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Supporting Information to

A Bioinspired Light Induced Avenue for the Design of Patterned Functional Interfaces

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Materials

Acetic acid (Roth, 100%, p.a.), acetonitrile (MeCN, p.a., Fischer), dry acetonitrile (dry MeCN, 99.5% Acros, extra dry, stored over molecular sieve), Al_2O_3 (active basic and active neutral, Merck, for column chromatography), chloroform-d^1 ($CDCl_3$) (99.8 %, EURISO-TOP), Cu(II)Br_2 (Fluka, 99%), Cu(I)Br (Fluka, 98 %) cyclohexane (VWR, p.a.), dichloromethane (DCM, VWR, p.a.), dry dichloromethane (dry DCM, Acros, extra dry, stored over molecular sieve), 4-(dimethylamino)-pyridine (DMAP, Acros, 99%), ethanol (p.a., VWR), dry ethanol (Acros, extra dry), ethyl acetate (Merck, anal. grade), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl, Alfa Aesar), hydrochloric acid (HCl, 37 %, Roth), N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, Merck, 98%), magnesium sulfate ($MgSO_4$, Roth, >99%) sand (VWR), silica gel (Merck), sodium bicarbonate (≥ 99 %, Roth), sodium chloride (≥ 99.8 %, Roth), *tert*-butyl dimethylchlorosilane (TBDMS-Cl) (97 %, ABCR), tetra-*n*-butylammonium fluorid (Alfa Aesar, 1 M in THF), tetrahydrofuran (THF, p.a., VWR) dry tetrahydrofuran (dry THF, Acros, extra dry, stored over molecular sieve), toluene (p.a., VWR), dry toluene (Acros, 99% and extra dry, stored over molecular sieve), 2,2,2-trifluoroethyl methacrylate (TFEMA, TCI, 98 %), tris(hydroxymethyl)methylamine (Tris buffer) (> 99 %, Acros), dimethyl sulfoxide-D^6 (DMSO-D^6) (99.8 %, EURISO-TOP) were used as received.

Photoenol-COOH **(1)** was prepared as described in [11b]. PEG-maleimide was synthesized by the reported procedure.[16] 3-(3,4-bis((tert-butyldimethylsilyl)oxy)phenyl)-2-((tert-butoxycarbonyl)amino) propanoic acid (DOPA-$TBDMS_2$) **(3)** was prepared in a two-step procedure according to reference.[17] 2-(1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethyl-2-bromo-2-methyl-propanoate was prepared according to reference [18]. The maleimide carrying peptide sequence (Peptide-maleimide) was kindly provided by Katharina Linkert and Professor Hans Börner (HU Berlin, Germany).

Characterization methods

^{1}H NMR and ^{13}C NMR spectroscopy was performed using a Bruker Ascend 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz). All samples were dissolved in chloroform-D^1 or DMSO-D^6. The δ-scale is referenced to the internal standard trimethylsilane (TMS, δ = 0.00 ppm).

ESI-MS (electrospray ionization-mass spectrometry) spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the *m*/*z* range 195-1822 using a standard comprising caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621, all from Aldrich). A constant spray voltage of 4.5 kV and a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature were set to 60 V, 110 V, and 275 °C, respectively. The polymer samples were prepared in a THF / methanol solution (ratio 3 : 2) mixed with sodium trifluoroacetate, and were injected directly to the ionization source.

XPS (X-ray photoelectron spectroscopy) measurements were performed using a K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). All the samples were analyzed using a microfocused, monochromated Al Kα X-ray source (400 µm spot size). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. Data acquisition and processing using the Thermo Avantage software is described elsewhere.[19] The spectra were fitted with one or more Voigt profiles (BE uncertainty: ± 0.2 eV). The analyzer transmission function, Scofield sensitivity factors[20], and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[21] All spectra were referenced to the C1s peak of hydrocarbon at 285.0 eV binding energy controlled by means of the well known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

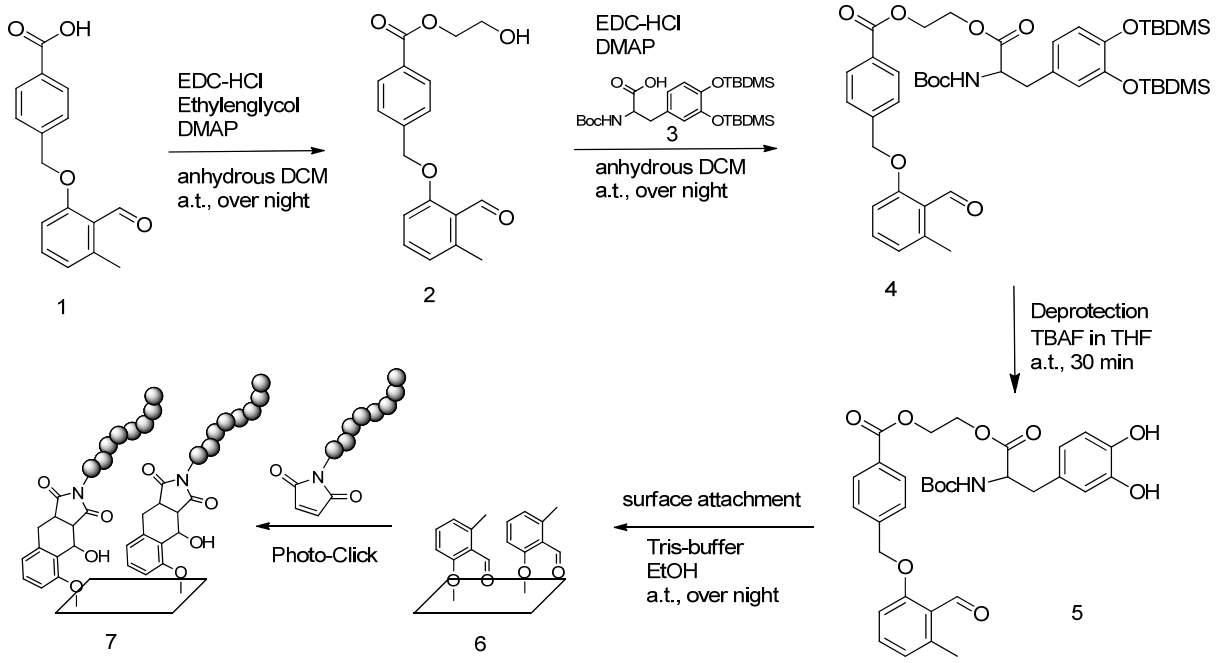
ToF-SIMS (time-of-flight secondary ion mass spectrometry) was performed on a TOF.$SIMS^5$ instrument (ION-TOF GmbH, Münster, Germany), equipped with a Bi cluster liquid metal primary ion source and a non-linear time of flight analyzer. The Bi source was operated in the “bunched” mode providing 0.7 ns Bi^{1+} ion pulses at 25 keV energy and a lateral resolution of approx. 4 µm. The short pulse length allowed for high mass resolution to analyze the complex mass spectra of the immobilized organic layers. Images

larger than the maximum deflection range of the primary ion gun of 500×500 μm^2 were obtained using the manipulator stage scan mode. Negative polarity spectra were calibrated on the C^-, C_2^-, and C_3^- peaks. Positive polarity spectra were calibrated on the C^+, CH^+, CH_2^+, and CH_3^+ peaks. Primary ion doses were kept below 10^{11} ions/cm^2 (static SIMS limit).

