

Supporting Information

Chemiluminescent Self-Reporting Supramolecular Transformations on Macromolecular Scaffolds

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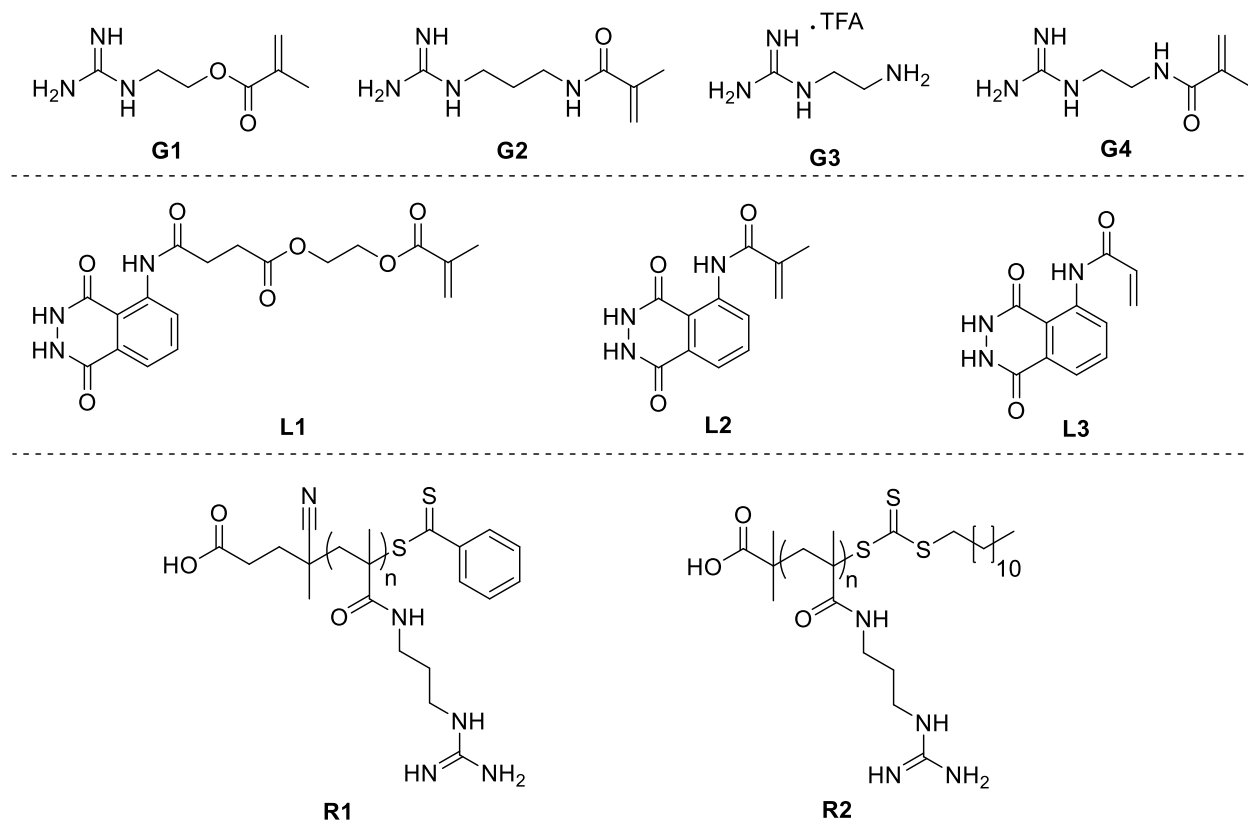
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A Additional data and figures

A.1 Overview of targeted guanidine- / luminol monomers and RAFT-derived polymers



Scheme S1: Overview of targeted guanidine- / luminol-derivative monomers (**G1-G4**, **L1-L3**) and RAFT-polymers (**R1-R2**).

