Supplementary Material (ESI) for Soft Matter

Supporting Information

"Nanostructured Polymer Brushes and Protein Density Gradients

on Diamond by Carbon Templating"

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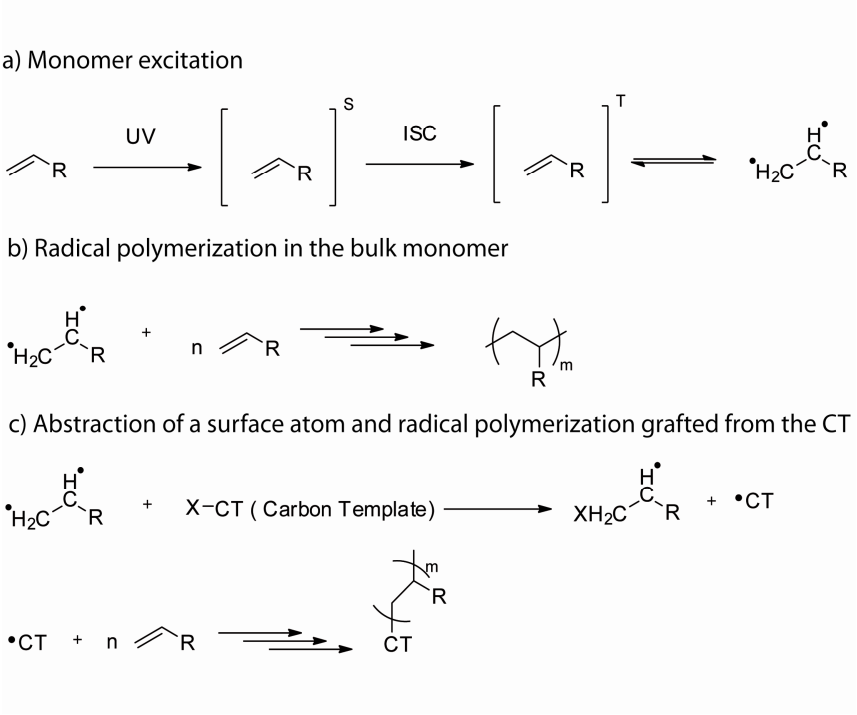
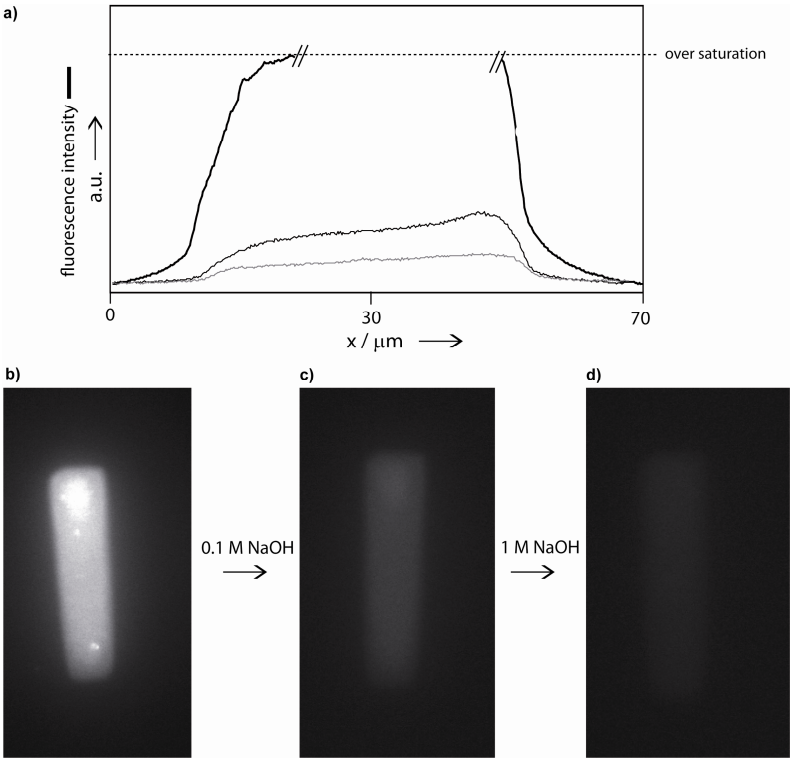
Supporting information 1: Self-initiated photografting and photopolymerization



