Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Enhancing the photochemical reversibility of coumarin-containing polymers by molecular orientation control

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Experimental section

NMR Spectroscopy

^{1}H- and ^{13}C-NMR-Spectra were recorded on an AV-300 (BRUKER, 300 MHz) or an AV-500 (BRUKER, 500 MHz). The δ chemical shift scale was calibrated using the residual solvent signal for dimethyl sulfoxide-d_6 or chloroform-*d*.

Mass spectroscopy

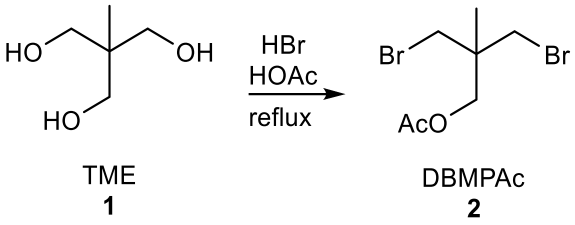
HR-ESI mass spectra were acquired with an LTQ-FT ULTRA mass spectrometer (THERMO FISCHER SCIENTIFIC) using acetonitrile as solvent.

Chemicals

The compounds were synthesized using the following starting materials from the stated manufacturers with given purities: Trimethylolethane (TME, ACROS ORGANICS, 97%), hydrogen bromide in acetic acid (MERCK, 33 wt%), 4-methylumbelliferone (4MC, ALFA AESAR, 97%), potassium carbonate (ACROS ORGANICS, 99+%), potassium iodide (GRÜSSING, 99.5%), *N,N*-dimethylformamide (DMF, ROTH, ≥99.5%), dichloromethane (DCM, anhydrous, ≥99.8%, SIGMA ALDRICH), triethylamine (TEA, GRÜSSING, 99%), methacrylic acid chloride (MAACl, SIGMA ALDRICH, ≥97%), methyl methacrylate (MMA, ACROS ORGANICS, 99%), azobis(isobutyronitril) (AIBN, SIGMA ALDRICH, 98%), ethylene glycol dimethacrylate (EGDMA, ≥97.5%, SIGMA ALDRICH). All other chemicals and solvents were of at least technical grade. Solvents and monomers were distilled before use.

Synthesis of compounds

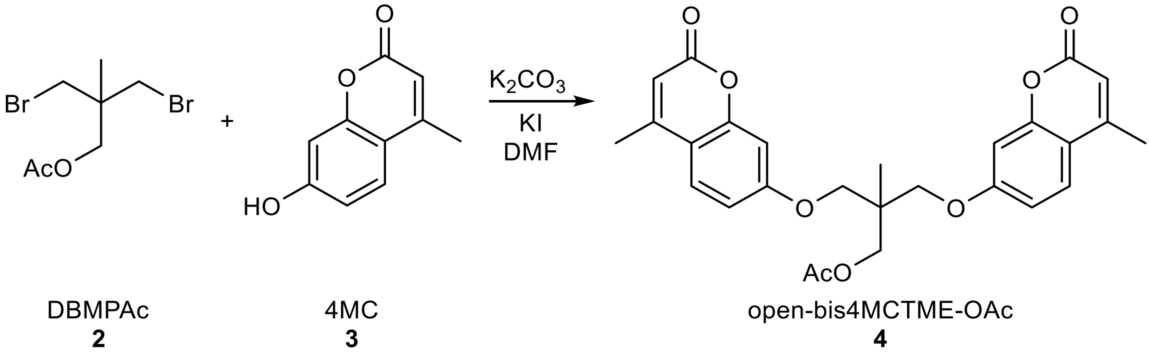
3-bromo-2-(bromomethyl)-2-methylpropyl acetate DBMPAc **2**:



50.00 g (0.42 mol) trimethylolethane (TME) were added to 250 mL HBr (33 wt% in HOAc). The solution was refluxed for three days. After cooling to room temperature and the addition of water, the solution was extracted with dichloromethane, washed with water and brine, dried over $MgSO_4$, and filtrated. Removement of all volatile compounds *in vacuo* yielded approx. 120 g of slightly colored crude product, which was distilled under reduced pressure. The fraction boiling at 74 °C (oil bath temperature 100 °C, 0.024 mbar) was collected to give 102.52 g (0.36 mol, 86%) of DBMPAc as a colorless, viscous liquid.