A.2 Additional figures

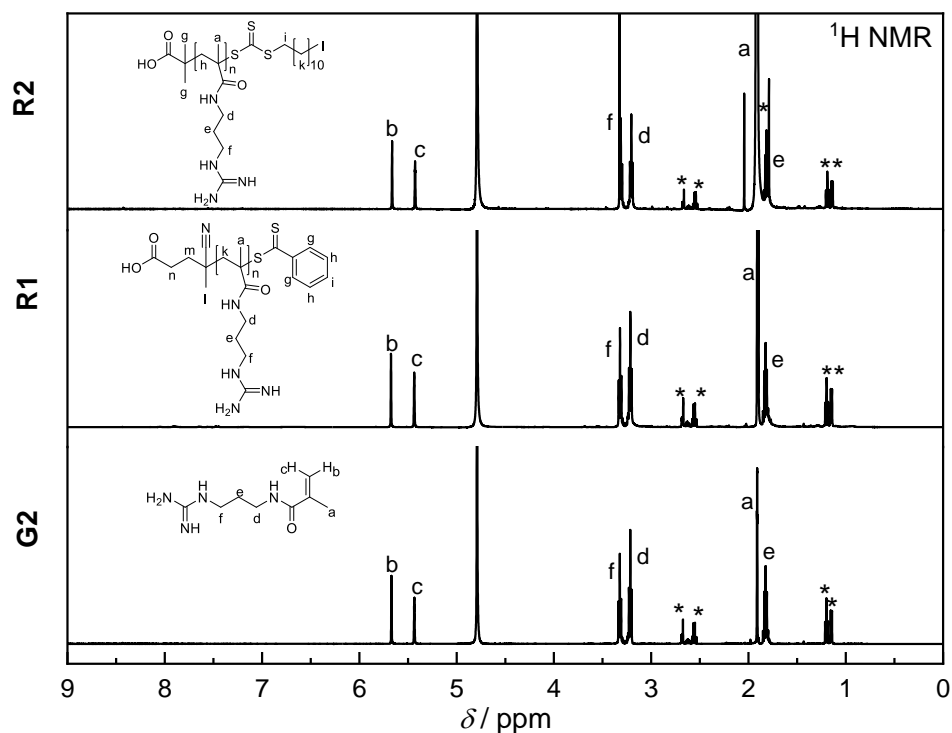


Figure S1: ^1H NMR (500 MHz) spectra of the guanidine-derivative **G2** and the targeted RAFT-polymers **R1** and **R2**. The spectra were recorded in D_2O at ambient temperature.

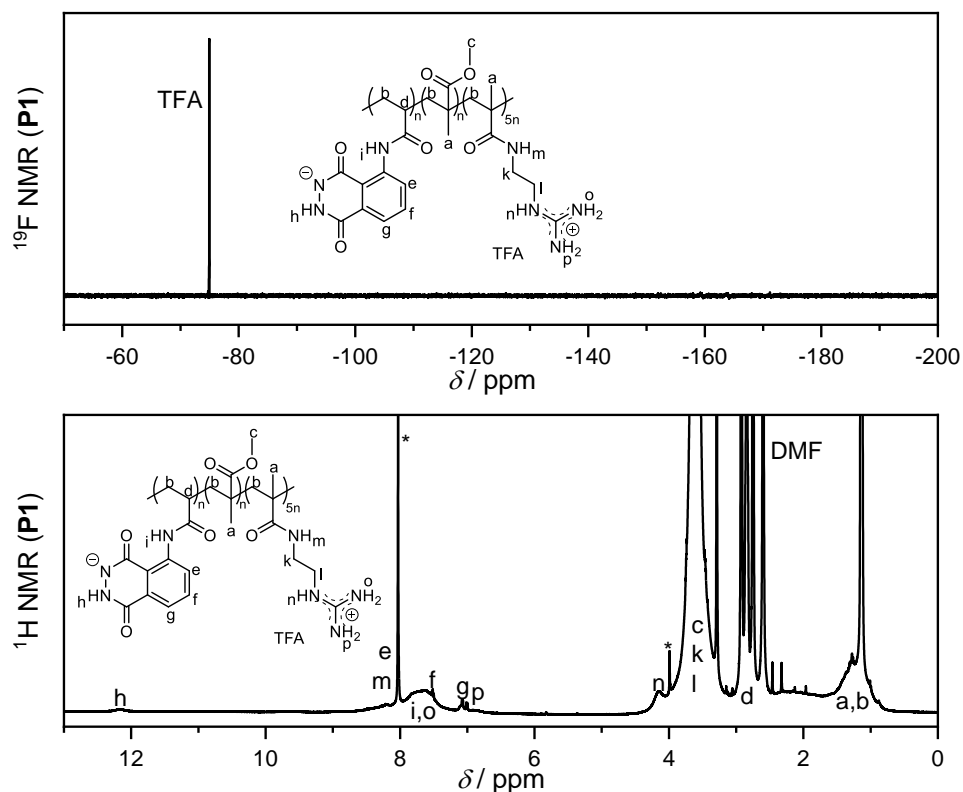


Figure S2: ^1H NMR (500 MHz) and ^{19}F NMR spectrum of **P1** in DMF-d_7 at ambient temperature.

