Electronic Supplementary Information:

Instrumentation

For optical and fluorescent microscopy imaging an Olympus CKX 41 microscope was operated with an Olympus XC 10 camera and a X-Cite® Series 120Q by Lumen Dynamics as the irradiation source. For fluorescent images suitable filters were used. Data processing was carried out with the software Stream Essentials (v. 1.9). Images were taken at 50-fold magnification with an exposure time of 600 ms. Insertion of scale bars and image corrections were carried out with ImageJ (v. 1.51).

AFM measurements were performed using a Nano Wizard(JPK Instruments AG) in tapping mode under air on silicon surfaces. The obtained images were processed with Gwyddion (v. 2.40).

XPS analyses of surfaces were done with a Kratos Axis Ultra (Kratos) using monochromated Al Kα irradiation with an excitation energy of 1486.6 eV. For region scans a pass energy of 0.02 eV was employed. The data were analyzed with CasaXPS Software Suite v2315. All spectra were calibrated to the binding energy of the C1s-orbital in aliphatic carbon-carbon chains (285 eV).

NMR spectra were recorded on an AV-300-spectrometer with 300.1 Hz (^{1}H), 75.5 Hz (^{13}C) (*Bruker*, Karlsruhe, Germany) and a Avance II 400 spectrometer with 400 Hz (^{1}H), 100 Hz (^{13}C) (*Bruker*, Karlsruhe, Germany). All measurements were performed in deuterated solvents. The chemical shifts (δ) are reported in parts per million (ppm) and relative to the residual solvent signals. The measured coupling constants are given in Hertz (Hz).

Chemicals

All chemicals were purchased from Acros Organics, Fischer Scientific GmbH, Schwerte, Germany, Aldrich, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany and Alfa Aesar, Alfa Aesar GmbH & Co KG, Karlsruhe, Germany and used without further purification.

Preparation of PDMS stamps

Poly(dimethyl siloxane) (PDMS) stamps were prepared from Sylgard 184 provided by Dow Corning. PDMS and curing agent were mixed in a ratio of 10:1 and stirred for 10 min by hand. The mixture was poured onto a structured silicon wafer and cured at 80°C overnight. After removing the PDMS from the silicon waver the structured stamps were cut out with a scalpel and treated for 55 min with a UV ozonizer (PSD-UV, Novascan Technologies Inc.). If not used immediately, the PDMS stamps were stored in deionized water.

Preparation of octenyltrichlorosilane SAMs

Glass or silicon surfaces were cut into pieces of 28 x 14 mm. The pieces were sonicated in pentane, acetone and deionized water for 3 min each. Then they were immersed into a freshly prepared solution of piranha (H_2SO_4/H_2O_2 – 3/1) and stirred for 30 min, before they were extensively washed with deionized water and dried under an argon stream. The clean and dry surfaces were then immersed in a freshly prepared solution of octenyltrichlorosilane (0.1 vol%) in toluene (20 ml) for 1 h. Afterwards the surfaces were washed with dichloromethane, ethanol and deionized water.

Microcontact printing

The ink solution contained 50 mM of ATRP-TAD[1] in acetonitrile. The freshly prepared ink solution (30 µl (for patterned stamps) or 60 µl (for flat stamps)) was placed on a freshly oxidized PDMS stamp for 1 min of incubation. The stamp was then dried with an argon stream before it was placed on an octenyltrichlorosilane SAM. The stamp was pressed gently to the surface. After a reaction time of 10 min the stamp was removed, and the surface was extensively washed with dichloromethane, ethanol and deionized water before they were used for polymerization.

Surface initiated polymerization for PCDA-PHEA brushes

Hydroxyethyl acrylate (3.03 g, 26.1 mmol), β-cyclodextrin acrylate (1.40 g, 1.3 mmol) and a solution (100 µL) of ethyl-α-bromo isobutyrate (1.8 mg, 9.4 µmol) in DMF (1 ml) were added to a schlenk tube containing initiator functionalized substrates. A vortexed solution (1 mL) of Cu(II)Br2 (0.5 mg, 2.2 µmol) and tris[2-(dimethylamino)ethyl]amine (3.6 mg, 11 µmol) in DMF (10 mL) was added. The solution was sonicated. Then the tube was purged with argon and subjected to three freeze/thaw circles with intermediate argon purges. Afterwards ascorbic acid (24 mg, 141 µmol) was added und argon and the tube was placed in an oil bath at 80 °C for 16 h. The surfaces were sonicated in DMF (15 min), MeOH (15 min) and deionized water (15 min) and dried in an argon stream.