^{1}H-NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ = 4.00 (s, 2H), 3.56 (s, 2H), 2.06 (s, 3H), 1.10 (s, 3H) *ppm*. **^{13}C-NMR** (75 MHz, DMSO-*d*$_6$; 300 K): δ = 170.0, 66.0, 40.2, 38.7, 20.5, 19.5 *ppm.*
HRMS (ESI+, ACN): calculated for $C_7H_{12}Br_2O_2Na$: 308.9102, found: 308.9105.

open-bis4MCTME-OAc **4**:

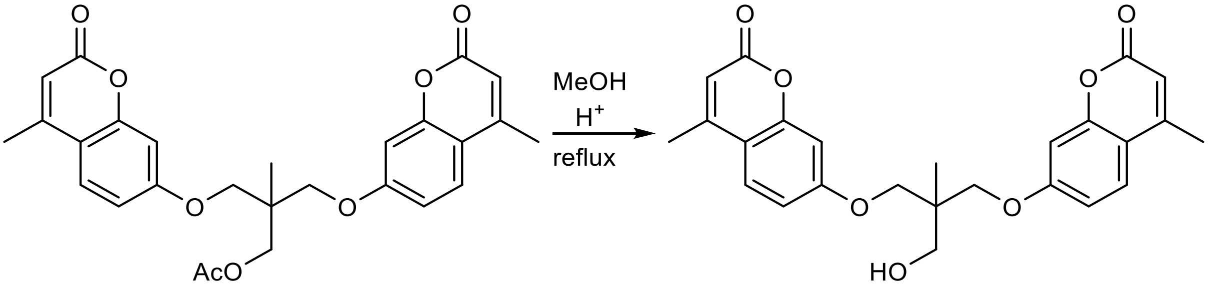


10.00 g (34.72 mmol, 1.00 eq) DBMPAc **2**, 12.25 g (69.53 mmol, 2.00 eq) 4-methylumbelliferone (4MC, **3)**, and catalytic amounts of KI were dissolved in 250 mL DMF. Under intense stirring, 19.20 g (138.88 mmol, 4.00 eq) K_2CO_3 were added. The suspension was heated to 70 °C for three days. DMF was removed under reduced pressure. The residue was dissolved in 120 mL ethyl acetate, washed with 5% aq. HCl (2 x 100 mL), water (3 x 100 mL), 10wt% aq. NaOH (2x 100 mL) and brine (2 x 50 mL). The organic phase was dried over $MgSO_4$, filtrated, and evaporated to dryness. After recrystallisation from isopropanol/acetonitrile 1:1 (v/v) and drying under fine vacuum, 11.62 g (24.28 mmol, 70%) of the acetylated product open-bis4MCTME-OAc **4** were received as off-white solid.

^{1}H-NMR (300 MHz, DMSO-d_6, 300 K): δ = 7.65 (d, ^3J = 9.5 Hz, 2H), 6.97 (dd, ^3J = 6.8 Hz, ^4J = 2.5 Hz, 4H), 6.19 (d, ^4J = 1.0 Hz, 2H), 4.17 (s, 3H), 4.11 (s, 4H), 2.37 (d, ^4J = 1.0 Hz, 6H), 2.03 (s, 3H) *ppm*. **^{13}C-NMR** (75 MHz, DMSO-d_6; 300 K): δ = 170.2, 161.5, 160.0, 154.6, 153.2, 126.4, 113.2, 112.5, 111.2, 101.4, 70.0, 65.2, 20.5, 18.0, 16.7 *ppm.*

HRMS (ESI+, ACN): calculated for $C_{27}H_{26}O_8Na$: 501.1520, found: 501.1508.

open-bis4MCTME-OH **5**:



open-bis4MCTME-OAc
4

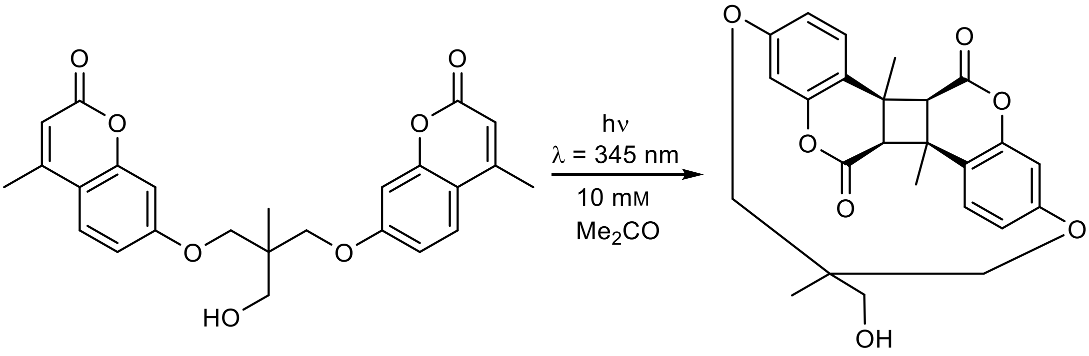
open-bis4MCTME-OH
5

5.00 g (10.45 mmol) of the acetate **4** were refluxed in 45 mL MeOH and 15 mL 6 M aq. HCl for 12 h. The aqueous phase was extracted with DCM. After washing with water and brine, drying over $MgSO_4$ and filtration, the solvent was removed under reduced pressure. 4.12 g (9.41 mmol, 90%) of open-bis4MCTME-OH **4** were received as colorless solid after drying under fine vacuum.