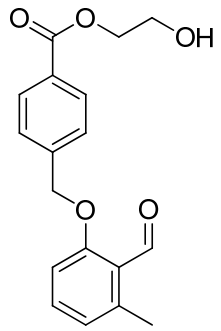
Contact Angle Measurement: The wettability of the samples was examined by the dynamic water drop method using a custom-made contact angle system. A 10 µL drop was placed on the surface. The volume increase and the advancing contact angle was record when the drop was 25 µL. Data were evaluated using a tangent leaning algorithm.

Synthesis

Reaction Sequence



Synthesis protocols



Synthesis of 2-hydroxyethyl 4-((2-formyl-3-methylphenoxy)methyl)benzoate ***(Photo-Gly) (2)***

4-((2-formyl-3-methylphenoxy)methyl)benzoic acid (Photo-COOH) **(1)** (0.500 g, 1.850 mmol) and EDC·HCl (1.064 g, 5.55 mmol) were dissolved in dry DCM (30 mL) under a nitrogen atmosphere. After 20 minutes, ethane-1,2-diol (0.4 mL, 7.15 mmol) and DMAP (0.045 g, 0.370 mmol) were added. The mixture was stirred over night at ambient temperature. Water was added and the organic fraction was washed with water (3×), $NaHCO_3$ (1×), brine (3×) and again water (3×). The organic fraction was dried over $MgSO_4$ and purified *via* column chromatography (cyclohexene : ethyl acetate = 1 : 1, rf = 0.33) to give a white solid (0.070 g, yield: 60.2 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.76 (s, 1H, aldehyde), 8.10 (d, *J* = 7.8 Hz, 2H, (-CH-C**H**-(C-(C=O)-O-)-C**H**-CH-)), 7.51 (d, *J* = 7.7 Hz, 2H, (-C**H**-CH-(C-(C=O)-O-)-CH-C**H**-)), 7.36 (t, *J* = 8.1 Hz, 1H, Me-C-CH-C**H**-CH-(C-O-CH_2-)-), 6.85 (d, *J* = 8.1 Hz, 2H, Me-C**H**-CH-C**H**-(C-O-CH_2-)-), 5.23 (s, 2H, CH-(C-CH-)-O-C$\mathbf{H_2}$-(C-CH-)-CH-), 4.48 (d, *J* = 2.8 Hz, 2H, -(C=O)-O-C$\mathbf{H_2}$-CH_2-OH), 3.98 (d, *J* = 2.8 Hz, 2H, -(C=O)-O-CH_2-C$\mathbf{H_2}$-OH), 2.59 (s, 3H, CH-(C-CH-)-**Me**). ^{13}C NMR (101

MHz, $CDCl_3$) δ = 192.14 (aldehyde), 166.68 (-(**C**=O)-O-CH_2-), 162.02 (-CH-(**C**-O-CH_2)-C-), 142.50 (-CH-(**C**-CH_2-)-CH-), 141.82 (Me-**C**-CH-CH-CH-(C-O-CH_2-)-), 134.55 (Me-C-CH-**C**H-CH-(C-O-CH_2-)-), 130.29 (-CH-**C**H-(C-(C=O)-O-)-**C**H-CH-), 129.84 (-**C**H-CH-(C-(C=O)-O-)-CH-**C**H-, -CH-CH-(**C**-(C=O)-O-)-CH-CH-), 127.04 (Me-C-**C**H-CH-CH-(C-O-CH_2-)-), 124.90 ((H-C=O)-**C**-CH-), 110.46 (Me-C-CH-CH-**C**H-(C-O-CH_2-)-), 70.06 (-CH-(C-CH-)-O-**C**H_2-(C-CH-)-CH-), 66.93 (-(C=O)-O-**C**H_2-CH_2-OH), 61.62 (-(C=O)-O-CH_2-**C**H_2-OH), 21.63 (**Me**-C-CH-CH-CH-(C-O-CH_2-)-). m / z [$M+Na^+$] = 337.17.

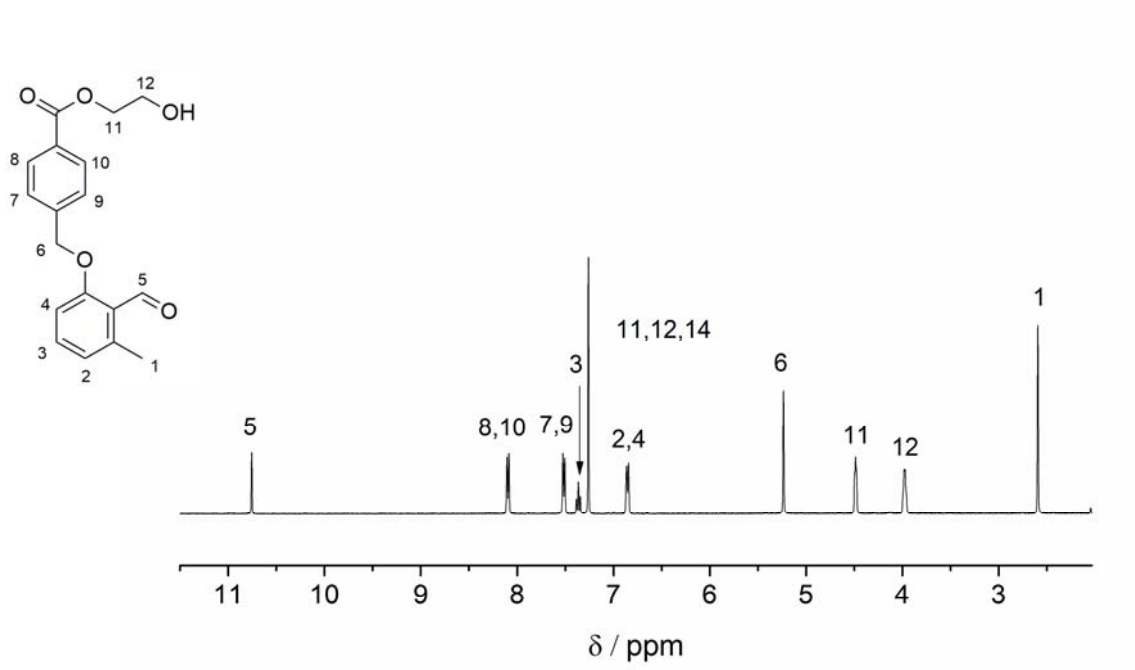
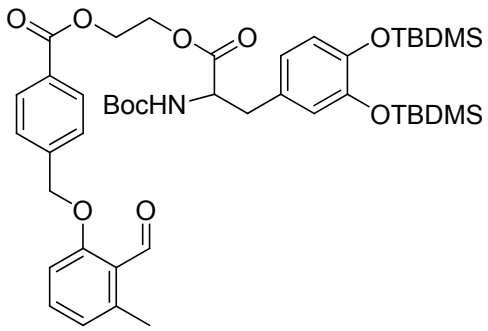