Surface initiated polymerization for PAAPA-PHEA brushes

Hydroxyethyl acrylate (3.03 g, 26.1 mmol), AAP acrylate (1.50 g, 3.9 mmol) and a solution (100 µL) of ethyl-α-bromo isobutyrate (1.8 mg, 9.4 µmol) in DMF (1 ml) were added to a schlenk tube containing initiator functionalized substrates. A vortexed solution (1 mL) of Cu(II)Br2 (0.5 mg, 2.2 µmol) and tris[2-(dimethylamino)ethyl]amine (3.6 mg, 11 µmol) in DMF (10 mL) was added. The tube was purged with argon and subjected to three freeze/thaw circles with intermediate argon purges. Afterwards ascorbic acid (24 mg, 141 µmol) was added und argon and the tube was placed in an oil bath at 80 °C for 16 h. The surfaces were sonicated in DMF (15 min), MeOH (15 min) and deionized water (15 min) and dried in an argon stream.

[1] O. Roling, K. De Bruycker, B. Vonhören, L. Stricker, M. Körsgen, H. F. Arlinghaus, B. J. Ravoo, F. E. Du Prez, *Angew. Chem. Int. Ed.*, 2015, **54**, 13126-13129.

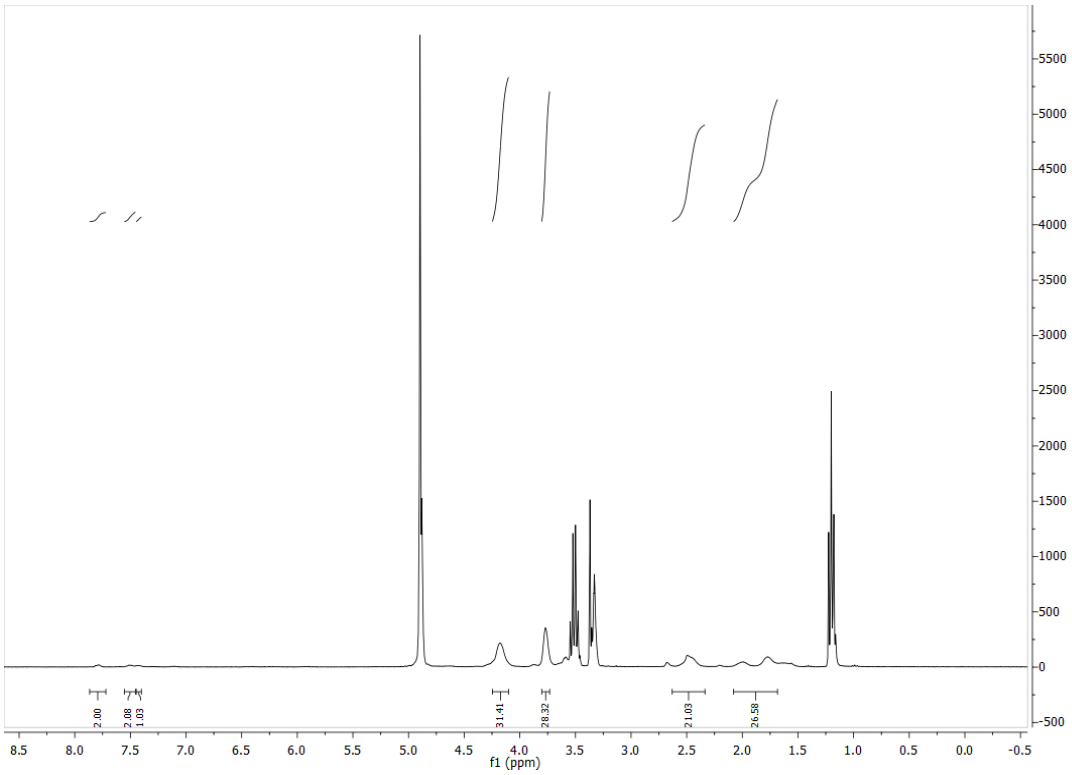


Figure S1: ^{1}H-NMR (300 MHz, MeOD) of PAAPA-PHEA polymerized in solution.

Preparation of Ir(dfppy)$_2$-Ad stained PCDA-PHEA surfaces

After polymerization process a solution of Ir(dfppy)$_2$-Ad in water (50 µM) was placed on the dried PCDA-PHEA glass surfaces. The interaction time was set to 10 min. After that time the surfaces were rinsed with deionized water, dried with an argon stream, and analysed by fluorescence microscopy.