^{1}H-NMR (300 MHz, DMSO-d_6, 300 K): δ = 7.63 (d, ^3J = 8.4 Hz, 2H), 6.96 (m, 4H), 6.17 (s, 2H), 4.82 (t, ^3J = 5.2 Hz, 1H), 3.99-4.07 (m, 4H), 3.52 (d, ^3J = 5.2 Hz, 2H), 2.36 (s, 1H), 1.10 (s, 3H) *ppm*. **^{13}C-NMR** (75 MHz, DMSO-d_6; 300 K): δ = 161.9, 160.0, 154.6, 153.2, 126.3, 113.1, 112.4, 111.1, 101.3, 70.1, 62.7, 40.8, 18.0, 16.6 *ppm.*

HRMS (ESI+, ACN): calculated for $C_{25}H_{24}O_7Na$: 459.1414, found: 459.1411.

closed-bis4MCTME-OH **6:**



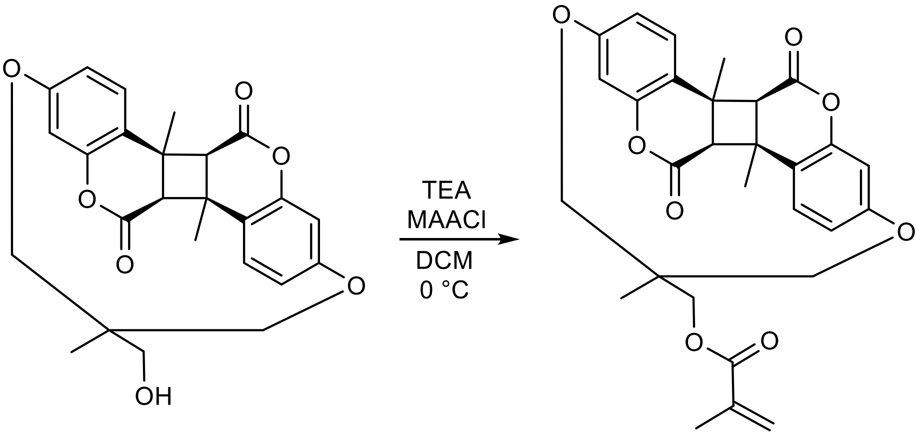
open-bis4MCTME-OH
5

closed-bis4MCTME-OH
6

open-bis4MCTME-OH **5** (4.36 g, 10.00 mmol) was dissolved in acetone (1000 mL). The solution was irradiated with UV-light (λ = 345 nm) in a flow reactor. At the end of the reaction, the solvent was removed and the raw product was adsorbed on silica. Purification by column chromatography (*n*-pentane/ethyl acetate 3:2) yielded 3.70 g (8.5 mmol, 85%) of closed-bis4MCTME-OH **6** as colorless solid.

^{1}H-NMR (300 MHz, DMSO-d_6, 300 K): δ = 6.86 (d, ^3J = 8.9 Hz, 2H), 6.63-6.58 (m, 2H), 6.07 (dd, ^2J = 13.9 Hz, ^4J = 2.5 Hz, 2H), 4.72 (t, ^3J = 5.22 Hz, 1H), 4.03-3.88 (m, 2H), 3.70 (t, ^3J = 5.22 Hz, 3H), 3.55 (s, 2H), 1.56 (s, 6H), 0.98 (s, 3H) *ppm*.
^{13}C-NMR (125 MHz, DMSO-d_6; 300 K): δ = 165.1, 160.3, 160.1, 149.9, 125.6, 115.5, 114.8, 114.7, 101.8, 69.9, 68.8, 62.8, 53.8, 42.6, 42.0, 27.6, 16.1 *ppm*.
HRMS (ESI+, ACN): calculated for $C_{25}H_{24}O_7Na$: 459.1414, found: 459.1410.

closed-bis4MCTME-MA **7**:



closed-bis4MCTME-OH
6

closed-bis4MCTME-MA
closed ICD-MA 7

For the attachment of the polymerizable group, 2.75 g (6.30 mmol, 1.00 eq) closed-bis4MCTME-OH **6** and 0.96 mL (6.93 mmol, 1.10 eq) triethylamine were dissolved in 40 mL dry DCM. The solution was cooled to 0 °C. 0.68 mL (6.93 mmol, 1.10 eq) MAACl were added dropwise. The solution was stirred overnight in the dark. The residue was adsorbed on silica and purified by column chromatography (DCM/MeOH 100:1). 3.02 g (5.99 mmol, 95%) of closed-bis4MCTME-MA **7** were received as white, crystalline solid.

