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XPS-Characterization of (Photo-) Click-Conjugated Polymers

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Introduction

Modular ligation chemistry belongs to the powerful methods to modify surfaces and designates reactions proceeding under mild conditions, with quantitative yield and orthogonal reactivity. As one of the few surface sensitive methods to provide information on chemical binding states in a non-destructive manner, X-ray photoelectron spectroscopy (XPS) was chosen as a powerful tool to prove the successful step-wise functionalization of gold and silicon surfaces.

Experimental

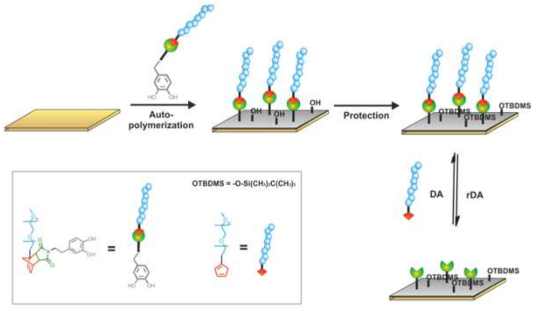
X-ray Photoelectron Spectroscopy (XPS):

ThermoFisher Scientific **K-Alpha** Spectrometer

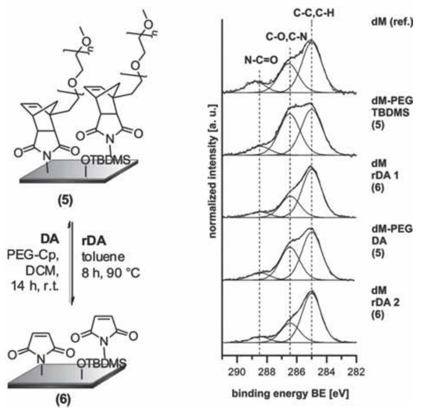
- Micro-focused mono-AlKα X-ray source,
- Charge compensation with low energy electrons and Ar$^+$-Ions,
- Avantage software for data acquisition and processing.

Biomimetic Polymer-Switching System on Gold Surfaces[1]

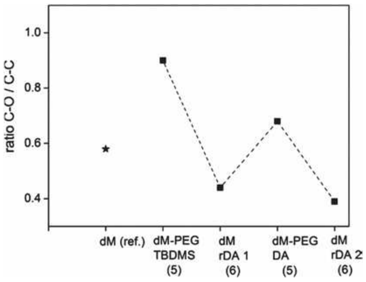
Mussel adhesives feature the ability to attach to a wide variety of material, such as metals, wood, glass and even Teflon. The combination of synthetically mimicked mussel adhesives and the well-known principles of modular ligation (i.e. Click) chemistry provide opportunities for defined and orthogonal surface modifications, which can be accomplished on a wide variety of materials. Here we present the use of a biomimetic precursor molecule, which performs an autopolymerization process under aqueous maritime conditions on important surfaces, such as gold substrates, and which possesses the capability to operate as a *switch* for the covalent linkage and delinkage of polymer chains equipped with an appropriate diene group.



Diels-Alder (DA) and retro-Diels-Alder (rDA) reaction of dopamine-maleimide-PEG on gold surfaces.



Schematic representation of DA and rDA reactions of dM-PEG on the surface of a gold substrate (left) and corresponding C 1s spectra (right). dM (reference) illustrates the surface attachment of pure dM on the gold substrate.

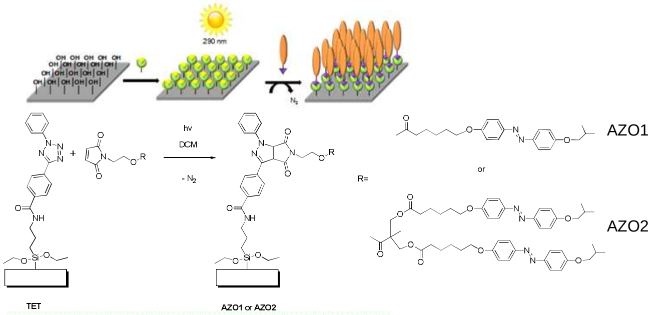


C 1s intensity ratios of components assigned to C–O and C–C bonds. The DA / rDA system is depicted in squares and a dashed line, while the ratio for pure dM (reference) on the surface is labeled with an asterisk.