Figure 1 *^{1}H-NMR spectrum of Photo-Gly (2).*



Synthesis of 2-((3-(3,4-bis((tert-butyldimethylsilyl)oxy)phenyl)-2-((tert-butoxycarbonyl)-amino)propanoyl)-oxy)ethyl 4-((2-formyl-3-methylphenoxy)methyl)benzoate ***(Photo-DOPA-TBDMS$_2$) (4)***

3-(3,4-bis((tert-butyldimethylsilyl)oxy)phenyl)-2-((tert-butoxycarbonyl)amino)propanoic acid (DOPA-TBDMS$_2$) **(3)** (0.063 g, 0.119 mmol) and EDC·HCl (0.069 g, 0.358 mmol) were dissolved in dry DCM (40 mL). After 20 minutes, Photo-Gly **(2)** (0.045 g, 0.143 mmol) and DMAP (0.015 g, 0.119 mmol) were added. The mixture was stirred for 22 h at ambient temperature. DCM (20 mL) was added and the

mixture was washed with brine (3×) and water (3×). The organic phase was dried over $MgSO_4$ and the solvent was removed. Purification was performed *via* column chromatography (cyclohexane : ethyl acetate = 1 : 1, rf=0.65) to give a white oil (m=0.065 g, yield: 66.3 %). ^{1}H-NMR (250 MHz, $CDCl_3$) δ = 10.75 (s, 1H, aldehyde), 8.08 (d, *J*=8.3 Hz, 2H, (-CH-C**H**-(C-(C=O)-O-)-C**H**-CH-)), 7.50 (d, *J*=8.3 Hz, 2H, (-C**H**-CH-(C-(C=O)-O-)-CH-C**H**-)), 7.35 (t, J = 7.9 Hz, 1H, Me-C-CH-C**H**-CH-(C-O-CH_2-)-), 6.84 (d, *J*=8.1, 2H, Me-C-C**H**-CH-C**H**-(C-O-CH_2-)-), 6.60 (m, 3H, arom. H at DOPA-OTBDMS), 5.22 (s, 2H, CH-(C-CH-)-O-C**H$_2$**-(C-CH-)-CH-), 4.93 (s, 1H, -N**H**-Boc), 4.64 – 4.38 (m, 5H, -(C=O)-O-C**H$_2$**-C**H$_2$**-O-, -NH-C**H**((C=O)-O-)-CH_2-arom.), 2.96 (s, 2H, -NH-CH((C=O)-O-)-C**H$_2$**-arom.), 2.59 (s, 3H, **Me**-C-CH-CH-CH-(C-O-CH_2-)-), 1.41 (s, 9H, **Boc**), 0.97 (s, 18H, **tBu** at TBDMS), 0.17 (s, 12H, **Me** at TBDMS). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.07 (aldehyde), 171.93 (-NH-CH((**C**=O)-O-)-CH_2-arom.), 166.03 (arom-(**C**=O)-O-CH_2-CH_2-), 162.03 (-CH-(**C**-O-CH_2)-C-), 155.21 (-NH-(**C**=O)-O-tBu), 146.90 (-C-CH-(**C**-OTBDMS)-(C-OTBDMS)-CH-CH), 146.16 (-C-CH-(C-OTBDMS)-(**C**-OTBDMS)-CH-CH-), 142.48 (-CH-(**C**-CH_2-)-CH-), 141.84 (Me-**C**-CH-CH-CH-(C-O-CH_2-)-), 134.53 (Me-C-CH-**C**H-CH-(C-O-CH_2-)-), 130.34 (-CH-**C**H-(C-(C=O)-O-)-**C**H-CH-), 129.65 (-**C**H-CH-(C-(C=O)-O-)-CH-**C**H-, -CH-CH-(**C**-(C=O)-O-)-CH-CH-), 128.88 (-NH-(CH-(C=O))-CH_2-**C**-) 127.03 (Me-C-**C**H-CH-CH-(C-O-CH_2-)-), 124.88 ((H-C=O)-**C**-CH-), 123.84 (-C-CH-(C-OTBDMS)-(C-OTBDMS)-CH-**C**H-), 122.29 (-C-CH-(C-OTBDMS)-(C-OTBDMS)-**C**H-CH-), 121.21 (-C-**C**H-(C-OTBDMS)-(C-OTBDMS)-CH-CH-), 110.43 (Me-C-CH-CH-**C**H-(C-O-CH_2-)-), 80.03 ((-NH-(C=O)-O-**C**-Me_3), 70.04 (-CH-(C-CH-)-O-**C**H_2-(C-CH-)-CH-), 63.10 (-(C=O)-O-**C**H_2-CH_2-O-(C=O)-CH), 62.78 (-(C=O)-O-CH_2-**C**H_2-O-(C=O)-CH), 54.43 (-NH-(**C**H-(C=O))-CH_2-C-), 37.50 (-NH-(CH-(C=O))-**C**H_2-C-), 28.43 (-$SiMe_2$-**C**-Me_3), 26.06 (-NH-(C=O)-O-C-**Me$_3$**), 21.63 (-$SiMe_2$-C-**Me$_3$**), 18.56 (CH-(C-CH-)-**Me**), 1.16 (-Si**Me$_2$**-tBu). m / z [$M+Na^+$] = 844.50