^{1}H-NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ = 6.88 (dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz, 2H), 6.63 (dt, ^3J = 8.6 Hz, ^4J = 1.8 Hz, 2H), 6.13 (s, 3H), 5.75 (m, 2H), 4.17-4.01 (m, 4H), 3.77 (m, 2H), 3.55 (s, 2H), 1.94 (s, 3H), 1.56 (s, 6H), 1.07 (s, 3H) *ppm*.
^{13}C-NMR (75 MHz, DMSO-*d*$_6$; 300 K): δ = 166.4, 165.0, 160.0, 159.9, 149.9, 135.7, 126.1, 125.6, 115.8, 114.7, 102.1, 102.0, 69.0, 66.2, 53.8, 42.7, 27.6, 18.0, 16.1 *ppm*.
HRMS (ESI+, ACN): calculated for $C_{29}H_{28}O_8H$: 505.1868, found: 505.1851.

Structural assignment of the dimer core

The exact chemical structure of the dimeric coumarin core of the closed-variant molecule was determined via ^{1}H-NMR-spectroscopy. It was identified as the *syn*-head-to-tail isomer based on its singlet signal at 1.56 *ppm* for the methyl group next to the cyclobutane ring. For a detailed discussion about the possible isomers, see reference.[S1]

Polymer composition

For the determination of the polymer composition, the material was analyzed via ^{1}H-NMR-spectroscopy. Small amounts of polymer were dissolved in deuterated chloroform. The recorded spectrum is given in Figure S1.

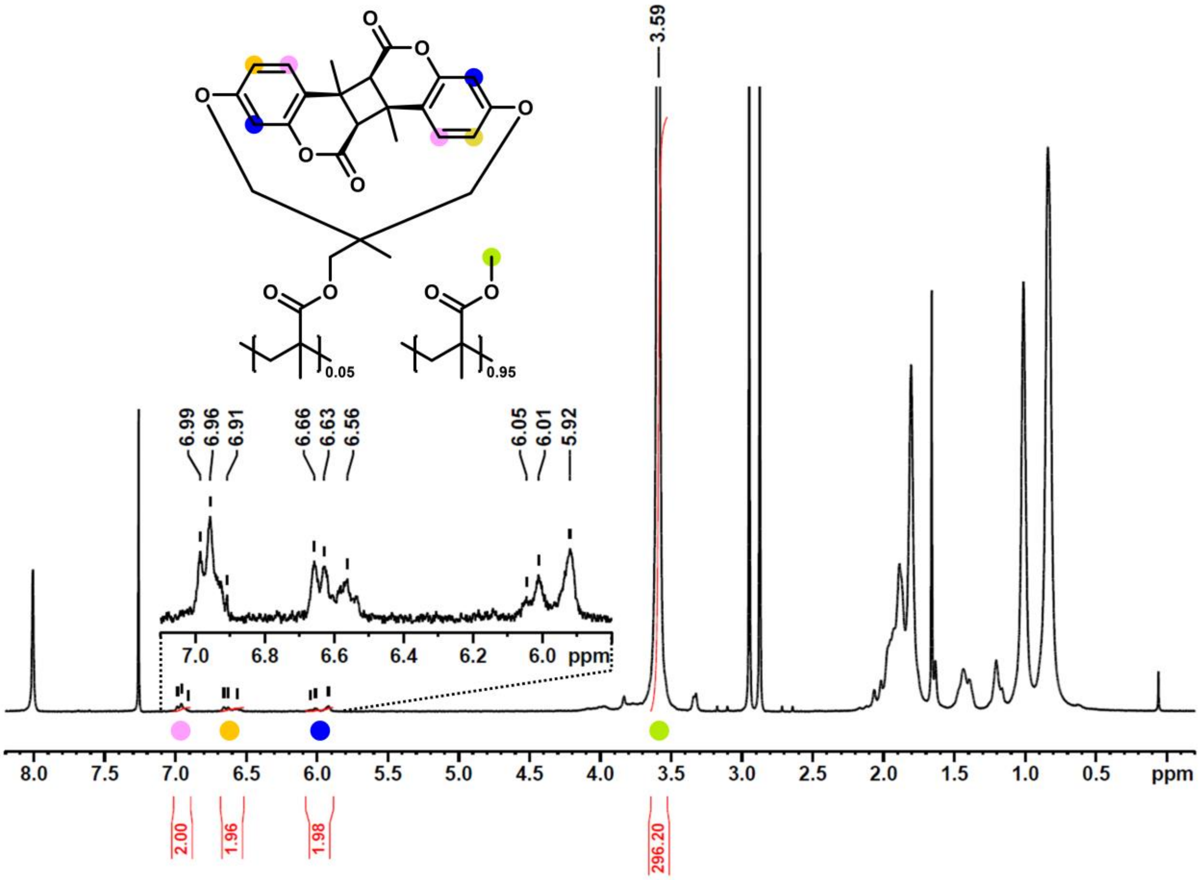


Figure S1: ^{1}H-NMR-Spectrum ($CDCl_3$, 300 K) of the synthetized polymer. The signals are assigned to the chemical structure by different colors. The ratio between the aromatic coumarin-dimer signals and the methyl ester signal of MMA indicates a weight proportion of 4.85% of the ICD-structure.

