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Characterization of Hybrid Materials Designed via Photo-Induced Ligation Chemistries

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Introduction

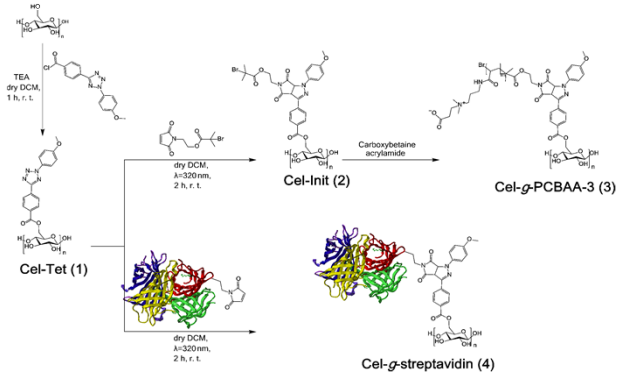
The current work presents different photochemical reactions which allow the grafting of various (natural and artificial) polymeric structures onto a diverse set of surfaces in a spatially controlled manner.

Experimental

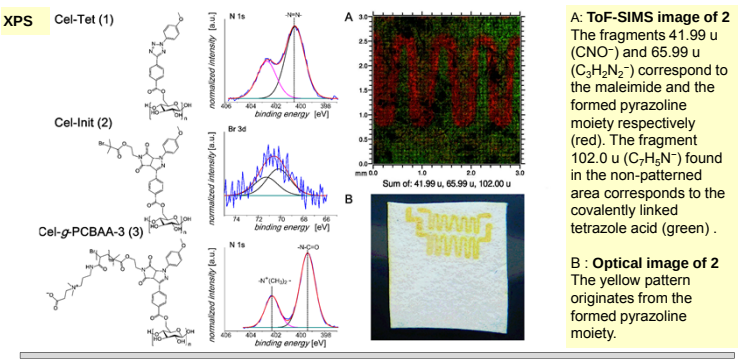
- ***X-ray Photoelectron Spectroscopy (XPS):***
  ThermoFisher Scientific **K-Alpha** Spectrometer
- ***Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)***
  ION-TOF GmbH **ToF.SIMS[5]** Spectrometer

Photo-Patterning of Non-Fouling Polymers and Biomolecules on Paper[1]

We focus on the synthesis and in depth characterization of the newly generated hybrid materials, thereby providing the technological base for a novel avenue for the development of biosensing materials as well as bioactive, non-fouling, flexible and inexpensive surfaces based on cellulose substrates.[1]
By employing nitrile imine-mediated tetrazole-ene cycloaddition (NITEC), streptavidin was grafted onto cellulose whereas non-fouling poly(carboxybetaine acrylamide) brushes were generated in a grafting-from approach, where the initiator was previously attached via NITEC. This leads to spatially-resolved functionalization of paper with both non-fouling polymer brushes as well as functional protein entities. Streptavidin is photo-immobilized with remarkable efficiency, opening the possibility to generate new materials for biomedical applications.



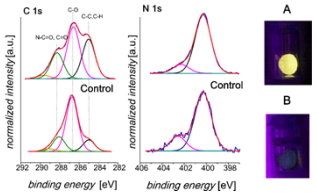
Synthetic routes for the preparation of photo-patterned poly(carboxybetaine acrylamide) brushes from cellulose via surface initiated single electron transfer living radical polymerization (SET-LRP) and the immobilization of streptavidin. The cellulose surface was firstly arylated with a tetrazole acid chloride to generate Cel-Tet (1). The maleimide-initiator was photo-patterned on Cel-Tet (1) to obtain Cel-Init (2) and exploited for grafting poly(CBAA-3) brushes by SET-LRP to finally yield Cel-*g*-PCBAA-3 (3). The second route is based on the photo-triggered immobilization of streptavidin functionalized with maleimide on Cel-Tet (1) in PBS to yield Cel-*g*-streptavidin (4).



A: **ToF-SIMS image of 2** The fragments 41.99 u (CNO^-) and 65.99 u ($C_3H_2N_2^-$) correspond to the maleimide and the formed pyrazoline moiety respectively (red). The fragment 102.0 u ($C_7H_8N^-$) found in the non-patterned area corresponds to the covalently linked tetrazole acid (green) .

B : **Optical image of 2** The yellow pattern originates from the formed pyrazoline moiety.

C 1s and N 1s XP spectra of Cel-*g*-streptavidin (4) (top) and the control sample (bottom). The control was conducted utilizing (1) and pure streptavidin to evidence clearly that the immobilization of streptavidin is exclusively occurring through the maleimide-tetrazole linkage.



A: **Optical image of 4** 366 nm irradiation: **Fluorescence** of Cel-*g*-streptavidin confirms the formation of pyrazoline moiety and the successful grafting.

