F_3: 393.2 g/mol.

4. Synthesis of 2-(6-ferrocenemethylhexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone **4.** (6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone (420 mg, 1.43 mmol) was

dissolved in 15 mL dry chloroform and ferrocenemethanol (500mg, 2.3mmol) dissolved in 2 mL dry chloroform was added. After addition of one drop of dibutyltindilaurate, the resulting solution was refluxed and stirred for 20 hours. The crude product was purified by column chromatography on silica using dichloromethane as an eluent: isolated yield 35%. ^{1}H-NMR (250 MHz, $CDCl_3$): δ 13.1 (s, 1H, CH_3-C-N$\underline{H}$), 11.9 (s, 1H, CH_2-NH-(C=O)-N$\underline{H}$), 10.1 (s, 1H, CH_2-N$\underline{H}$-(C=O)-NH), 5.8 (s, 1H, C$\underline{H}$=C-CH_3), 5.1-4.9 (m, 1H, N$\underline{H}$-(C=O)-O and 2H, ferrocene-C$\underline{H}_2$-O-(C=O)), 4.3-4.1 (m, 9H, C$\underline{H}$=CH), 3.3 (m, 2H, C$\underline{H}_2$-NH-(C=O)-NH), 3.2 (m, 2H, C$\underline{H}_2$-NH(C=O)-O), 2.2 (s, 3H, C$\underline{H}_3$-C=CH), 1.6-1.4 (m, 8H, CH_2-C$\underline{H}_2$-CH_2); mass(FAB-MS), *m/z* = 508.2 (M+H) and 1017.1(2M-H). Calculated for $C_{24}H_{31}N_5O_4Fe$: 509.2 g/mol.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy provided information about the composition of the self-assembled layers. XPS spectra exhibit peaks associated with C1s, F1s (or Fe2p), N1s, O1s and S2p. Peak positions were referenced to the binding energy of C1s electrons at 284.8 eV. The binding energies of N1s, O1s and S2p were found at 399.3 eV, 531.9 eV, 161.9 (bound sulfur), and 163.1 eV (unbound sulfur), respectively, in agreement with results reported in the literature for organic samples that contain these elements [3].

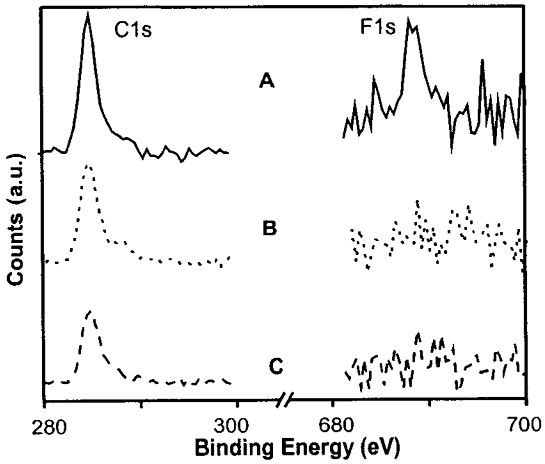

*Figure S1 C1s (284.8 eV) and F1s (688.5 eV) signals in XPS spectra of (A) [Au-1+3] (solid lines); (B) after DMSO rinsing, [Au-1] (dotted lines); (C) reference sample of SAM of 11-mercapto-1-undecanol on gold after treating with **3** in $CHCl_3$ (dashed lines).*

The data shown in Figure S1 confirm that a DMSO rinse of [Au-**1** + **3**] removes only the upper leaflet of the bilayer-type assembly (compare A vs. B) and that there is no non-specific adsorption of **3** onto a hydroxyalkanethiol SAM (C).

Differential Pulse Voltammetry

The data presented in Figure S2 show that a DMSO rinse of [Au-**1** + **4**] removes **4** from the assembly (compare A vs. B) and that there is no non-specific adsorption of **4** onto a hydroxy alkanethiol SAM (C). **3** and **4** in $CHCl_3$, respectively.