Preparation of sulforhodamin labelled β-CD stained PAAPA-PHEA surfaces

After polymerization process a solution of sulforhodamin labelled β-CD in water (25 mg/ 500 µL) was placed on the dried PAAPA-PHEA glass surfaces. The interaction time was set to 10 min. After that time the surfaces were rinsed with deionized water, dried with an argon stream, and analysed by fluorescence microscopy.

β-CD and AAP polymers

β-CD polymer was obtained from Sigma Aldrich and used as received. AAP acrylamide copolymer was synthesized as described in the literature.[2] In brief, AAPA (208 mg, (0.5 mmol, 1 eq.) and acrylamide (267 mg, 37.5 mmol, 75 eq.) were dissolved in DMF (40 mL) and AIBN (0.3 mg) was added so that the total monomer/initiator ratio was 300:1. Subsequently, the mixture was stirred overnight at 60°C. The resulting turbid solution was precipitated by the addition of MeOH and the solid was collected by centrifugation (10000 RCF, 2 min).

[2] H. Yamaguchi, Y. Kobayashi, R. Kobayashi, Y. Takashima, A. Hashidzume, A. Harada, *Nature Commun.*, 2012, **3**, Article number: 603.

Supramolecular gluing

SysI: To adhere two PAAPA-PHEA surfaces to one of the surfaces a drop of deionized water was added and to the other a drop of a β-CD-polymer in deionized water was given. After 10 min of interaction time, the surfaces were gently rinsed with deionized water to remove excess β-CD polymer. Then, the surfaces were pressed onto each other and dried for 60 min before further use.

SysII: To adhere two PCDA-PHEA surfaces to one of the surfaces a drop of deionized water was added and to the other a drop of an AAP acrylamide copolymer in deionized water was given. After 10 min of interaction time, the surfaces were gently rinsed with deionized water to remove excess AAP acrylamide copolymer. Then, the surfaces were pressed onto each other and dried for 60 min before further use.

SysIII: To adhere a PCDA-PHEA surface to a PAAPA-PHEA surface a drop of deionized water was added to both surfaces. After 10 min the surfaces were pressed onto each other and dried for 60 min before further use.

Maximum weight tests

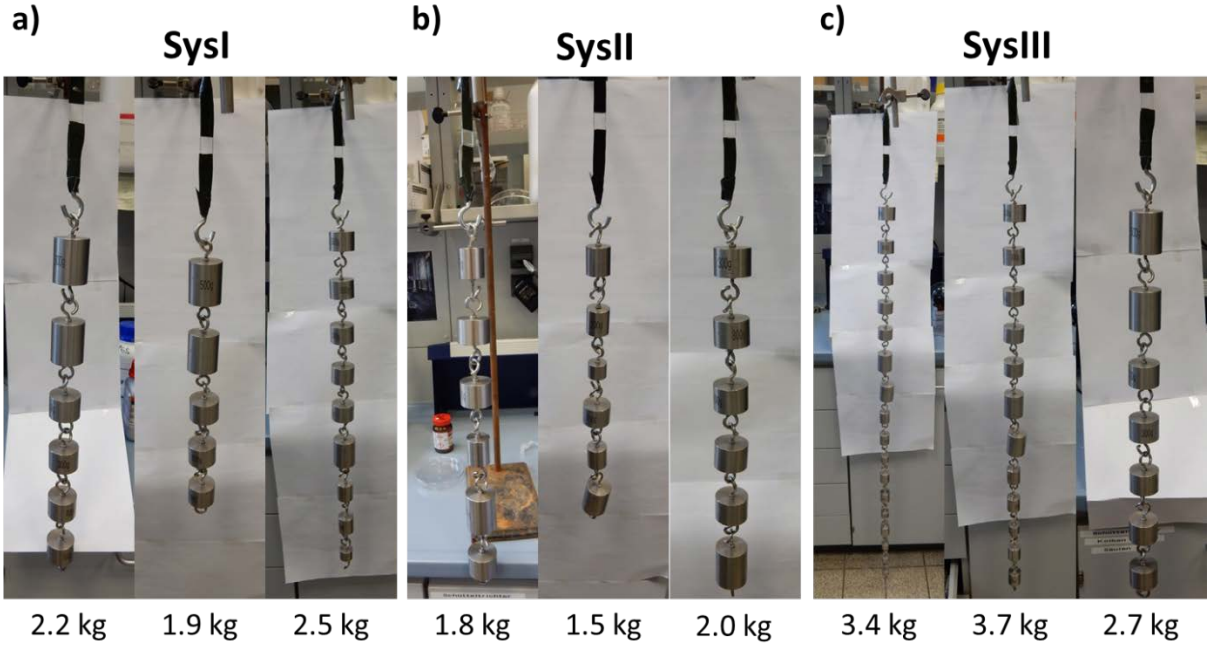


Figure S2: Maximum weight test of all three systems to calculate an average weight.

