Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Fluorescent Polymers from Non-Fluorescent Photoreactive Monomers

Jan O. Mueller,[a,b] *Dominik Voll,*[a,b] *Friedrich G. Schmidt,*[c] *Guillaume Delaittre**[a,d] *and Christopher Barner-Kowollik**[a,b]

[a] Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany.

[b] Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

[c] Evonik Industries AG, Paul-Baumann-Strasse 1, 45764 Marl, Germany.

[d] Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

Synthetic procedures

Synthesis of tetrazole acid chloride

(4-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)benzoyl chloride)

Tet-acid (4-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)benzoic acid, 3.00 g, 10.1 mmol, 1.00 eq) was suspended in dry THF (80 mL) and $SOCl_2$ (12.05 g, 7.34 mL, 101.3 mmol, 10.0 eq) was added under inert atmosphere. The mixture was heated to reflux (75 °C) for 3.5 h and the volatiles were subsequently removed under reduced pressure. The residue was dissolved two times in dry THF (40 mL) and dried in vacuum to remove the excess of $SOCl_2$. The resulting product was used without further purification steps as starting material for the synthesis of $\mathbf{M_1}$ and $\mathbf{M_2}$.

Synthesis of $\mathbf{M_1}$

2-(Acryloyloxy)ethyl 4-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)benzoate ($\mathbf{M_1}$)

Tetrazole acid chloride (3.10 g, 9.86 mmol, 1.00 eq) was dissolved in dry THF (80 mL) and added dropwise to a cooled solution (0 °C) of 2-hydroxyethyl acrylate (HEA, 11.5 g, 11.3 mL, 98.6 mmol, 10.0 eq) and pyridine (2.92 g, 3.00 mL, 37.0 mmol, 3.75 eq) in dry THF (15 mL). After complete addition, the reaction mixture was stirred at 0 °C for an additional hour before it was stirred at ambient temperature overnight. All purification steps were carried out in a yellow light laboratory using a high pressure sodium lamp (refer to the *Materials section*). The precipitate was subsequently removed by filtration. The solution was diluted with DCM (300 mL) and washed 2 times with HCl (5 %, 2 × 130 mL), distilled water (2 × 130 mL) and brine (2 × 130 mL). The organic phase was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The crude monomer $\mathbf{M_1}$ was washed two times with cold ethanol and

subsequently dried under reduced pressure. The pure monomer **M_1** was obtained by column chromatography (silica gel, CH/EA (1:1)) as a white solid; yield: 0.75 g (19 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 8.33 (d, J^3 = 8.6 Hz, 2H, a), 8.19 (d, J^3 = 8.7 Hz, 2H, b), 8.11 (d, J^3 = 9.2 Hz, 2H, c), 7.07 (d, J^3 = 9.2 Hz, 2H, d), 6.47 (m, 1H, e), 6.17 (m, 1H, f), 5.88 (m, 1H, g), 4.60 (m, 4H, h, i), 3.90 (s, 3H, k). ^{13}C NMR ($CDCl_3$, 100 MHz) δ / ppm: 166.08 (C, a), 165.92 (C, b), 164.22 (C, c), 160.85 (C, d), 131.64 (C, e), 130.47 (C, f), 128.13 (C, g), 127.08 (C, h), 121.61 (C, i), 114.89 (C, k), 63.09 (C, l), 62.34 (C, m), 55.83 (C, n).

Synthesis of M_2

Step 1

3-Hydroxypropyl fumarate

Monoethyl fumarate (10.0 g, 87.6 mmol, 1.00 eq), 1,3-propanediol (25.3 mL, 26.6 g, 350 mmol, 4.00 eq), and 4-dimethylaminopyridine (4-DMAP, 214 mg, 17.5 mmol, 0.02 eq) were dissolved in dry THF (200 mL). The solution was cooled to 0 °C in an ice bath and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide-hydrochloride (EDC-HCl, 21.8 g, 114 mmol, 1.30 eq) was added portion-wise to the stirred solution. After complete addition, the reaction mixture was stirred at 0 °C for an additional hour before it was stirred at ambient temperature overnight. The solvent was removed under reduced pressure and the residue was dissolved in diethyl ether (400 mL). The organic layer was washed two times with HCl (5 %, 3 × 150 mL), saturated $NaHCO_3$ solution (3 × 150 mL), and distilled water (3 × 150 mL). The organic phase was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The crude product was purified via column chromatography (silica gel, CH/EA (1:1)) to afford a light yellow oil; yield: 4.48 g (25 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ / ppm: 6.83 (s, 2H, a), 4.34 (t, J^3 = 6.2 Hz, 2H, b),

4.24 (q, J^3 = 7.1 Hz, 2H, c), 3.71 (m, 2H, d), 2.05 (bs, 1H, e), 1.91 (p, J^3 = 6.2 Hz, 2H, f), 1.30 (t, J^3 = 7.1 Hz, 3H, g). ^{13}C NMR ($CDCl_3$, 100 MHz) δ/ ppm: 165.39 (C, a), 165.03 (C, b), 134.09 (C, c), 133.37 (C, d), 62.34 (C, e), 61.52 (C, f), 59.05 (C, g), 31.64 (C, h), 14.18 (C, i).

Step 2

Ethyl 3-(4-(2-(4-methoxyphenyl)-2*H*-tetrazol-5-yl)benzoyloxy)propyl fumarate (**M_2**)

Tetrazole acid chloride (2.30 g, 7.31 mmol, 1.00 eq) was dissolved in dry THF (60 mL) and added dropwise to a cooled solution (0 °C) of ethyl 3-hydroxypropyl fumarate (refer to step 1, 4.43 g, 21.9 mmol, 3.00 eq) and pyridine (2.17 g, 2.21 mL, 27.4 mmol, 3.75 eq) in dry THF (12 mL) via a syringe. After complete addition, the reaction mixture was stirred at 0 °C for an additional hour before it was stirred at ambient temperature overnight. All purification steps were carried out in a yellow light laboratory using a high pressure sodium lamp (refer to the *Materials section*). The precipitate was subsequently removed by filtration. The solution was diluted with DCM (250 mL) and washed 2 times with HCl (5 %, 2 × 100 mL), distilled water (2 × 100 mL) and brine (2 × 100 mL). The organic phase was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The crude monomer M_2 was washed two times with cold ethanol to remove major impurities and subsequently dried under reduced pressure. The pure monomer M_2 was obtained by column chromatography (silica gel, CH/EA: (1/1)) as a white solid; yield: 1.41 g (40 %). ^{1}H NMR ($CDCl_3$, 400 MHz) δ/ ppm: 8.33 (d, J^3 = 8.3 Hz, 2H, a), 8.18 (d, J^3 = 8.3 Hz, 2H, b), 8.12 (d, J^3 = 9.1 Hz, 2H, c), 7.08 (d, J^3 = 9.1 Hz, 2H, d), 6.86 (s, 2H, e), 4.48 (t, J^3 = 6.2 Hz, 2H, f), 4.41 (t, J^3 = 6.2 Hz 2H, g) 4.25 (q, J^3 = 7.1 Hz, 2H, h), 3.91 (s, 3H, i), 2.22 (p, J^3 = 6.2 Hz, 2H, k), 1.31 (t, J^3 = 7.1 Hz, 3H, l). ^{13}C NMR ($CDCl_3$, 100 MHz) δ/ ppm: 166.04 (C, a), 164.99 (C, b), 164.24 (C, c), 160.86 (C, d), 134.26 (C, e), 133.25 (C, f),

131.69 (C, g), 130.36 (C, h), 127.09 (C, i), 121.63 (C, k), 114.91 (C, l), 61.90 (C, m), 55.85 (C, n), 28.17 (C, o), 14.24 (C, p).

Photopolymerization procedure

All photopolymerization samples were prepared in crimp-top vials (refer to the *Materials section*) containing 2 mg **M_1** or **M_2** and 20 µL THF or DMAC (c = 100 mg mL^{-1}) if not otherwise stated. The vials were sealed with appropriate caps and directly irradiated in a custom-built photoreactor. After the desired reaction time, the solvent of each sample was removed under reduced pressure. Subsequently, NMR spectra (in $CDCl_3$) and GPC (in THF or DMAC) were measured.

