Supporting Information

Renewable, Fluorescent, and Thermoresponsive: Cellulose Copolymers *via* Light-induced Ligation in Solution

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Materials

p-Anisidine (ABCR, 99%), 2-bromo-2-methylpropionic acid (Acros, 98%), carbon disulfide (Sigma-Aldrich, 99.9%), *N*-(dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC; Roth, 99%), 4-(dimethylamino)pyridine (DMAP; Sigma Aldrich, 99%), dimethyl carbonate (Acros, 99%), *N,N*-dimethylformamide (DMF; VWR Analpur), dimethyl sulfoxide (DMSO; Carl Roth, 99.8%), 1-dodecanethiol (Acros, 98%), furan (Acros, 99%), 4-formylbenzoic acid (TCI, 98%), hydrochloric acid (Roth, 37%), maleic anhydride (Alfa Aesar, 98%), potassium carbonate

(technical), potassium phosphate monohydrate (Sigma Aldrich, puriss.), pyridine (Sigma Aldrich, 99.8%), sodium nitrite (Alfa Aesar, 98%), *p*- toluenesulfonyl hydrazide (Alfa Aesar, 98%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; Sigma Aldrich, 98%) and triethylamine (Merck, 99%) were used as received. All other solvents were of analytical grade and used as received. 1-Butyl-3-methylimidazolium chloride (BMIMCl; Aldrich, 95%), lithium chloride (Sigma Aldrich, 99%), and Whatman filter paper no. 5 were stored in a desiccator over silica gel. 2,2'-Azobis(2-methylpropionitrile) (AIBN; Fluka, 98%) was recrystallized twice from methanol. Ethanolamine (Acros, 99%) was dried over molecular sieve (3 Å) prior to use. N-Isopropylacrylamide (NIPAM; TCI, 98%) was recrystallized twice from hexane and stored at -20 °C.

Characterization Methods

NMR measurements were performed on a Bruker Ascend spectrometer operating at 400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei. The chemical shifts δ were referenced to the solvent residual signals, respectively ($\delta_H(CHCl_3)$=7.26, δ_H(DMSO)=2.50, $\delta_C(CHCl_3)$=77.16, δ_C(DMSO)=39.52). *J* values are given in Hz. The degree of substitution (*DS*) of cellulose 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (cellulose-tetrazole) was determined according to a procedure adopted from literature.[1, 2] A defined amount of maleic acid as standard and a defined amount of cellulose-tetrazole were dissolved in DMSO-d_6. The *DS* was calculated using the integral ratio of the ^{1}H NMR resonance corresponding to the aromatic protons **d**, **e**, **i**, **j** of cellulose-tetrazole (Figure S1) and the resonance corresponding to the double bond protons of maleic acid (δ = 6.27 ppm).

Size exclusion chromatography (SEC). SEC with *N,N*-dimethylacetamide (DMAc) containing 0.03 wt% LiBr as eluent was performed for PNIPAM with a sample concentration of 2 g L^{-1} on a Polymer Laboratories PL-GPC 50 Plus Integrated System comprising an autosampler, a PLgel

5 µm bead-size guard column (50 × 7.5 mm) followed by three PLgel 5 µm MixedC columns (300 × 7.5 mm), and a refractive index detector at 50 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated against linear poly(methyl methacrylate) standards with molecular weights ranging from 700 to 2 × 10^6 Da. The samples were filtered through polytetrafluorethylene (PTFE) membranes with a pore size of 0.2 µm prior to injection. SEC of cellulose-*graft*-copolymers, cellulose-tetrazole and Whatman filter paper no. 5 was performed at a sample concentration of 1-2 g $L^{-1}$with DMAc containing 10 g L^{-1} LiCl as eluent at 70 °C on an Agilent Series 1200 HPLC system including an isocratic pump (G1310A), an autosampler (G1329A), a thermostat controlled column compartment (G1316A) and a refractive index detector (G1362A) that was kept at 50 °C, at a flow rate of 0.5 mL min^{-1}. Separation was achieved on a SEC column (PSS, GRAM analytical, 300 × 8.00 mm, 10 µm particle size, 3000 Å porosity) with precolumn (50 × 8.00 mm). Linear poly(methyl methacrylate) standards with molecular weights ranging from 4300 to 3.73 × 10^6 g mol^{-1} were used for calibration. The samples were filtered through PTFE membranes with a pore size of 0.45 µm prior to injection. Dissolution of Whatman filter paper no. 5 was achieved in a solvent exchange procedure from literature.[2-4]

Determination of conversion from SEC measurements. In order to determine the conversion *via* SEC, samples which have not been irradiated, t = 0 h, and samples which have been irradiated for 5 h were isolated from the reaction mixture and injected at a defined sample concentration (c(s)), where m(s) is the mass of the sample, m(solv) is the mass of the solvent and ρ(solv) is the density of DMAc at 25°C.

$$c(s) = \frac{m(s) * \rho(solv)}{m(solv) + m(s)} \qquad \text{eq. S1}$$

Thus, the mass of injected PNIPAM injected (m(PNIPAM in, 0 h)) can be calculated for t = 0 h, where the initial mass of cellulose-tetrazole (m(cell(0)), and PNIPAM m(PNIPAM(0)) and the injection volume (V(in)) is known.

$$\text{m(PNIPAM in, 0 h)} = \frac{\text{m(PNIPAM(0))}}{\text{m(PNIPAM(0))} + \text{m(cell(0))}} * \text{c(s)} * \text{V(in)} \qquad \text{eq. S2}$$

The refractive index (RI) detector response is directly proportional to the mass concentration. Thus, the integral of the RI detector response from peak minimum to peak minimum for the PNIPAM homopolymer I(RI,PNIPAM), can be used to calculate m(PNIPAM in,5 h).

$$\text{m(PNIPAM in, 5 h)} = \frac{\text{m(PNIPAM in, 0 h)}}{\text{I(RI,PNIPAM,0 h)}} * \text{I(RI,PNIPAM, 5 h)} \qquad \text{eq. S3}$$

Finally, the conversion of tetrazole can be calculated using the initial molar ratio of PNIPAM/tetrazole (x) and m(PNIPAM,5 h), which is calculated from eq. S2 and m(PNIPAM in, 5h).

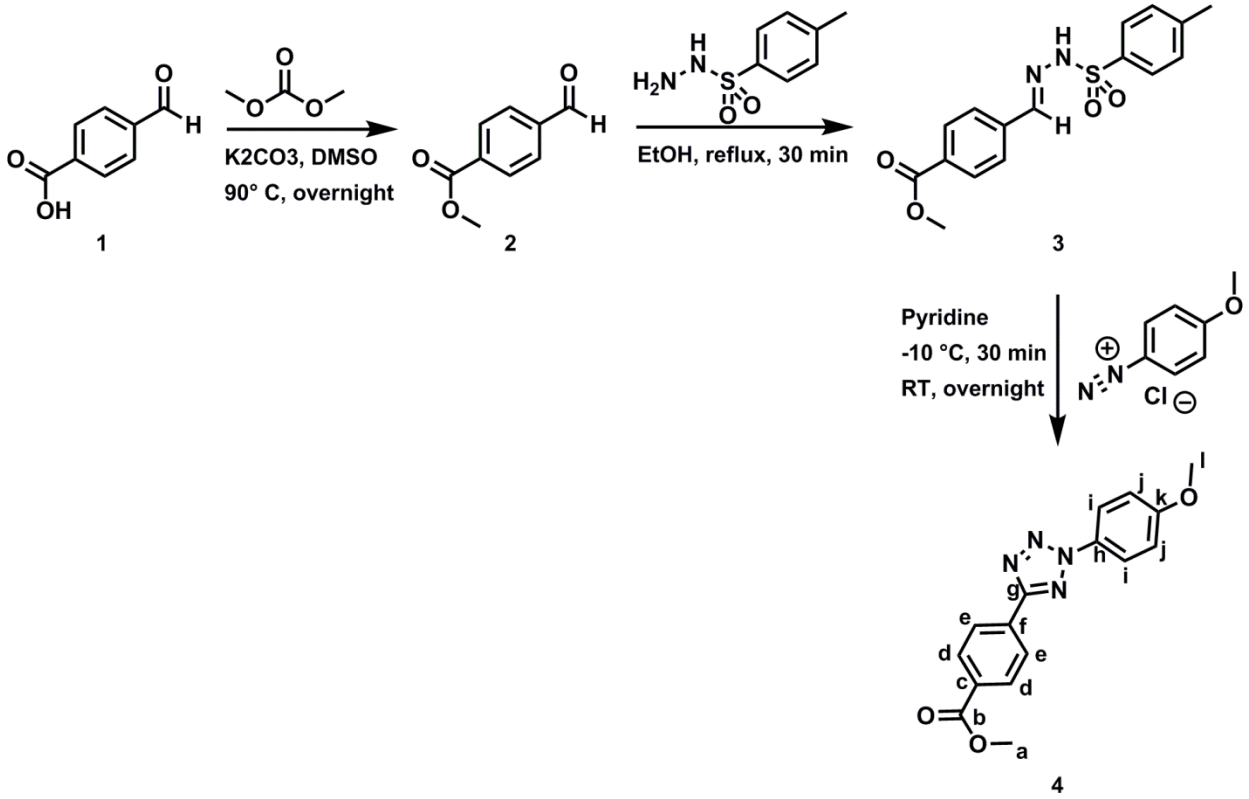
$$\text{conversion(tetrazole)} = \frac{\text{m(PNIPAM (0))} - \text{m(PNIPAM,(5 h))}}{\text{m(PNIPAM(0))}} * \text{x} \qquad \text{eq. S4}$$

UV-vis measurements. UV/vis spectra were recorded on a Cary 300 Bio UV-vis spectrophotometer (Varian) at ambient temperature in DMSO from 200 nm to 800 nm with a resolution of 1 nm and a slit width of 2 nm.