Reusability tests

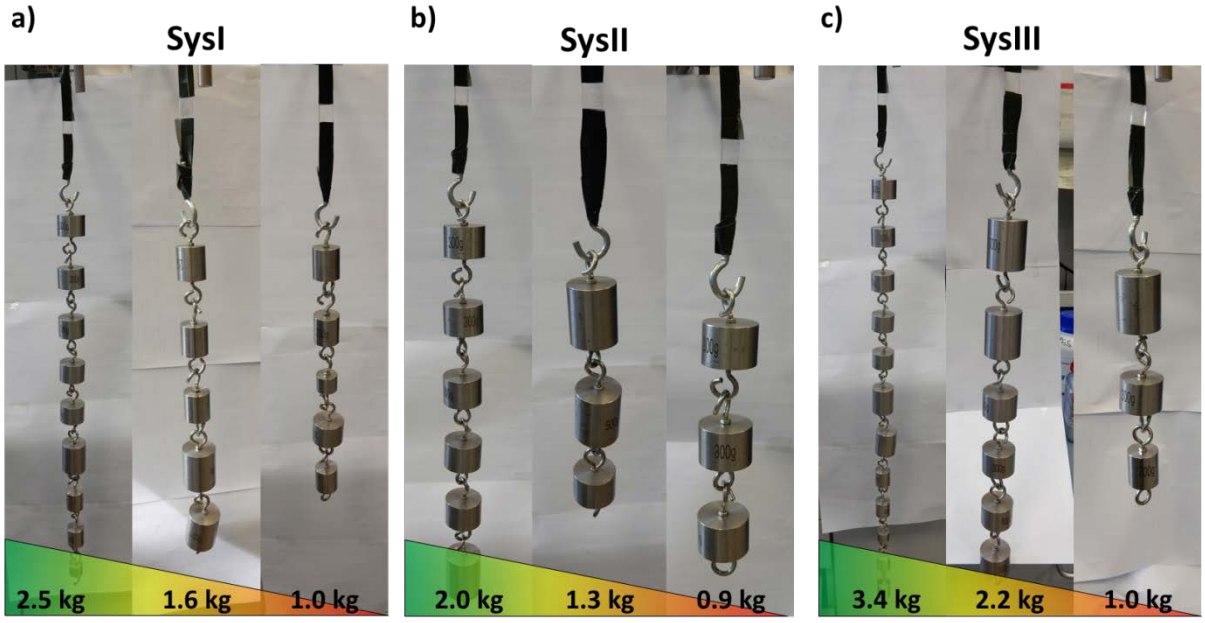


Figure S3: Three different repeated gluing experiments of the PAAPA-PHEA and PCDA-PHEA surfaces with cleaning step in between. a) SysI: First gluing 2.5 kg*cm^{-1}; second gluing 1.6 kg*cm^{-1}; third gluing 1.0 kg*cm^{-1}; b) SysII: First gluing 2.0 kg*cm^{-1}; second gluing 1.3 kg*cm^{-1}; third gluing 0.9 kg*cm^{-1}; c) SysIII: First gluing 3.4 kg*cm^{-1}; second gluing 2.2 kg*cm^{-1}; third gluing 1.0 kg*cm^{-1}.

XPS N1s signal of PAAPA-PHEA surfaces

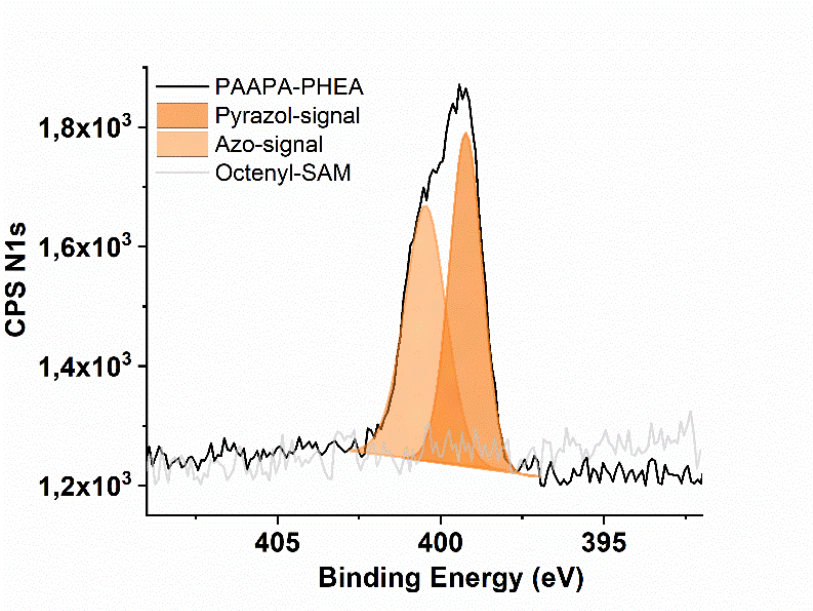


Figure S4: XPS measurement of the nitrogen region from the PAAPA-PHEA surfaces.