Materials

Tetrazole acid (**tet-acid**) was synthesized according to literature.[1] Cyclohexane (CH, VWR, GPR RECTAPUR), dichloromethane (DCM, VWR, AnalaR NORMAPUR), dichloromethane (DCM, Arcos Organics, extra dry, 99.8 %), diethyl ether (Et_2O, Fisher Chemical, reagent grade), 4-dimethylaminopyridine (4-DMAP, Fluka Analytical, purum, >98 %), ethyl acetate (EA, VWR, AnalaR NORMAPUR), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide-hydrochloride (EDC-HCl, Carl Roth, ≥99 %), hydrochloric acid (HCl, 37 %, Carl Roth), 2-hydroxyethyl acrylate (HEA, Aldrich, 96 %, contains monomethyl ether hydroquinone as inhibitor), magnesium sulfate ($MgSO_4$, Carl Roth, ≥99 %), monoethyl fumarate (Aldrich, 95 %), 1,3-propanediol (Aldrich, 98 %), pyridine (Alfa Aesar, 99+ %), silica gel (Merck, Geduran Si 60, 40-63 µm, for column chromatography), sodium chloride (NaCl, Carl Roth, >99.8 %), sodium hydrogen carbonate ($NaHCO_3$, Carl Roth, ≥99 %), tetrahydrofuran (THF, Acros Organics, extra dry, 99.5 %, stabilized), and thionyl chloride ($SOCl_2$, Aldrich, ReagentPlus, ≥99 %) were used as received. Chloroform-d_1 ($CDCl_3$, EURISO-TOP, 99.8 %,) was utilized for all NMR measurements. For ESI-MS measurements tetrahydrofuran (THF, Scharlau, Multisolvent, stabilized with BHT), and methanol (MeOH, Carl Roth, ROTISOLV HPLC ultra gradient grade) were used as solvent as received. For GPC measurements tetrahydrofuran (THF, Scharlau, Multisolvent, stabilized with BHT), and dimethylacetamide (DMAC, Aldrich, CHROMASOLV Plus for HPLC, ≥99 %) were used as solvent as received. For photopolymerization reactions tetrahydrofuran (THF, Scharlau,

[1] C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns, A. S. Goldmann, M. Bastmeyer and C. Barner-Kowollik, *Adv. Mater.*, 2013, **25**, 6123.

Multisolvent, stabilized with BHT), and dimethylacetamide (DMAC, Aldrich, CHROMASOLV Plus for HPLC, ≥99 %) were used as solvent as received.

Purification of the monomers and the polymerization sample preparation were conducted in a laboratory illuminated by a high pressure sodium lamp (SYLVANIA TWINARC, SHP-S, 50 W, E27) (yellow light) due to the photosensitivity of $\mathbf{M_1}$ and $\mathbf{M_2}$. The photopolymerization reactions were performed utilizing crimp-top vials (VWR, crimp neck vial, 0.7 mL, 40×7 mm, clear glass, conical) and the corresponding caps (VWR, cap alu 8 mm, silicon white/PTFE red 1.3 mm).

Characterization

Size exclusion chromatography (SEC). To determine molecular weight distributions (MWD) a SEC system (Polymer Laboratories PL-GPC 50 Plus) comprised of an auto injector, a guard column (PLgel Mixed C, 50 × 7.5 mm) followed by three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 μm bead-size) and a differential refractive index detector was employed. THF was used as the eluent at 35 °C, with a flow rate of 1 mL·min^{-1}. The SEC system was calibrated using narrow poly(methyl methacrylate) standards ranging from 600 to 6 × 105 g mol^{-1} (Polymer Standards Service (PSS), Mainz, Germany). The resulting molecular weight distributions were determined by universal calibration using Mark-Houwink parameters for polystyrene (K = 14.1 × 10^{-5} dL g^{-1}, α = 0.7).

NMR spectroscopy. The synthesized compounds were analyzed *via* ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker Avance 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz). Samples were dissolved in $CDCl_3$. The δ-scale was referenced with tetramethylsilane (δ = 0.00) as internal standard. Abbreviations used in the description of the materials' syntheses include singlet (s), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

Electrospray ionization - mass spectrometry (ESI-MS). ESI-MS spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m*/*z* range of 195-1822 using a standard containing 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 was used. Nitrogen was applied at a dimensionless sweep gas flow-rate of 2 (approx. 3 L min^{-1}) and a dimensionless sheath gas flow-rate of 12 (approx. 1 L min^{-1}) were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 60 V, 110 V, and 300 °C respectively.

Fluorescence and UV-Vis spectroscopy. Fluorescence emission spectra were recorded for samples in quartz cuvettes loaded with a sample volume of 230 µL on a Varian Cary Eclipse Fluorescence Spectrometer. UV-Visible spectroscopy was performed using a Varian Cary 300 Bio spectrophotometer featuring a thermostatted sample cell holder. Absorption spectra were measured for 1.0×10^{-4} mol L^{-1} samples in acetonitrile solution from 200 to 800 nm with a resolution of 1 nm and slit width of 2 nm in a 1 cm UV cuvette.

Size exclusion chromatography

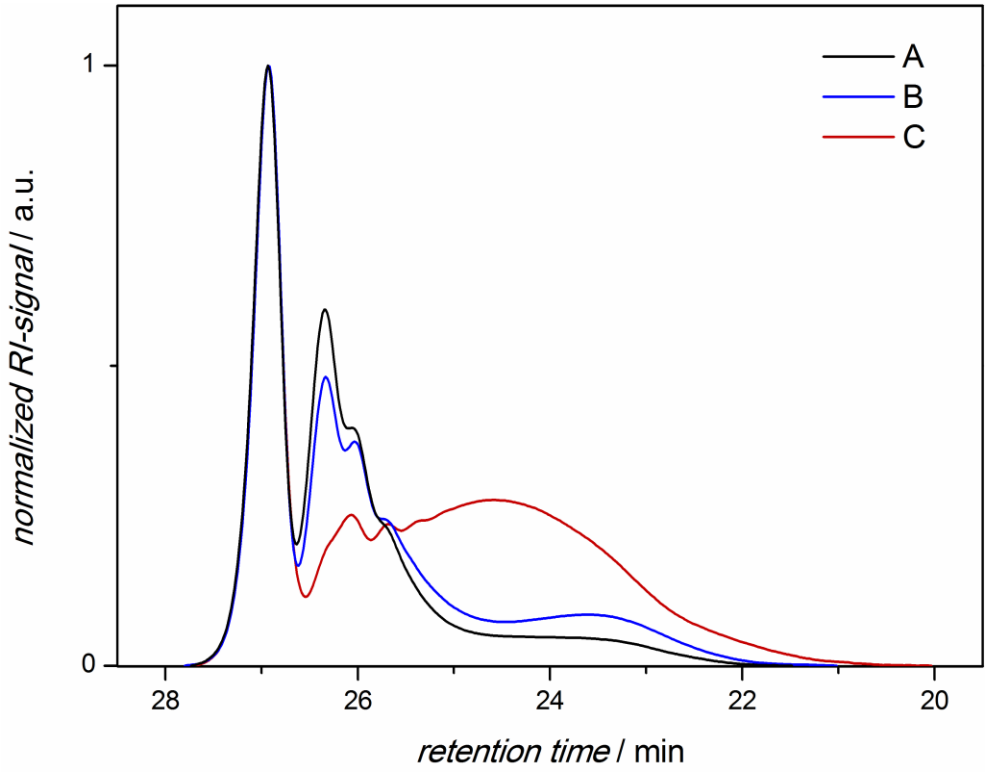


Fig. S1 SEC chromatograms of the crude **Ppy$_1$** samples of the concentration study conducted with monomer **M$_1$** (2 mg) in THF for 24 h utilizing DMAC as eluent. A: 2 mg mL^{-1}, M_n = 1,600 g mol^{-1}, M_w = 2,700 g mol^{-1}, *PDI* = 1.69. B: 10 mg mL^{-1}, M_n = 1,800 g mol^{-1}, M_w = 3,700 g mol^{-1}, *PDI* = 2.07. C: 40 mg mL^{-1}, M_n = 2,400 g mol^{-1}, M_w = 6,000 g mol^{-1}, *PDI* = 2.56.

An increasing amount of high molar mass material compared to the dimer signal was found with increasing concentration of the reaction medium.

