

Surface Functionalization of Conjugated Microporous Polymer Thin Films and Nanomembranes using Orthogonal Chemistries

P. Lindemann,^a A. Schade,^b L. Monnereau,^b W. Feng,^c K. Batra,^a H. Gliemann,^a P. Levkin,^c S. Bräse,^{b,c} C. Wöll^a and M. Tsotsalas^{a*}

Experimental Section

Chemicals: All chemicals were purchased from commercial sources and used without further purification, if not indicated otherwise. Tetrahydrofuran (THF) was purchased from Acros Organics; toluene was purchased from Alfa Aesar. Acetone, ethyl acetate and ethanol were purchased from Prolabo. Tetrakis-(acetonitrile)-copper(I) hexafluorophosphate and poly(methyl methacrylate) (PMMA) average M_w 996,000 were purchased from Aldrich. Iodine and potassium iodide were purchased from Sigma-Aldrich. Tetrakis(4-azidophenyl)-methane (TPM-azide) and tetrakis(4-ethynylphenyl)methane (TPM-alkyne) were synthesized as described in literature.^[1] Rhodamine-SH was synthesized according to literature.^[2]

Safety in the Handling of Sodium Azide and other Azides: Sodium azide is toxic (LD_{50} oral (rats) = 27 mg kg⁻¹) and can be absorbed through the skin. It decomposes explosively upon heating to above 275 °C. Some organic and other covalent azides are classified as toxic and highly explosive, and appropriate safety measures must be taken at all times.^[3]

Substrates: As sacrificial substrate a 150 nm gold film on mica was used. For analytical measurements the membrane was transferred to a Si(100) wafer coated with 5 nm titanium and 100 nm gold (Au/Ti/Si). The substrates were obtained by Georg-Albert-PVD, Germany and were stored in inert argon atmosphere until use.

Infrared reflection absorption spectroscopy (IRRAS): The IRRAS-spectra were recorded on a Bruker Vertex 80 purged with dried air. The IRRAS accessory (A518) has a fixed angle of incidence of 80°. The data were collected on a narrow band liquid nitrogen cooled MCT detector. Perdeuterated hexadecanethiol-SAMs on Au/Ti/Si were used for reference measurements. The absorption band positions are given in wave numbers $\tilde{\nu}$ in cm⁻¹.

Self-assembled monolayer (SAM) preparation: For SAM formation a clean gold substrate (2.2 cm × 2.2 cm) was rinsed with pure ethanol and then immersed in a solution of 11-thioacetyl-undecane acid-propargyl amide^[4] (with a concentration of 1 mmol/L) in ethanol for 18 h. Afterwards the substrate was taken out, rinsed thoroughly with ethanol and dried in a nitrogen stream.^[5]

Preparation of Conjugated Microporous Polymer (CMP) films: The synthesis is explained in more detail in reference^[6], briefly: Tetrakis(4-azidophenyl)-methane (TPM-azide), tetrakis(4-ethynylphenyl)methane (TPM-alkyne) and tetrakis(acetonitrile)copper(I) hexafluorophosphate were dissolved in water free THF ($c = 2$ mmol/L). The synthesis was carried out under inert conditions using a Schlenk line. Solutions of TPM-azide and TPM-alkyne were alternatingly added to the SAM coated substrate together with Cu(I)catalyst; after each step the substrate was rinsed with THF. The reaction time for each step was 30 min. After eight cycles, the coated substrate was taken out from the reaction solution, rinsed with THF, ethanol and dried in a nitrogen stream.^[6a]

Preparation of the membrane from SAM on sacrificial substrate: To obtain free-standing membranes, the CMP-film was grown on sacrificial substrates using the above described procedure. The membrane was then obtained by following a procedure described in literature.^[6-7] First PMMA was spin coated as a supporting layer and afterwards the mica was removed by floating in solutions of I₂/KI/H₂O; KI/H₂O and in the last step by immersing the substrate in H₂O. The retaining gold film was etched in a solution of I₂/KI/H₂O. The membrane was washed 3 times on water.^[7] Afterwards the membrane was transferred to either a glass slide or a gold coated Si-wafer and the PMMA was dissolved in acetone. The obtained membrane size was 2 cm × 2 cm)

Surface modification: For the surface modification the membrane was completely wetted with either 1H,1H,2H,2H-perfluorodecanethiol (10%_{v/v} in ethyl acetate), cysteamine hydrochloride (10%_w in ethanol/water 1:3) or 3-mercaptopropionic acid (10%_{v/v} in ethanol). For the thiol-yne reaction the samples were covered with a quartz glass slide and irradiated with UV-light ($\lambda = 260$ nm; Intensity = 5 mW/cm²) for 60 seconds. Afterwards the sample was rinsed thoroughly with the same solvent of the reaction solutions and dried in a nitrogen stream.

The rhodamine-SH patterning was achieved according to a reported procedure.^[8] Briefly, the membrane was wetted with the dye solution (4 mg/mL in acetone), covered with a quartz photomask, and irradiated by UV light through the photomask for 60 s. Afterwards the sample was rinsed thoroughly with acetone and dried in a nitrogen stream. The fluorescence images were taken on an optical microscope AxioPlan 2 imaging (Zeiss) equipped with an Axio CAM MRm and used with filter number 15 (Rhod)

- [1] O. Plietzsch, C. I. Schilling, M. Tolev, M. Nieger, C. Richert, T. Muller, S. Bräse, *Organic & biomolecular chemistry* **2009**, *7*, 10.
- [2] L. Li, J. Li, X. Du, A. Welle, M. Grunze, O. Trapp, P. A. Levkin, *Angewandte Chemie International Edition* **2014**, *53*, 3835-3839.
- [3] S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem., Int. Ed.* **2005**, *44*, 5188-5240.
- [4] M. Kleinert, T. Winkler, A. Terfort, T. K. Lindhorst, *Organic & biomolecular chemistry* **2008**, *6*, 2118-2132.
- [5] R. Chelmowski, D. Käfer, S. D. Köster, T. Klasen, T. Winkler, A. Terfort, N. Metzler-Nolte, C. Wöll, *Langmuir : the ACS journal of surfaces and colloids* **2009**, *25*, 11480-11485.
- [6] aP. Lindemann, M. Tsotsalas, S. Shishatskiy, V. Abetz, P. Krolla-Sidenstein, C. Azucena, L. Monnereau, A. Beyer, A. Götzhäuser, V. Mugnaini, H. Gliemann, S. Bräse, C. Wöll, *Chemistry of Materials* **2014**, *26*, 7189 - 7193; bP. Lindemann, Y. Träutlein, C. Wöll, M. Tsotsalas, *J. Vis. Exp.* **2015**, *106*, e53324.
- [7] M. Ai, S. Shishatskiy, J. Wind, X. Zhang, C. T. Nottbohm, N. Mellech, A. Winter, H. Vieker, J. Qiu, K.-J. Dietz, A. Götzhäuser, A. Beyer, *Advanced materials* **2014**, *26*, 3421 - 3426.
- [8] W. Feng, L. Li, E. Ueda, J. Li, S. Heißler, A. Welle, O. Trapp, P. A. Levkin, *Advanced Materials Interfaces* **2014**, *1*, DOI: 10.1002/admi.201400269.