Supporting Information

Figure S1. Scanning force microscopy height image and profile of reference gold. Height image and height profile of the scratched unmodified gold surface used as the electrode to determine the thickness of the gold which is used in the correction for determining the polymer thickness. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited.
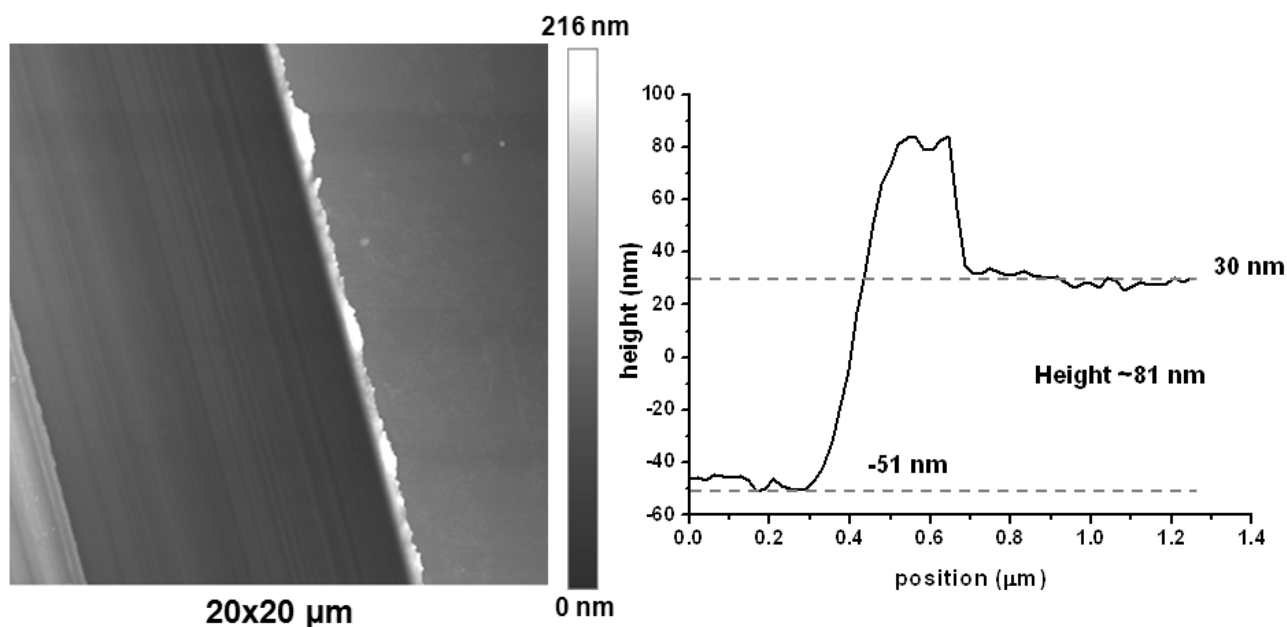

Figure S2. Scanning force microscopy height image and profile of $OEGMA_{475}$, 30 min. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with $OEGMA_{475}$ for 30 min. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.
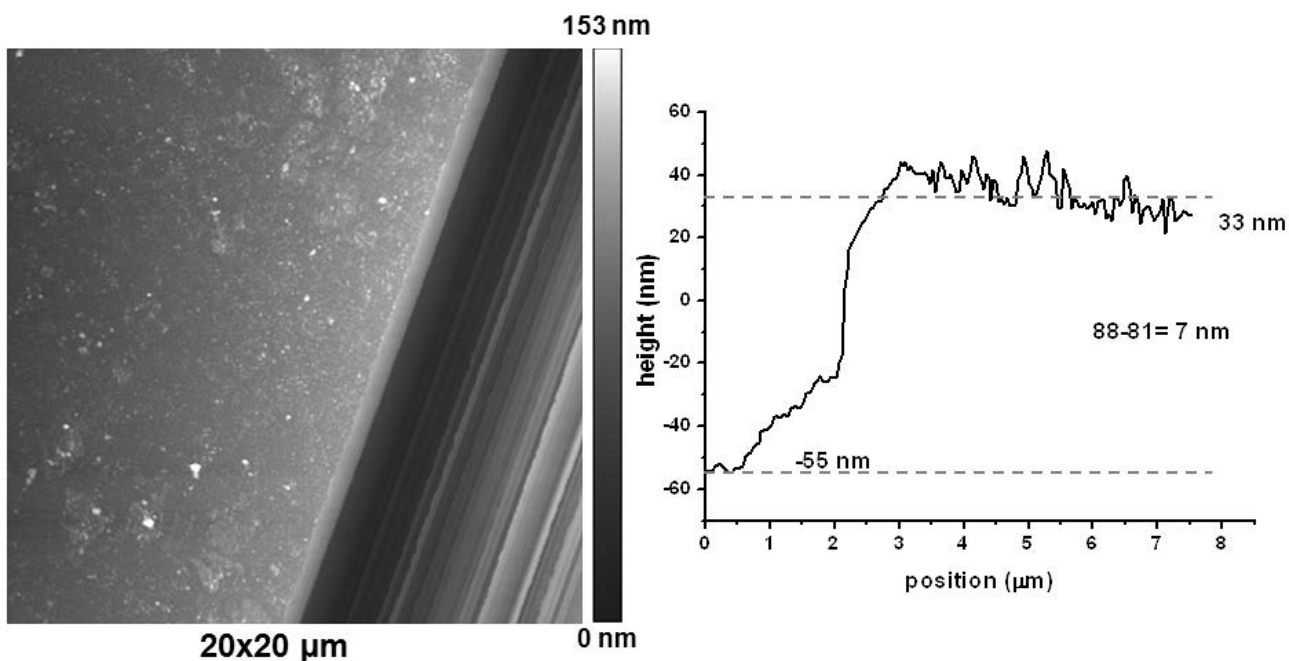