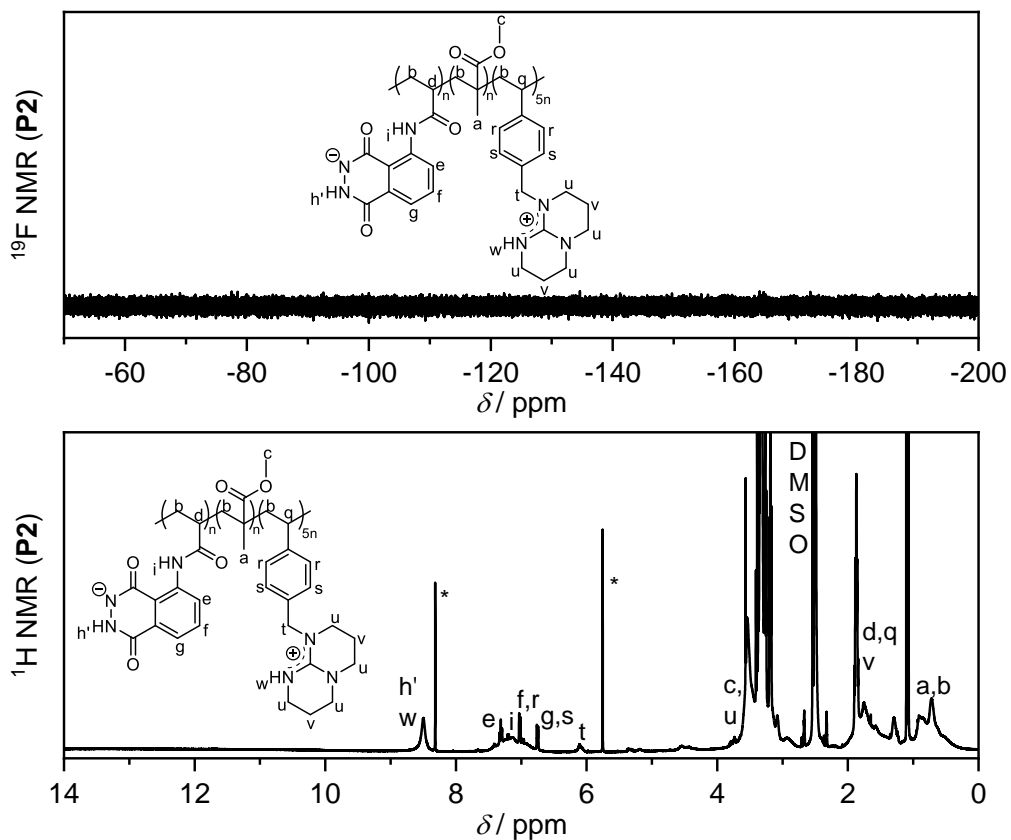


Figure S3: ¹H NMR (400 MHz) and ¹⁹F NMR spectrum of P2 in DMSO-d₆ at ambient temperature.