Size exclusion chromatography

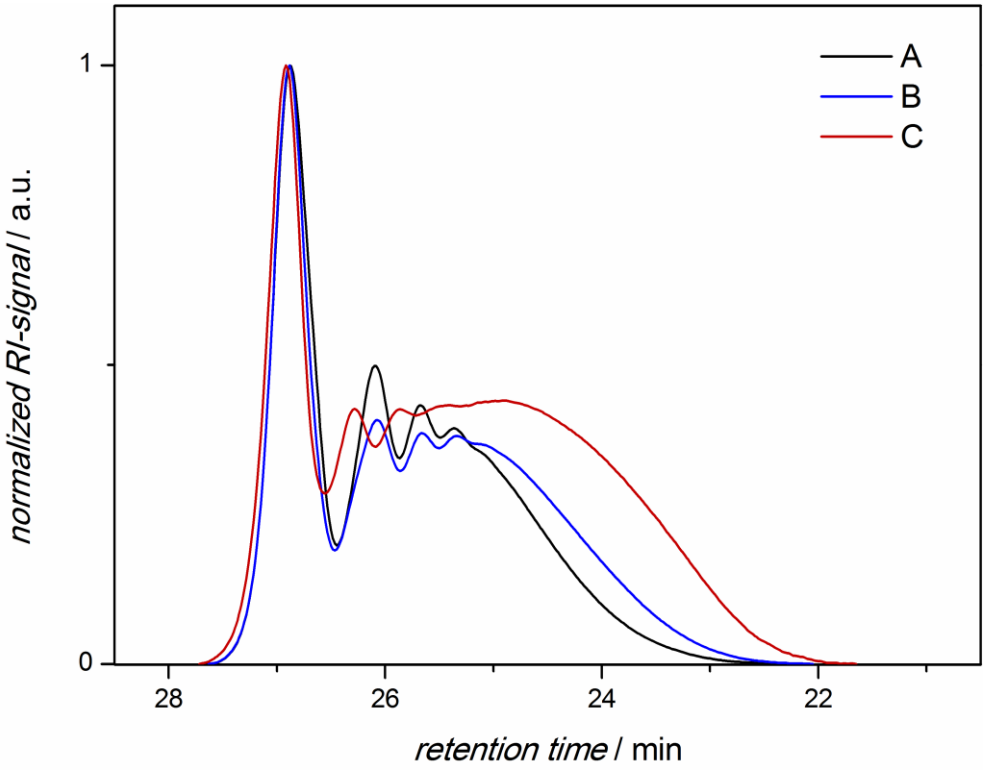


Fig. S2 SEC chromatograms of the crude **Ppy$_1$** samples of the total batch size study conducted with monomer **M$_1$** in DMAC (100 mg mL^{-1}) for 24 h utilizing DMAC as eluent. A: 10 mg, M_n = 2,100 g mol^{-1}, M_w = 3,300 g mol^{-1}, PDI = 1.56. B: 5 mg, M_n = 2,300 g mol^{-1}, M_w = 4,000 g mol^{-1}, PDI = 1.73. C: 5 mg, M_n = 2,600 g mol^{-1}, M_w = 5,400 g mol^{-1}, PDI = 1.73.

When the total batch size was reduced from 10 mg, over 5 mg, to 2 mg an increasing amount of high molar mass material compared to the dimer signal was found after the same irradiation time.

Electrospray-ionization mass spectrometry

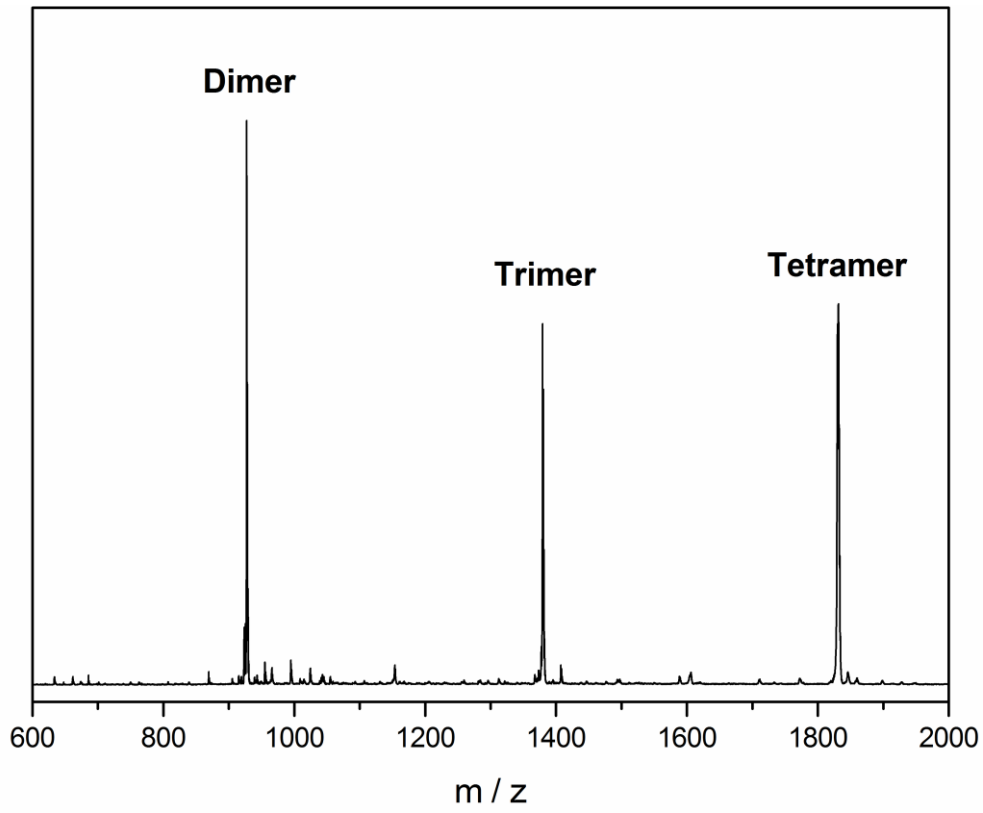
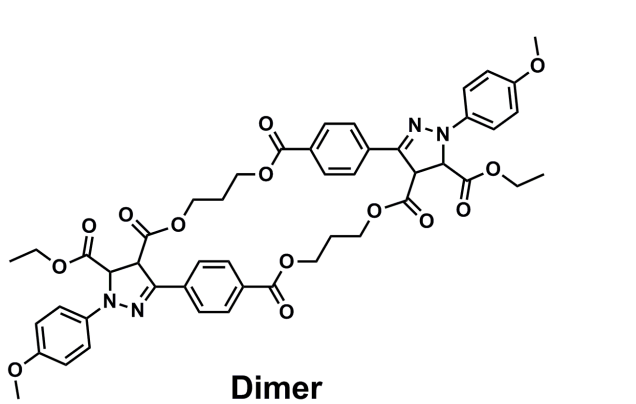


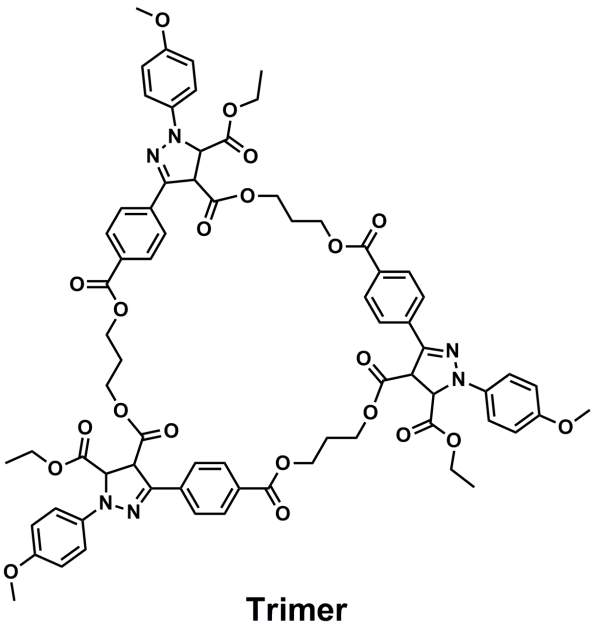
Fig. S3 ESI-MS spectrum of the low molecular weight material accumulated during the polymerization process of monomer **M_2**.

Table S1 Experimental and theoretical *m*/*z* values of the low molecular weight termination product corresponding to the ESI-MS spectrum in Fig. S3. Proposals of the respective structures are provided in Scheme S1.

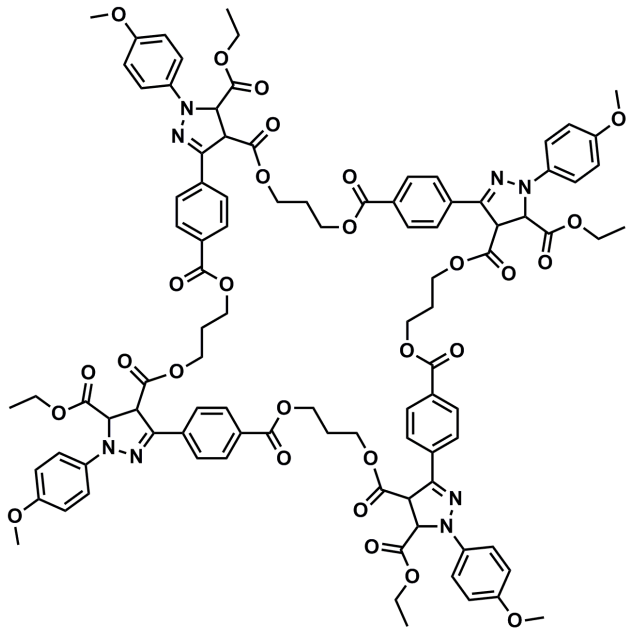
Signal	m/z_{exp}	m/z_{theo}	Sum formula
Dimer	927.50	927.31	$C_{48}H_{48}N_4O_{14}Na^+$
Trimer	1379.58	1379.46	$C_{72}H_{72}N_6O_{21}Na^+$
Tetramer	1831.50	1831.63	$C_{96}H_{96}N_8O_{28}Na^+$



Dimer



Trimer



Tetramer

Scheme S1 Structures of the cyclic small molecular weight termination products.

