Electronic Supplementary Information (ESI)

Introduction of anti-fouling coatings at the surface of supramolecular elastomeric materials via post-modification of reactive supramolecular additives

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Surface characterization



Figure S1. AFM height and amplitude micrographs of the different surfaces, PCLdiUPy height (a) and amplitude (d), PCLdiUPy with 10 mol% height (b) and amplitude (e) and PCLdiUPy with 10 mol% UPy-Tz and reacted with star-PEG-BCN height (c) and amplitude (f). Scale bars represent 100 nm.



Characterization of surface reaction

b.



Figure S2. Surface reaction of the UPy-Tz (**2**) with a model compound BCN-NH₂ (**9**), a) Reaction scheme of the UPy-Tz (**2**) with the BCN-NH₂ (**9**) to form the reaction product UPy-TZ-BCN (**10**), MW = 1185.8 g·mol⁻¹ and b) Surface MALDI-ToF MS spectrum of the different surfaces, PCLdiUPy incubated with BCN-NH₂ (**9**), PCLdiUPy with UPy-Tz and PCLdiUPy with UPy-Tz incubated with BCN-NH₂ (**9**), yielding the reaction product (**10**). Masses of interest: UPy-Tz (**2**): m/z 1190.3 (observed: m/z 1191.3) and UPy-Tz where the UPy-moiety is cleaved off ($\Delta m/z$ 151) m/z 1138.2 (observed: m/z 1040.6) and UPy-Tz-BCN product (**10**): m/z 1485.8 (observed: m/z 1487.4) and the reaction product (**10**) with the UPy-moiety cleaved m/z 1334.6 (observed: m/z: 1339.2).

Method:

Surface MALDI-ToF MS. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) was performed on an Autoflex Speed MALDI-MS (Bruker) using an α -cyano-4-hydroxycinnamic acid (CHCA) matrix. Surface MALDI-ToF MS experiments were performed on drop-cast samples on a MTP 384 target plate polished steel TF. Dropcast were prepared by 3 μ L 50 mg $\mathbb{P}mL^{-1}$ PCLdiUPy + 10 mol% UPy-Tz and directly deposited on the MALDI plate. Next, drop-cast spots were incubated with 10 μ L 100 μ M BCN-NH₂ (**9**) solution for 70 minutes, after which the reaction solution was discarded from the MALDI plate and the spots were washed 3 times with 10 μ L milli-Q water. Subsequently 1 μ L CHCA in 49.5/49.5/1 MeCN/water/TFA (v/v/v%) was spotted on each surface and allowed to dry for 30 minutes. MALDI-ToF Ms measurements were performed in positive linear mode (method: 700-2000 Da), 2500 shots per spot and a laser power of 60%.

Protein adsorption measurements



Figure S3. Overview of the modelled mass adsorption of BSA (30 mg·mL⁻¹) as determined by QCM-D using a Voigt-Voinova viscoelastic model on the different surfaces, pristine PCLdiUPy and PCLdiUPy with 10 mol% UPy-Tz. Different star-PEG-BCN concentrations (1 mg·mL¹, 0.5 mg·mL⁻¹ and 0.1 mg·mL⁻¹ were immobilized on the PCLdiUPy with 10 mol% UPy-Tz surfaces to tune surface properties. Adsorption is represented as mean \pm SD (n \geq 4).



Figure S4. Overview of the modelled mass adsorption as determined by QCM-D using a Voigt-Voinova viscoelastic model. BSA (30 mg·mL⁻¹), γ -globulin (10 mg·mL⁻¹), fibrinogen (3 mg·mL⁻¹) and the corresponding protein mixture (Vroman series) on both PCLdiUPy and PCLdiUPy with 10 mol% UPy-Tz spin coated supramolecular surfaces conjugated with star-PEG BCN. Adsorption is represented as mean ± SD (n ≥ 2).

Cell attachment studies



Figure S5. Fluorescence microscopy graphs of HK-2 cells on spincoated surfaces after 24 hours of culture. Upper row represents images of PCLdiUPy (a) the pristine material or incubated with either mono-functional-PEG-BCN, bi-functional-PEG-BCN or star-PEG-BCN (from left to right). Lower row represents Images of PCLdiUPy with 10 mol% UPy-Tz incorporated (b) the pristine material or incubated with either mono-functional-PEG-BCN, bi-functional-PEG-BCN or star-PEG-BCN (from left to right). The actin skeleton is stained with Phalloidin (green), the nuclei are stained with DAPI (blue). Scale bars represent 100 μm.



Figure S6. Fluorescence microscopy graphs of HK-2 cells on spincoated surfaces after 72 hours of culture on a) PCLdiUPy and b) PCLdiUPy with 10 mol% UPy-Tz. The actin skeleton is stained with Phalloidin (green), the nuclei are stained with DAPI (blue) and the focal adhesions were stained with Atto-555 (red). Scale bars represent 20 μ m.

Synthesis and characterization



Figure S7. Characterization of the monofunctional-PEG-BCN (**3**) synthesis, a) MALDI-ToF MS spectra of the methoxy-PEG-amine prior to (upper spectrum) and after (lower spectrum) BCN-functionalization and b) ¹ H NMR spectrum of the monofunctional-PEG-BCN (**3**).



Figure S8. Characterization of the bifunctional-PEG-BCN (**4**) synthesis, a) MALDI-ToF MS spectra of the PEGdiamine prior to (upper spectrum) and after (lower spectrum) BCN-functionalization and b) ¹H NMR spectrum of the bifunctional-PEG-BCN (**4**).



Figure S9. Characterization of the star-PEG-BCN (**5**) synthesis, a) MALDI-ToF MS spectra of the star-PEG-tetraamine prior to (upper spectrum) and after (lower spectrum) BCN-functionalization and b) ¹ H NMR spectrum of the star-PEG-BCN (**5**).