Supplementary Information to

Amphiphilic Polyether-based Block Copolymers as Crosslinkable Ligands for Au-Nanoparticles

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Thioacetic acid-S-(3-chloropropyl)ester (1). Thioacetic acid (28.7 mL, 0.4 mol) and allyl chloride (32.6 mL, 0.4 mol) were mixed and allowed to stir at 55 °C for 3 h. The following distillation under reduced pressure gave 32 mL (61 %) of 1 (84 °C, 13 mbar). ¹H-NMR (300 MHz, CDCl₃): 3.58 ppm (t, 2 H, -CH₂-Cl), 3.01 ppm (t, 2 H, -S-CH₂-), 2.33 ppm (s, 3 H, -CO- CH_3), 2.04 ppm (p, 2 H, -CH₂-CH₂-CH₂-)

3-Chloropropyl thiol (2). 25 mL (0.19 mol) of 1 were dissolved in 150 mL of methanol. After addition of 33 mL of concentrated aqueous HCl the mixture was stirred at 65 °C for 3.5 h. Subsequently, the solution was cooled to room temperature and neutralized with aqueous NaOH. The mixture was extracted with chloroform three times and the organic layers were collected. The solvent was removed under reduced pressure and 15 mL of a colorless liquid were obtained (81 %). The material was used without further purification. ¹H-NMR (300 MHz, CDCl₃): 3.66 ppm (t, 2 H, -CH₂-Cl), 2.68 ppm (q, 2 H, HS-CH₂-), 2.02 ppm (p, 2 H, -CH₂-CH₂-), 1.35 ppm (t, 1 H, -SH)

S-(*t***-Butyldimethylsilyl)-3-chloropropyl thiol (3).** 12.5 g (184 mmol) of imidazole were dissolved in 30 mL of DMF. After the addition of 14.2 mL (147 mmol) of 3-chloropropyl thiol the mixture was cooled to 0 °C and flushed with argon. 23 g (153 mmol) of TBDMS-chloride dissolved in 50 mL of DMF were added dropwise over a period of 40 minutes. The reaction was then allowed to stir for 2 h at 0 °C and subsequently 1 h at room temperature. The mixture was poured into 200 mL of an aqueous NaOH solution (1.25 M) and extracted with DCM. The organic layers were collected and washed with water to remove most of the DMF. After evaporation of the solvent the distillation under reduced pressure gave 25 mL (71 %) of 3 (70 °C, $5 \cdot 10^{-2}$ mbar). ¹H-NMR (300 MHz, CDCl₃): 3.67 ppm (t, 2 H, $-CH_2$ -Cl), 2.66 ppm (t, 2 H, $-S-CH_2$ -), 2.04 ppm (p, 2 H, $-CH_2$ -CH₂-CH₂-), 0.96 ppm (s, 9 H, $-Si-C(CH_3)_3$), 0.27 ppm (s, 6 H, $-Si(CH_3)_2$)



Figure S1 ¹H-NMR spectrum of the thiol-ene click product of the reaction of thioacetic acid with allyl chloride (thioacetic acid-S-(3-chloropropyl)ester) (1).



Figure S2 ¹H-NMR spectrum of the S-deprotected 3-chloropropyl thiol (2).



Figure S3 ¹H-NMR spectrum of the silyl protected thiol modified termination group (*tert*-butyl((3-chloropropyl)thio)dimethylsilane) (3), the endcapping agent for the anionic polymerization of glycidyl ethers.



Figure S4 ¹H-NMR spectrum of the silyl protected, thiol modified poly(ethylene oxide)₅₄*block*-poly(allyl glycidyl ether)₇ (PEO₅₄-*b*-PAGE₇-S-TBDMS).

Separated NMR signals of the C_3 spacer of the endgroup could not be observed. We assume that the broad signal at 1.9 ppm can be referred to as residual water entrapped by the PEO segment.



Figure S5 ¹H-NMR spectrum of the thiol modified poly(ethylene oxide)₅₄-*block*-poly(allyl glycidyl ether)₇ (PEO₅₄-*b*-PAGE₇-SH).

Separated NMR signals of the endgroup could not be observed. The signal at 3.4 ppm can probably be attributed to the first methylene group of the C_3 spacer next to the PAGE block. We assume that the broad signal at 2.5 ppm can be assigned to residual water entrapped by the PEO segment.



Figure S6 ¹H-NMR spectrum of the silyl protected, thiol modified poly(ethylene oxide)₄₅*block*-poly(furfuryl glycidyl ether)₇ (PEO₄₅-*b*-PFGE₇-S-TBDMS).