NMR spectra kinetic study

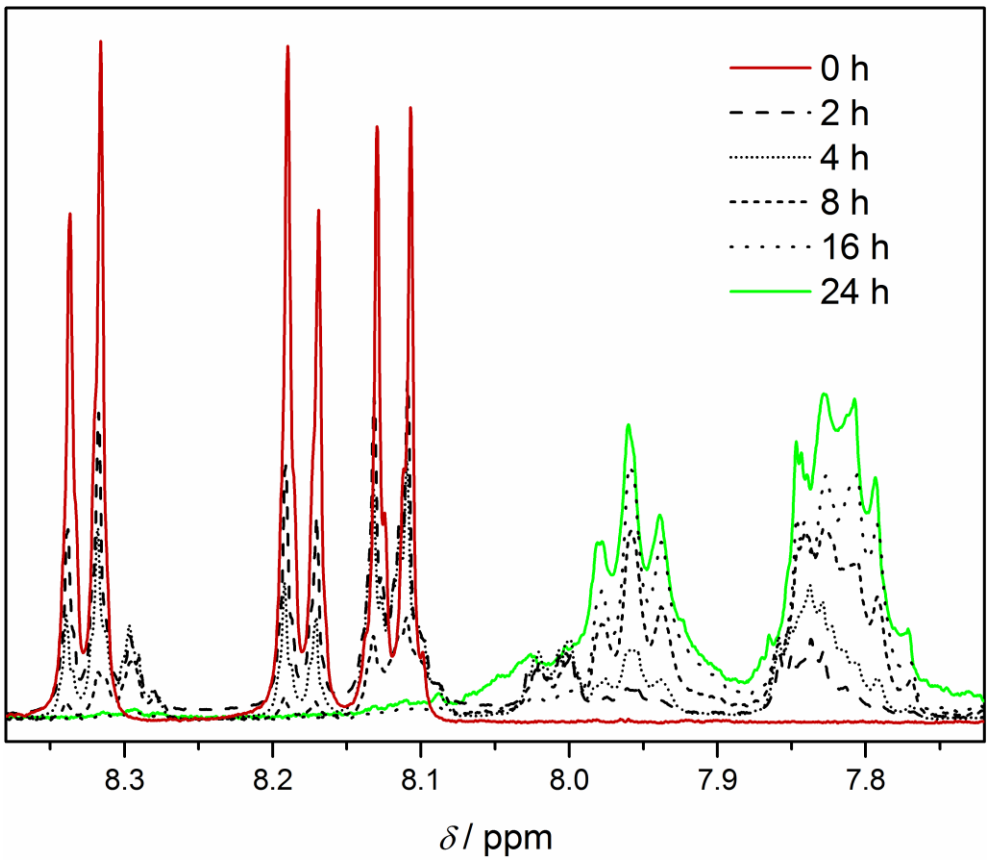


Fig. S4 ^{1}H NMR spectra of the **Ppy$_2$** samples in the kinetic study conducted with 1 UV-lamp irradiating monomer **M$_2$** in THF (100 mg mL^{-1}) utilizing $CDCl_3$ as solvent for NMR measurements.

NMR spectra kinetic study

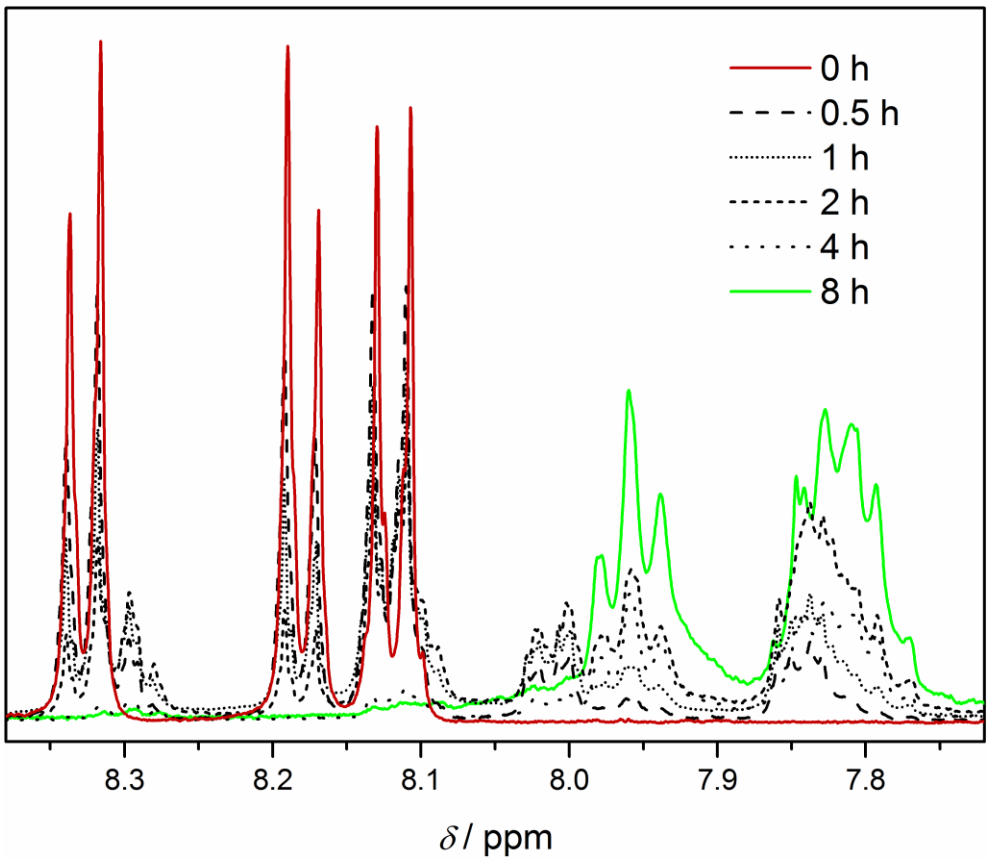


Fig. S5 ^{1}H NMR spectra of the **Ppy$_2$** samples in the kinetic study conducted with 3 UV-lamps irradiating monomer **M$_2$** in THF (100 mg mL^{-1}) utilizing $CDCl_3$ as solvent for NMR measurements.

SEC chromatograms kinetic study

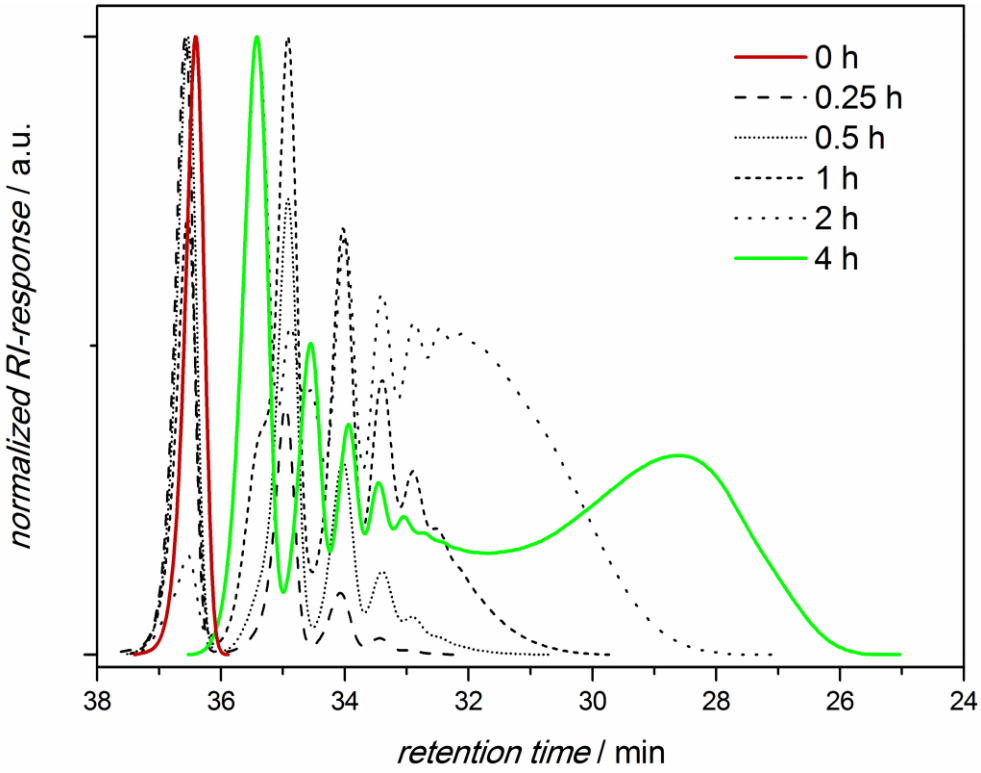


Fig. S6 SEC chromatograms of the **Ppy_2** samples of the kinetic study conducted with 5 UV-lamps irradiating monomer **M_2** in THF (100 mg mL^{-1}) utilizing THF as eluent for SEC analysis.