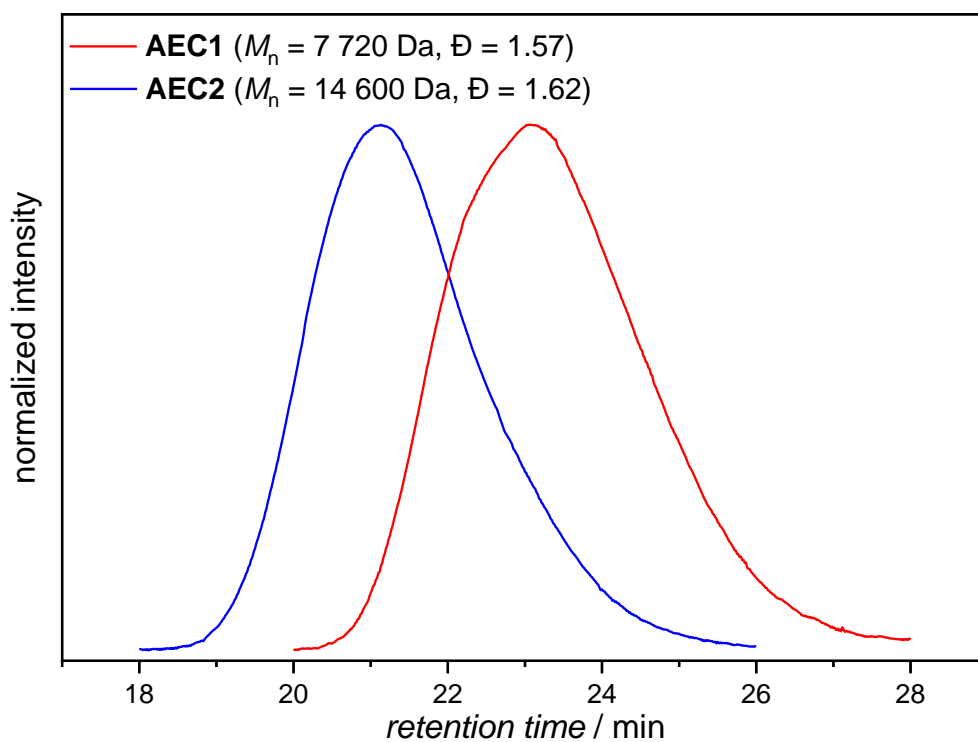


Figure S4: SEC elution traces of AEC1 and AEC2 in THF at 30°C

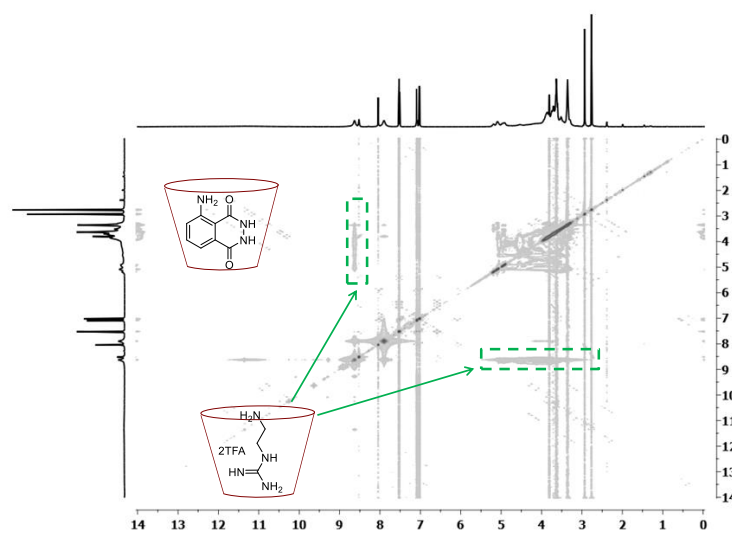
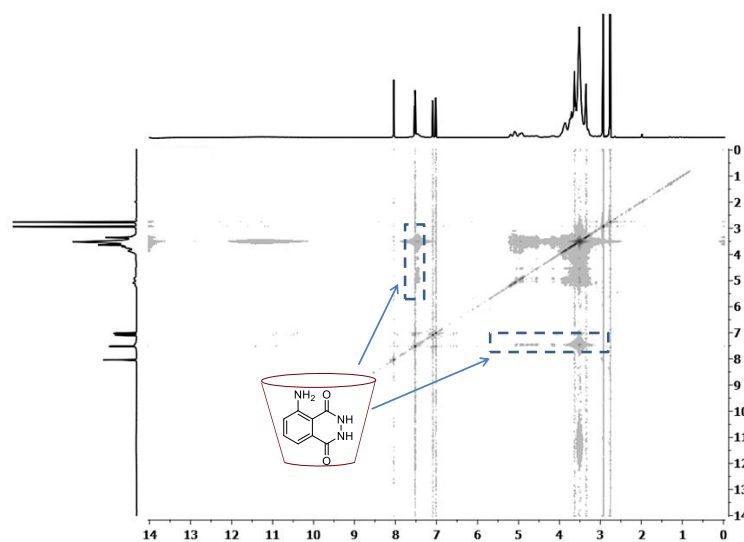
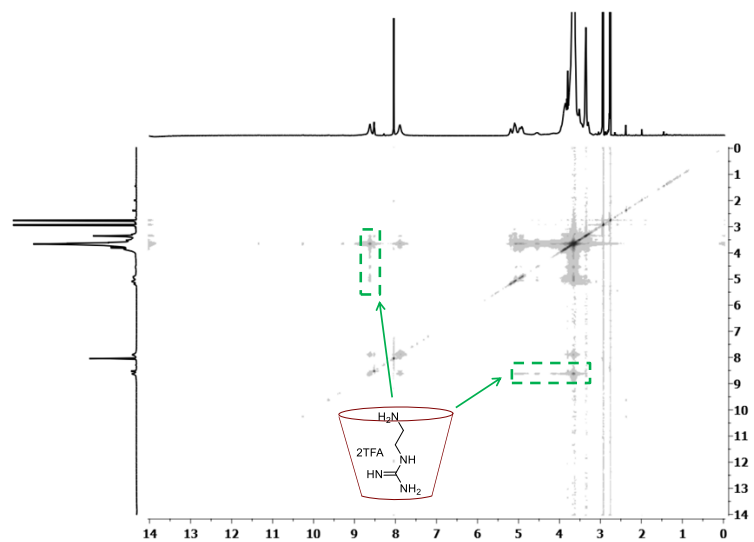