Figure S3. Scanning force microscopy height image and profile of $OEGMA_{475}$, 60 min. Height image and height profile of the modified gold surface (across an unmodified area, surface defect) used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with $OEGMA_{475}$ for 60 min. The lowest point is considered to be the gold-layer and the polymer layer thickness was taken as the average height difference.
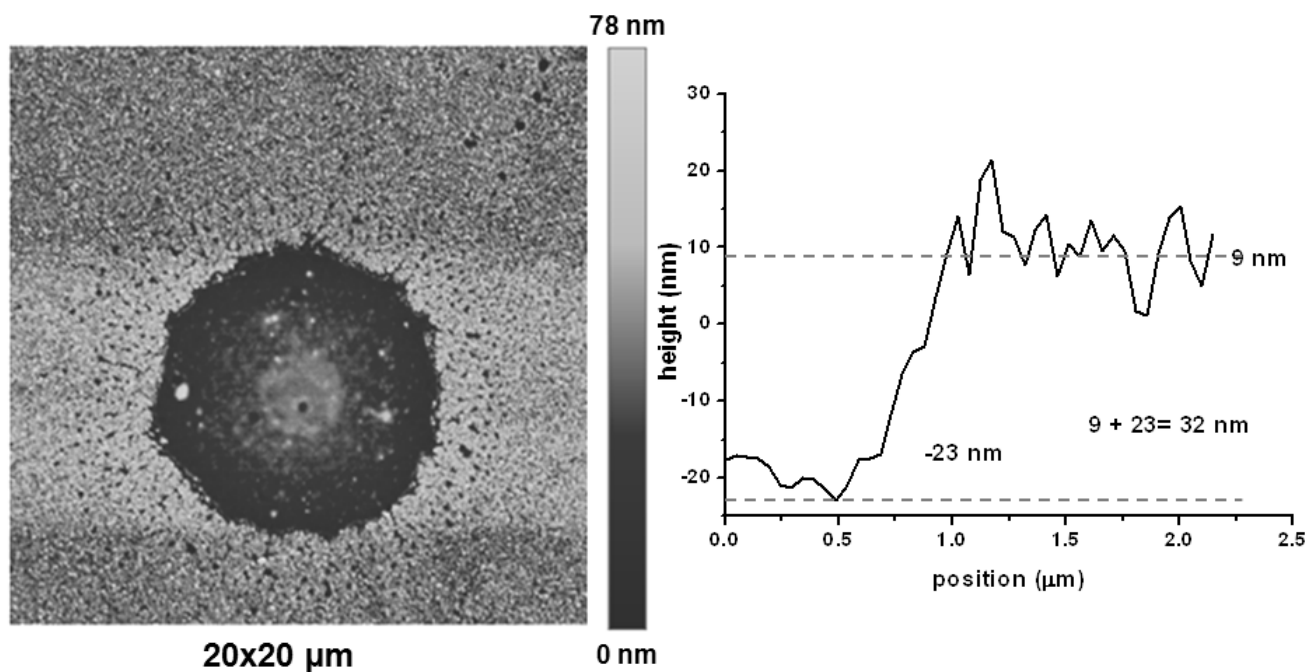

Figure S4. Scanning force microscopy height image and profile of $OEGMA_{475}$, 120 min. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with $OEGMA_{475}$ for 120 min. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.