Fluorescence measurements. Fluorescence emission spectra were recorded on a Varian Cary Eclipse spectrometer at an excitation wavelength of 400 nm in quartz cuvettes with a sample volume of 200 µL and a sample concentration of 0.5 g L^{-1} in water. The spectra were recorded from 420 nm to 780 nm at an excitation slit width of 5 nm, an emission slit width of 10 nm, a resolution of 0.5 nm, and a scan rate of 30 nm min^{-1}.

Cloud point determination. Cloud points were measured on a Cary 300 Bio UV/vis spectrophotometer (Varian) at 600 nm in the temperature range from 7 °C to 60 °C at a heating rate of 0.3 °C min^{-1}. For sample preparation, 100 µL of a solution of polymer in DMSO with a concentration of 20 g L^{-1} were added to 3.9 mL of water while stirring vigorously and cooling with an ice bath, resulting in an aqueous solution with a sample concentration of 0.5 g L^{-1}.

Experimental Procedures



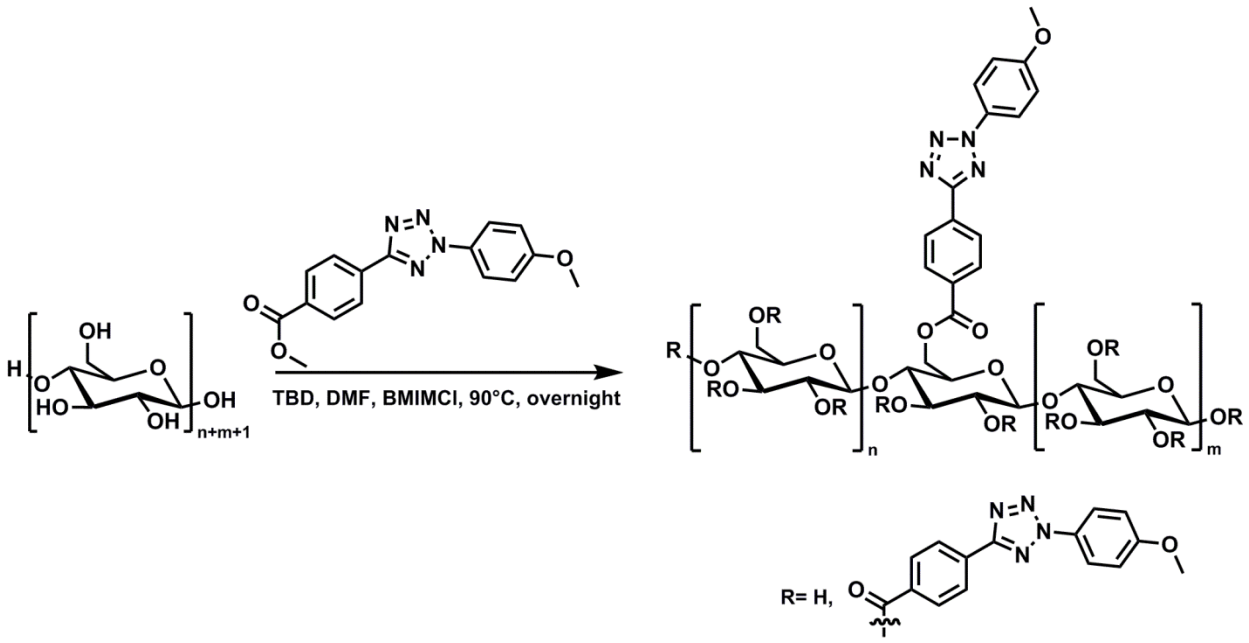
Scheme S1: Synthesis of methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (**4**).

Methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (4)

Methyl 4-formylbenzoate (**2**) was synthesized according to a literature procedure.[5] Subsequently, **2** was transformed into the tetrazole **4** *via* Methyl 4-((2-tosylhydrazono)methyl)benzoate (**3**) following a literature procedure.[6] The tetrazole **4** was obtained in an overall yield of 31%. For NMR annotation see Scheme S1.

^{1}H NMR (400 MHz, $CDCl_3$):[δ, ppm] = 8.29 (d, J = 8.5 Hz, 2H, d), 8.16 (d, J = 8.5 Hz, 2H, e), 8.08 (d, J = 9.1 Hz, 2H, i), 7.04 (d, J = 9.1 Hz, 2H, j), 3.94 (s, 3H, a), 3.87 (s, 3H, l). ^{13}C NMR

(100 MHz, $CDCl_3$): [δ, ppm] = 166.61 (b), 164.19 (g), 160.77 (k), 131.79 (f), 131.47 (c), 130.40 (h), 130.28 (i), 126.97(d) , 121.51(e) , 114.82 (j), 55.77 (l) , 52.41 (a).



Scheme S2: Synthesis of cellulose 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (cellulose-tetrazole).

Cellulose 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (cellulose-tetrazole)

Cellulose starting material Whatman filter paper no. 5 (0.55 g, 3.38 mmol anhydroglucose unit, 1.00 eq) was cut into square pieces of approximately 5 mm width and dissolved in BMIMCl (21.38 g) at 90 °C for 24 h to yield a 2.5 wt% solution. DMF (19 mL) was added dropwise. Subsequently, TBD (0.14 g, 1.02 mmol, 0.30 eq), and methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (1.99 g, 6.42 mmol, 1.90 eq) were added and the reaction mixture was stirred at 90 °C overnight. The reaction vessel was capped by a perforated septum to ensure the release of methanol. The reaction mixture was cooled to ambient temperature and the cellulose-

tetrazole was precipitated in water (600 mL). The crude product was washed with water (300 mL), ethyl acetate (300 mL) and acetone (600 mL). The crude product was redissolved in DMSO (40 mL), reprecipitated in water (800 mL), washed with water (300 mL) and acetone (2 × 300 mL) and dried at 70 °C *in vacuo* overnight. Cellulose-tetrazole was obtained as a white solid with a *DS* of 0.24 (0.71 g, 92%).

^{1}H NMR (400 MHz, DMSO-d_6):[δ, ppm] = 8.49-7.41(b, 6H, d, e, i), 7.22 (b, 2H, j), 5.90-2.70 (b, cellulose-H 1-6), 3.88 (s, 3H, l). ^{13}C NMR (100 MHz, DMSO-d_6): [δ, ppm] = 166.12 (b), 163.53(g), 160.60 (k), 131.63-128.97 (f, c, i, h), 126.97 (d), 121.89 (e), 115.21 (j), 102.79 (1), 80.48(4), 76.82-71.35 (5, 3, 2), 60.26 (6), 55.80 (l).

Regeneration of residual methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate

Excess methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate was regenerated after the synthesis of cellulose-tetrazole. After the removal of ethyl acetate and acetone the residue was redissolved in acetone (20 mL), reprecipitated in water (600 mL) and washed with water (300 mL) and ethanol (300 mL). The regenerated methyl 4-(2-(4-methoxyphenyl)-*2H*-tetrazol-5-yl) benzoate (1.03 g, 52%) was reused for the synthesis of cellulose-tetrazole (DS = 0.21, 88%).