Figure S5: NOESY spectra from top to bottom: **G3** + Me- β -CD, luminal + Me- β -CD and **G3** + luminal + Me- β -CD. All spectra were recorded in DMF- d_7 at 300K.

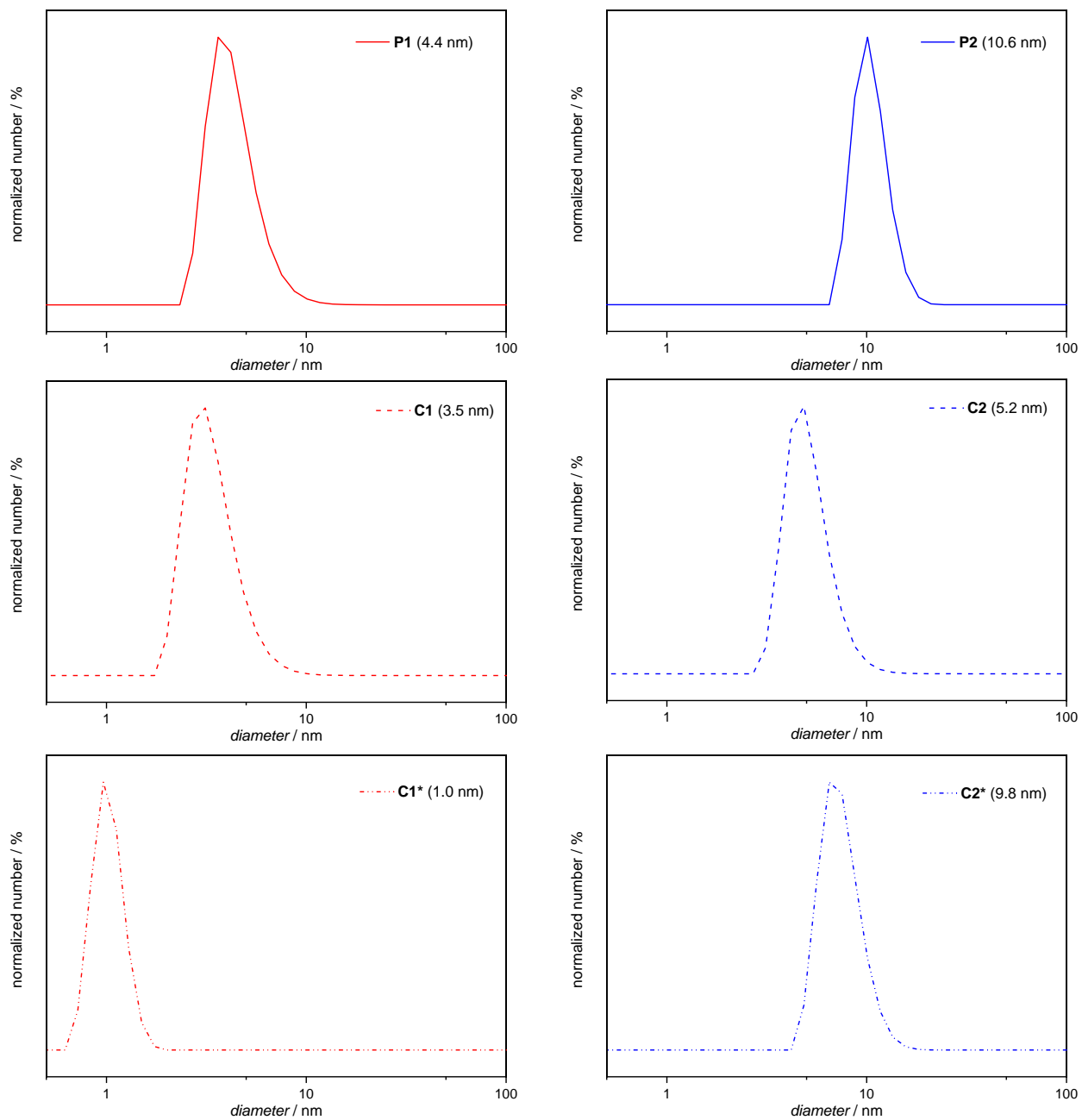


Figure S6: Single DLS traces of **P1**, **P2**, **C1**, **C2**, **C1*** and **C2*** (the traces are shown combined in Figure 1 in the main text). All traces were recorded in DMF at 20°C with a concentration of 1 mg mL⁻¹.

