Supporting Information

**Wavelength Selective Polymer Network Formation of End-Functional Stars-Polymers**

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Materials

2,2'-Azobis(2-methylpropionitrile) (AIBN) was recrystallized twice from methanol and stored at -19 °C. 4-Chloromethyl-styrene was distilled and stored at -19 °C. 4-Bromostyrene was passed through a column of basic alumina to remove inhibitor and subsequently stored at -19 °C. 2-Hydroxy-6-methylbenzaldehyde, 4-(2-phenyl-2H-tetrazol-5-yl)benzoic acid, 4,10-dioxatricyclo-[5.2.1.0(2,6)]dec-8-ene-3,5-dione, and the maleimide containing copolymer were synthesized according to a literature procedure. All other chemicals were used as supplied by the manufacturers.

Synthesis of 2-(4-(bromomethyl)benzyloxy)-6-methylbenzaldehyde†

1,4-Bis(bromomethyl)benzene (8.26 g, 31.3 mmol, 3 equiv), K₂CO₃ (2.16 g, 15.65 mmol, 1.5 equiv) and 18-crown-6 (49 mg, 0.185 mmol, 0.18 equiv) were stirred in 100 mL of acetone at 40 °C. 2-Hydroxy-6-methylbenzaldehyde (1.41 g, 10.36 mmol, 1 equiv) dissolved in 25 mL of acetone was added dropwise and the mixture was stirred at 40 °C over night. After filtration, the solvent was removed under reduced pressure. The solid was suspended in cold acetone, the residue filtered off

† The identical polymer as in reference 4 was employed in the current project.

‡ M. K. acknowledges help in the optimization of the reaction procedure by Dipl. Chem. Marcel Langer, KIT, Karlsruhe, Germany.
and washed with cold acetone. The solvent was again removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 19:1, \( R_f = 0.25 \)) to afford a white solid (1.78 g, 54 %).  

\( ^1\)H-NMR (CDCl\(_3\), 400 MHz) \( \delta \)/ppm: 10.73 (s, 1H, CHO), 7.4 (m, 5H, paraAr and para to CHO), 6.8 (m, 2H, meta to CHO), 5.15 (s, 2H, OCH\(_2\)), 4.51 (s, 2H, BrCH\(_2\)), 2.59 (s, 3H, CH\(_3\)).  

\( ^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \)/ppm: 192.2 (CHO), 162.1 (OC\(_{arom}\)), 142.2 (OCH\(_2\)C\(_{arom}\)), 137.8 (CH\(_3\)C\(_{arom}\)), 136.5 (BrCH\(_2\)C\(_{arom}\)), 134.4 (CH\(_3\)CCH\(_2\)), 129.4 (BrCH\(_2\)C\(_{H}\)), 127.6 (OCH\(_2\)CC\(_{H}\)), 124.5 (CH\(_3\)CC\(_{H}\)), 123.6 (CHO\(_{arom}\)), 110.3 (OC\(_{H}\)), 70.1 (OCH\(_2\)), 33.0 (BrCH\(_2\)), 21.5 (CH\(_3\)).  

MS: (ESI) \( m/z \) calculated for C\(_{16}\)H\(_{15}\)BrO\(_2\) [M+Na]\(^+\): 341.0153, found 341.0153.

**Figure S 1** \( ^1\)H-NMR spectrum of 2-(4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde in CDCl\(_3\) at 400 MHz.

**Figure S 2** \( ^{13}\)C-NMR spectrum of 2-(4-(bromomethyl)benzyl)oxy)-6-methylbenzaldehyde in CDCl\(_3\) at 100 MHz.
Synthesis of 4-arm photo-enol RAFT agent (TetraPE-RAFT)

\[
\text{Br-}\text{CH}_2\text{CHO} + \text{CS}_2 + \left[\text{O-}\text{C-SH}\right]_4 \xrightarrow{\text{K}_3\text{PO}_4} \left[\text{O-}\text{C-S-S-CO}\right]_4
\]