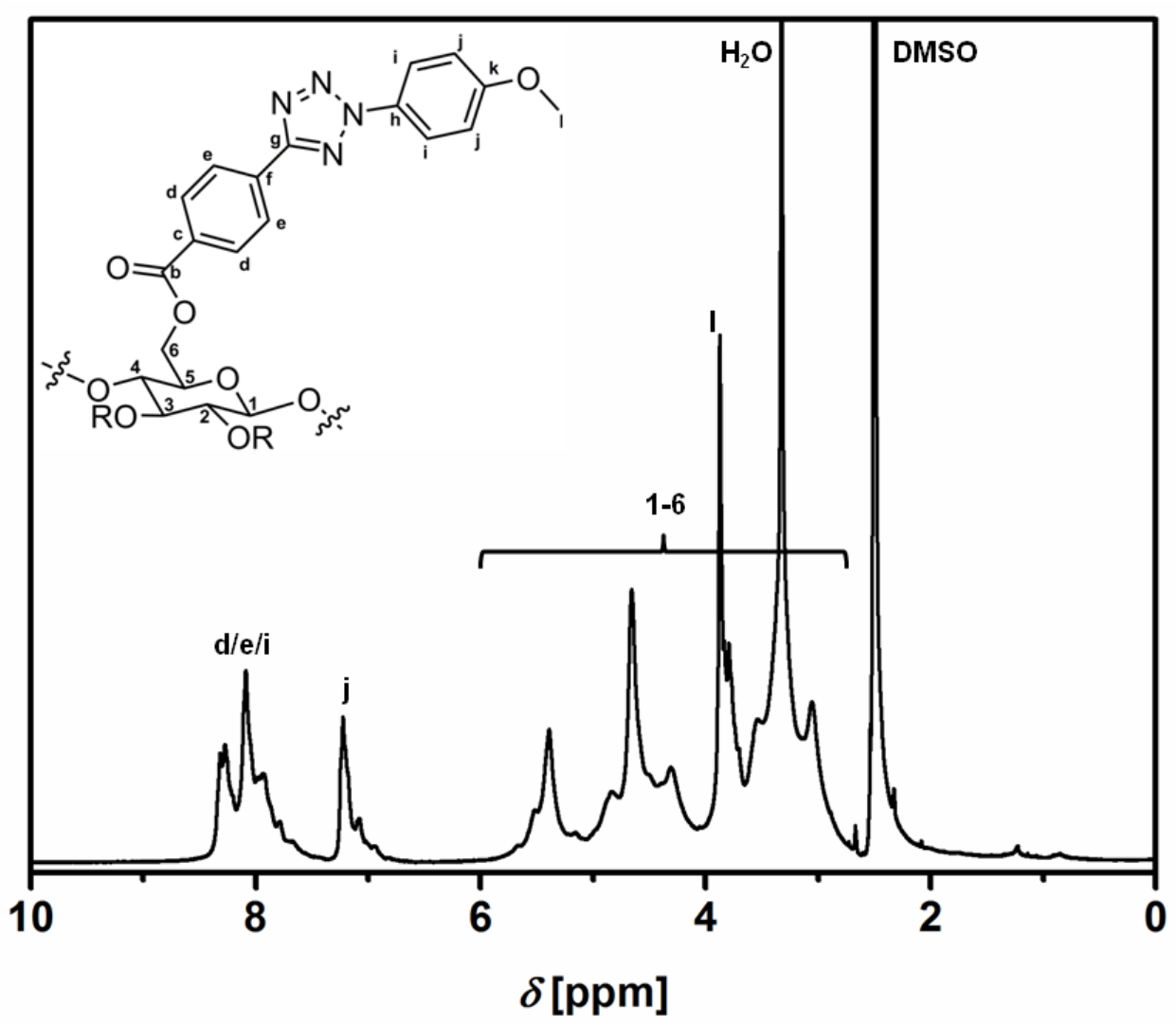


Figure S1: ^{1}H NMR of cellulose-tetrazole in DMSO-d_6 as solvent.

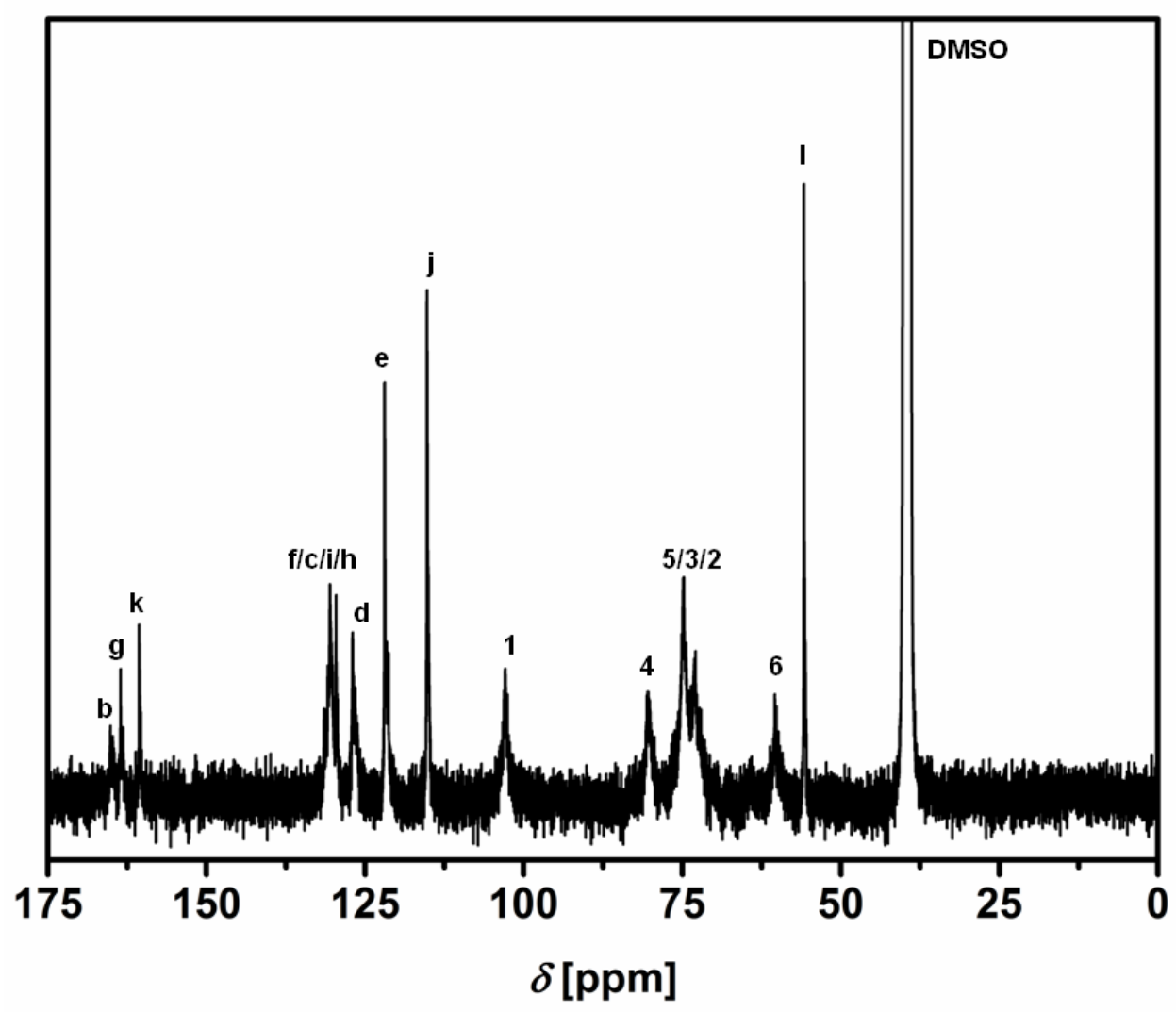


Figure S2: ^{13}C NMR of cellulose-tetrazole in DMSO-d_6 as solvent. For the assignment of the resonances refer to Figure S1.