SEC chromatograms kinetic study

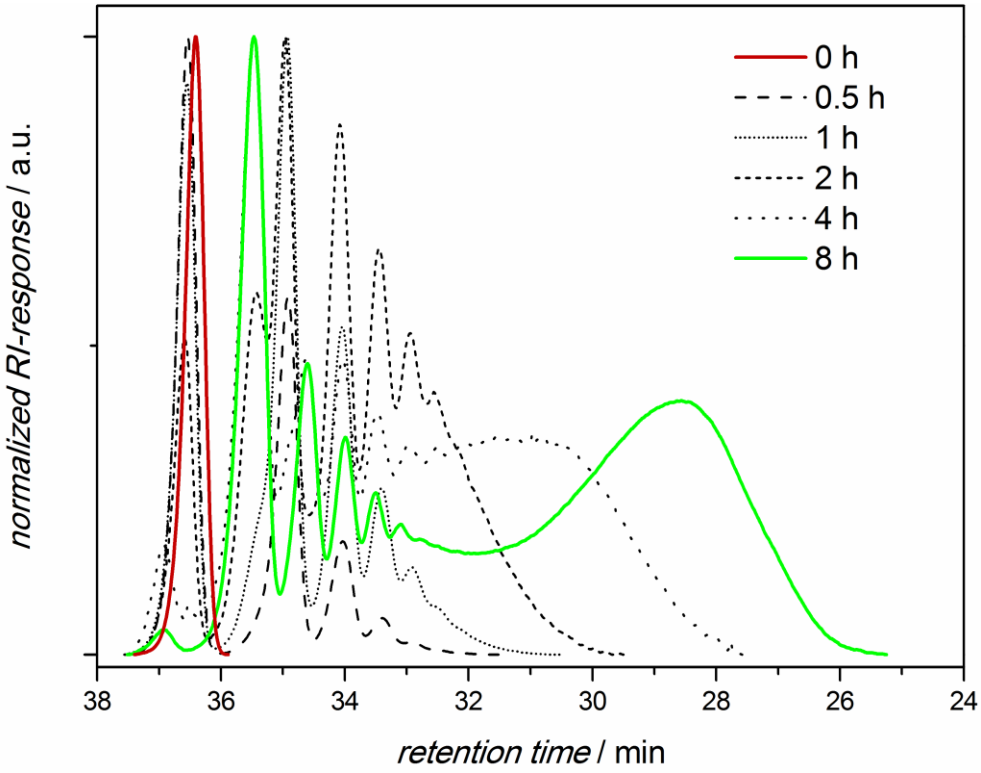


Fig. S7 SEC chromatograms of the **Ppy_2** samples of the kinetic study conducted with 3 UV-lamps irradiating monomer **M_2** in THF (100 mg mL^{-1}) utilizing THF as eluent for SEC analysis.

SEC chromatograms kinetic study

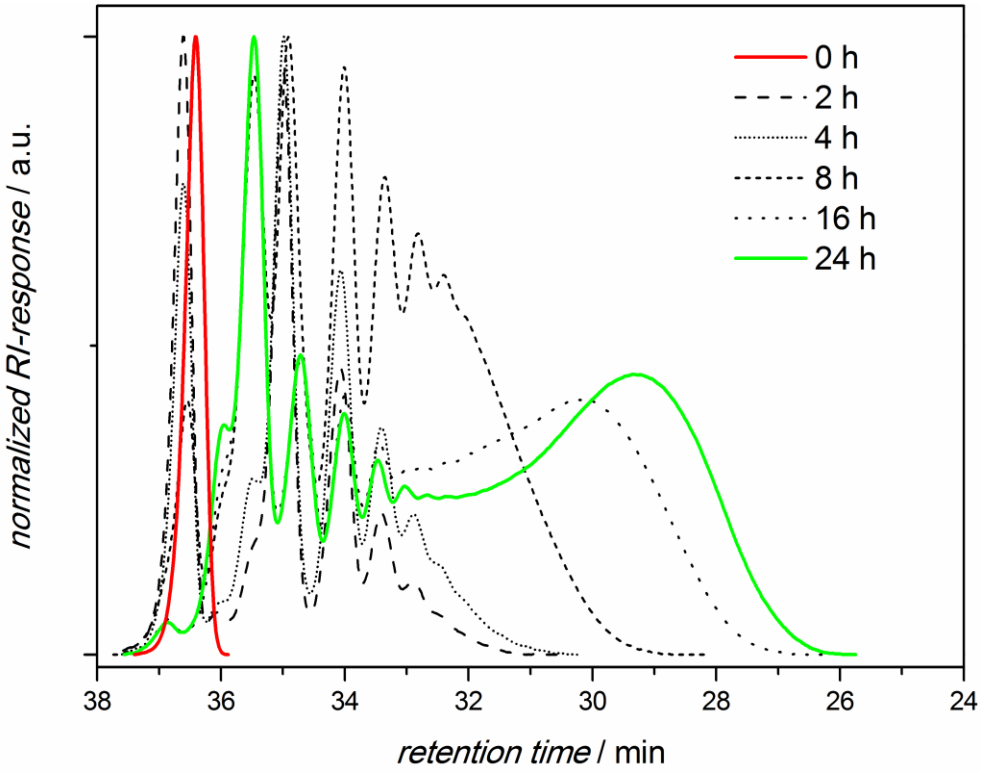


Fig. S8 SEC chromatograms of the **Ppy_2** samples of the kinetic study conducted with 5 UV-lamps irradiating monomer **M_2** in THF (100 mg mL^{-1}) utilizing THF as eluent for SEC analysis.

Calculations concerning the kinetic study

The conversion values for the kinetic study were determined by comparison of the integration values of a proton resonance in $\mathbf{M_2}$ and $\mathbf{Ppy_2}$. Therefore, equation 1 (Eq. S1) was applied, where $\boldsymbol{x}$ refers to the integral of the monomer signal and $\boldsymbol{x'}$ is assigned to the integration value of the correlating product resonance. In order to obtain the plotted values, resonances **a**;**a'** (Fig. 2a, Main Text) were inserted for $\boldsymbol{x}$;$\boldsymbol{x'}$, yet the integration values for the pairings **b**;**b'**, **k**;**k'**, or **l**;**l'** deliver similar values.

$$\boldsymbol{conversion}\ [\%] = \frac{\mathbf{100}\times \boldsymbol{x'}}{\boldsymbol{x}+\boldsymbol{x'}} \qquad \textbf{Eq. S1}$$

The kinetic parameters (Table S2) were determined by exponentially fitting the experimental data applying equation S2, which corresponds to a pseudo first order process. The kinetic plots and the corresponding fits are depicted in Fig. S9.

$$\boldsymbol{c_t} = \boldsymbol{c_0} \times \boldsymbol{e^{-kt}} + \boldsymbol{A} \qquad \textbf{Eq. S2}$$

Carothers equation for the weight average molecular weight ($\boldsymbol{M}_\mathbf{w}$), where $\boldsymbol{M_0}$ displays the molar mass of the photomonomer and $\boldsymbol{p}$ represents the conversion.

$$\boldsymbol{M_w} = \boldsymbol{M_0}\frac{\mathbf{1}+\boldsymbol{p}}{\mathbf{1}-\boldsymbol{p}} \qquad \textbf{Eq. S3}$$