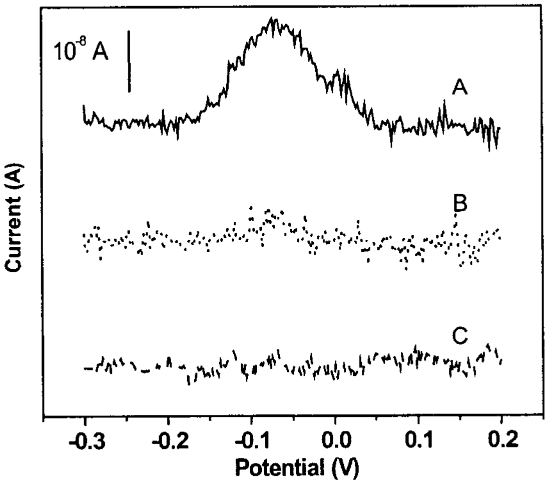

Figure S2. DPV scans of (A) [Au-1+4] (solid lines); (B) after DMSO rinsing, [Au-1] (dotted lines); (C) reference sample of SAM of 11-mercapto-1-undecanol on gold after treating with 4 in $CHCl_3$ *(dashed lines).*

Surface Plasmon Resonance

The measured reflectivity curves (Figure S3) were modeled with a matrix-formalism based on the Fresnel equation [4, 5] and the layer thicknesses were thus obtained.

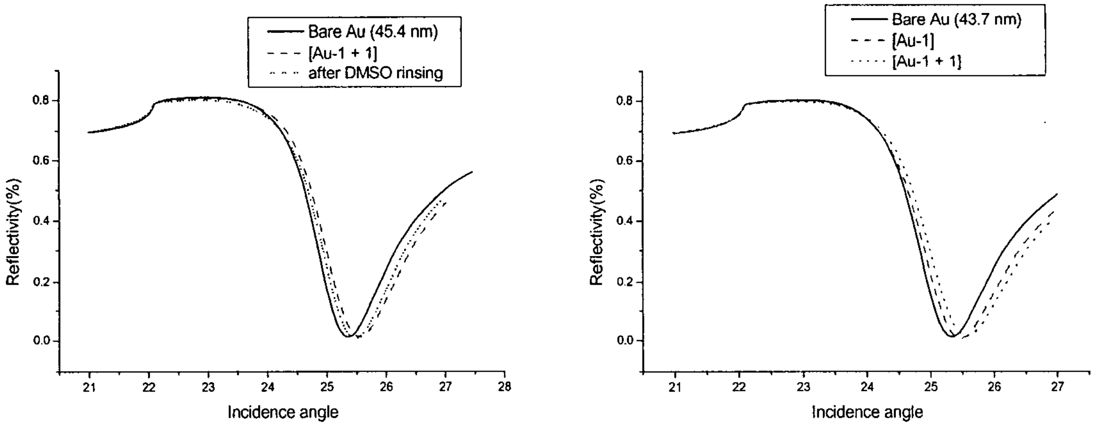

Figure S3. Reflectivity scans measured in SPR experiments. The minimum corresponds to the coupling angle. Left: Gold layer (solid line); complex formed in $CHCl_3$ *on Au, [Au-**1**+**1**] (dashed line); after rinsing with DMSO, [Au-**1**] (dotted line). Right: Gold layer (solid line); monolayer of **1** on Au assembled from DMSO, [Au-**1**] (dashed line); complex formed on monolayer of [Au-**1**] by assembly from* $CHCl_3$*, [Au-**1**+**1**] (dotted line).*

The SPR data shown in Table S1 supports the observation that 2-ureido-4[1H]-pyrimidinone-hydroxyalkane disulfide **1** assembled onto Au from $CHCl_3$ leads to a bilayer structure ([Au-**1** + **1**]); the upper leaflet of the bilayer is not affected by a treatment in $CHCl_3$ overnight, but can be removed by a treatment of the layer in hot $CHCl_3$; it can also be washed off by DMSO.

Table S1. Optical thicknesses measured by SPR against air.

Thickness (nm) of 1 assembled on Au in $CHCl_3$	Thickness (nm) of layers after dipping in $CHCl_3$ for 20 hours	Thickness (nm) of [Au-**1** + **1**] after treatment in boiling $CHCl_3$	Thickness (nm) of [Au-**1** + **1**] after DMSO rinse
1.5 ± 0.2	1.6 ± 0.2	0.9 ± 0.2	0.8 ± 0.2

References

[1] Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874-878.

[2] Häussling, L. Ph.D. Thesis, University of Mainz, Germany, 1991.

[3] Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F. *Handbook of X-Ray Photoelectron Spectroscopy*; Muilenberg, G. E. (Ed.); Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979.

[4] (a) Rothenhäusler, B.; Knoll, W. *Nature*, **1988**, *332*, 615 - 617. (b) Kretschmann, E.; Raether, H. *Z. Naturforsch.* **1968**, *23A*, 2135 - 2136.

[5] Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*, Elsevier, Amsterdam, 1987.