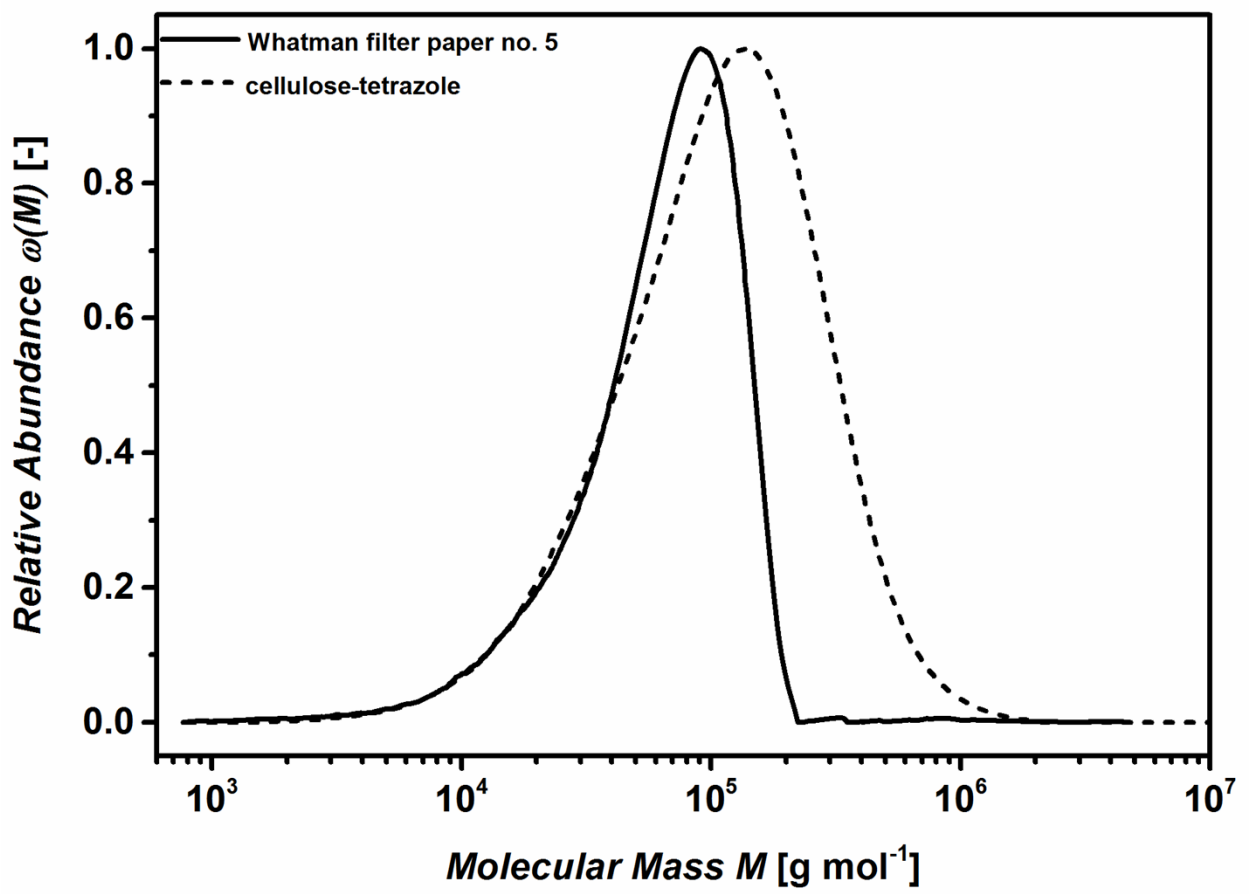
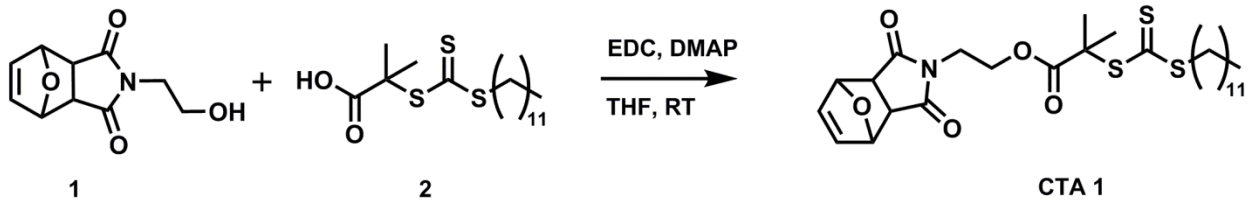


Figure S3: SEC traces of cellulose starting material Whatman filter paper no. 5 (solid line) and cellulose-tetrazole (dashed line). Whatman filter paper no. 5: $M_{n,SEC}$ = 41000 g mol^{-1}, $Đ$ = 1.93. Cellulose-tetrazole: $M_{n,SEC}$ = 62000 g mol^{-1}, $Đ$ = 2.56.

RAFT-agent synthesis



Scheme S3: Synthesis of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid 2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester (**CTA 1**).

2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid 2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.$0^{2,6}$]dec-8-en-4-yl) ethyl ester (CTA 1)

4-(2-Hydroxyethyl)-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (**1)** and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (**2)** were synthesized according to literature procedures.[7, 8] Subsequently, **CTA 1** was synthesized according to a procedure adopted from literature.[9, 10] To a solution of acid **2** (2.08g, 5.72 mmol, 1.00 eq) in 83 mL dry tetrahydrofuran (THF) alcohol **1** (1.79 g, 8.58 mmol, 1.50 eq) and DMAP (0.14 g, 1.14 mmol, 0.20 eq) were added at ambient temperature. The reaction mixture was cooled to 0 °C and EDC (3.29 g, 17.15 mmol, 3.00 eq) was added. After stirring for 1 h at 0 °C the reaction mixture was stirred at ambient temperature over night. The solvent was removed under reduced pressure and the residue was dissolved in 40 mL dichloromethane. The resulting solution was washed with saturated $NaHCO_3$ solution (100 mL), brine (3 × 100 mL), and water (3 × 100 mL). The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel with cyclohexane/ethyl acetate (1:1) as the eluent and subsequent recrystallization from *n*-hexane. **CTA 1** was obtained as a yellow solid (1.55 g, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): [δ, ppm] = 6.50 (s, 2H, CH=CH), 5.24 (s, 2H, CHOCH), 4.23 (t, J = 5.4 Hz, 2H, CH_2O), 3.76 (t, J = 5.4 Hz, 2H, NCH_2), 3.23 (t, J = 7.4 Hz, 2H, SCH_2), 2.85 (s, 2H, CHCON), 1.74 – 1.52 (m, 8H, C-$(CH_3)_2$, SCH_2CH_2), 1.43 – 1.02 (m, 18H, CH_2-$(CH_2)_9$-CH_3), 0.87 (t, J = 6.8 Hz, 3H, CH_2-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): [δ, ppm] = 221.79 (C=S), 175.90 (CON), 172.81 (COO), 136.66 (CH=CH), 80.97 (CHO), 62.28 (CH_2O), 56.05 ($C(CH_3)_2$), 47.64 (2C, CH), 37.67 (NCH_2), 37.14 (S-CH_2), 32.02 (CH_2-CH_2-CH_3), 29.73 (2 × $CH_{2,aliphatic}$), 29.66 ($CH_{2,aliphatic}$), 29.55 ($CH_{2,aliphatic}$), 29.44 ($CH_{2,aliphatic}$), 29.20 ($CH_{2,aliphatic}$), 29.08 ($CH_{2,aliphatic}$), 27.91 ($CH_{2,aliphatic}$), 25.23 ($C(CH_3)_2$), 22.79 (CH_2CH_3), 14.23 (CH_2CH_3).

Exemplary RAFT-Polymerization of NIPAM with CTA 1

NIPAM (2.07 g, 18.28 mmol, 128 eq), **CTA 1** (0.08 g, 0.14 mmol, 1.00 eq), AIBN (3.06 mg, 0.019 mmol, 0.13 eq), and furan (133.8 µL, 1.96 mmol, 13.7 eq) were added into a Schlenk tube and dissolved in DMF (5.1 mL). After three freeze-pump-thaw cycles, the Schlenk tube was filled with argon and placed in an oil bath at 60 °C. The polymerization was stopped after 2 h by cooling the reaction mixture in liquid nitrogen and opening the Schlenk tube to the atmosphere. Furan was removed under reduced pressure and the polymer was collected by dialysis against water for three days using a SpectraPor6 dialysis tube (MWCO=1000 Da) and subsequent lyophilization (0.53 g, 22% conversion). The conversion was determined gravimetrically. SEC (**PNIPAM-1**): $M_{n,SEC}$ = 4800 g mol^{-1}, $Đ$ = 1.20. $M_{n,NMR}$ was calculated from the ^{1}H NMR integral ratio of the resonances corresponding to protons **i** and **c** (Figure S4). $M_{n,NMR}$(**PNIPAM-1**) = 4000g mol^{-1}.

Exemplary deprotection of the maleimide endgroup of PNIPAM polymers

PNIPAM-1 was placed in a Schlenk flask and heated to 105 °C for 24 h under vacuum. Complete removal of furan was monitored by ^{1}H NMR spectroscopy (Figure S5). $M_{n,SEC}$ = 4800 g mol^{-1}, $Đ$ = 1.21. $M_{n,NMR}$ was calculated from the integral ratio of the resonances corresponding to protons **i** and **e** (Figure S5). $M_{n,NMR}$(PNIPAM-1) = 4000g mol^{-1}.

Table S1: Experimental conditions for the synthesis of **PNIPAM 1-3** *via* RAFT-polymerization employing **CTA 1**. All polymerizations were performed at 60 °C under inert conditions.