Pentaerythritol tetrakis(3-mercaptopropionate) (454 mg, 0.929 mmol, 1 equiv), CS\textsubscript{2} (849 mg, 11.15 mmol, 12 equiv) and K\textsubscript{3}PO\textsubscript{4} (1.19 g, 5.58 mmol, 6 equiv) were stirred in 15 mL THF for 30 minutes. 2-(4-(Bromomethyl)benzyl)-6-methylbenzaldehyde (1.78 g, 5.58 mmol, 6 equiv) was added and the pale yellow liquid turned intensively yellow. After stirring at ambient temperature over night the remaining K\textsubscript{3}PO\textsubscript{4} was filtered off and the solvent removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 2:1, R\textsubscript{f}=0.5) to afford a yellow solid (665 mg, 41\%). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz) δ/ppm: 10.71 (s, 4H, C\textsubscript{H}O), 7.35 (m, 20H, paraAr and para to CHO), 6.8 (m, 8H, meta to CHO), 5.11 (s, 8H, OCH\textsubscript{2}), 4.61 (s, 8H, SC\textsubscript{H}2C\textsubscript{arom}), 4.14 (s, 8H, CCH\textsubscript{2}OC(O)), 3.61 (t, J=6.8 Hz, 8H, SC\textsubscript{H}2CH\textsubscript{2}C(O)), 2.80 (t, J=6.8 Hz, 8H, SCH\textsubscript{2}CH\textsubscript{2}C(O)), 2.57 (s, 12H, CH\textsubscript{3}). \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz) δ/ppm: 222.4 (SC(S)S), 192.1 (CHO), 170.7 (OC(O)), 162.1 (OC\textsubscript{arom}), 142.1 (OCH\textsubscript{2}C\textsubscript{arom}), 135.9 (CH\textsubscript{3}C\textsubscript{arom}), 134.9 (SCH\textsubscript{2}C\textsubscript{arom}), 134.4 (CH\textsubscript{3}CCH\textsubscript{CH}), 129.6 (SCH\textsubscript{2}C\textsubscript{CH}), 127.6 (OCH\textsubscript{2}C\textsubscript{CH}), 124.5 (CH\textsubscript{3}C\textsubscript{CH}), 110.3 (OC\textsubscript{CH}), 70.1 (OCH\textsubscript{2}), 62.4 (C\textsubscript{CH}2OC(O)), 41.1 (SCH\textsubscript{2}C\textsubscript{arom}), 33.0 (SCH\textsubscript{2}CH\textsubscript{2}C(O)), 31.2 (SCH\textsubscript{2}CH\textsubscript{2}C(O)) 21.5 (CH\textsubscript{3}). UV-Vis: (acetonitrile) λ\textsubscript{max} = 309, 257 nm. MS: (ESI) m/z calculated for C\textsubscript{85}H\textsubscript{80}O\textsubscript{16}S\textsubscript{12} [M+Na\textsuperscript{+}]: 1767.2300, found 1767.2335.

![Figure S3](image-url) **Figure S3** \textsuperscript{1}H-NMR spectrum of TetraPE-RAFT in CDCl\textsubscript{3} at 400 MHz.
Figure S 4 13C-NMR spectrum of TetraPE-RAFT in CDCl3 at 100 MHz.

Figure S 5 UV-Vis spectrum of TetraPE-RAFT in acetonitrile.

Synthesis of 2-hydroxyethyl 4-(bromomethyl)benzoate

\[
\begin{align*}
\text{Br}^+ & \quad \text{OH} \\
\text{O} & \quad \text{O} \\
\text{HO} \quad \text{OH} & \quad \text{DCC, DMAP}
\end{align*}
\]

4-(Bromomethyl)benzoic acid (3.0 g, 13.97 mmol, 1 equiv), 4-dimethylaminopyridine (341 mg, 2.79 mmol, 0.2 equiv) and ethylene glycol (2.6 g, 41.9 mmol, 3 equiv) were dissolved in 50 mL dry THF. Subsequently, dicyclohexylcarbodiimide (3.17 g, 15.37 mmol, 1.1 equiv) dissolved in 15 ml dry THF was added dropwise. The reaction proceeded over night at ambient temperature. After filtration the solvent was removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 1:1, Rf=0.5) to afford a white solid (2.4 g,
66 %). $^1$H-NMR (CDCl$_3$, 400 MHz) δ/ppm: 8.02 (d, $^3$J=8.1 Hz, 2H, OC(O)CH$_{arom}$), 7.45 (d, $^3$J=8.1 Hz, 2H, BrCH$_2$CH$_{arom}$), 4.49 (s, 2H, BrCH$_2$), 4.46 (t, $^3$J=4.5 Hz, 2H, C(O)OCH$_2$), 3.95 (t, $^3$J=4.5 Hz, 2H, HOCH$_2$).