UV/vis measurements of AAP acrylamide polymer on a PCDA-PHEA surface

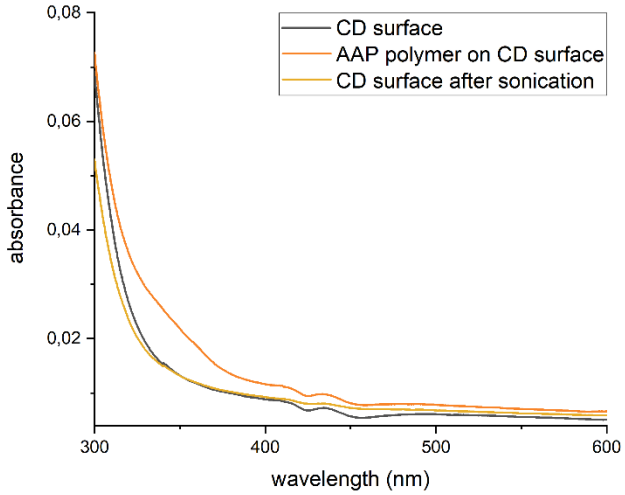


Figure S5: UV/vis-measurement of PCDA-PHEA surface (black), an AAP acrylamide polymer interacting with the PCDA-PHEA surface (orange) and the same PCDA-PHEA surface after sonication in deionized water (yellow).

AFM measurements of PAAPA-PHEA and PCDA-PHEA surfaces after gluing and rupture

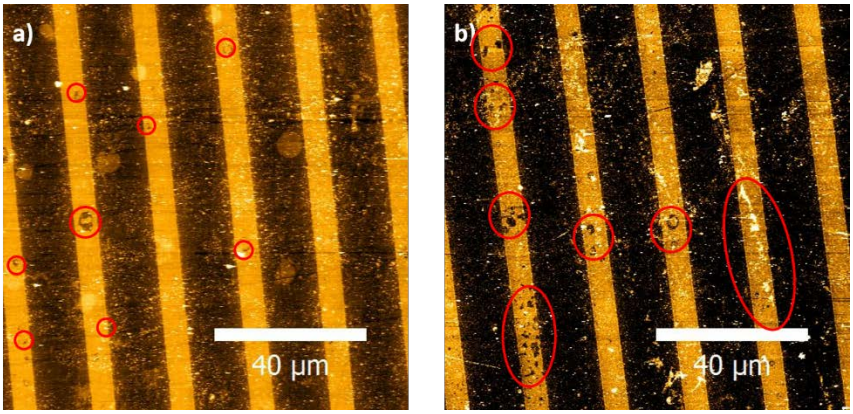
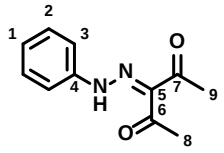


Figure S6: a) PCDA-PHEA surface after gluing and rupture with little holes on the brushes, where polymer brushes were ripped out. b) PAAPA-PHEA surface after gluing and rupture with little holes on the brushes, where polymer brushes were ripped out.

Synthesis:

The synthesis of the AAP acrylate was carried out according to a literature procedure.[3]

3-(2-Phenylhydrazono)pentane-2,4-dione



$NaNO_2$ (0.61 g, 8.86 mmol, 1.2 eq.) dissolved in a minimum amount of water was added dropwise to a solution of aniline (0.67 mL, 7.38 mmol, 1.0 eq.) in AcOH (11 mL) and HCl (12 M, 1.7 mL) at 0 °C. After stirring for 30 minutes the resulting diazonium salt was transferred to a suspension of pentane-2,4-dione (0.98 mL, 9.6 mmol, 1.3 eq.) and NaOAc (1.82 g, 22.14 mmol, 3 eq.) in EtOH (7.4 mL) and water (4.5 mL). The mixture was stirred for 30 min and the resulting yellow precipitate was collected *via* vacuum filtration. After washing with water and water/EtOH (1:1) the yielded solid was dried under vacuum affording the desired compound.