By comparison of the aromatic signals of coumarin (6.99 – 5.95 *ppm*) with the terminal methyl ester protons of MMA, the composition was found to be 4.85 wt% (98.73 eq MMA), which is close to the feeding ratio of 5.00 wt% (95.76 eq MMA).

Differential scanning calorimetry (DSC)

DSC measurements were performed on a Mettler Toledo DSC 3 under N_2 flow (10 mL·min^{-1}). Temperature profiles (two heating and cooling cycles each) with heating rates of 10 °C·min^{-1} were used to determine the glass transition temperatures from the second heating cycle. The second heating cycle is shown in Figure S2.

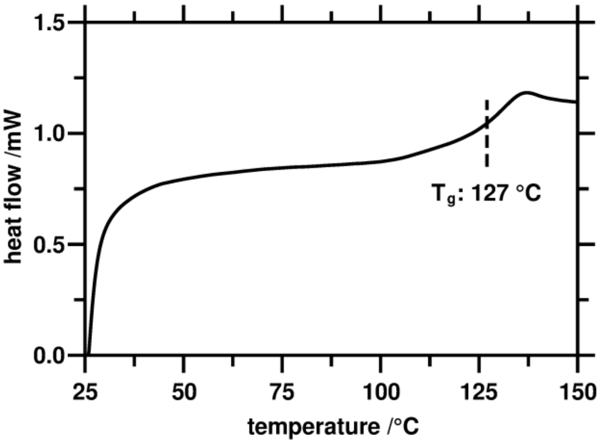


Figure S2: second heating cycle of the DSC measurement with a glass transition point of 127 °C.

Size exclusion chromatography (SEC)

SEC measurements were performed on an SEC system equipped with a SHIMADZU LC20AD pump, WYATT OPTILAB REX refractive index detector, and four PLGEL 5µ Mixed-C columns at 35 °C using THF as an eluent with a flow rate of 1 mL·min^{-1}. The analytic system was calibrated using linear PMMA standards from POLYMER LABORATORIES. The obtained molecular weight distributions are shown in

Figure S3. The molecular weight of the as-prepared polymer was determined to be 118,000 g·mol^{-1} with a dispersity of Đ = 1.74. After one cycle of illumination, the molecular weight remained at 118,000 g·mol^{-1} with a slightly higher Đ (1.80).

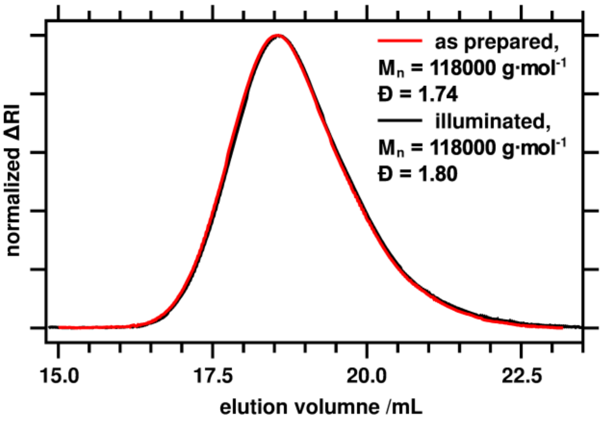
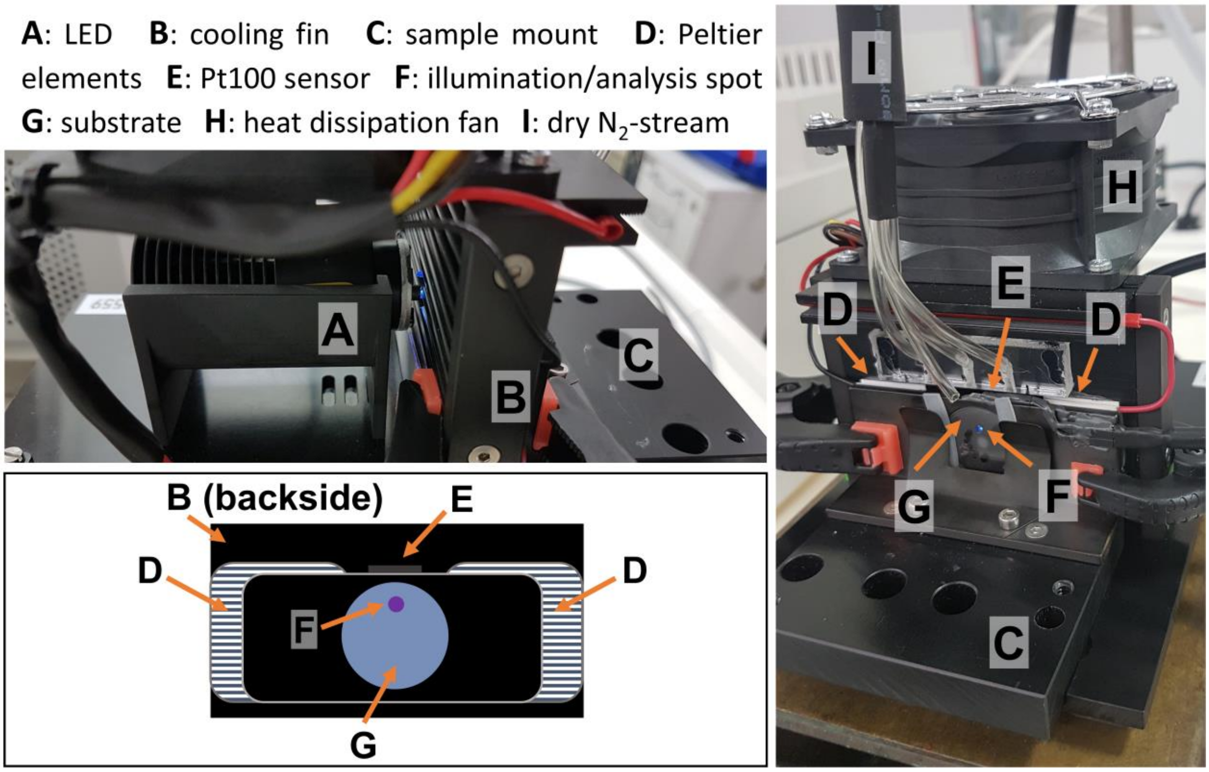