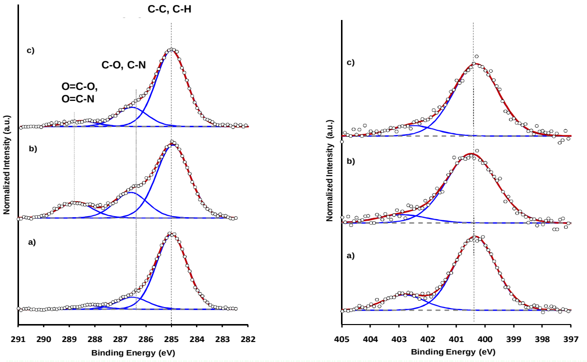
C 1s Spectra

The increase and decrease of intensity ratios of C-O to C-C bonds prove the successful DA/rDA process. The DA reaction does not seem to proceed to full conversion, possibly associated with the steric requirements of the polymer coil.

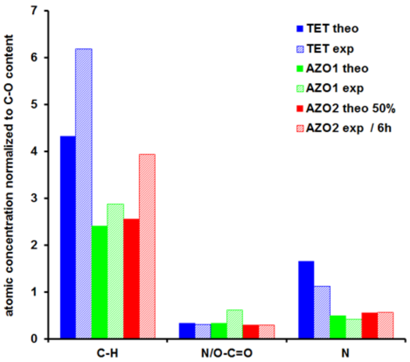
Photochemical Generation of Light Responsive Surfaces[2]



Azobenzene-functionalization of a silicon substrate



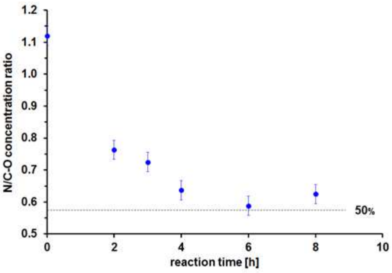
Comparison of C 1s (left) and N 1s (right) spectra of (a) **TET**, (b) **AZO1** and (c) **AZO2** functionalized silicon wafers



Left:
Bar chart comparing theoretical and experimental C 1s and N 1s peak abundances for the silicon wafers **TET**, **AZO1** and **AZO2**. Intensities are normalized to the (C-O, C-N) content.

For **AZO2** a theoretical reaction yield of 50% is assumed, the experimental data are based on 6 h reaction time. The high intensity the C-H components is due to adventitious carbon.

Right:
Time dependent evolution of the N/(C-O, C-N) ratio of **AZO2**. Dashed line indicates the assumed max. 50% reaction yield (cf. S5), 0 h reaction time represents pure wafer **TET**.
Error bars represent standard deviations of the measurements.



N 1s Spectra

In comparison with **TET** the N/(C-O, C-N) ratio decreased on the functionalized surface (**AZO1 and AZO2**) evidencing the presence of azobenzene on the surface.

In the case of **AZO2** the experimental result is not in agreement with the theoretical value evidencing *incomplete functionalization* of the surface.

The intensity of the N/(C-O, C-N) ratio was chosen as a sensor for the reaction evolution.

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[1] Corinna M. Preuss, Anja S. Goldmann, Vanessa Trouillet, Andreas Walther, Christopher Barner-Kowollik, Macromolecular Rapid Communications, 2013, 34, 640-644.
[2] Eva Blasco , Milagros Piñol, Luis Oriol, Bernhard V. K. J. Schmidt, Alexander Welle, Vanessa Trouillet, Michael Bruns, and Christopher Barner-Kowollik, Advanced Functional Materials 2013, 23, 4011-4019.