$^{13}$C-NMR (CDCl$_3$, 100 MHz) δ/ppm: 166.3 (ester), 142.9 (BrCH$_2$C), 130.1 (OC(O)C), 129.7 (OC(O)C), 129.0 (BrCH$_2$C), 66.7 (C(O)OC), 61.3 (HOC), 32.1 (BrC).

MS: (ESI) m/z calculated for C$_8$H$_7$BrO$_2$ [M+Na]$: 280.9784, found 280.9784.

**Figure S 6** $^1$H-NMR spectrum of 2-hydroxyethyl 4-(bromomethyl)benzoate in CDCl$_3$ at 400 MHz.

**Figure S 7** $^{13}$C-NMR spectrum of 2-hydroxyethyl 4-(bromomethyl)benzoate in CDCl$_3$ at 100 MHz.
Synthesis of (4-(Bromomethyl)benzoyloxy)ethyl 4-(2-phenyl-2H-tetrazol-5-yl)benzoate

2-Hydroxyethyl 4-(bromomethyl)benzoate (526 mg, 2.03 mmol, 1 equiv), 4-dimethylaminopyridine (25 mg, 0.2 mmol, 0.1 equiv) and 4-(2-phenyl-2H-tetrazol-5-yl)benzoic acid (541 mg, 2.03 mmol, 1 equiv) were dissolved in 20 mL of THF. Subsequently, dicyclohexylcarbodiimide (524 mg, 2.53 mmol, 1.25 equiv) dissolved in 10 ml THF was added dropwise. The reaction proceeded over night at ambient temperature. After filtration the solvent was removed under reduced pressure and the crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 4:1, Rf=0.4) to afford a slightly red solid (481 mg, 47 %). ¹H-NMR (CDCl₃, 400 MHz) δ/ppm: 8.34 (d, ³J=8.5 Hz, 2H, middle ring, ortho to ester), 8.21 (d, ³J=8.6 Hz, 4H, 4H of monosubstituted ring), 8.04 (d, ³J=8.3 Hz, 2H, BrCH₂CCH₂), 7.5 (m, 5H, remaining aromatic protons), 4.70 (s, 4H, C(O)OC₂H₅C₂H₅OC(O)), 4.50 (s, 2H, BrCH₂). ¹³C-NMR (CDCl₃, 100 MHz) δ/ppm: 165.8 (C(O)OCH₂CH₂OC(O)), 164.3 (NC₄), 142.9 (BrCH₂C), 136.8 (NC₅), 131.5, 131.4, 130.3, 130.2, 129.9, 129.7, 129.1, 127.0, 119.9 (remaining aromatic carbons), 63.0, 62.8 (C(O)OCH₂CH₂OC(O)), 32.1 (BrCH₂). MS: (ESI) m/z calculated for C₂₄H₁₉BrN₄O₄ [M+Na]⁺: 529.0487, found 529.0508.

Figure S 8 ¹H-NMR spectrum of the tetrazole-functionalized precursor in CDCl₃ at 400 MHz.
Synthesis of 4-arm tetrazole RAFT agent (TetraTet-RAFT)