Figure S3: SEC measurements for the polymer as prepared and after illumination (λ = 265 nm and λ = 345 nm).

Illumination of the polymer thin films

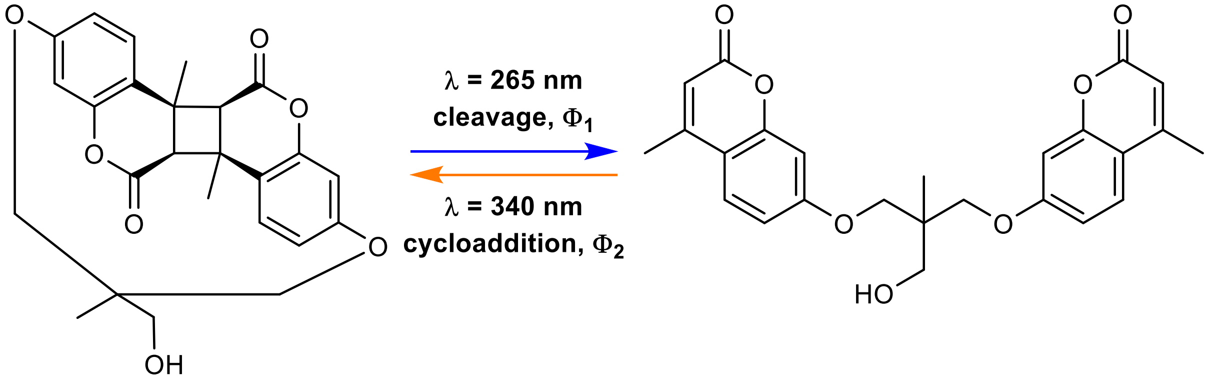
For the illumination of the polymer thin films, two different mounted UV-LEDs (λ = 265 nm: THORLABS M265L3, P = 2 mJ·cm^{-2}, λ = 345 nm: THORLABS M340L4, P = 20 mJ·cm^{-2}) hooked to a laboratory power supply were used. The thin films on the substrates were heated / cooled (depending on the polarity) with two Peltier elements, on which the substrate was fixed by two clips. The temperature was measured next to the sample with a Pt100 sensor. The sample mount was constantly blown with dry nitrogen gas to prevent air moisture condensation. In Scheme S1, the illumination setup is shown.



Scheme S1: Photography and schematic representation of the illumination apparatus. Middle Left: LED Setup. The wavelength was changed by changing the LED inside the mount. Bottom left: Schematic representation along the illumination axis as a description of the arrangement which is shown on the right.

Reversibility control experiment in solution

Analog to the reaction in the polymer matrix, the reaction was investigated in solution. Hereby, a solution ($5\cdot10^{-5}$ M in acetonitrile) of the closed configuration alcohol species was illuminated with alternating wavelength, as shown in Scheme S2.



closed configuration

open configuration

Scheme S2: Reversible reaction for determination of photochemical parameters.

The concentration of the open configuration molecule was determined by LAMBERT-BEER-law. The extinction coefficient $\varepsilon_{319\ \mathrm{nm}}$ is 26162 $\mathrm{L\cdot(mol\cdot cm)^{-1}}$. The development of the concentration over the illumination cycles is given in Figure S4.