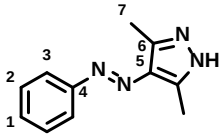
Yield: 1.21 g (5.90 mmol, 80%) as yellow solid.

^{1}H-NMR: (300 MHz, $CDCl_3$) δ = 14.74 (s, 1H, NH), 7.44 – 7.39 (m, 4H, H-2, H-3), 7.25 – 7.16 (m, 1H, H-1), 2.61 (s, 3H, H-8), 2.50 (s, 3H, H-9) ppm.

^{13}C-NMR: (75 MHz, $CDCl_3$) δ = 198.09 (C-6), 197.27 (C-7), 141.65 (C-4), 133.34 (C-5), 129.80 (C-2), 126.04 (C-1), 116.40 (C-3), 31.84 (C-8), 26.80 (C-9) ppm.

MS (m/z): (ESI, MeOH) Calculated for $[C_{11}H_{12}N_2O_2Na]^+$: 227.0791, found 227.0800.

(*E*)-3,5-Dimethyl-4-(phenyldiazenyl)-1*H*-pyrazole



Hydrazine x hydrate (0.23 mL, 5.74 mmol, 1 eq.) was added to a solution of 3-(2-phenylhydrazono)pentane-2,4-dione (1.20 g, 5.74 mmol, 1 eq.) dissolved in EtOH and refluxed for 3 hours. Concentration under reduced pressure yielded the resulting arylazopyrazole without further purification.

Yield: 1.15 g (5.74 mmol, quantitative) as orange solid.

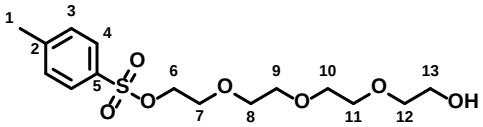
^{1}H-NMR: (400 MHz, $CDCl_3$) δ = 9.73 (s, 1H, NH), 7.93 – 7.74 (m, 2H, H-3), 7.52 – 7.42 (m, 2H, H-2), 7.42 – 7.35 (m, 1H, H-1), 2.62 (s, 6H, H-7) ppm.

^{13}C-NMR: (101 MHz, $CDCl_3$) δ = 153.67 (C-4), 141.62 (C-6), 134.87 (C-5), 129.66 (C-1), 129.05 (C-2), 121.98 (C-3), 12.30 (C-7) ppm.

MS (m/z): (ESI, MeOH) Calculated for $[C_{11}H_{12}N_4H]^+$: 201.1135, found 201.1135.

[3] S. Sagebiel, L. Stricker, S. Engel, B. J. Ravoo, *Chem. Commun.*, 2017, **53**, 9296-9299.

2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl-4-methylbenzenesulfonate (TsO-TEG-OH)



To a solution of tetraethylene glycol (22.0 g, 113 mmol, 10.3 eq.) in THF (4 mL), a solution of NaOH (690 mg, 17.1 mmol, 1.6 eq.) in water (4 mL) was added at 0 °C. At the same temperature a solution of *p*-toluenesulfonyl chloride (2.08 g, 10.9 mmol, 1 eq.) in THF (13 mL) was added dropwise over 1 hour and stirred for 2 hours at 0 °C. The solution was poured into ice-water and the layers were separated. The aqueous layer was extracted with DCM (3 × 50 mL) and the organic layers were combined, washed with water (2 × 50 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The desired compound was used in the next step without further purification.

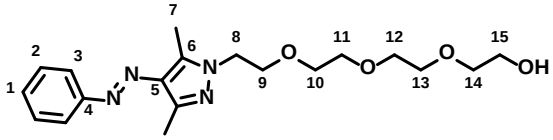
Yield: 3.50 g (10.1 mmol, 92%) as yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.3 Hz, 2H, H-4), 7.33 (d, *J* = 7.7 Hz, 2H, H-3), 4.15 (t, *J* = 4.9 Hz, 2H, H-6), 3.72 – 3.55 (m, 14H, H-7, H-8, H-9, H-10, H-11, H-12, H-13), 2.43 (s, 3H, H-1) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 144.93 (C-2), 133.04 (C-5), 129.93 (C-3), 128.07 (C-4), 72.56, 70.83, 70.74, 70.56, 70.42, 69.36, 68.79, 61.82 (C-6, C-7, C-8, C-9, C-10, C-11, C-12, C-13), 21.75 (C-1) ppm.

MS (m/z): (ESI, MeOH) Calculated for $[C_{15}H_{23}N_3O_6SNa]^+$: 396.1200, found 396.1197.