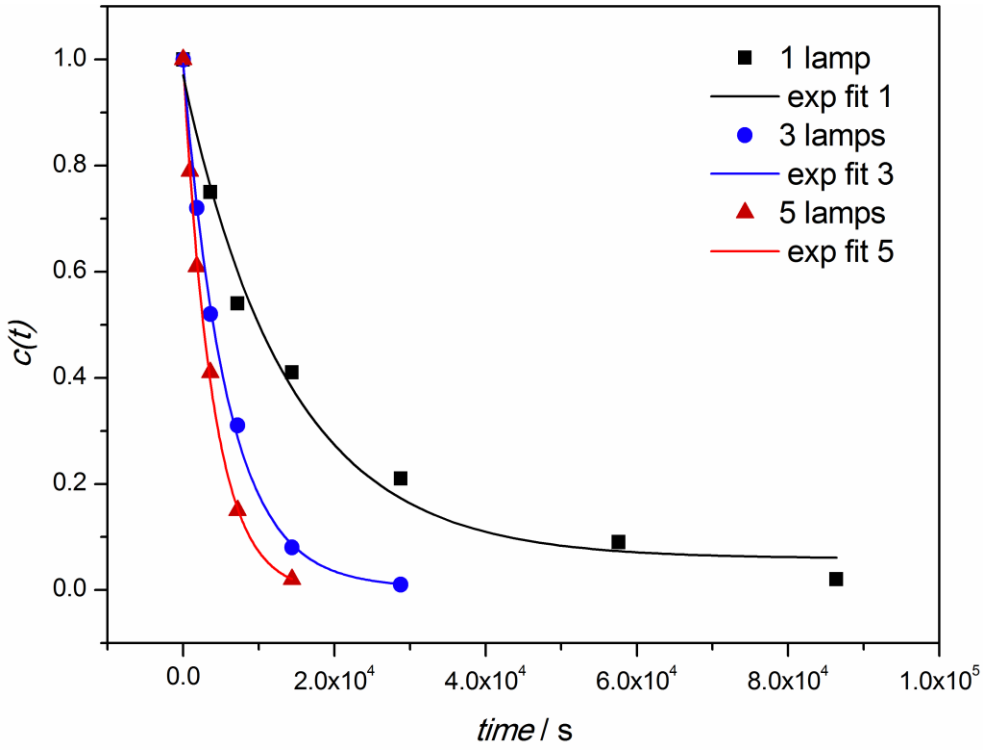


Fig. S9 Kinetic plots displaying the tetrazole decay under variation of the irradiation intensity. The exponential fits correlate with Eq. S2.

Table S2 Parameters of Eq. S2 and their respective standard deviation (σ) determined from the kinetic plots of Fig. S9.

entry	c_0	$\sigma(c_0)$	A	$\sigma(A)$	k [s^{-1}]	$\sigma(k$ [s^{-1}])
1 lamp	0.911	$5.92\ 10^{-2}$	$5.92\ 10^{-2}$	$3.48\ 10^{-2}$	$7.23\ 10^{-5}$	$1.03\ 10^{-5}$
3 lamps	0.988	$1.94\ 10^{-2}$	$4.56\ 10^{-3}$	$1.55\ 10^{-2}$	$1.73\ 10^{-4}$	$8.80\ 10^{-6}$
5 lamps	1.000	$1.76\ 10^{-2}$	$4.77\ 10^{-3}$	$1.63\ 10^{-2}$	$2.56\ 10^{-4}$	$1.22\ 10^{-5}$

UV-lamp specification

- *Arimed B6*, Cosmedico GmbH, Stuttgart, Germany. Compact low-pressure fluorescent lamp, 36 W, λ_{max} = 320 nm (±30 nm).

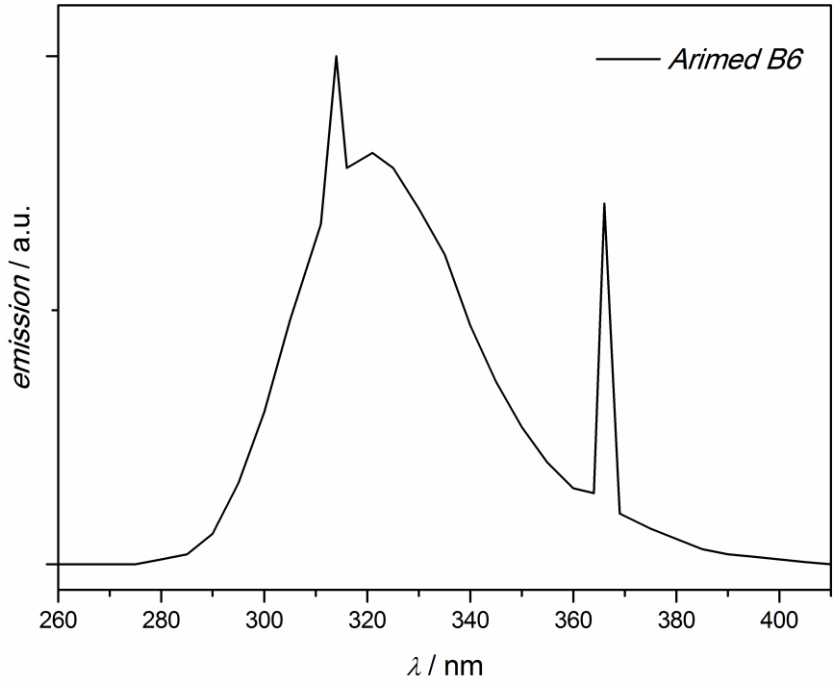


Fig. S10 Emission spectrum of the UV-lamp *Arimed B6*

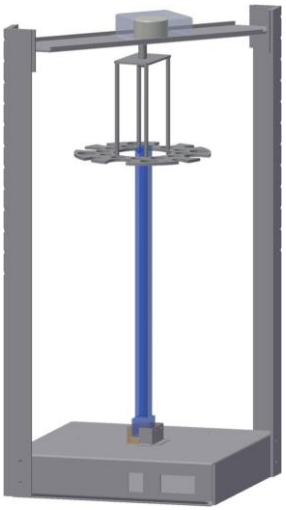
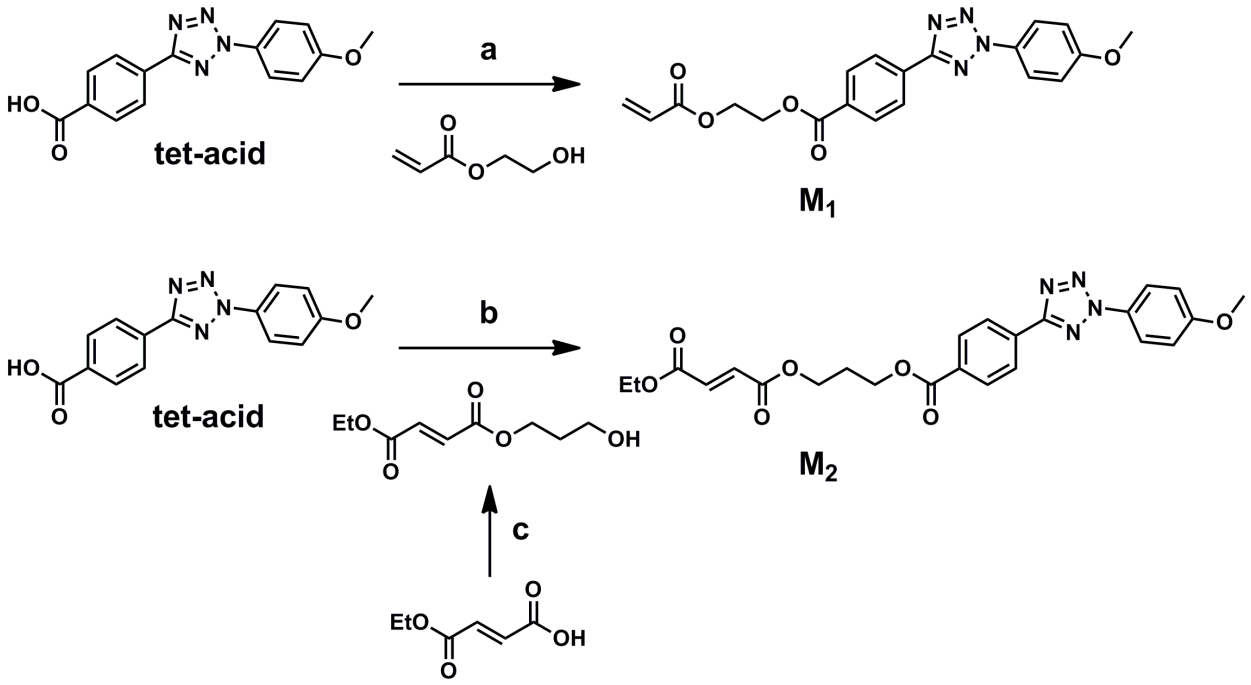


Fig. S11. Illustration of the custom-built photoreactor employed in the current study.

Synthesis of monomers M_1 and M_2



Scheme S1 Synthetic strategy for producing the monomers $\mathbf{M_1}$ and $\mathbf{M_2}$. a) 1. $SOCl_2$, dry THF, 4 h, 75 °C; 2. Dry THF, pyridine, 0 °C – RT, overnight. b) 1. $SOCl_2$, dry THF, 4 h, 75 °C; 2. Dry THF, pyridine, 0 °C – RT, overnight. **c**: Dry THF, 1,3-propanediol, EDC-HCl, 4-DMAP, 0 °C – RT, overnight.