	$[M]_0$ [mol L^{-1}]	$[M]_0$/[CTA 1]/[AIBN]	[CTA 1]/[furan]	*conversion* [%]	*t* [h]
PNIPAM-1	3.58	128/1/0.13	1/14	22	2
PNIPAM-2	3.47	183/1/0.13	1/14	24	2
PNIPAM-3	3.49	347/1/0.13	1/14	31	3

Table S2: SEC and ^{1}H NMR data of PNIPAM polymers before and after the deprotection of the maleimide endgroup.

Polymer	$M_{n,NMR}$ [g mol^{-1}]	$M_{n,SEC}$ [g mol^{-1}]	$Đ$
PNIPAM-1 protected	4000	4800	1.20
PNIPAM-1 deprotected	4000	4800	1.21
PNIPAM-2 protected	8200	10400	1.21
PNIPAM-2 deprotected	8300	10400	1.22
PNIPAM-3 protected	19000	20300	1.23
PNIPAM-3 deprotected	19400	20300	1.23

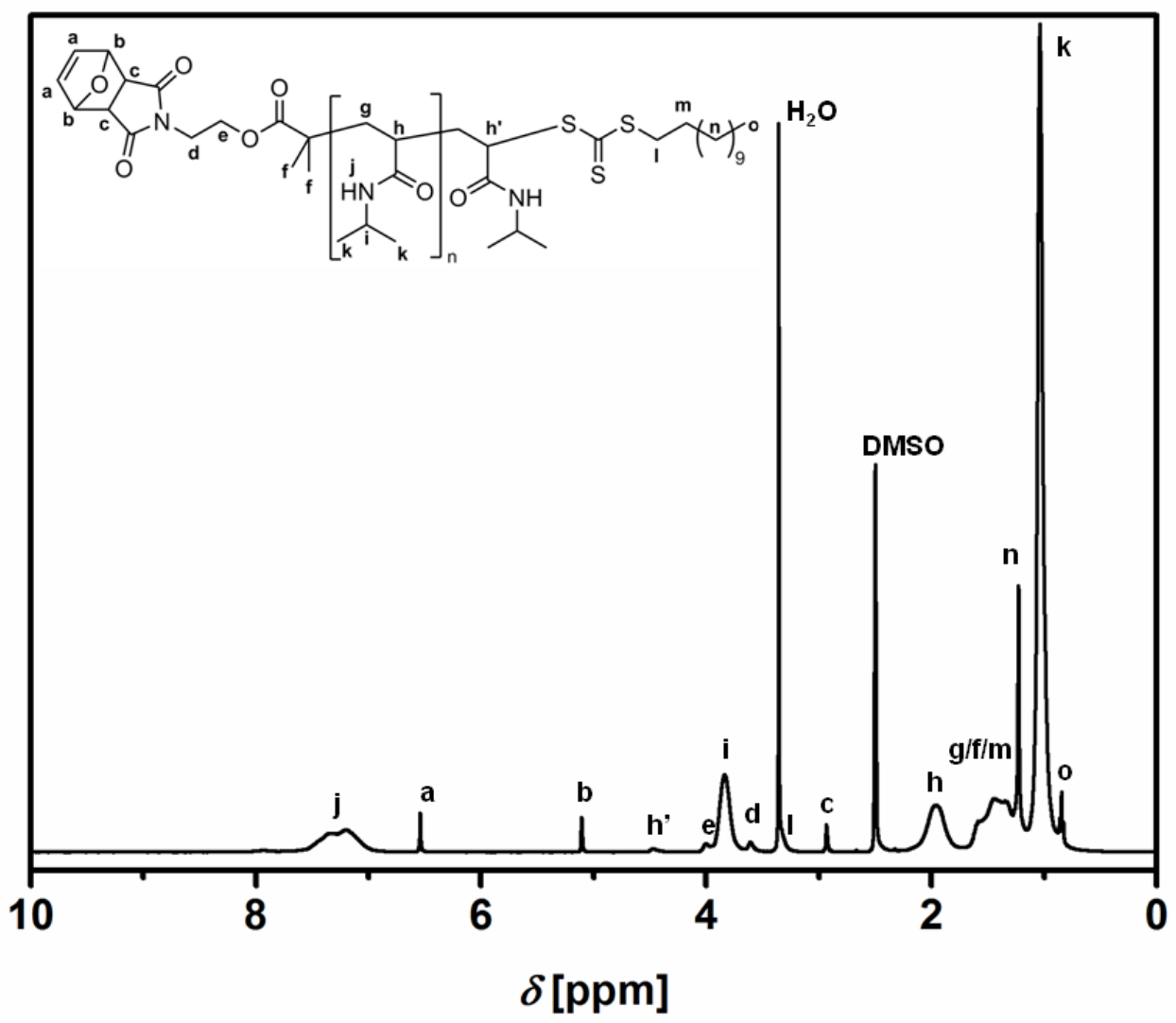


Figure S4: ^{1}H NMR spectrum of furan protected **PNIPAM-1** in DMSO-d_6 as solvent.

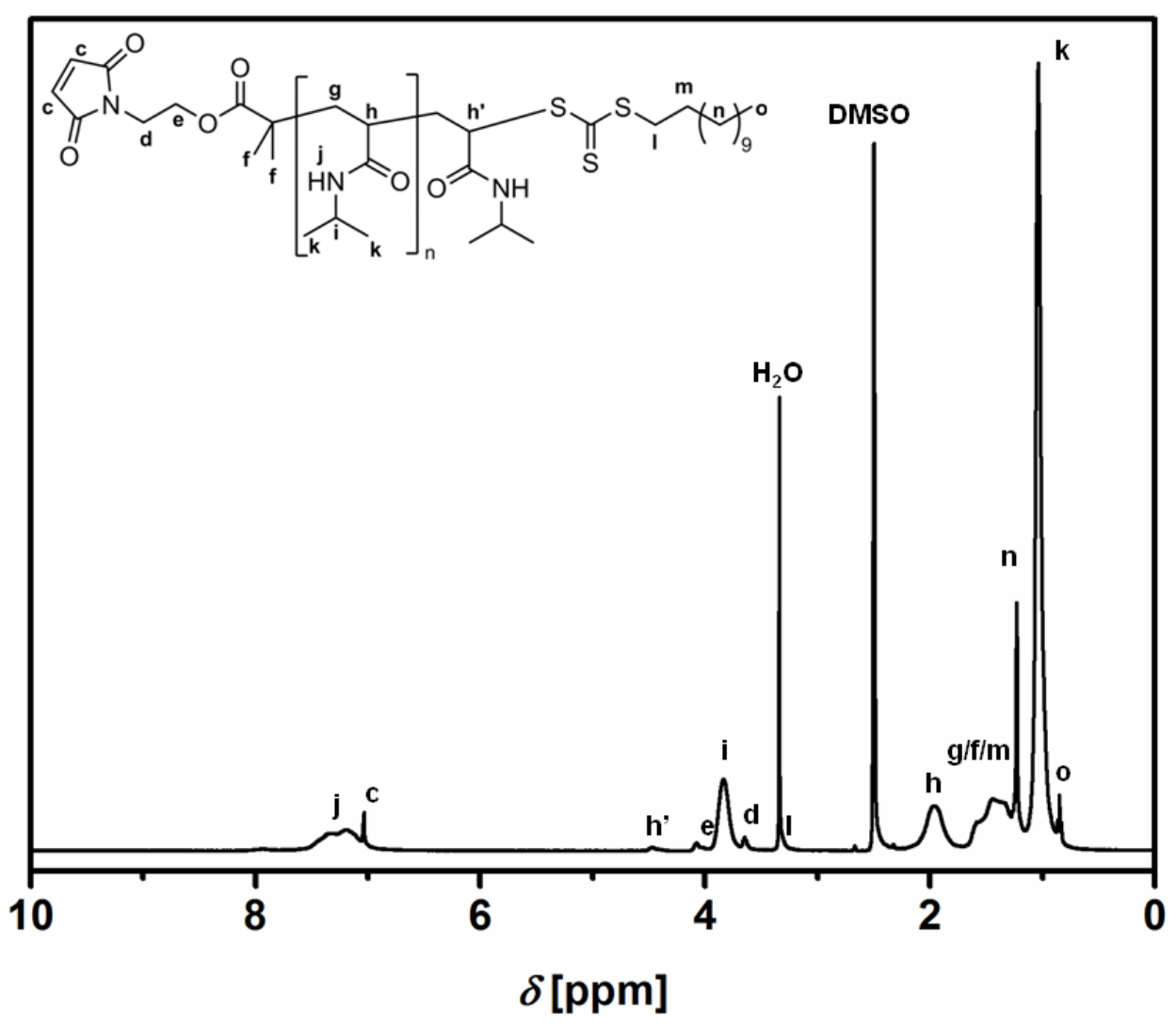


Figure S5: ^{1}H NMR spectrum of **PNIPAM-1** after deprotection of the maleimide endgroup in DMSO-d_6 as solvent.