Pentaerythritol tetrakis(3-mercaptopropionate) (122.5 mg, 0.251 mmol, 1 equiv), CS₂ (229.2 mg, 3.01 mmol, 16 equiv) and K₃PO₄ (319 mg, 1.50 mmol, 8 equiv) were stirred in 10 mL THF for 30 minutes. (4-{(Bromomethyl)benzoyloxy)ethyl 4-((2-phenyl-2H-tetrazol-5-yl)benzoate (757 mg, 1.50 mmol, 8 equiv) dissolved in 6 mL THF was added and the pale yellow liquid turned red. After stirring at ambient temperature for 10 days the remaining K₃PO₄ was filtered off and the solvent removed under reduced pressure. The crude product was purified via column chromatography (silica gel, cyclohexane/ethyl acetate 3:1 to regain the excess precursor and afterwards cyclohexane/ethyl acetate 2:3 to release the product) to afford a slightly red solid (288 mg, 46 %).

\[ ^1H-NMR \ (CDCl_3, 400 MHz) \delta/\text{ppm}: \ 8.31 \ (m, 8H, middle ring, ortho to ester), \ 8.18 \ (m, 16H, 4H of monosubstituted ring), \ 8.00 \ (m, 8H) \text{ and } 7.5 \ (m, 20H, \text{remaining aromatic protons}), \ 4.68 \ (s, 16H, \text{C(O)OC}_2\text{H}_5\text{C}_H\text{OC(O)}), \ 4.61 \ (m, 8H, \text{SC}_2\text{H}_2\text{C}_H\text{arom}), \ 4.11 \ (s, 8H, \text{CCH}_2\text{OC(O)}), \ 2.76 \ (m, 8H, \text{SCH}_2\text{C}_H\text{arom}), \ 3.58 \ (m, 8H, \text{SC}_2\text{H}_2\text{CH}_2\text{C(O)O}), \ 2.76 \ (m, 8H, \text{SCH}_2\text{C}_H\text{arom}), \text{13C-NMR (CDCl}_3, 100 MHz) \delta/\text{ppm}: \ 221.9 \ (SC(S)S), \ 170.8 \ (\text{SC}_2\text{H}_2\text{C}_H\text{OC(O)}), \ 2.76 \ (m, 8H, \text{SCH}_2\text{C}_H\text{arom}), \text{MS: (ESI) } m/z \text{ calculated for C}_{117}H_{100}N_{16}O_{24}S_{12} \ [M+Na]^+: \ 2519.3637, \text{ found } 2519.3794. \text{ UV-Vis: (dichloromethane) } \lambda_{\text{max}} = 287 \text{nm.} \]
Figure S 10 $^1$H-NMR spectrum of TetraTet-RAFT in CDCl$_3$ at 400 MHz.

Figure S 11 $^{13}$C-NMR spectrum of TetraTet-RAFT in CDCl$_3$ at 100 MHz.
RAFT polymerizations

A solution of AIBN (7.6 mg, 0.046 mmol, 0.40 equiv), TetraPE-RAFT (201.7 mg, 0.115 mmol, 1.00 equiv), and 4-chloromethyl-styrene (1.41 g, 9.24 mmol, 80 equiv) in toluene (1.1 mL) was deoxygenated with four consecutive freeze-pump-thaw cycles. The reaction was placed into a preheated oil-bath at 60 °C for 8 h. The reaction was stopped by cooling in an ice-bath and exposing the reaction mixture to oxygen. The polymer was isolated via two-fold precipitation in cold methanol and subsequent drying under vacuum to afford 300 mg of a yellow powder. $M_n = 4400$ g mol$^{-1}$, $D = 1.28$ (GPC in THF, polystyrene calibration); $M_n = 5300$ g mol$^{-1}$ (NMR, comparison of the integrals between 10.85 – 10.6 ppm and 7.60 – 6.0 ppm).

Figure S 12 UV-Vis spectrum of TetraTet-RAFT in dichloromethane.
**Figure S 13** GPC trace in THF (PS calibration) of 4-chloromethyl-styrene polymerized with TetraPE-RAFT.

**Figure S 14** $^1$H-NMR spectrum of 4-chloromethyl-styrene polymerized with TetraPE-RAFT in CDCl$_3$ at 400 MHz. Comparison of repetition unit resonance integrals (c, 7.6 – 6.0 ppm) to end group resonance integrals (a, 10.85 – 10.6 ppm) results in $M_n = 4400$ g mol$^{-1}$.