Spectroscopic data of monomers M_1 and M_2

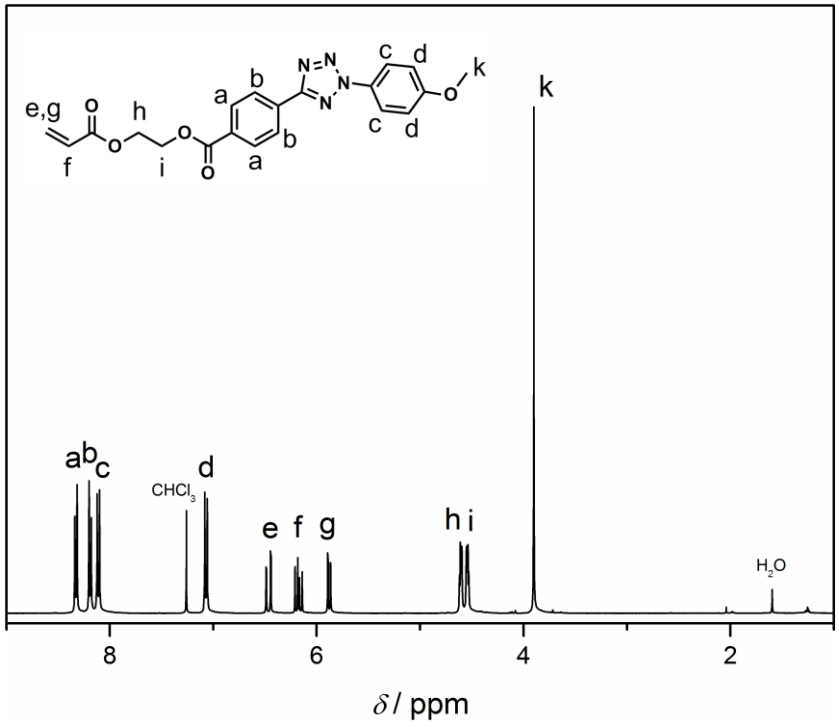


Fig. S12 ^{1}H-NMR spectrum of **M_1** recorded in $CDCl_3$.

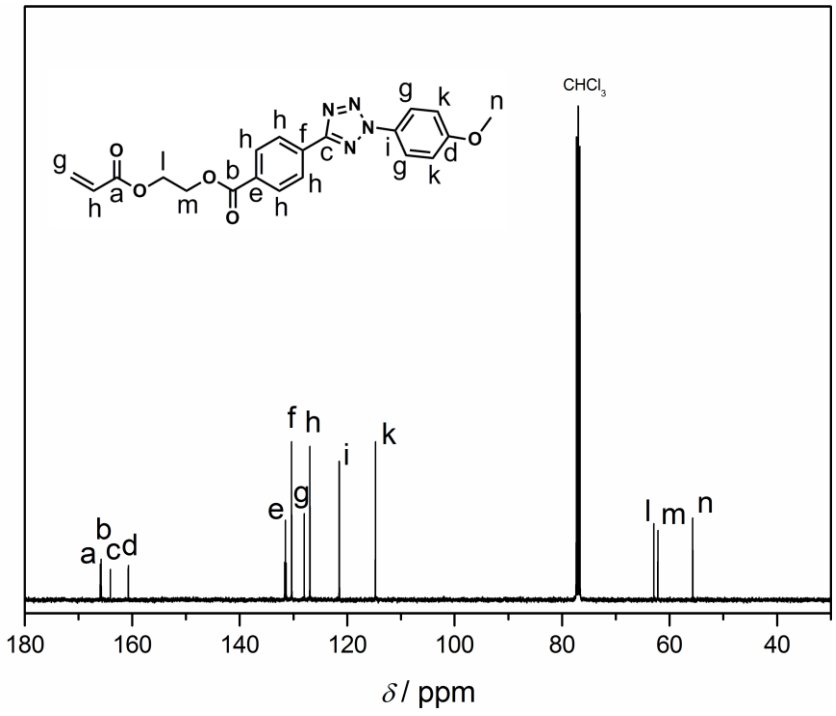


Fig. S13 ^{13}C-NMR spectrum of **M_1** recorded in $CDCl_3$.

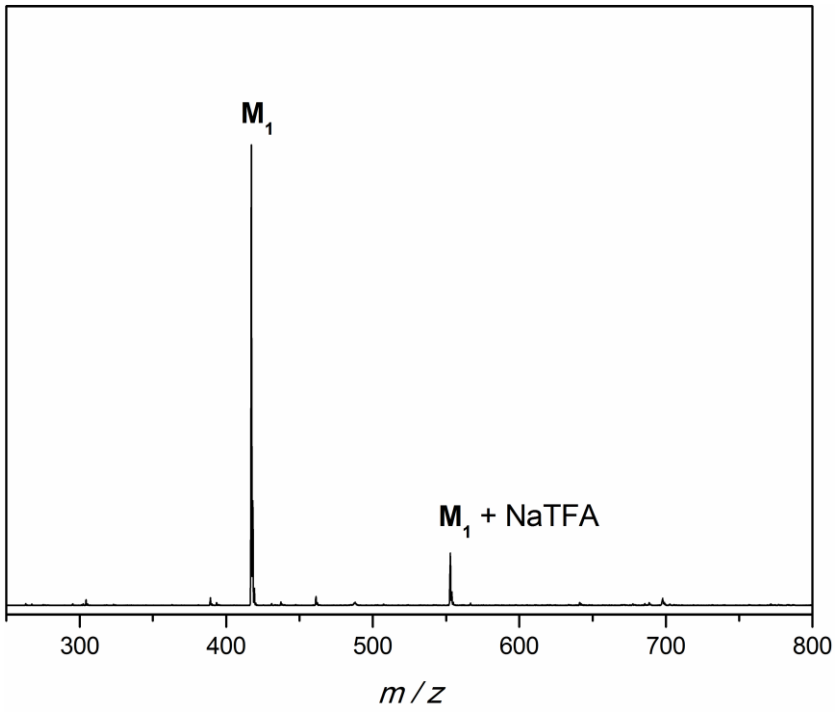


Fig. S14 ESI-MS spectrum of $\mathbf{M_1}$ recorded in THF/MeOH (3:2) doped with sodium trifluoro acetate (NaTFA).

Table S3 Experimental and theoretical *m*/*z* values of $\mathbf{M_1}$ corresponding the ESI-MS spectrum in Fig. S14.

Signal	m/z_{exp}	m/z_{theo}	Sum formula
$\mathbf{M_1}$	417.25	417.12	$C_{20}H_{18}N_4O_5Na^+$
$\mathbf{M_1}$ + NaTFA	552.92	553.09	$C_{22}H_{18}N_4\,F_3O_7Na_2^+$

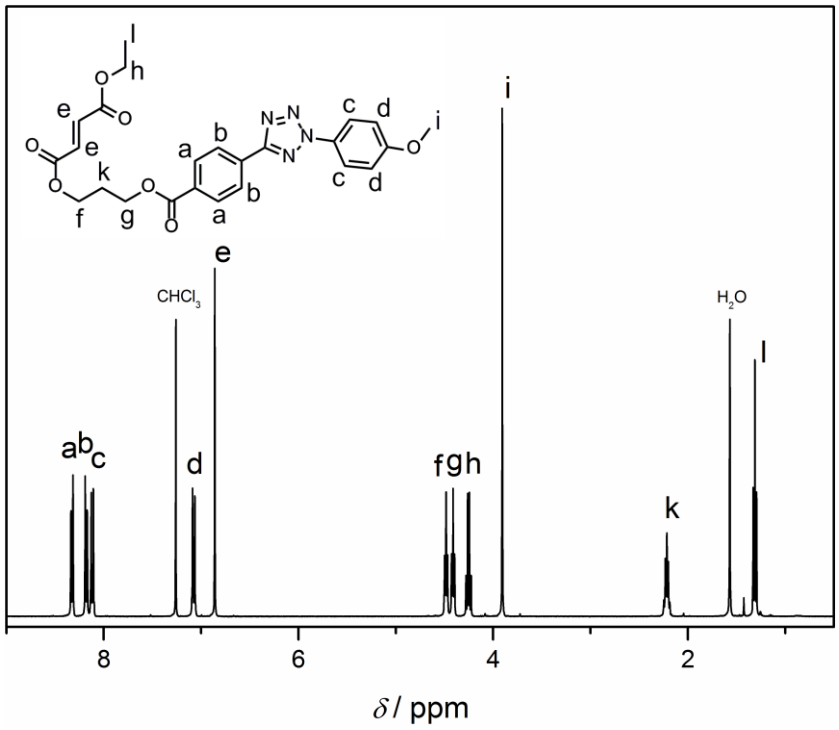


Fig. S15 ^{1}H-NMR spectrum of **M_2** recorded in $CDCl_3$.