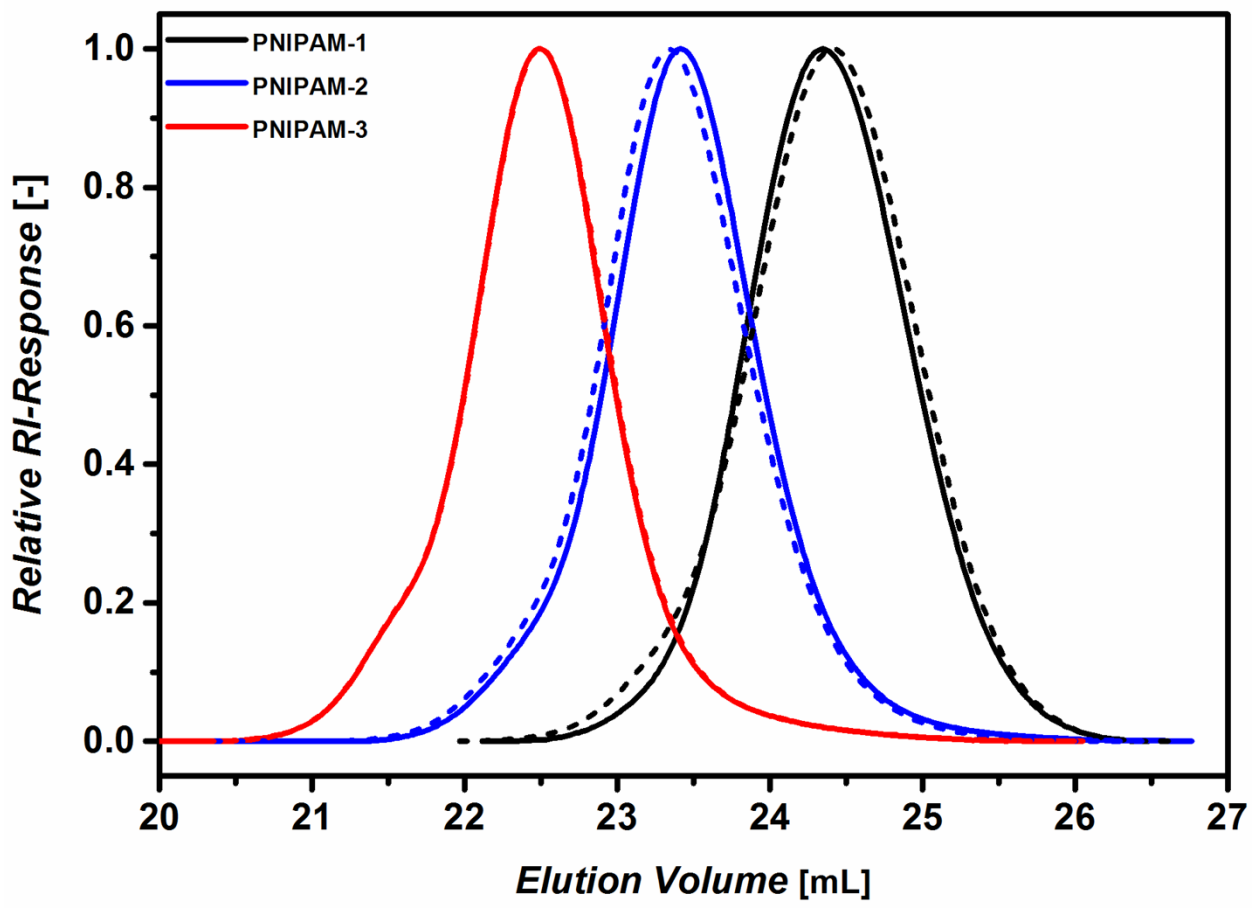
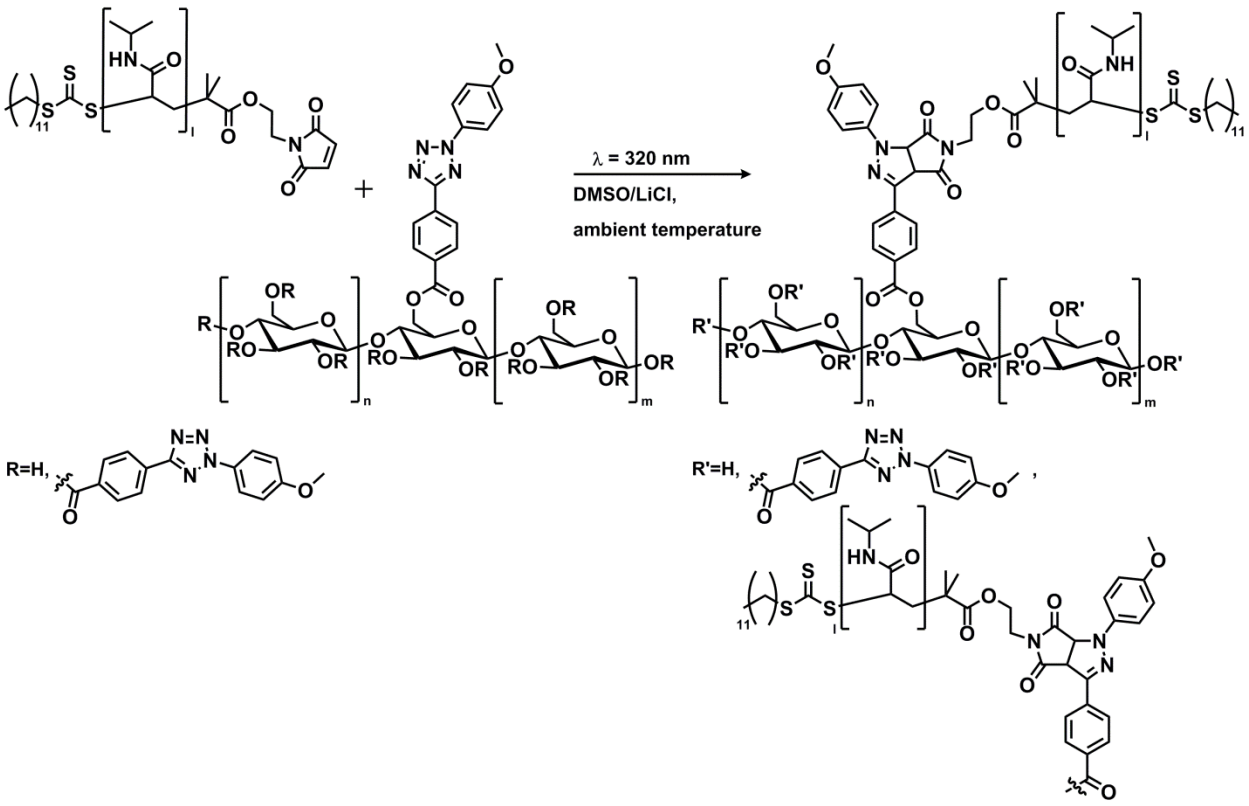


Figure S6: SEC traces of PNIPAM polymers. Solid lines represent the polymers with the furan protected maleimide endgroup and dotted lines refer to the respective polymers after deprotection of the endgroup.



Scheme S4: Light-induced synthesis of cellulose-*graft*-PNIPAM-copolymers.

Exemplary procedure for grafting of maleimide end-capped PNIPAM onto cellulose-tetrazole

PNIPAM-1 (0.17 g, 0.036 mmol, 1.70 eq), cellulose-tetrazole (*DS* = 0.24, 0.021 mmol tetrazole, 1.00 eq), and LiCl (4 g L^{-1} DMSO) were dissolved in DMSO (13.3 mL) in an air-tight crimped quartz vial. The reaction mixture was irradiated for 5 h, while stirring vigorously. The reaction was performed in a custom-built photoreactor equipped with a single compact low-pressure fluorescent lamp (36 W, Arimed B6, λ_{max} = 320 nm, Figure S7 and S11), and a magnetic stirrer. Subsequently, the reaction mixture was transferred to a SpectraPor6 dialysis tube (MWCO = 1000 Da), dialyzed against water for 3 days, and lyophilized. For the removal of PNIPAM-1 homopolymer, the crude product was dissolved in DMSO (5 mL) and added to cold

acetone (40 mL). Cold diethyl ether (approximately 20 mL) was added until the solution became turbid. The sample was stored in the refrigerator overnight, the precipitate was collected by decantation of solvent, and the residue was dried at 70 °C *in vacuo* overnight. The purification procedure was repeated until SEC traces confirmed removal of homopolymer (1-3 times). $M_{n,SEC}$ = 100000 g mol^{-1}, $Đ$ = 15.11.