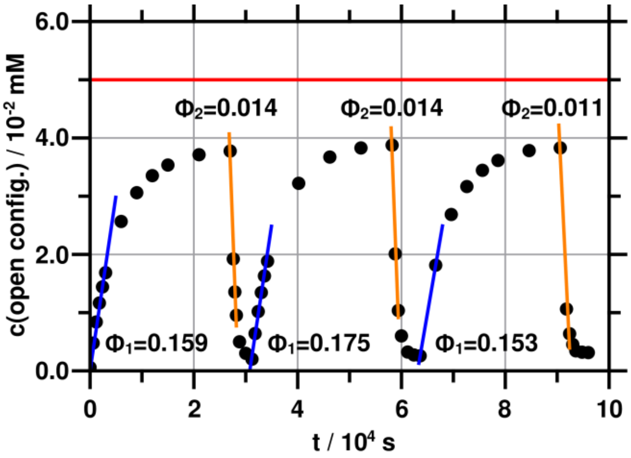


Figure S4: Reversibility cycles of the reaction shown above with the quantum yields of the reaction. The corresponding rate constants are given in Table S1. Red line: maximal possible concentration, blue line: rate constant determination of cycloreversion, orange line: rate constant determination of cycloaddition.

The photochemical parameters (rate constant k and quantum yield ϕ) were determined as described elsewhere.[S2] The values for every reaction over three cycles are given in Table S1.

Table S1: Concentration values, rate constants, and quantum yield for the reversible reaction shown in Scheme S2 and Figure S4.

reaction type	**concentration /10^{-5} M**	**rate constant k /10^{-7} mMs^{-1}**	**quantum yield ϕ /%**
start	0.06	-	-
cycloreversion 1	3.78	5.41	15.91
cycloaddition 1	0.20	23.95	1.42
cycloreversion 2	3.88	5.94	17.46
cycloaddition 2	0.26	23.66	1.40
cycloreversion 3	3.83	5.19	15.26
cycloaddition 3	0.31	18.49	1.10

Over all three cycles, good reversibility is found. Hereby, a non-complete cleavage reaction is observed as the concentration does not reach the value of $5 \cdot 10^{-5}$ M, but a value of approx. 76% of this value ($3.8 \cdot 10^{-5}$ M), which is described by a forward-backward equilibrium under illumination with 265 nm UV light.[S3] The quantum yields and rate constants of the cleavage reaction are in a typical range for coumarin dimers.[S4] Noteworthy is the remarkable high quantum yield ($\phi \approx 10^{-2}$) for the cyclization reaction, especially in these low concentrated solution without added sensitizers.[S5] In addition, the rate constant of the reaction is nearly concentration independent, indicating a reaction with zeroth order kinetics, as expected for the intramolecular [2+2]-cycloaddition. The here-found combination of high k and ϕ is an explanation for the efficient preparative procedure of the intramolecular closed-type structures.[S1] Furthermore, no significant amounts of side products were identified by HPLC analysis after the three illumination cycles, which demonstrates the high degree of reversibility and the remaining isomer purity.

Absorbance trend by illumination

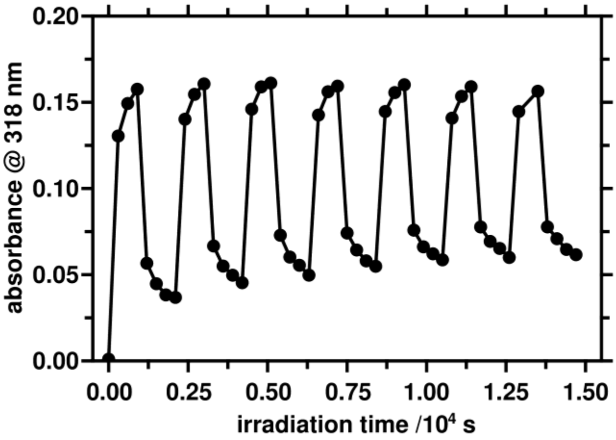


Figure S5: Absorbance trend for illumination series at 10 °C.

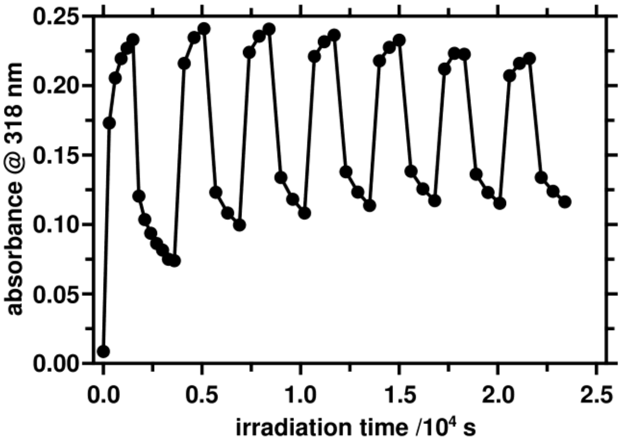


Figure S6: Absorbance trend for illumination series at 35 °C.