A solution of AIBN (3.7 mg, 0.023 mmol, 0.40 equiv), TetraTet-RAFT (140.0 mg, 0.056 mmol, 1.00 equiv), and 4-bromostyrene (825 mg, 4.51 mmol, 80 equiv) in toluene (2.5 mL) was deoxygenated with three consecutive freeze-pump-thaw cycles. The reaction was placed into a preheated oil-bath at 60 °C for 8 h. The reaction was stopped by cooling in an ice-bath and exposing the reaction mixture to oxygen. The polymer was isolated via precipitation in cold methanol and subsequent drying under vacuum to afford 247 mg of a yellow powder. $M_n = 3800$ g mol$^{-1}$, $\mathcal{D} = 1.13$.
(GPC in THF, polystyrene calibration); $M_n = 6750 \text{ g mol}^{-1}$ (NMR, comparison of the integrals between 8.4 – 8.25 ppm and 7.7 – 6.0 ppm).

Figure S 15 GPC trace in THF (PS calibration) of 4-bromostyrene polymerized with TetraTet-RAFT.

Figure S 16 $^1$H-NMR spectrum of 4-bromostyrene polymerized with TetraTet-RAFT in CDCl$_3$ at 400 MHz. Comparison of repetition unit resonance integrals (c, 7.7 – 6.0 ppm) to end group resonance integrals (a, 8.4 – 8.25 ppm) results in $M_n = 6750 \text{ g mol}^{-1}$. 
Synthesis of $2',2''-(\text{nitrilotris(ethane-2,1-diyl)})\text{tris(3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione)}$

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} & \quad \text{NH}_2 \\
\text{N} & \quad \text{NH}_2 & \quad + & \quad 3 & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

A solution of 4,10-dioxatricyclo[5.2.1.0(2,6)]dec-8-ene-3,5-dione (5.66 g, 34 mmol, 5 equiv) in 150 mL of methanol was cooled to 0 °C in a 2-neck round bottom flask equipped with a condenser and a dropping funnel. The dropping funnel was loaded with a solution of tris(2-aminoethyl)amine (1.00 g, 6.85 mmol, 1 equiv) in 50 mL of methanol which was added dropwise to the reaction mixture over a period of 30 min. Subsequent to addition, the mixture was heated to reflux for 3 h. The mixture turned yellow. Then, the reaction mixture was concentrated to 75 mL and left to crystallize at 4°C. The obtained pale yellow crystals were filtered and washed with 50 mL of ethyl acetate. Residual solvent was evaporated under reduced pressure. Yield: 945 mg (24 %). $^1\text{H NMR}$ (CDCl$_3$, 400 MHz) $\delta$/ppm: 6.49 (s, 2H), 5.19 (s, 2H), 3.40 (t, 2H), 2.89 (s, 2H), 2.59 (t, 2H).

Synthesis of tris(2-maleimidoethyl)amine

\[
\begin{align*}
\text{O} & \quad \text{N} & \quad \text{N} & \quad \text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

$2',2''-(\text{nitrilotris(ethane-2,1-diyl)})\text{tris(3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione)}$ (0.5 g, 0.85 mmol, 1 equiv) was dissolved in 30 mL of toluene in a round bottom flask, equipped with a condenser. The reaction mixture was heated to reflux for 7 h. Then the solvent was removed under reduced pressure. Subsequently, the residue was dissolved in ethyl acetate and passed over a short silica column. After removal of the solvent, the product was obtained as an off-white solid. Yield: 260 mg (84 %). $^1\text{H NMR}$ (CDCl$_3$, 400 MHz) $\delta$/ppm: 6.67 (s, 2H), 3.51 (t, 2H), 2.70 (t, 2H).

Light-induced network formation

The 4-arm end-functional RAFT star polymer and tris(2-maleimidoethyl)amine were dissolved in dichloromethane. The solution was deoxygenated via purging with nitrogen for 2 min and irradiated in custom made photo reactor (see Figure S 17 and Figure S 21) until network formation could be
observed. The solvent was removed under reduced pressure and the solid washed three times with dichloromethane. Weigh-ins and reaction conditions can be found in Table S 1.

Table S 1 Weigh-ins and reaction details of light–induced network formation reactions.