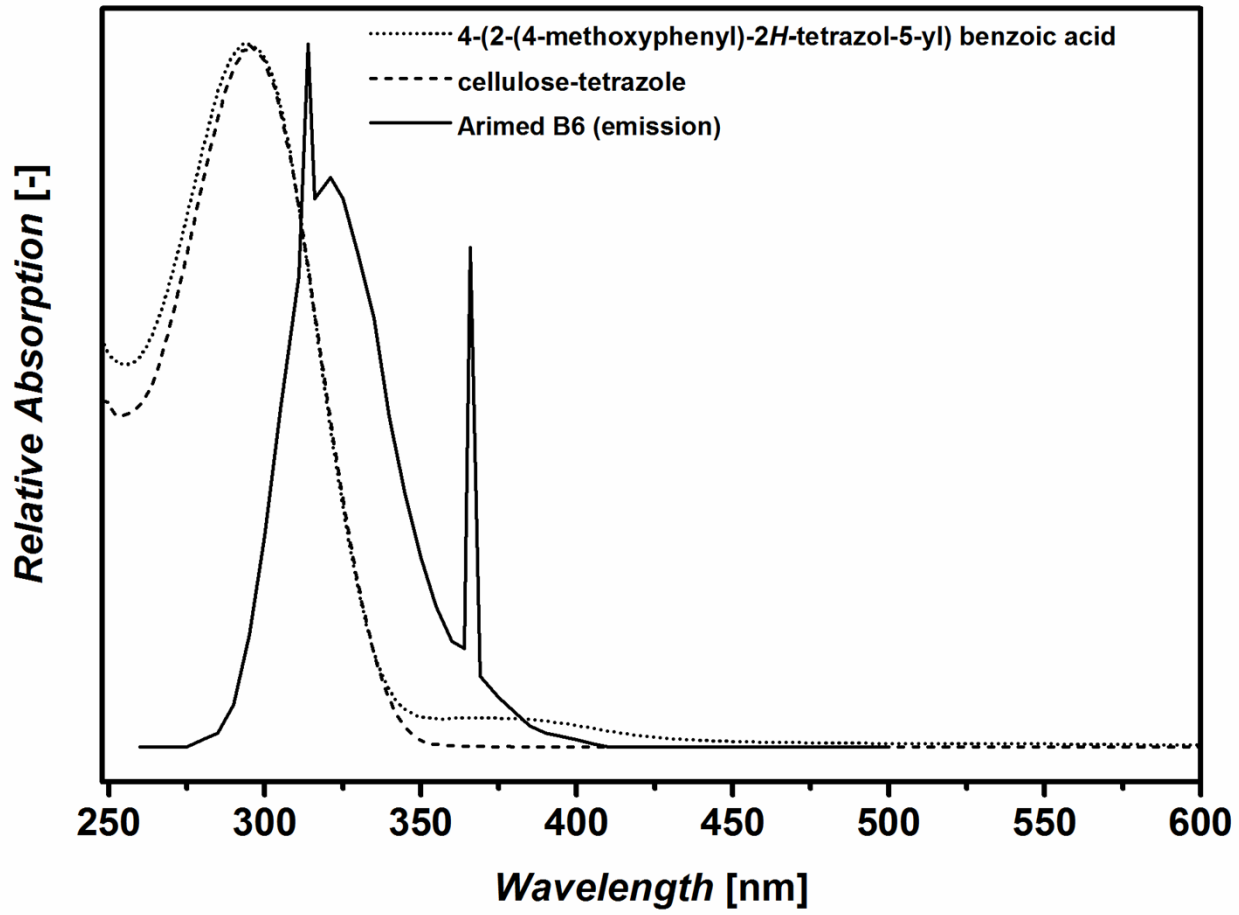


Figure S7: UV-vis absorption spectra of 4-(2-(4-methoxyphenyl)-2*H*-tetrazol-yl) benzoic acid and cellulose-tetrazole in DMSO and emission spectrum of the Arimed B6 lamp used in this work. The absorbtion and emission is given relative to the peak maximum, respectively.

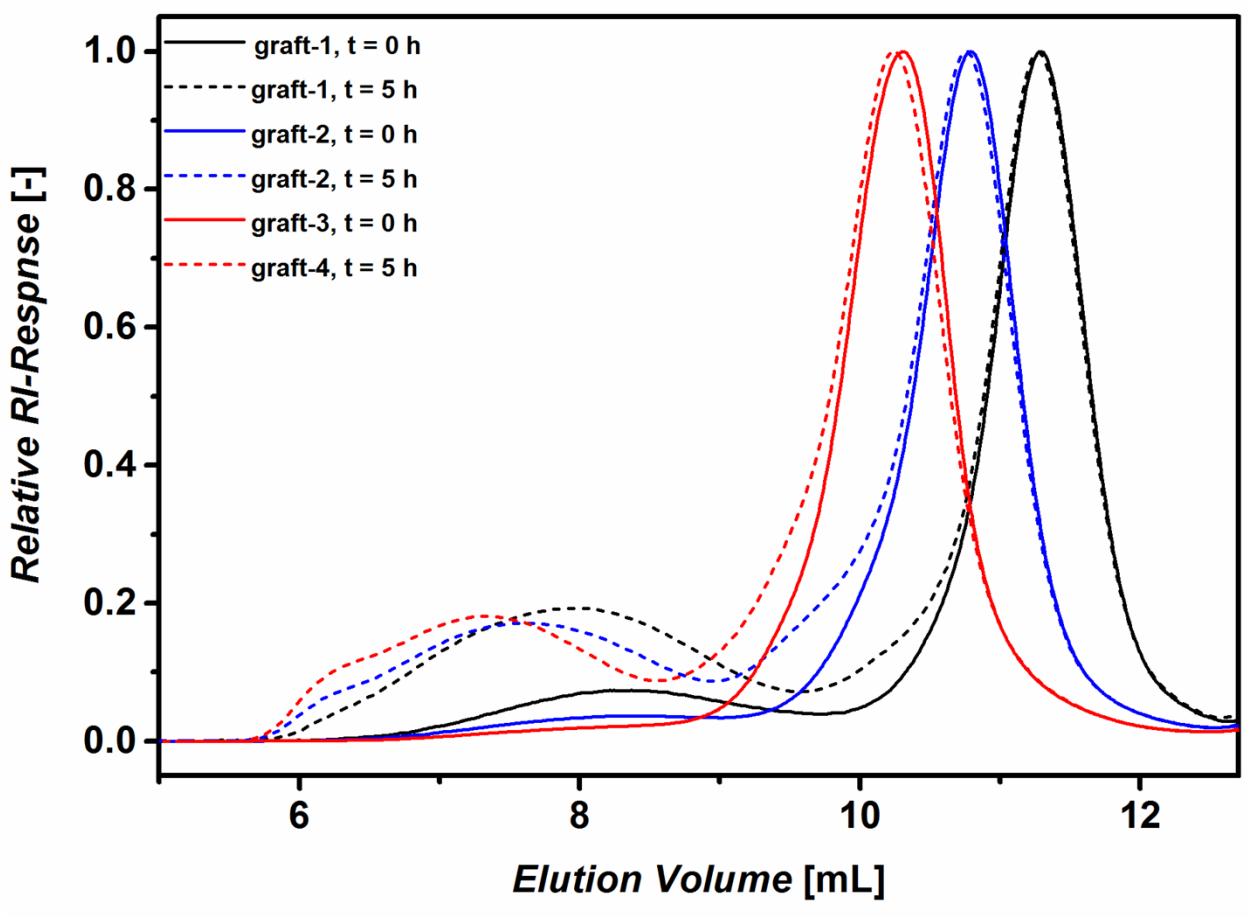


Figure S8: SEC traces of **graft 1-3** before removal of PNIPAM homopolymer at t = 0 h and after irradiation for 5 h. The RI-response is given relative to the peak maximum corresponding to free PNIPAM for all samples.