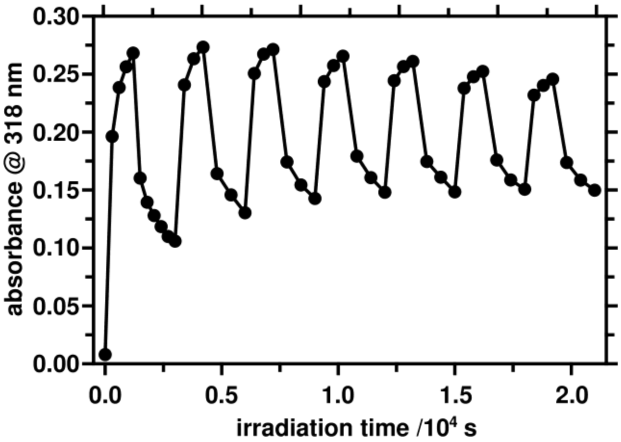


Figure S7: Absorbance trend for illumination series at 60 °C.

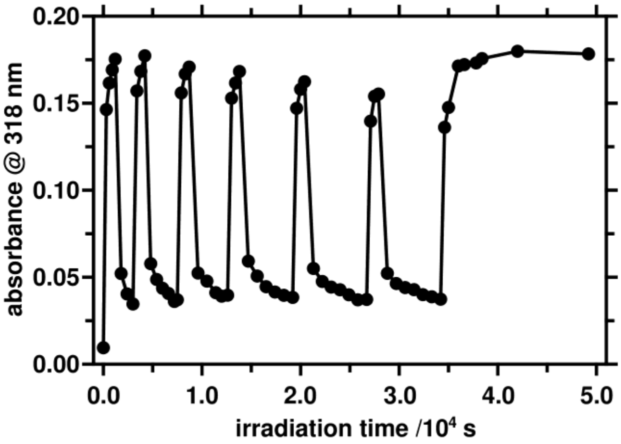


Figure S8: Absorbance trend for illumination series at 10 °C with prolonged illumination intervals for cycloaddition reaction.

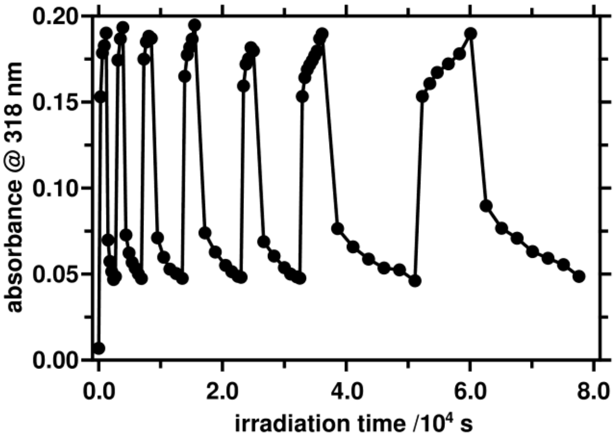


Figure S9: Absorbance trend for illumination series at 10 °C with prolonged illumination intervals for both wavelengths.

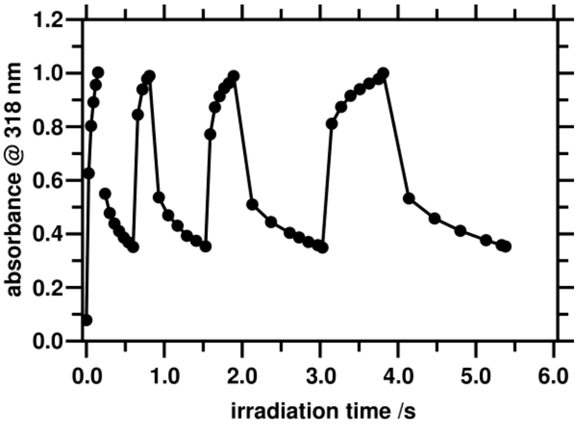


Figure S10: Absorbance trend for illumination series of the crosslinked polymer at 10 °C with prolonged intervals for both wavelengths, experiment 1.

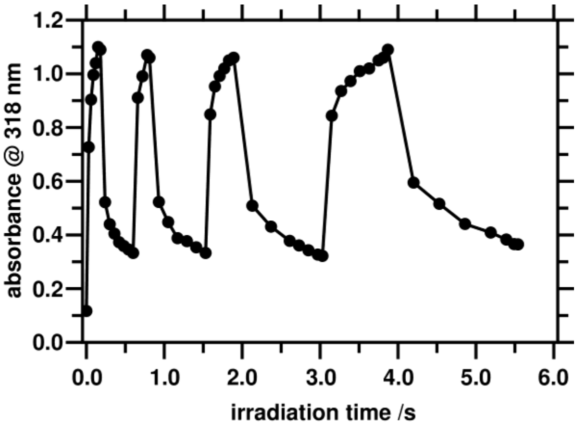


Figure S11: Absorbance trend for illumination series of the crosslinked polymer at 10 °C with prolonged intervals for both wavelengths, experiment 2.

References

S1 S. Inacker, J. Fanelli, S. I. Ivlev, N. A. Hampp, *Macromolecules*, 2022, **55**, 8461-8471.

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