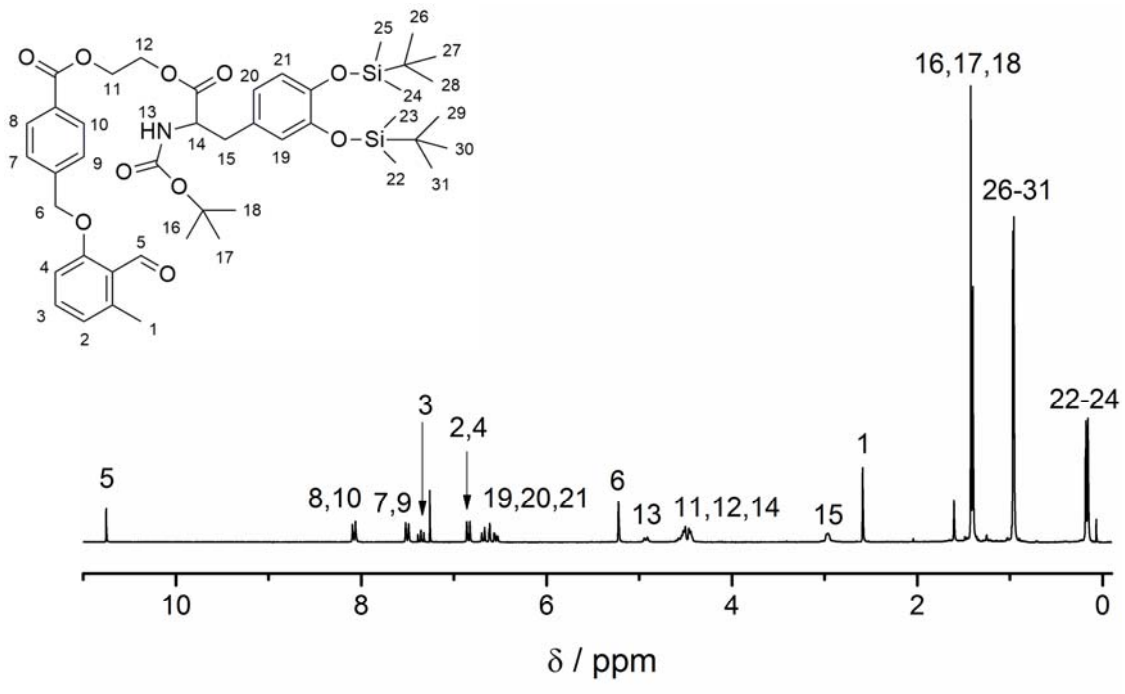
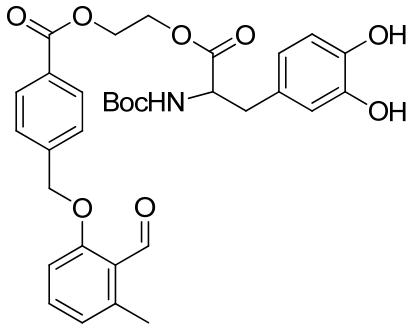
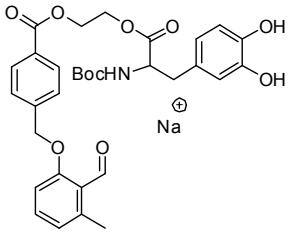


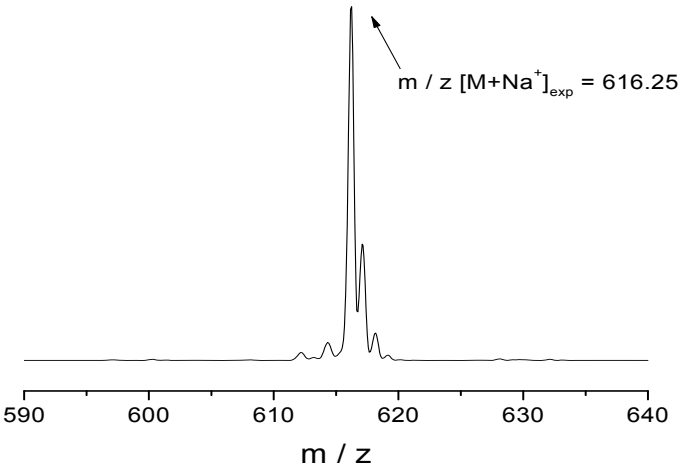
Figure 2 *^{1}H-NMR spectrum of Photo-DOPA-TBDMS$_2$ (4).*



Synthesis of 2-((2-((tert-butoxycarbonyl)amino)-3-(3,4-dihydroxyphenyl)propanoyl)oxy)ethyl 4-((2-formyl-3-methylphenoxy)methyl)benzoate ***(Photo-DOPA) (5)***

Photo-DOPA-$TBDMS_2$ **(4)** (0.4 g, 0.487 mmol) was dissolved in THF (2 mL). TBAF (0.973 mL, 0.973 mmol) in THF (1.0 M) was added and the mixture was stirred for 30 minutes at ambient temperature. The solvent was removed. The raw product was dissolved in DCM and washed with water (2×), HAc diluted (0.05 M) (2×), brine (2×) and water (2×). The organic fraction was dried over $MgSO_4$ and the solvent removed. m / z $[M+Na^+]$ = 616.25. The product was applied for the surface reactions immediately.





Synthesis of maleimide functional PTFEMA ***(PTFEMA-maleimide)***

In a 20 mL Schlenk tube, equipped with a stirring bar, 2,2,2-trifluoroethyl methacrylate (TFEMA, 2.94 g, 17.5 mmol), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 19.1 mg, 0.11 mmol), Cu(II)Br_2 (1.2 mg, 0.006 mmol), and 2-(1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethyl-2-bromo-2-methyl-propanoate (313.3 mg, 0.88 mmol) were dissolved in 2 mL anhydrous toluene. The tube was sealed with a stopper and three freeze-pump-thaw cycles were employed to remove oxygen from the solution. Next, Cu(I)Br (6.6 mg, 0.05 mmol) was added while the solution was frozen under a nitrogen atmosphere and a further freeze-pump-thaw cycle was conducted. The polymerization was

carried out in an oil bath at 60°C for 2 h and was quenched by cooling in an ice bath and flushed with air. The reaction mixture was then diluted with THF, passed through a column with neutral Al_2O_3 in order to remove the copper catalyst and precipitated in ice cold n-hexane. $M_{n,SEC}$ = 3700 g mol^{-1}, $Đ$ = 1.27 (THF SEC, PMMA calibration). The deprotection of the furan-protected malemide moiety was conducted by immersing PTFEMA-Mal-furan (0.5 g, 0.072 mmol) in toluene (10 mL) and refluxation for 5 h. Subsequently, the solvent was removed *in vacuo* resulting in MI-PTFEMA. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.74 (s, 2H, C**H**=C**H**), 4.34 (s, C**H$_2$**-CF_3), 4.22 – 4.13 (m, 2H, O-C**H$_2$**), 3.88 – 3.76 (m, 2H, N-C**H$_2$**), 2.16 – 1.88 (m, -C**H$_2$** backbone), 1.82 (s, 6H, -C**H$_3$**), 1.18 – 0.86 (m, -C**H$_3$** backbone).