Figure S5. Scanning force microscopy height image and profile of HEMA, 30 min. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with HEMA for 30 min. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.
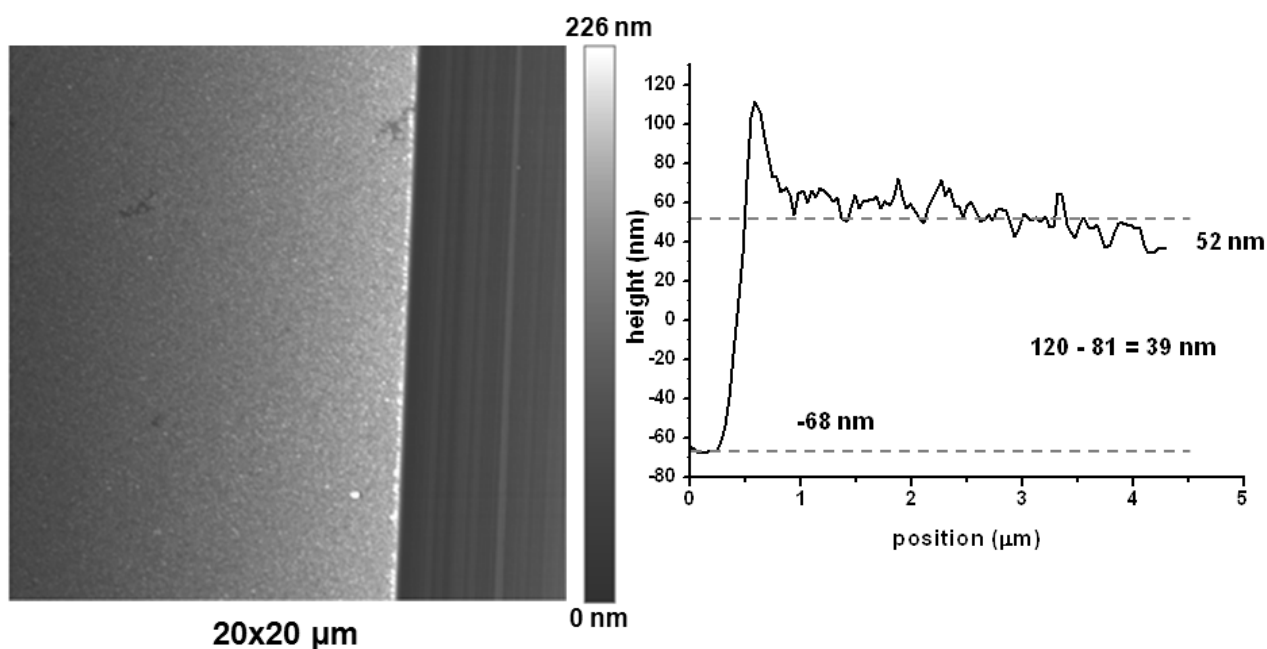

Figure S6. Scanning force microscopy height image and profile of HEMA, 60 min. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with HEMA for 60 min. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.