<table>
<thead>
<tr>
<th>Type of RAFT star polymer</th>
<th>Amount of tris(2-maleimidoethyl) amine</th>
<th>Amount of solvent</th>
<th>Light source</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>Power of light source</th>
<th>Irradiation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>10.2 mg</td>
<td>1.2 mg</td>
<td>200 µL</td>
<td>PL-L</td>
<td>355 nm</td>
<td>36 W</td>
</tr>
<tr>
<td>PE</td>
<td>10.0 mg</td>
<td>1.1 mg</td>
<td>100 µL</td>
<td>LED</td>
<td>375 nm</td>
<td>3·3 W</td>
</tr>
<tr>
<td>Tet</td>
<td>11.1 mg</td>
<td>0.8 mg</td>
<td>150 µL</td>
<td>Arimed-B6</td>
<td>320 nm</td>
<td>36 W</td>
</tr>
<tr>
<td>Tet</td>
<td>5.9 mg</td>
<td>0.6 mg</td>
<td>100 µL</td>
<td>LED</td>
<td>375 nm</td>
<td>3·3 W</td>
</tr>
</tbody>
</table>

Figure S 17 Schematic drawing of the custom-built photo-reactor employed in the current contribution.
**Figure S 18** Emission spectrum of the employed compact low-pressure fluorescent lamp Arimed B6.

**Figure S 19** Emission spectrum of the employed compact low-pressure fluorescent lamp Philips CLEO Compact PL-L.
**Figure S 20** Emission spectrum of the LEDs as measured by the supplier.5

**Figure S 21** Image of the LEDs on cooling elements. For the reaction the LEDs are put in the photo reactor, as it offers cooling fans and protection from harmful irradiation. The sample is placed slightly elevated between the three LEDs.

**Figure S 22** Fluorescence of the entire network sample (approx. 1 cm wide) and a peeled off piece (approx. 2 mm) irradiated at 366 nm.
**Direct Laser Writing**

Photo-resists were prepared by dissolving the photo-active star polymer (33.0 mg of photo-enol star polymer, 37.5 mg of tetrazole star polymer) and the maleimide containing copolymer (20.0 mg) in a mixture of 127 µL acetophenone and 121.6 µL γ-butyrolactone and subsequent filtering through a syringe filter (0.2 µm pore size).

3D polymer structures were fabricated using a costum-built Direct Laser Writing system by means of two-photon photo-polymerization. The system employs a Ti:Sa femtosecond laser source (Spectra-Physics MaiTai HP) which pumps an optical parametric oscillator (Spectra-Physics Inspire HF100) to generate femtosecond laser pulses with a center wavelength of 640 nm. The laser beam is focused by an oil-immersion objective lens with a magnification of 100x and a numerical aperture of 1.4 (Leica HCX PL APO 100x/1.4 CS). Relative 3D movement of sample and focal spot is realized by a 3D piezo stage. Standard microscopy cover slides were used as substrates. An average laser power of 4 mW and a piezo scan speed of 100 µm·s⁻¹ were used for structuring. To remove excess photo-resist after writing, the samples were developed in acetone for 15 min and rinsed with isopropanol.

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**Figure S 23** Full comparison of the NMR spectra of the 4-arm tetrazole star polymer, the trimaleimide linker and the reaction mixture after 5 h irradiation at 375 nm. No novel signals and no shift of existing signals indicate no reaction.
XPS results

Figure S 24 C 1s XP spectra of the photo-enol functional RAFT star polymer (top) and the networks formed from it (middle with UV-lamp, bottom with LED). The higher intensity for carbon bound to hetero-atoms stems from the incorporation of the trimaleimide crosslinker.
Figure S 25 N 1s XP spectra of the photo-enol functional RAFT star polymer (top) and the networks formed from it (middle with UV-lamp, bottom with LED). The precursor polymer does not contain nitrogen, whereas the networks contain nitrogen stemming from the trimaleimide crosslinker.