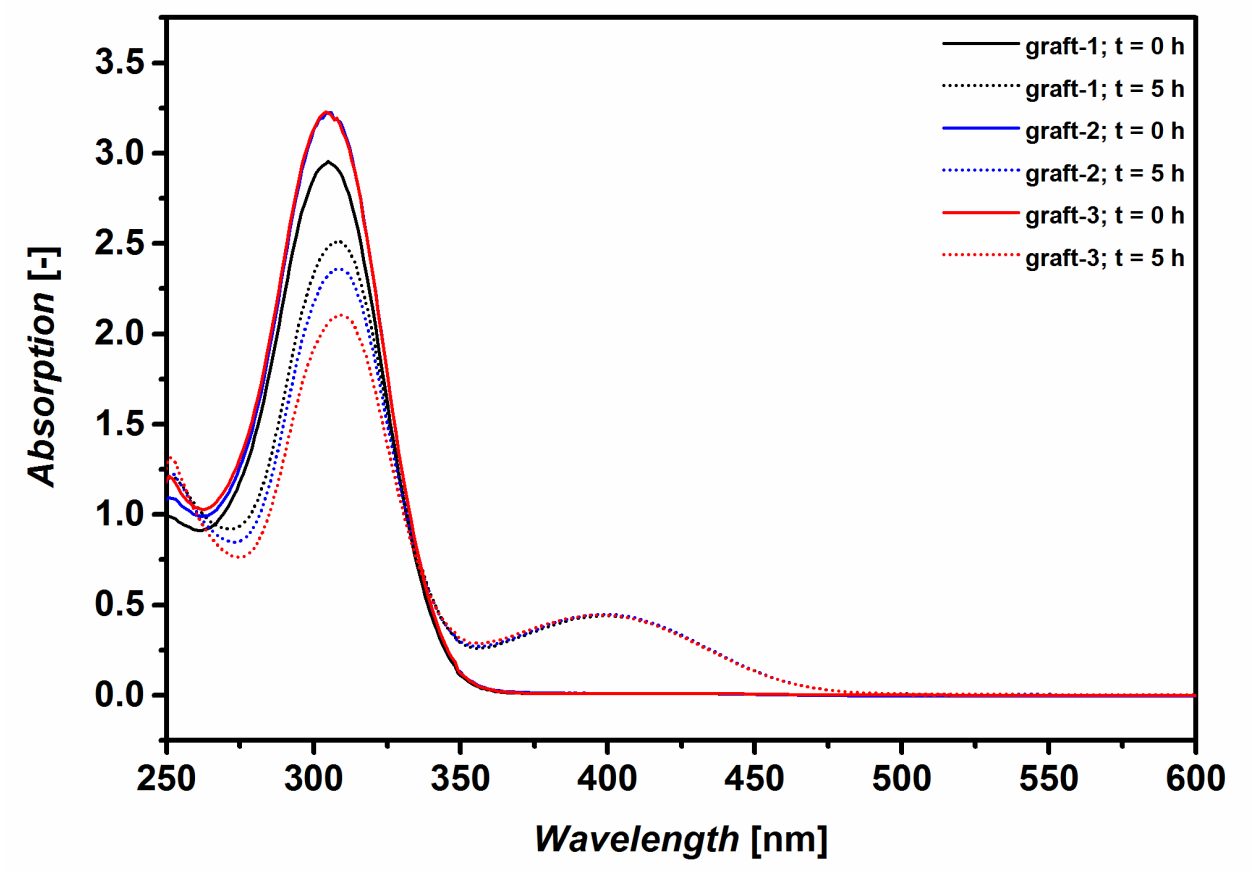


Figure S9: UV-vis absorption spectra of **graft 1-3** before (t = 0 h) and after irradiation (t = 5 h) in DMSO. **Graft-1** was measured at a sample concentration c(**graft-1**) = 2.3 g L^{-1}, and **graft 2-3** were measured at sample concentrations c(**graft-2**) = 4.8 g L^{-1}, and c(**graft-3**) = 9.1 g L^{-1}, respectively.

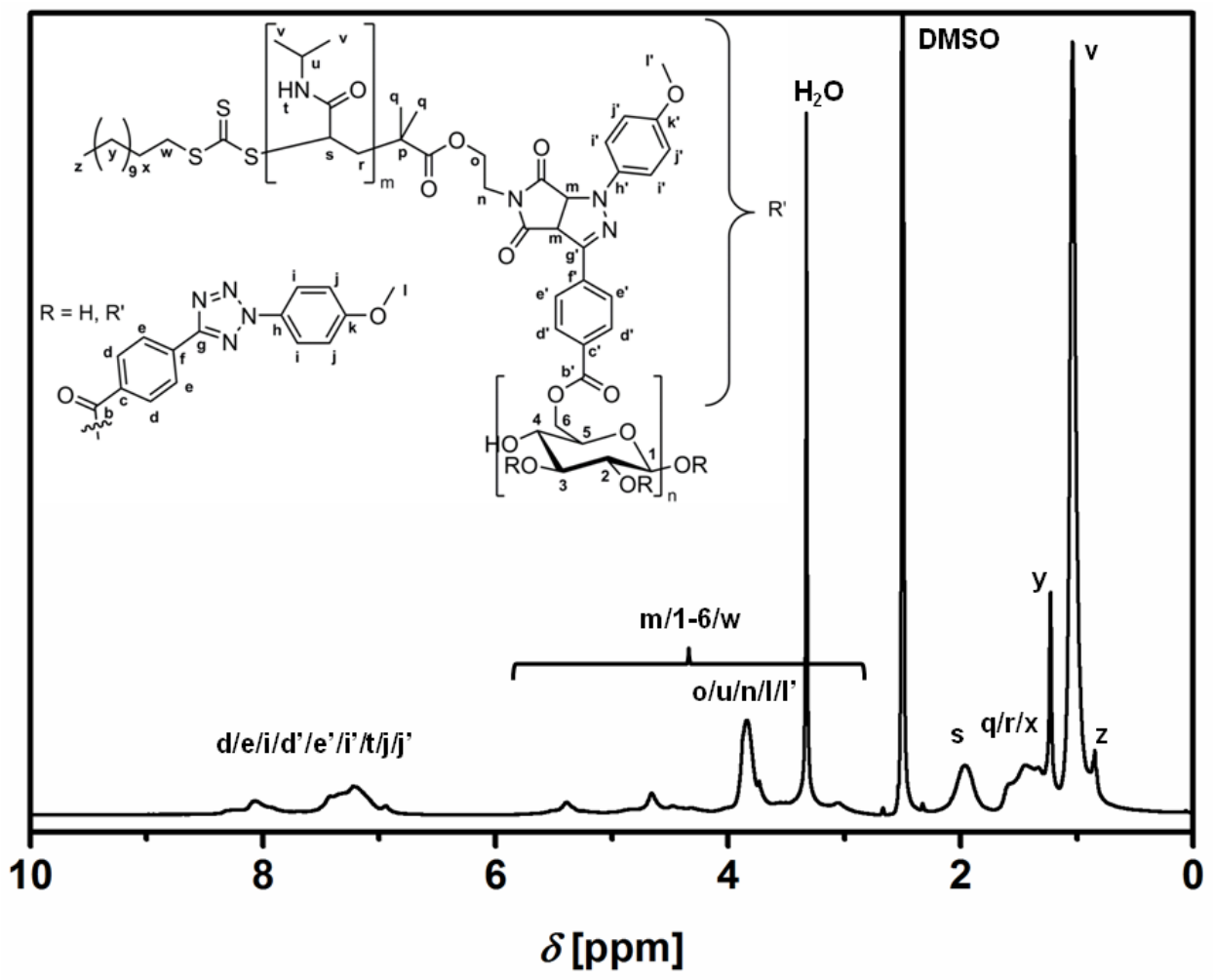


Figure S10: ^{1}H NMR of **graft-1** in DMSO-d_6 as solvent.

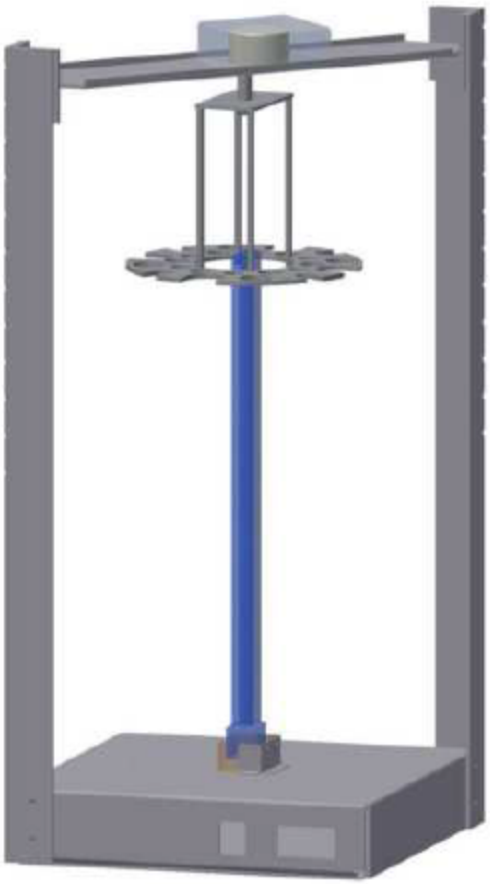


Figure S11: Illustration of the custom-built photoreactor used in the current work.

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