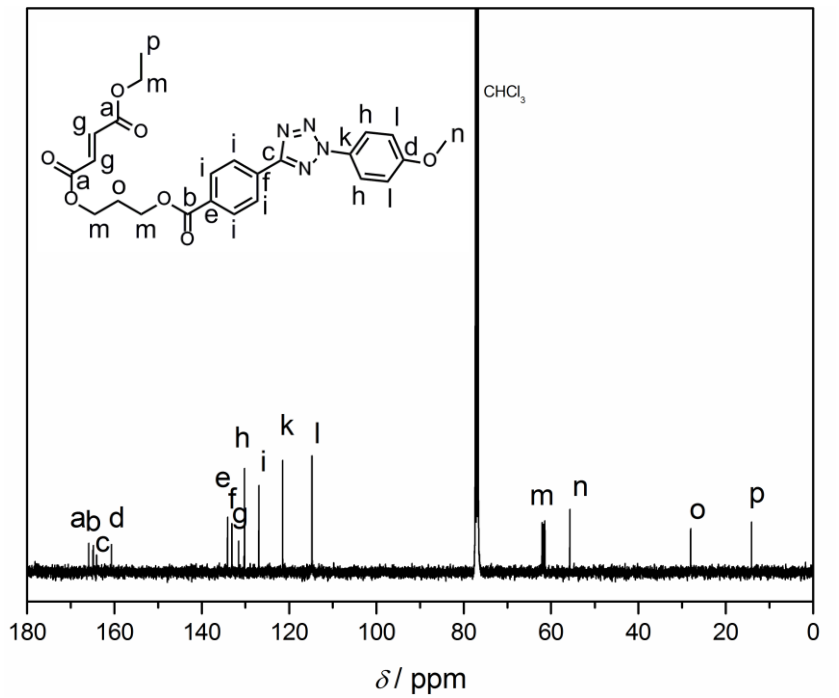


Fig. S16 ^{13}C-NMR spectrum of **M_2** recorded in $CDCl_3$.

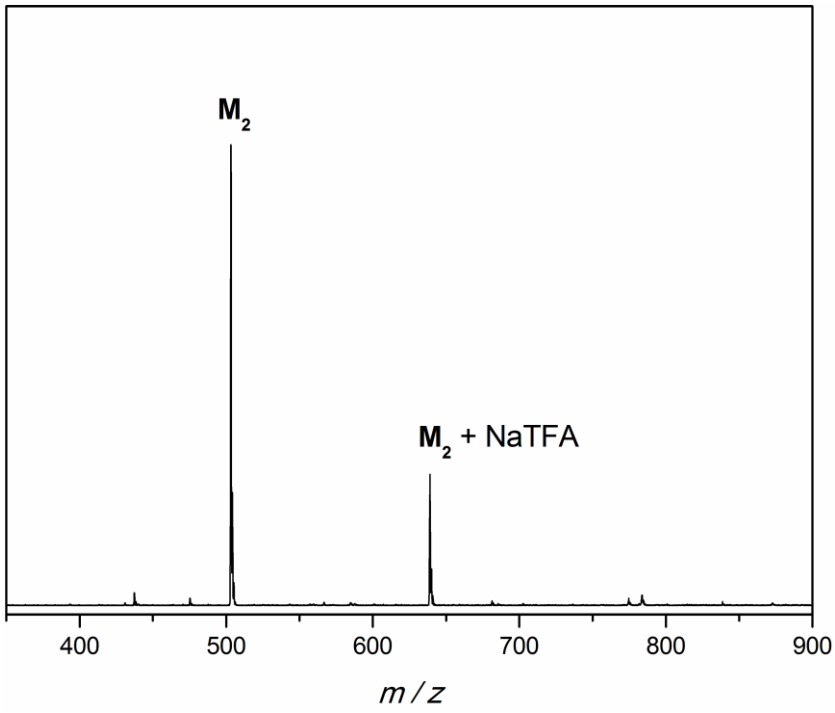


Fig. S17 ESI-MS spectrum of **M_2** recorded in THF/MeOH (3:2) doped with sodium trifluoro acetate (NaTFA).

Table S4 Experimental and theoretical *m*/*z* values of **M_2** corresponding the ESI-MS spectrum in Fig. S17.

Signal	m/z_{exp}	m/z_{theo}	Sum formula
M_2	503.25	503.15	$C_{24}H_{24}N_4O_7Na^+$
M_2 + NaTFA	639.00	639.13	$C_{26}H_{24}N_4F_3O_9Na_2^+$

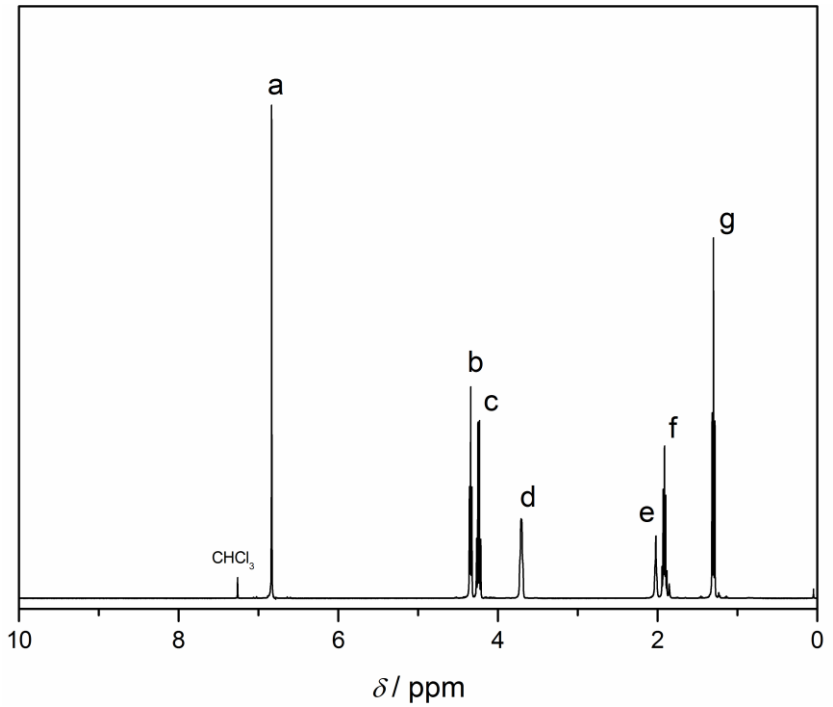


Fig. S18 ^{1}H-NMR spectrum of ethyl **3-hydroxypropyl fumarate** recorded in $CDCl_3$.

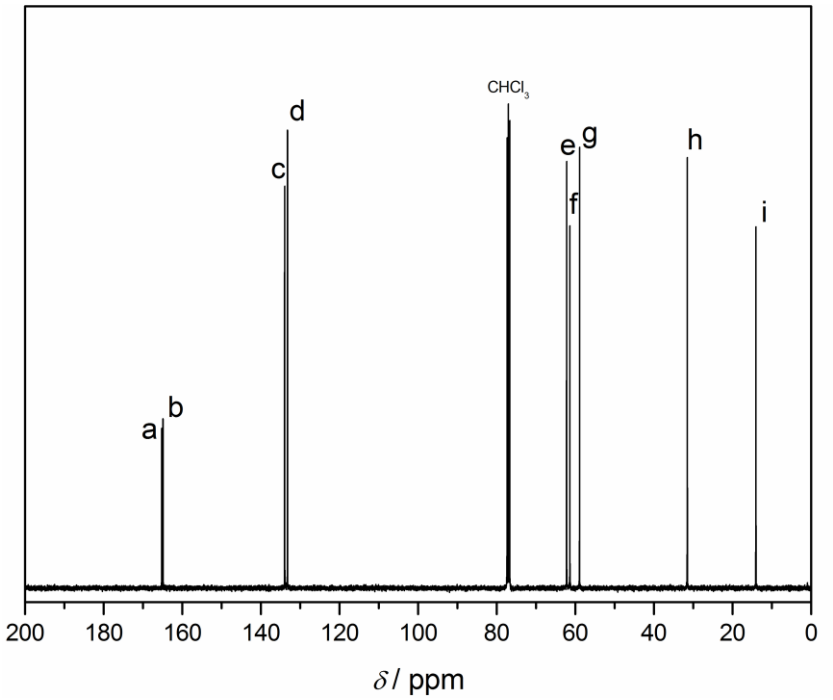


Fig. S19 ^{13}C-NMR spectrum of **3-hydroxypropyl fumarate** recorded in $CDCl_3$.