Figure S 26 S 2p XP spectra of the photo-enol functional RAFT star polymer (top) and the networks formed from it (middle with UV-lamp, bottom with LED). There is no significant change.
Figure S 27 Cl 2p XP spectra of the photo-enol functional RAFT star polymer (top) and the networks formed from it (middle with UV-lamp, bottom with LED).
Figure S 28 C 1s XP spectra of the tetrazole functional RAFT star polymer (top) and the network formed from it (bottom). The higher intensity for carbon bound to hetero-atoms stems from the incorporation of the trimaleimide crosslinker.

Figure S 29 N 1s XP spectra of the tetrazole functional RAFT star polymer (top) and the network formed from it (bottom). The change in peak ratio stems from the incorporation of the trimaleimide crosslinker and the expulsion of nitrogen.
The second peak in the network sample most probably stems from an oxidation side reaction.

Figure S 30 S 2p XP spectra of the tetrazole functional RAFT star polymer (top) and the network formed from it (bottom). The second peak in the network sample most probably stems from an oxidation side reaction.

Figure S 31 Br 3d XP spectra of the tetrazole functional RAFT star polymer (top) and the network formed from it (bottom).
Analysis

Gel permeation chromatography (GPC)
GPC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 mm bead-size guard column (50 × 7.5 mm) followed by three PL gel 5 mm MixedC columns (300 × 7.5 mm) and a differential refractive index detector using THF at 35 °C as the eluent with a flow rate of 1 mL·min⁻¹. The GPC system was calibrated using linear polystyrene standards ranging from 476 to 2.5·10⁶ g·mol⁻¹. All GPC calculations were carried out relative to polystyrene calibration (Mark-Houwink parameters $K = 14.1·10^{-5}$ dL·g⁻¹, $\alpha = 0.70$).

Electrospray ionization-mass spectrometry (ESI-MS)
Mass spectra were recorded on a Q Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific). A constant spray voltage of 4.7 kV and a dimensionless sheath gas of 5 were applied. The capillary temperature and the S-lens RF level were set to 320 °C and 62.0, respectively. The samples were dissolved with a concentration of 0.05 mg·mL⁻¹ in a mixture of THF and MeOH (3:2) containing 100 µmol of sodium triflate and infused with a flow of 5 µL·min⁻¹.

Nuclear magnetic resonance (NMR) spectroscopy
NMR measurements were conducted on a Bruker Ascend 400 at 400 MHz for hydrogen nuclei. Samples were dissolved in CDCl₃ using residual solvent peaks for shift correction.

X-ray photoelectron spectroscopy (XPS)
XPS investigations were performed on a K-Alpha+ spectrometer (ThermoFisher Scientific, East Grinstead, UK) using a micro-focused, 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. The photoelectrons were detected at an emission angle of 0° with respect to the normal of the sample surface. The K-Alpha charge compensation system was employed during analysis, using electrons of 8 eV energy and low-energy argon ions to prevent any localized charge build-up. Data acquisition and processing using the Thermo Avantage software is described elsewhere. The spectra were fitted with one or more Voigt profiles (BE uncertainty: ± 0.2 eV). The analyzer transmission function, Scofield's sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2 M formalism. All spectra were referenced to the C 1s peak of hydrocarbon at 285.0 eV binding energy, controlled by means of the well-known photo-electron peaks of metallic Cu, Ag, and Au. Signals were divided by the maximum of the analyzed peak without background subtraction.
Ultraviolet-visible (UV-Vis) spectroscopy
UV-Vis spectra were recorded on a Varian Cary 300 Bio spectrophotometer. Spectra were recorded in acetonitrile or dichloromethane in a 10 mm path length cell. Spectra were collected between 200 and 800 nm. Samples were baseline corrected with respect to the pure solvent.

Emission measurements
Emission spectra were recorded on a spectral radiometer UVpad E from Opsytel Dr. Gröbel (Ettlingen, Germany) in a distance of ca. 4 cm to the lamp.

Fluorescence microscopy
Fluorescence micrographs of 3D structures generated by Direct Laser Writing were recorded with a laser scanning microscope (Zeiss LSM 510 Meta) using a laser diode with an emission wavelength of 405 nm as excitation source and an oil immersion objective lens with a magnification of 63x and a numerical aperture of 1.4.

References
5. Avonec Homepage (avonec.de), Accessed 27.08.2015.