Tetraethyleneglycol functionalized arylazopyrazole (AAP-TEG)



To a stirred solution of AAP (2.51 g, 12.53 mmol, 1 eq.) in 150 ml of dry acetonitrile, containing K_2CO_3 (8.66 g, 62.67 mmol, 5 eq.) and catalytic amounts of LiBr, tosylated tetraethyleneglycol (5.26 g, 15.1 mmol, 1.2 eq.) dissolved in acetonitrile (50 mL) was added and the reaction mixture was refluxed for 3 days under argon. It was then allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in DCM (120 mL), washed with water (100 mL) and brine (3 × 100 mL). The organic phase was dried over $MgSO_4$ and concentratedThe crude product was purified by column chromatography (SiO_2, DCM/MeOH 97:3, R_f = 0.18).

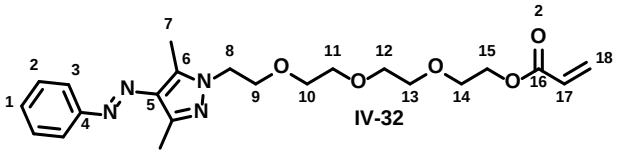
Yield: 4.21 g (11.19 mmol, 89%) as red oil.

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.72 (m, 2H, H-3), 7.46 (dd, *J* = 8.4, 6.9 Hz, 2H, H-2), 7.41 - 7.34 (m, 1H, H-1), 4.24 (t, *J* = 5.4 Hz, 2H, H-8), 3.88 (t, *J* = 5.4 Hz, 2H, H-9), 3.73 – 3.65 (m, 2H, H-10), 3.65 – 3.46 (m, 11H, OH, H-11, H-12, H-13, H-14, H-15), 2.63 (s, 3H, H-7), 2.51 (s, 3H, H-7) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$) δ = 153.70 (C-4), 142.51 (C-6), 140.67 (C-5), 135.03 (C-6), 129.52 (C-1), 129.04 (C-2), 121.90 (C-3), 72.59, 70.83, 70.73, 70.66, 70.46, 69.99, 61.82 (C-9, C-10, C-11, C-12, C-13, C-14, C-15), 49.17 (C-8), 14.12, 10.06 (C-7)ppm.

MS (m/z): (ESI, MeOH) Calculated for $[C_{19}H_{28}N_4O_4Na]^+$: 399.2003, found: 399.1999.

Synthesis of AAP acrylate



IV-32

Triethylamine (4.57 mL, 33 mmol, 3 eq.) was added to a solution of AAP-TEG (4.14 g, 11 mmol, 1 eq.) in dry DCM (50 mL). To this a solution of acryloylchloride (2.7 mL, 33 mmol, 3 eq.) in dry DCM (20 mL) was added dropwise at 0 °C. Afterwards the solution was allowed to warm to room temperature and was stirred for 18 h. Water was added (75 mL) and the layers were separated. The organic layer was washed with brine (3 × 75 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification via column chromatography (DCM/MeOH 98:2, R_f = 0.25) yielded the desired compound.

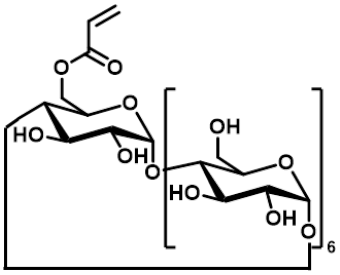
Yield: 4.2 g (9.76 mmol, 89%) as red oil.

^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.76 – 7.64 (m, 2H, H-3), 7.44 – 7.34 (m, 2H, H-2), 7.34 – 7.25 (m, 1H, H-1), 6.34 (dd, *J* = 17.3, 1.5 Hz, 1H, H-17), 6.06 (dd, *J* = 17.3, 10.4 Hz, 1H, H-18), 5.75 (dd, *J* = 10.4, 1.5 Hz, 1H, H-18), 4.28 – 4.11 (m, 4H, H-8, H-15), 3.79 (t, *J* = 5.4 Hz, 2H, H-9), 3.66 – 3.59 (m, 2H, H-10), 3.58 – 3.44 (m, 8H, H-11, H-12, H-13, H-14), 2.55 (s, 3H, H-7), 2.44 (s, 3H, H-7) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$) δ = 166.27 (C-16), 153.71 (C-4), 142.58 (C-6), 140.64 (C-5), 131.15 (C-18), 129.43 (C-17), 129.02 (C-1), 128.37 (C-2), 121.87 (C-3), 70.92, 70.73, 70.67, 70.06, 69.22 (C-9, C-10, C-11, C-12, C-13, C-14), 63.77 (C-15), 49.20 (C-8), 14.26, 10.06 (C-7) ppm.