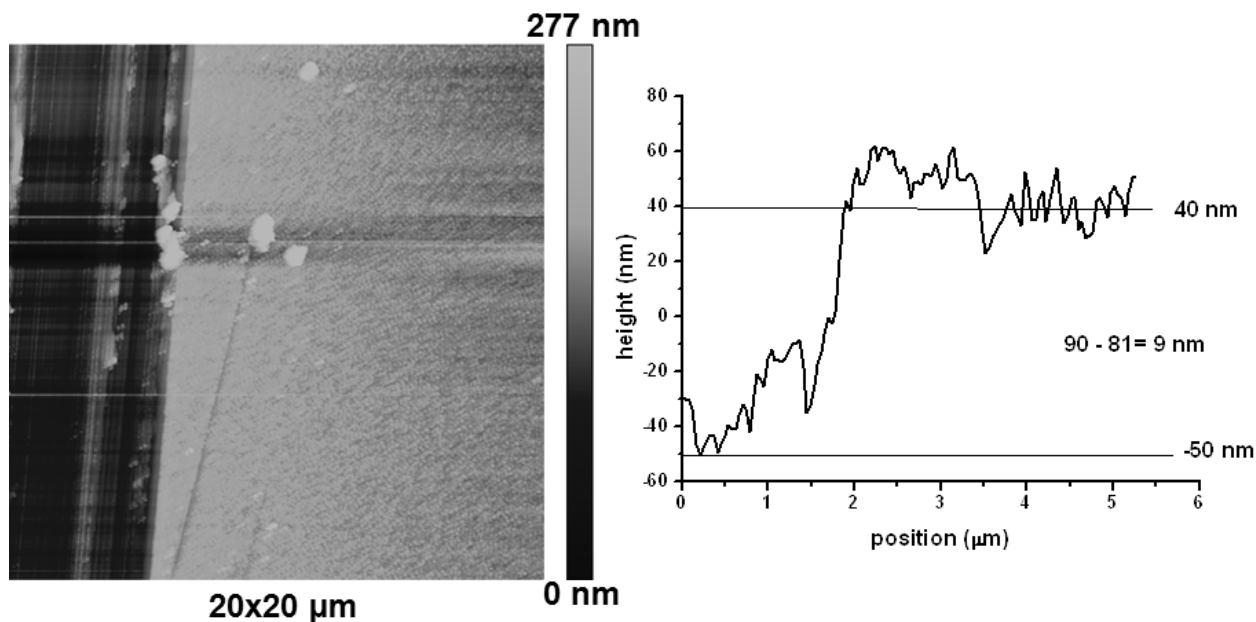
Figure S7. Scanning force microscopy height image and profile of HEMA, 120 min. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with HEMA for 120 min. The lowest point is considered to be the hard SiO_2-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.
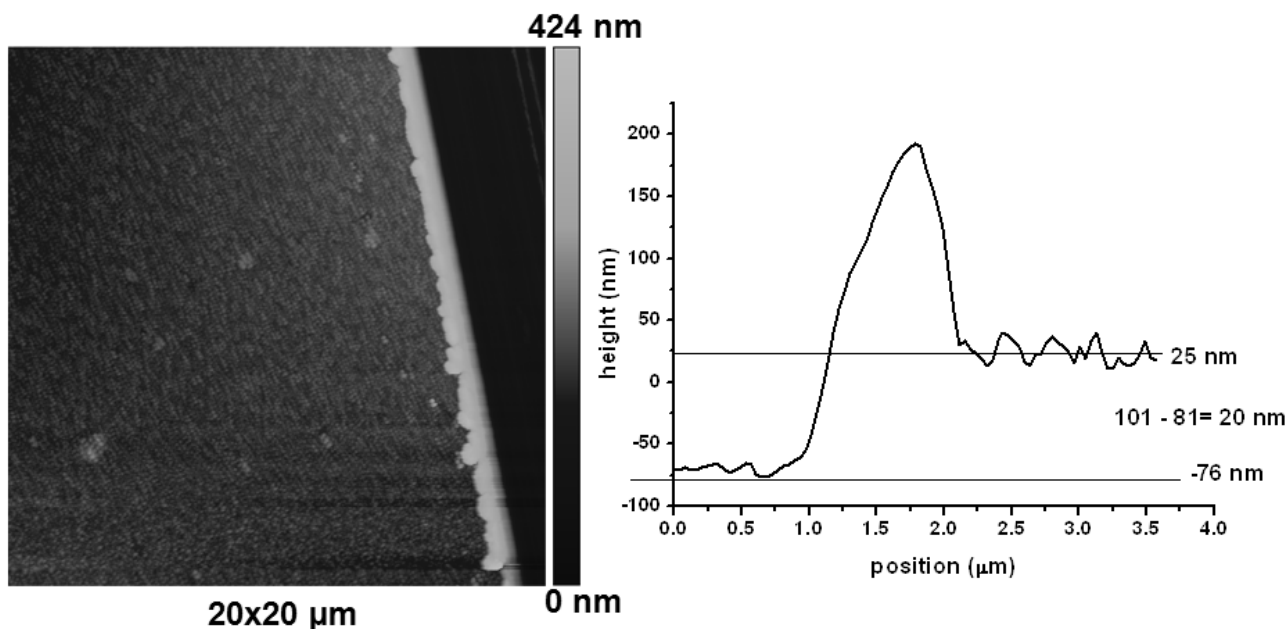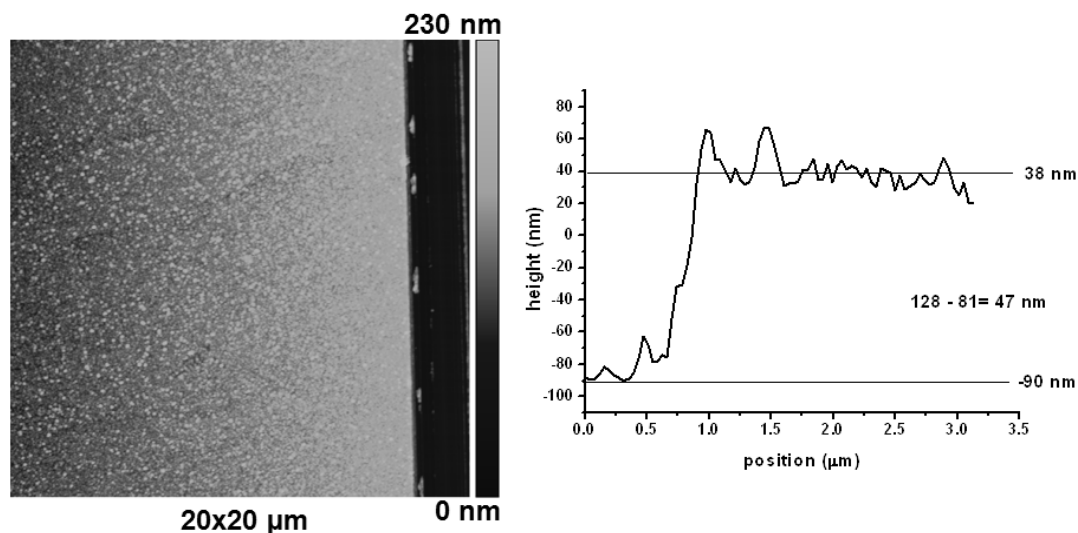

Figure S8. X-ray photoelectron spectroscopy (XPS) of the with $OEGMA_{475}$, 120 min modified surface. XPS analysis of the surface obtained from 120 min polymerization of $OEGMA_{475}$ gives three main signals: O, C and Au. The relative ratio of the atomic concentration between oxygen and carbon is ~27% (O) *vs*. 69% (C). No Cu is detected meaning that the concentration is below 0.1% (detection limit XPS).
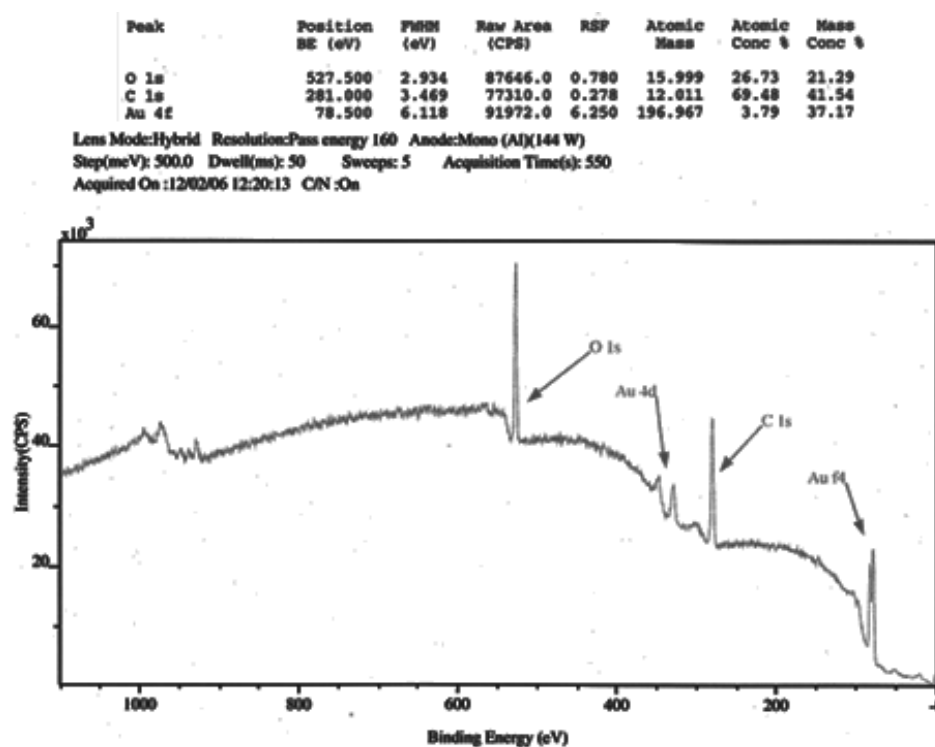
Peak	Position BE (eV)	FWHM (eV)	Raw Area (CPS)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
O 1s	527.500	2.934	87646.0	0.780	15.999	26.73	21.29
C 1s	281.000	3.469	77310.0	0.278	12.011	69.48	41.54
Au 4f	78.500	6.118	91972.0	6.250	196.967	3.79	37.17

Lens Mode:Hybrid Resolution:Pass energy 160 Anode:Mono (Al)(144 W)
Step(meV): 500.0 Dwell(ms): 50 Sweeps: 5 Acquisition Time(s): 550
Acquired On :12/02/06 12:20:13 C/N :On

Figure S9. Scanning force microscopy height image and profile of OEGMA$_{475}$, 120 min and Pt-wire in solution. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization is performed with OEGMA$_{475}$ for 120 min with the Pt-wire connection to the gold also in the solution. The lowest point is considered to be the hard SiO$_2$-support on which the gold-layer is deposited and the polymer layer thickness was taken as the average height corrected for the thickness of the gold layer.