B : **Control sample.**

Photo-Induced Functionalization of Spherical and Planar Surfaces via Caged Thioaldehyde End-Functional Polymers[2]

The present work shows the combination of the light-induced thioaldehyde ligation reaction with reversible addition-fragmentation chain transfer (RAFT) polymerization,[2] thus enabling the photo-induced grafting of any polymer synthesizable via RAFT onto surfaces carrying a nucleophilic motif or diene species, such as a carrier material coated with a poly(dopamine) (PDA) layer or porous cyclopentadiene-functionalized microspheres. By combination with a Direct Laser Writing (DLW) setup, any two-dimensional pattern can be encoded onto PDA-coated surfaces with micrometer resolution. Precision functionalized microspheres have a wide range of applications from pharmaceuticals and chromatography to organic synthesis.

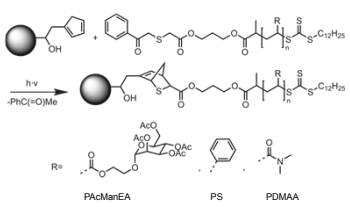
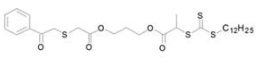
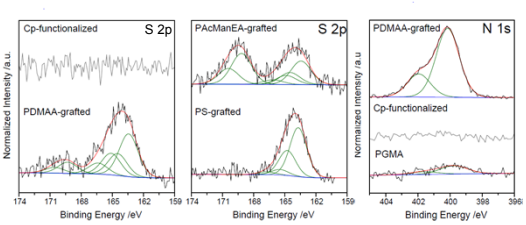


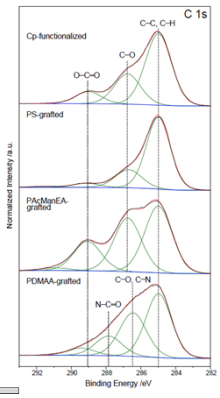
Photo-triggered grafting reactions of RAFT-polymers onto Cp-functionalized microspheres.

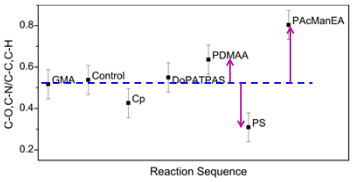


DoPATPAS used for a test reaction

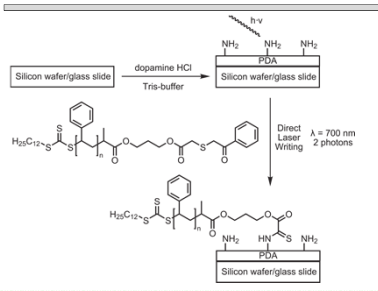


S 2p XP Spectra:
Sulfur can only be detected in all samples after the photografting.
N 1s XP Spectra:
The nitrogen increase proves the successful macromolecular grafting.
C 1s XP spectra:
Expected necessary carbon species.

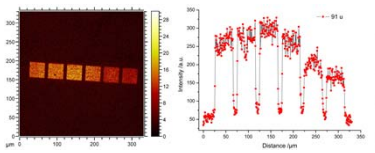




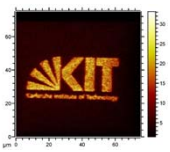
Comparison of the amount of carbon bound to oxygen or nitrogen and carbon bound to carbon or hydrogen based on the deconvolution of C 1s XP spectra. The values are in agreement with the theoretically expected changes for grafted-to polymers.



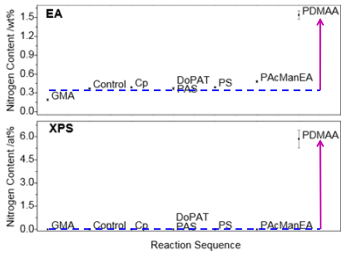
Synthetic route for the photo-patterning of PDA-interfaces



ToF-SIMS image of the $C_7H_7^+$ ion from PS grafted onto a PDA-functionalized silicon wafer (left) and intensity profile for the $C_7H_7^+$ signal across the squares of the DLW patterned structure (right) visualizing the lateral resolution of the obtained structures.



ToF-SIMS imaging of the sum of $C_7H_7^+$, $C_8H_9^+$, $C_9H_7^+$ and $C_9H_9^+$ signals from PS grafted onto a PDA-functionalized glass slide by DLW.



Nitrogen concentration for each sample: the nitrogen increase clearly proves the attachment of PDMMA.

KIT – University of the State of Baden-Wuerttemberg and
National Research Center of the Helmholtz Association

[1] T. Tischer, C. Rodriguez-Emmenegger, V. Trouillet, A. Welle, V. Schueler, J. O. Mueller, A.S. Goldmann, E. Brynda, and C. Barner-Kowollik, Adv. Mater. 2014, 26, 4087-4092.
[2] M. Kaupp, A.S. Quick, C. Rodriguez-Emmenegger, A. Welle, V. Trouillet, O.Pop-Georgievski, M. Wegener, and C.Barner-Kowollik, Adv. Funct. Mater. 2014, 24,5649–5661