Tris-buffer solution: A Tris buffer solution (0.3 M, pH = 8.5) was prepared following the procedure of Ryou *et al.*[6]

*Surface attachment of Photo-DOPA **(5)** on gold substrates, PET and graphite*

Gold substrates (1×1 cm^2), PET substrates (1×1 cm^2) and graphite substrates (1×1 cm^2) were employed. The gold substrates were cleaned with a plasma cleaner just before deposition.

In a saturated atmosphere of ethanol and water (1:1), the substrates were placed in a petri-dish and 60 µL of the freshly prepared Tris-buffer solution were added to each surface. Straight afterwards, Photo-DOPA **(5)** (2.7 mg, 4.55 µmol) was dissolved in dry EtOH (0.06 mL) (per sample) and added to each surface employing an Eppendorf pipette. The surfaces were left for 12 hours at ambient temperature under ethanol/water atmosphere. Afterwards, the surfaces were washed with milli-Q water, ethanol and were left in DCM for 15 minutes before they were washed with DCM again. The samples were dried in a nitrogen stream. Surface characterization was performed *via* XPS spectroscopy.

Surface Photo-Click reactions

For the Photo-Click reaction between the photoenol moiety and a maleimide-carrying polymer chain or peptide, a photoreactor as described by Pauloehrl *et al.* was employed (***Figure 3***).[11b] The samples were irradiated with a low-pressure fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany) emitting at 320 nm (± 30 nm, 36 W).[11b]

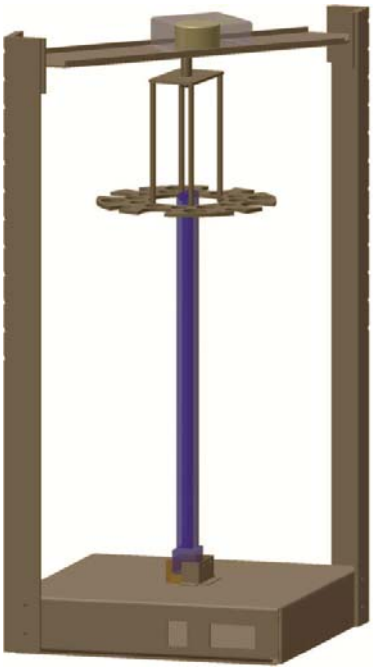


Figure 3 *Schematic setting of the photo-reactor. The Arimed B6 (Cosmedico GmbH, Stuttgart, Germany) in the middle (blue) emits irradiation in the UVA region (λ≈ 320 nm). The samples are situated in the wheel-shaped disc in the upper part of the reactor, which rotates while the samples are irradiated.*[11b] *The picture was drawn by Till Gruendling.*

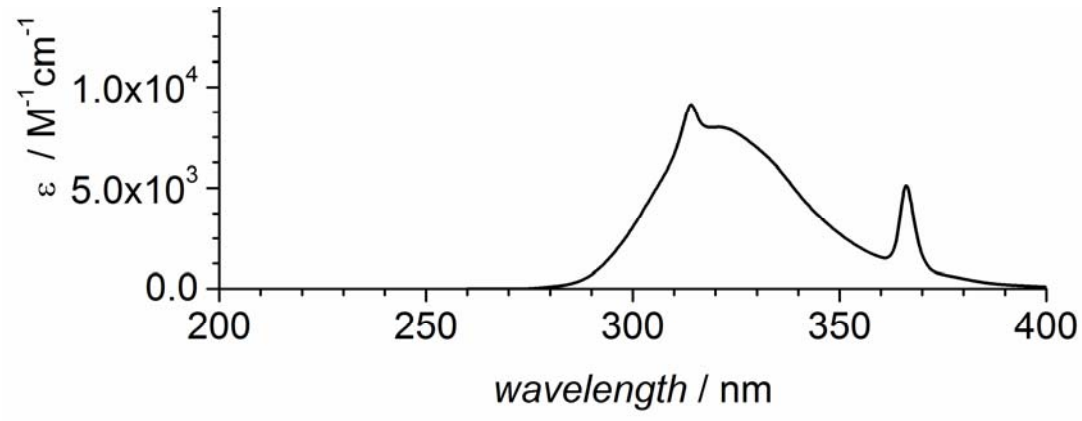
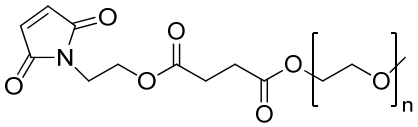


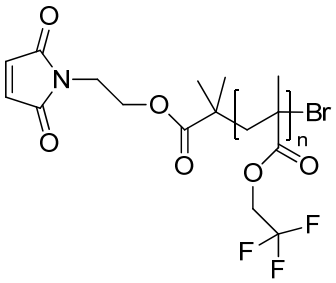
Figure 4 *Emission spectrum of the UVA lamp Arimed B6 (36 W, λ = 320 nm ± 30 nm).*

Employed maleimides

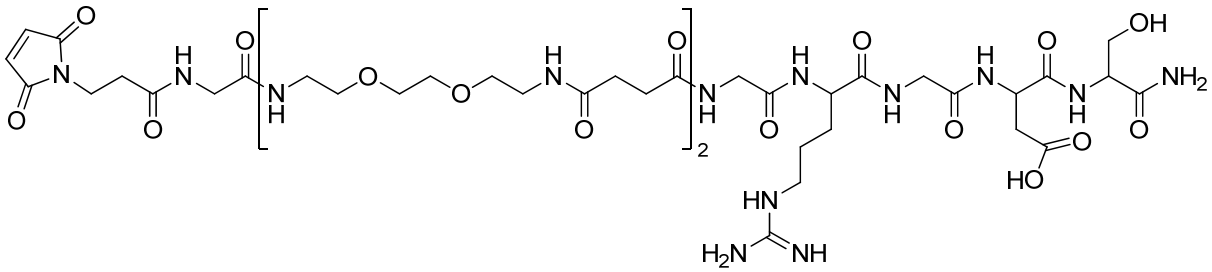
a) PEG-maleimide



b) PTFEMA-maleimide



c) Peptide-maleimide (PEP-Mal)



The Au-PE-DOPA surfaces were reacted with (a) PEG-maleimide, (b) PTFEMA-maleimide and a (c) PEP-maleimide. PET-PE-DOPA was photo-ligated with (c). The detailed procedures are depicted below.