Separated NMR signals of the C_3 spacer of the endgroup could not be observed. We assume that the signal at 1.9 ppm can be assigned to residual water entrapped by the PEO segment.



Figure S7 ¹H-NMR spectrum of the thiol modified poly(ethylene oxide)₄₅-*block*-poly(furfuryl glycidyl ether)₇ (PEO₄₅-*b*-PFGE₇-SH).

Separated NMR signals of the endgroup could not be observed. We assume that the signal at 1.9 ppm can be assigned to residual water entrapped by the PEO segment.

					Non-crosslinked			Crosslinked	
	HAuCl ₄	Ligand	Ratio	$NaBH_4$	⊢	Radius	Α (λ _{max})	<r<sub>h>_{z,app}</r<sub>	A (λ _{max})
	[g·L ⁻¹]	[g·L⁻¹]	Au:Lig.	[g·L ⁻¹]	[nm]ª	[nm] ^ь	[nm]º	[nm]ª	[nm]°
Au@PEO ₄₅ - <i>b</i> -PFGE ₇ -SH	0.1	13	1:16	0.1	11	3.9	534	8	516
	0.1	6.5	1:8	0.1	11	4.6	553	10	520
	0.1	3.3	1:4	0.1	10	4.7	563	10	535
	0.1	1.6	1:2	0.1	11	5.2	565	12	544
	0.1	0.8	1:1	0.1	13	5.4	565	15	550
	0.1	0.4	2:1	0.1	18	5.5	568	22	555
	0.1	0.2	4:1	0.1	27	6.2	571	28	560
	0.1	0.1	8:1	0.1	30	6.4	580	33	567
Au@PEO ₅₄ - <i>b</i> -PAGE ₇ -SH	0.1	13.8	1:16	0.1	1	2.2	523	1	506
	0.1	6.9	1:8	0.1	2	3.1	523	2	509
	0.1	3.5	1:4	0.1	2	2.9	526	4	525
	0.1	1.7	1:2	0.1	16	3.7	531	14	530
	0.1	0.9	1:1	0.1	13	4.2	545	19	544
	0.1	0.4	2:1	0.1	15	4.5	562	22	560
	0.1	0.2	4:1	0.1	16	5.8	566	21	564
	0.1	0.1	8:1	0.1	20	6.4	568	24	566

Table S1 Summarized concentrations, DLS- and UV/Vis data of Au-NPs with various Au:Lig.ratios of Au@PEO₄₅-*b*-PFGE₇-SH and Au@PEO₅₄-*b*-PAGE₇-SH.

^a obtained from DLS measurements; ^b obtained from transmission electron microscopy;

^c obtained from UV/Vis measurements



Figure S8 UV/Vis and DLS traces of $Au@PEO_{45}-b-PFGE_7-SH$ with different ratios between the polymer and the Au precursor.

- (A) UV/Vis spectra of Au-NPs with various Au@PEO₄₅-b-PFGE₇-SH ratios
- (B) Number-weighted DLS Contin plots of Au-NPs with various Au@PEO₄₅-*b*-PFGE₇-SH ratios
- (C) UV/Vis spectra of the shell-crosslinked Au-NPs with various Au@PEO₄₅-*b*-PFGE₇-SH ratios
- **(D)** Intensity-weighted DLS Contin plots of the shell-crosslinked Au-NPs with various Au@PEO₄₅-*b*-PFGE₇-SH ratios



Figure S9 UV/Vis and DLS traces of Au@PEO₅₄-*b*-PAGE₇-SH with different ratios between the polymer and the Au precursor.

- (A) UV/Vis spectra of Au-NPs with various Au@PEO₅₄-b-PAGE₇-SH ratios
- **(B)** Number-weighted DLS Contin plots of Au-NPs with various Au@PEO₅₄-*b*-PAGE₇-SH ratios
- **(C)** UV/Vis spectra of the shell-crosslinked Au-NPs with various Au@PEO₅₄-*b*-PAGE₇-SH ratios
- **(D)** Intensity-weighted DLS Contin plots of the shell-crosslinked Au-NPs with various Au@PEO₅₄-*b*-PAGE₇-SH ratios



Figure S10 FT-IR spectra of the Au@PEO₄₅-*b*-PFGE₇-SH dispersions before and after shell crosslinking. The spectra were recorded using pure DMAc as reference spectrum.



Figure S11 Magnified region of the FT-IR spectrum of the Au@PEO₄₅-*b*-PFGE₇-SH dispersions before and after shell crosslinking showing the signal of the C=O vibration of the crosslinker. The spectra were recorded using pure DMAc as reference spectrum.