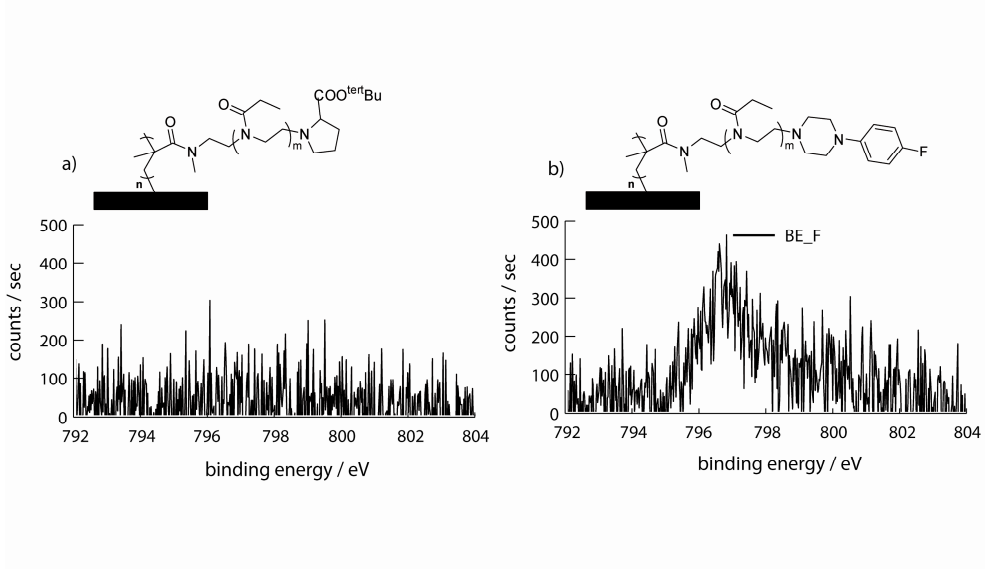
SI 1: Schematic mechanism of the SIPGP. a) Under UV irradiation the vinyl monomers absorb light and are excited to a singlet state S which is transformed to a triplet state T bearing two free radicals via intersystem crossing. b) These radicals can subsequently either initiate the polymerization of bulk monomer or c) lead to the abstraction of a CT surface atom with the suitable bond dissociation energy resulting in the generation of a surface radical. This induces the formation of polymer brushes grafted from the surface.

Supporting information 2: Stability of the polymer brush – GFP conjugates



SI 2: Comparison of the fluorescence of P(MA) bound GFP before and after treatment with NaOH (causing denaturation of the protein). All fluorescence micrographs were taken with the highest excitation intensity to obtain comparable results. a) Profile plot of the fluorescence intensity; The freshly biofunctionalized NCD sample revealed a strong fluorescence which reaches a level of oversaturation at the highest excitation intestity (thick black line); After treatment with 0.1 M NaOH over night, the fluorscence drastically descreases, although a clear contrast between the non-modified and the GFP-functionalized NCD persists (thin black line); Even after treatment in 1 M NaOH over night, a slight contrast in fluorescence remains visible, indicating a stabilization of the GFP molecules inside the polymer brush layer (grey line). b)-d) Fluorescence images of the GFP functionalized P(MA) gradient without denaturation procedure (b), after treatment in 0.1 M NaOH (c) and 1 M NaOH (d).

Supporting information 3: XPS analysis of the end group functionalized BBBs



SI 3: X-ray photoelectron spectroscopy (XPS) data of POx BBBs on NCD with differently terminated end groups after the LCROP. a) zoom into the spectra of P(IPOx-g-EtOx) BBBs terminated with proline-*tert*-butylester, b) zoom into the range of the fluorine binding energy for P(IPOx-g-EtOx) BBBs terminated with fluorophenyl piperazine. XPS is a powerful tool to demonstrate the presence of atoms introduced during the LCROP termination reaction. Since the discrimination between different compositions of only N/C/O is very difficult, we used a terminating agent with a characteristic fluorine atom as proof of priciple.