Photo-Click reaction of (a) and (b) on surfaces

The prepared photo-reactive surfaces were placed (upright) in a headspace vial (Pyrex, diameter 20 mm). 5 mg of PEG-maleimide (a) or PTFEMA-maleimide (b) were dissolved in 4 mL dry acetonitrile and the mixture was added to the vial. The vial was crimped air-tight using SBR seals with PTFE inner liner and was degassed with nitrogen for 30 minutes, before it was placed into the photo reactor and irradiated (λ = 320 nm) for 60 minutes. The surface was washed with acetonitrile, milli-Q water, left in DCM for 20 minutes and washed with DCM. The samples were dried in a nitrogen stream. Modified version of [11b]. Characterization was performed *via* XPS spectroscopy.

Photo-Click reaction of (c) on surfaces

The prepared photo-reactive surfaces were placed (upright) in a headspace vial (Pyrex, diameter 20 mm). 4 mg of Peptide-maleimide (c) were dissolved in 4 mL of a acetonitrile/milli-Q water mixture (3:1) and the mixture was added to the vial. The vial was crimped air-tight using SBR seals with PTFE inner liner and was degassed with nitrogen for 30 minutes, before it was placed into the photo reactor and irradiated (λ = 320 nm) for 60 minutes. The surface was washed with acetonitrile, milli-Q water, left in milli-Q water for 20 minutes and washed with acetonitrile again. The samples were dried in a nitrogen stream. Modified version of [11b]. Characterization was performed *via* XPS spectroscopy.

Area-resolved photo-patterning with PTFMA-maleimide

For the demonstration of area-resolved patterning *via* photo-ligation of a DOPA-photoenol surface and a maleimide-carrying molecule, the Au-Photo-DOPA (Au-PE-DOPA) surface and the PTFEMA-maleimide were employed as a model system. The freshly prepared Au-PE-DOPA surface was covered with a shadow mask and fixed in a holder to prevent irradiation of the whole surface (*Figure 5*). The unmasked part (meander structure) was uncovered. The experiment was performed with the equipment that was already described by Pauloehrl *et al*.[11b]

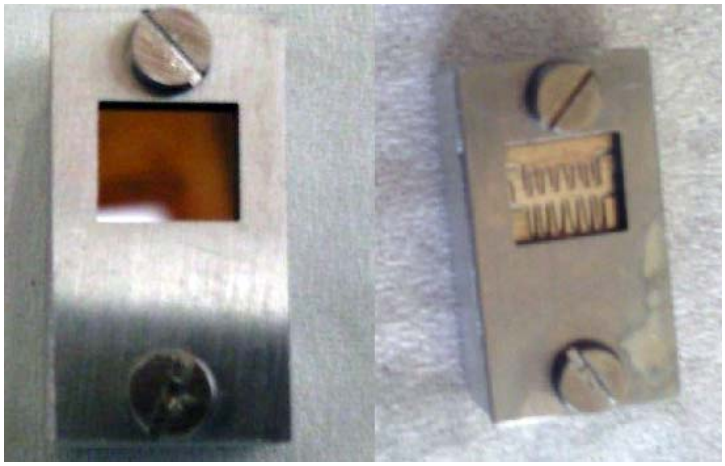


Figure 5 *Shadow mask for the photo patterning on the Au-PE-DOPA surface with a square cut in the metal plate (left) and the shadow mask that possesses a meander structure (right).*

The prepared photo-reactive surfaces (masked and in the holder) were placed (upright) in a headspace vial (Pyrex, diameter 20 mm). 5 mg of PTFEMA-maleimide (b) were dissolved in 4 mL dry acetonitrile and the mixture was added to the vial. The vial was crimped air-tight using SBR seals with PTFE inner liner and was degassed with nitrogen for 30 minutes, before it was placed into the photo reactor and irradiated (λ = 320 nm) for 60 minutes. The surface was washed with acetonitrile, milli-Q water, left in DCM for 20 minutes and washed with DCM. The samples were dried in a nitrogen stream. Characterization was performed *via* ToF-SIMS.

Surface characterization

Attachment of Photo-DOPA to graphite (graphite-PE-DOPA)