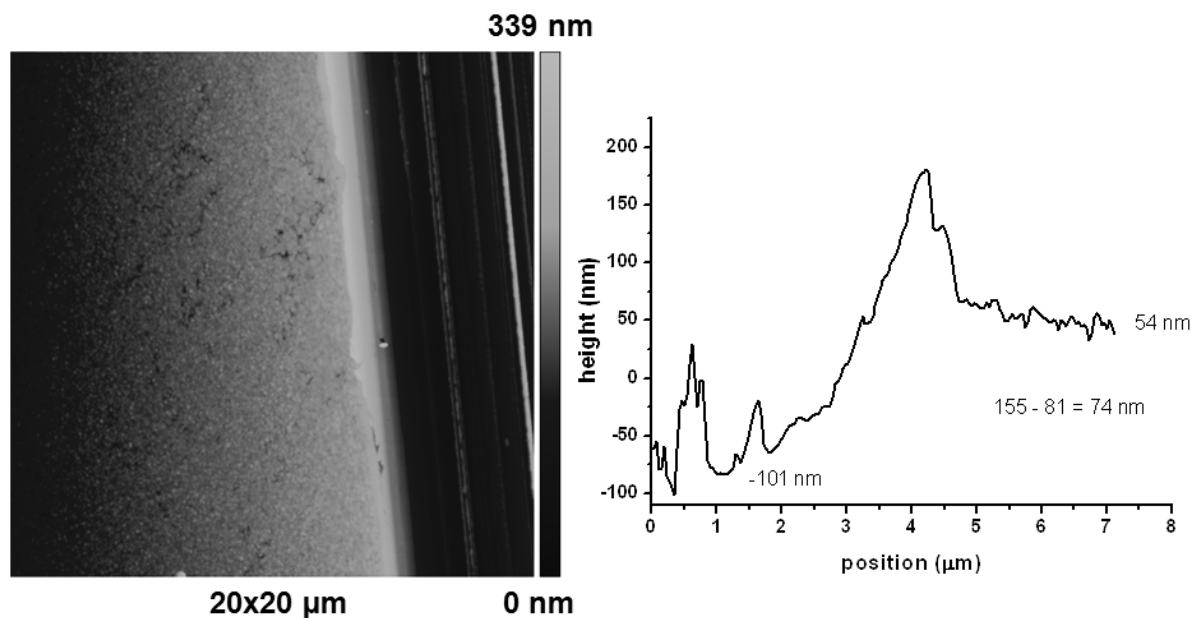

Figure S10. Scanning force microscopy height image and profile of HEMA, 120 min before and after removal of Cu-ions. Height image and height profile of the scratched modified gold surface used in the aqueous surface initiated *e*-ATRP reaction. Polymerization was performed with HEMA for 120 min and the surface was analyzed with respect to the layer thickness before and after extraction of the residual Cu-ions. No difference in height was observed.