MS (m/z): (ESI, MeOH) Calculated for $[C_{22}H_{30}N_4O_5Na]^+$: 453.2108, found 453.2103.

β-Cyclodextrin monoacrylate



Oven-dried β-CD (5.00 g, 4.4 mmol, 1 eq.) was dissolved under argon in dry NMP (60 mL) and cooled to 0°C. After the addition of Et_3N (3.9 mL, 30.8 mmol, 7 eq.) ancryloyl chloride (1.23 mL, 15.4 mmol, 3.5 eq.) was added dropwise. The mixture was allowed to warm to rt and stirred for 18 h. After the addition of ice-cold MeOH (130 mL) the solution was poured into acetone (500 mL). The resulting precipate was isolated by filtration and washed multiple times with acetone and dried under reduced pressure.

Yield: 2.64 g (2.20 mmol, 50%) as colourless solid.

^{1}H NMR (400 MHz, D_2O) δ = 6.50 – 6.37 (m, 1H), 6.30 – 6.13 (m, 1H), 6.07 – 5.95 (m, 1H), 5.05 (d, *J* = 3.8 Hz, 7H, H-1), 4.00 – 3.88 (m, 8H, H-5), 3.90 – 3.76 (m, 20H, H-2, H-3, H-6), 3.63 (dd, *J* = 9.9, 3.6 Hz, 8H, H-6), 3.57 (t, *J* = 8.9 Hz, 7H, H-4).

MS (m/z): (MALDI-MS (DHB Matrix, H_2O/ACN) Calculated for $[C_{45}H_{72}O_{36}Na]^+$: 1211.37, found 1211.52.

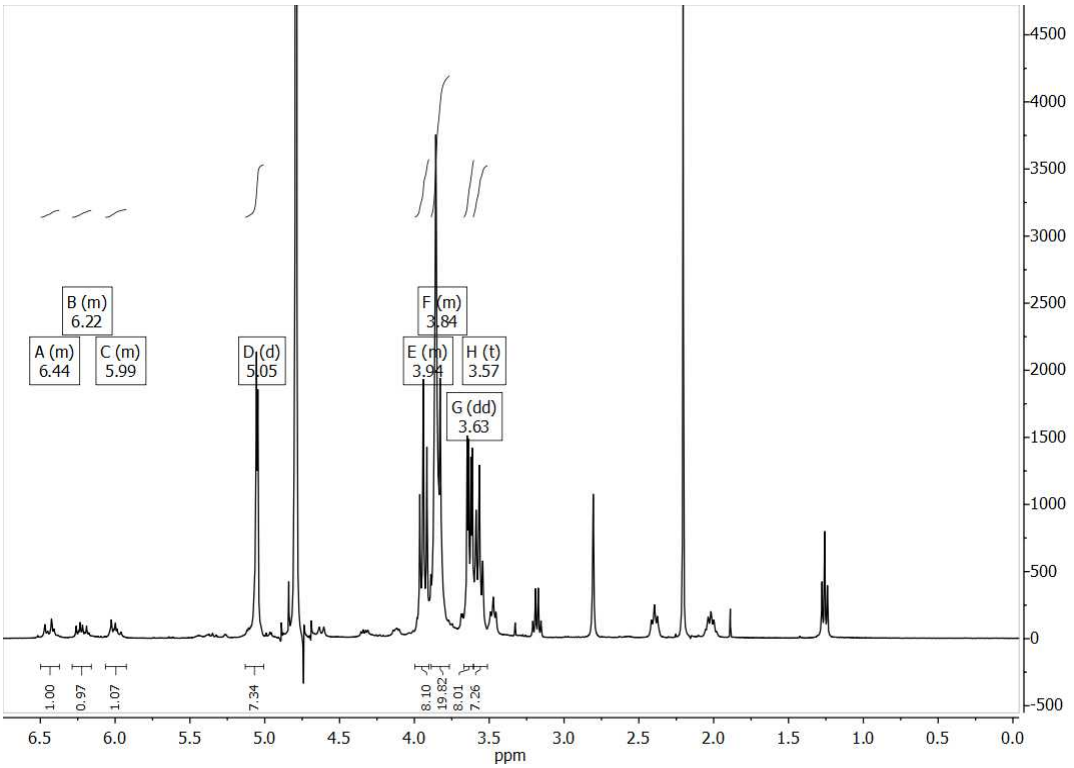


Figure S7: ^{1}H-NMR (400 MHz, D_2O) of β-cyclodextrin monoacrylate.