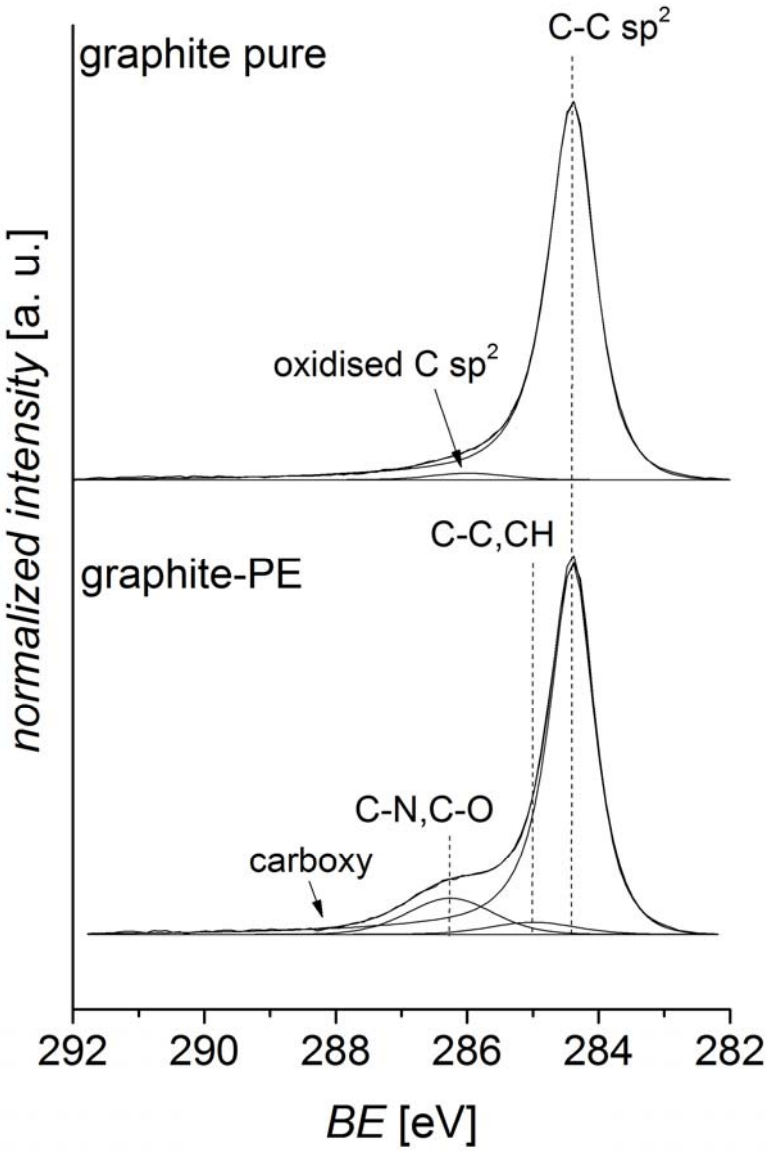


Figure 6 *The XPS data of the C1s orbital of the surface attachment onto graphite is depicted. The signal for the C-C sp^2 of the graphite substrate at 284.4 eV serves as reference peak (upper part). After the surface attachment of Photo -DOPA to form graphite-PE-DOPA, additional peaks appeared, such as the signal assigned to C-C and C-H bonds at 285.0 eV and the C-O and C-N signal at 286.3 eV. The signal for the corresponding carboxyl groups most likely vanishes in the characteristic tail caused by the graphite substrate. All peaks were compared with reference* [22] *and could be assigned.*

F 1s spectrum of Au-PE-DOPA-PTFEMA

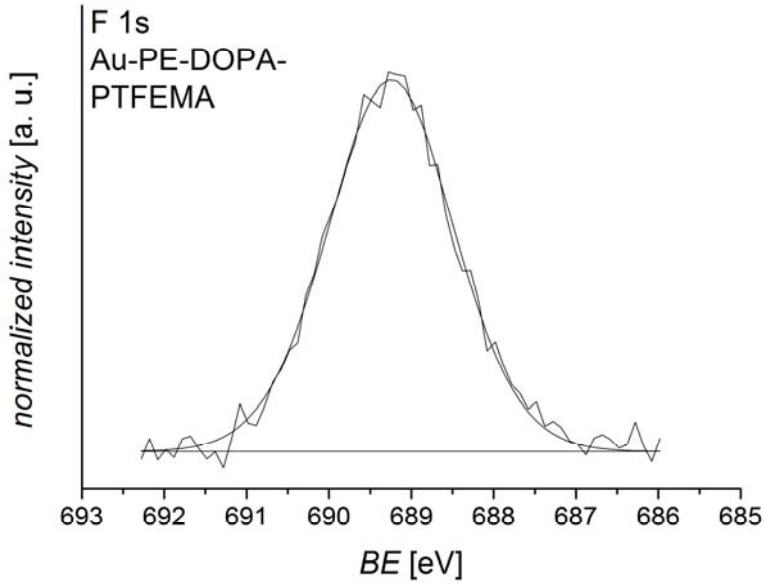


Figure 7 *F 1s spectrum of the Au-PE-DOPA surface after PTFEMA photo-grafting. The appearance of the C-F peak at 689.3 eV clearly approves the successful attachment.*[15a]

Photo-ligation of PEP-maleimide on PET-PE-DOPA

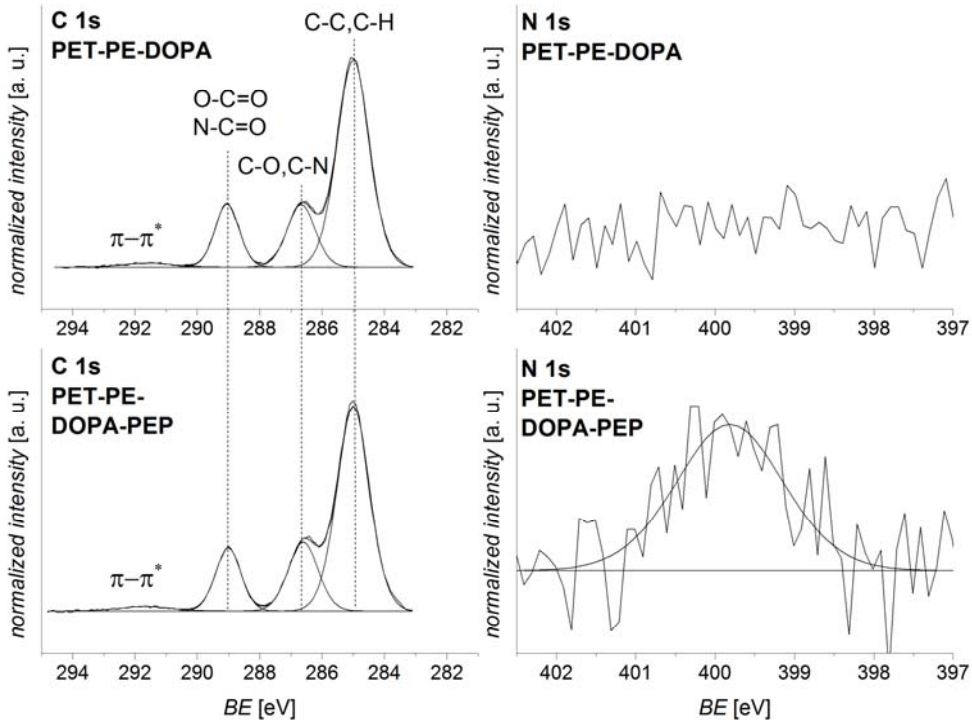


Figure 8 *The C 1s and N1s spectra of the photo-ligation of the PEP-maleimide to PET-PE-DOPA is depicted. The change in the C 1s spectrum is very slight due to the strong and dominant signals of the substrate itself. Therefore, the N 1s spectra are compared additionally, which clearly show the successful attachment as the signal in the N1s region exhibits a strong increase.*

[1] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426-430.

[2] a) M. d'Ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, *Angewandte Chemie-International Edition* **2009**, *48*, 3914-3921; b) J. Liebscher, R. Mrówczyński, H. A. Scheidt, C. Filip, N. D. Hădade, R. Turcu, A. Bende, S. Beck, *Langmuir* **2013**.

[3] a) O. Pop-Georgievski, N. Neykova, V. Proks, J. Houdkova, E. Ukraintsev, J. Zemek, A. Kromka, F. Rypaček, *Thin Solid Films* **2013**, *DOI: 10.1016/j.tsf.2012.11.128*; b) O. Pop-Georgievski, Š. Popelka, M. Houska, D. Chvostová, V. Proks, F. Rypáček, *Biomacromolecules* **2011**, *12*, 3232-3242.