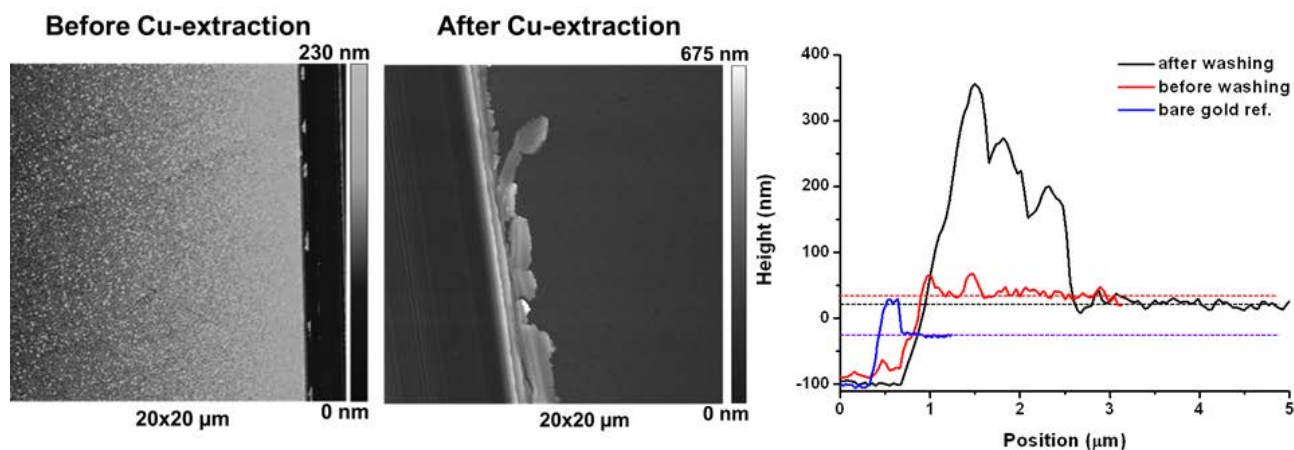
Figure S11. Electrochemical-quartz crystal microbalance (E-QCM) profile of polymerization of HEMA by surface initiated *e*-ATRP. The electropolymerization has been done on the EQCM at a scale factor of 200 Hz/V. The applied potential was set to −0.5 V *vs.* Ag/AgCl reference electrode. As counter electrode a platinum coil was used, which was separated by a glass frit filled with deinonized water from the reaction vessel. The data acquisition was set to record ten data points per second. The experiment was started with the pure 2.5% HEMA solution. The potential was applied for a certain time to show that there is no mass increase and hence polymerisation with initiator. Immediately after addition of the $Cu(II)Br_2/Me_6TREN$ complex a change in the quartz frequency, indicated by the observed change in analog potential output. The analog potential output can be calculated as such back to the relative frequency. Relative frequency (Hz) = analog voltage output (V) × scale factor (Hz/V). From the relative frequency the deposited mass on the electrode can be calculated by mass displacement (ng) = relative frequency/0.0566. (**A**) Initial polymerization reaction and (**B**) the re-initiated polymerization of and the isolated polymer layer. The average rate was calculated by determined by subtracting the increase in mass before initiation (instrumental error) from the increase in mass during polymerization.
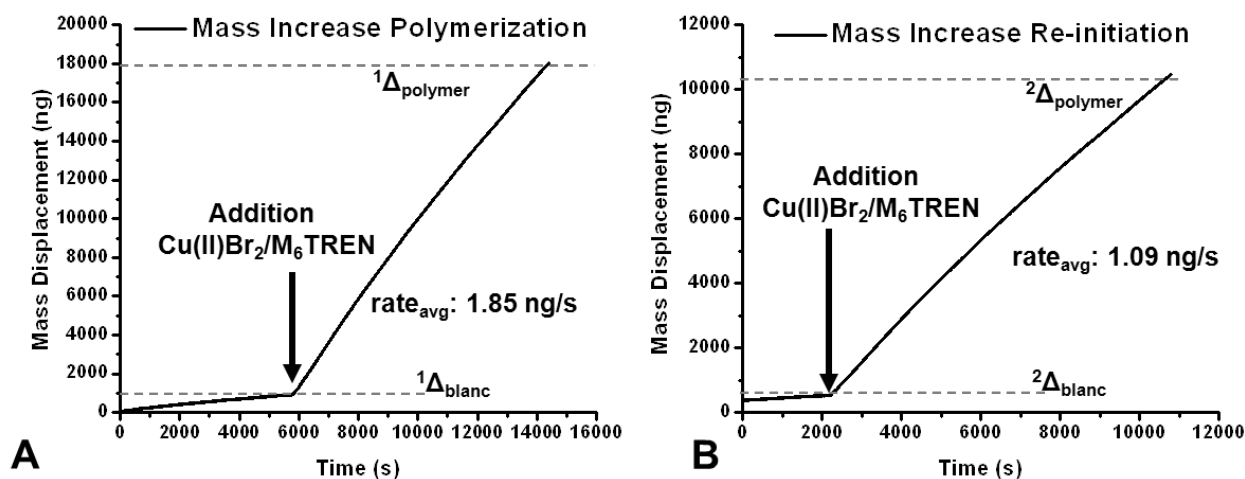
Figure S12. EQCM profile of mass increase due to possible electrochemical Cu-depostion. In order to investigate possible electrodeposition of Cu-species, a quartz electrode coated with the initiator was used in the same reaction-setup without monomer and only Cu(II)Br$_2$/Me$_6$TREN. The applied potential was again set to −0.5 V *vs.* Ag/AgCl electrode. This indicates Cu deposition on the electrode and a discoloration of the electrode could be observed only very slightly as a result of the Cu deposition. Though the deposition was found, the increase in mass is only a fraction of that what is obtain from the polymerization reaction.