[4] M. Yu, J. Hwang, T. J. Deming, *Journal of the American Chemical Society* **1999**, *121*, 5825-5826.

[5] M. d'Ischia, A. Napolitano, A. Pezzella, P. Meredith, T. Sarna, *Angewandte Chemie International Edition* **2009**, *48*, 3914-3921.

[6] M.-H. Ryou, Y. M. Lee, J.-K. Park, J. W. Choi, *Adv. Mater.* **2011**, *23*, 3066-3070.

[7] B. H. Kim, D. H. Lee, J. Y. Kim, D. O. Shin, H. Y. Jeong, S. Hong, J. M. Yun, C. M. Koo, H. Lee, S. O. Kim, *Adv. Mater.* **2011**, *23*, 5618-5622.

[8] a) G. Bilic, C. Brubaker, P. B. Messersmith, A. S. Mallik, T. M. Quinn, C. Haller, E. Done, L. Gucciardo, S. M. Zeisberger, R. Zimmermann, J. Deprest, A. H. Zisch, *American Journal of Obstetrics and Gynecology* **2010**, *202*, 85 e81-89; b) K. C. L. Black, J. Yi, J. G. Rivera, D. C. Zelasko-Leon, P. B. Messersmith, *Nanomedicine* **2012**, *8*, 17-28; c) D. E. Fullenkamp, J. G. Rivera, Y.-k. Gong, K. H. A. Lau, L. He, R. Varshney, P. B. Messersmith, *Biomaterials* **2012**, *33*, 3783-3791; d) C. M. Haller, W. Buerzle, C. E. Brubaker, P. B. Messersmith, E. Mazza, N. Ochsenbein-Koelble, R. Zimmermann, M. Ehrbar, *Prenat. Diagn.* **2011**, *31*, 654-660; e) O. Pop-Georgievski, C. Rodriguez-Emmenegger, A. d. l. S. Pereira, V. Proks, E. Brynda, F. Rypacek, *Journal of Materials Chemistry B* **2013**, *1*, 2859-2867.

[9] a) O. Pop-Georgievski, S. t. p. n. Popelka, M. Houska, D. Chvostová, V. r. Proks, F. e. Rypáček, *Biomacromolecules* **2011**, *12*, 3232-3242; b) A. S. Goldmann, C. Schödel, A. Walther, J. Yuan, K. Loos, A. H. E. Müller, *Macromolecular Rapid Communications* **2010**, *31*, 1608-1615; c) J. Wang, M. N. Tahir, M. Kappl, W. Tremel, N. Metz, M. Barz, P. Theato, H.-J. Butt, *Adv. Mater.* **2008**, *20*, 3872-3876; d) K. J. Coyne, X.-X. Qin, J. H. Waite, *Science* **1997**, *277*, 1830-1832; e) C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns, A. S. Goldmann, M. Bastmeyer, C. Barner-Kowollik, *Adv. Mater.* DOI: 10.1002/adma.201302492; f) V. Proks, J. Jaroš, O. Pop-Georgievski, J. Kučka, Š. Popelka, P. Dvořák, A. Hampl, F. Rypáček, *Macromolecular Bioscience* **2012**, *12*, 1232-1242.

[10] a) J. A. G. King, A. Percival, N. C. Robson, G. A. Swan, *Journal of the Chemical Society C: Organic* **1970**, 1418-1422; b) P. A. Baldry, G. A. Swan, *Journal of the Chemical Society, Perkin Transactions 2* **1977**, 1346-1350; c) G. A. Swan, A. Waggott, *Journal of the Chemical Society C: Organic* **1970**, 1409-1418.

[11] a) T. Gruendling, K. K. Oehlenschlaeger, E. Frick, M. Glassner, C. Schmid, C. Barner-Kowollik, *Macromolecular Rapid Communications* **2011**, *32*, 807-812; b) T. Pauloehrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H. G. Börner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik, *Angewandte Chemie International Edition* **2012**, *51*, 1071-1074.

[12] K. K. Oehlenschlaeger, J. O. Mueller, N. B. Heine, M. Glassner, N. K. Guimard, G. Delaittre, F. G. Schmidt, C. Barner-Kowollik, *Angewandte Chemie International Edition* **2013**, *52*, 762-766.

[13] a) T. Pauloehrl, G. Delaittre, M. Bruns, M. Meißler, H. G. Börner, M. Bastmeyer, C. Barner-Kowollik, *Angewandte Chemie International Edition* **2012**, *51*, 9181-9184; b) T. Pauloehrl, A. Welle, M. Bruns, K. Linkert, H. G. Börner, M. Bastmeyer, G. Delaittre, C. Barner-Kowollik, *Angewandte Chemie International Edition* **2013**, 52, 9714–9718; c) T. Pauloehrl, A. Welle, K. K. Oehlenschlaeger, C. Barner-Kowollik, *Chemical Science* **2013**, *4*, 3503-3507.

[14] M. Bruns, C. Barth, P. Brüner, S. Engin, T. Grehl, C. Howell, P. Koelsch, P. Mack, P. Nagel, V. Trouillet, D. Wedlich, R. G. White, *Surface and Interface Analysis* **2012**, *44*, 909-913.

[15] a) R. Chebbi, A. Beicha, W. R. W. Daud, R. Zaamouche, *Applied Surface Science* **2009**, *255*, 6367-6371; b) S. Agraharam, D. W. Hess, P. A. Kohl, S. A. Bidstrup-Allen, *Journal of the Eletrochemical Society* **1999**, *146*, 1960-1965.

[16] M. Glassner, K. Kempe, U. S. Schubert, R. Hoogenboom, C. Barner-Kowollik, *Chemical Communications* **2011**, *47*, 10620-10622.

[17] B. P. Lee, K. Huang, F. N. Nunalee, K. R. Shull, P. B. Messersmith, *Journal of Biomaterials Science-Polymer Edition* **2004**, *15*, 449-464.

[18] G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornelissen, K. Velonia, *Journal of the American Chemical Society* **2005**, *127*, 2966-2973.

[19] K. L. Parry, A. G. Shard, R. D. Short, R. G. White, J. D. Whittle, A. Wright, *Surface and Interface Analysis* **2006**, *38*, 1497-1504.

[20] S. J.H, *J. Electron. Spectrosc. Relat. Phenom.* **1976**, *8*, 129-137.

[21] S. Tanuma, C. J. Powell, D. R. Penn, *Surface and Interface Analysis* **1994**, *21*, 165-176.

[22] N. Zydziak, C. Hubner, M. Bruns, A. P. Vogt, C. Barner-Kowollik, *Polymer Chemistry* **2013**, *4*, 1525-1537.