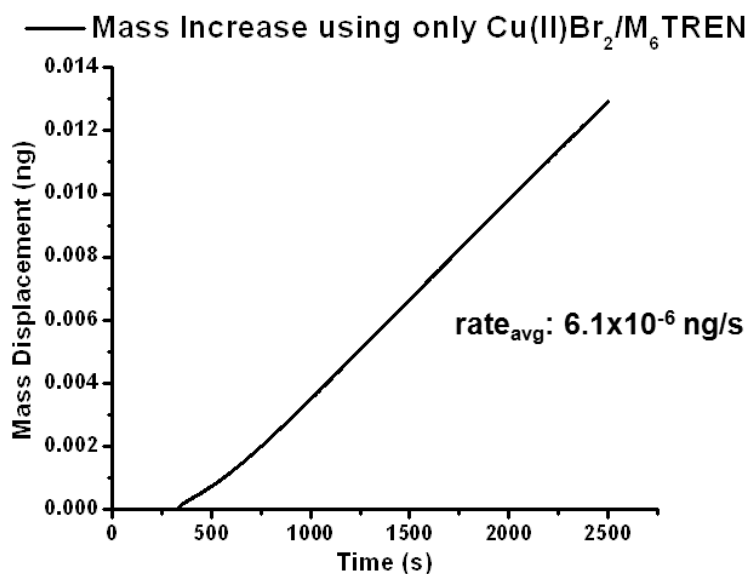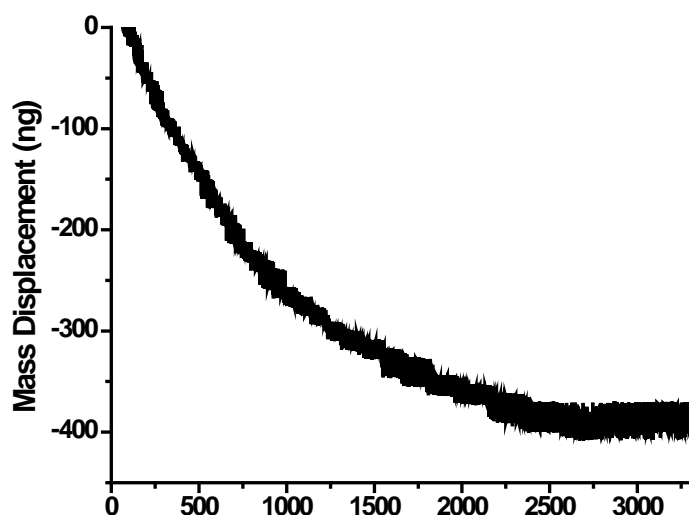
Figure S13. EQCM profile of mass decrease due to thiol-reduction and polymer removal. Detachment of surface tethered polymers was done via thiol-reduction at −2 V *vs.* Ag/AgCl reference electrode. It was ensured, that the solution did not contain any Cu^{+x} contamination. For that the electrode and the reaction vessel were rinsed several times with deionized water. A Cu^{+x} contamination in solution would lead to the deposition of pure Cu on the electrode and would result in a mass increase. The electrodes were arranged as in previous experiments. A slow decrease in surface confined mass was observed over a period of approximately one hour. After this period the weight of the electrode stabilized. Most likely the presence of residual Cu-species inside the polymer film forms a solid-Cu(0) layer which embeds the thiols and prevents further polymer detachment.