B Experimental procedures

B.1 Materials

Unless otherwise stated, all chemicals were used as received.

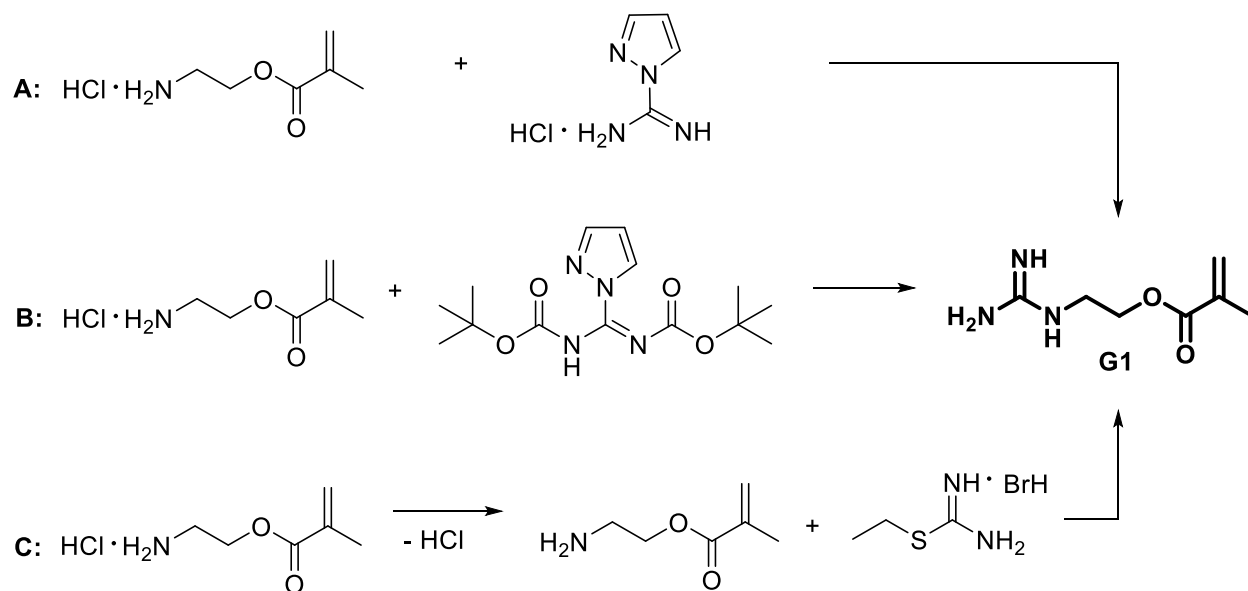
2- Aminoethylmethacrylate hydrochloride (Sigma Aldrich, 90 %, stabilized with ~ 500 ppm phenothiazine), 1*H*-Pyrazole-1-carboxamide hydrochloride (Sigma Aldrich, 99 %), diisopropylethylamine (Merck, 99 %), ethanol absolute (EtOH, VWR, max. 0.003 % H₂O), dichloromethane (VWR, 99.8 %, stabilized with 0.2 % of ethanol), ethylacetate (EtOAc, VWR, normapur), luminol (Alfa Aesar, 98 %), succinic anhydride (Merck, ≥ 98.0 %), pyridine (Acros Organics, extra dry, AcroSeal, 99.5 %), *N,N*-dimethylformamide (DMF, Acros Organics, 99.8 %, extra dry, over molecular sieves, AcroSeal), *N,N*-dimethylformamide (DMF, Acros Organics, extra pure, ≥ 99.0 %), hydrochloric acid (HCl, VWR, 32 %), 4-(dimethylamino)pyridine (DMAP, Sigma Aldrich, ≥ 99 %), thiourea (abcr, 99 %), 1-bromoethane (VWR, ≥ 99.0 %), triethylamine (TEA, Sigma Aldrich, ≥ 99 %), *N*-aminopropylmethacrylamide hydrochloride (Sigma Aldrich, 98 %, stabilized with ≤ 1.00 ppm MEHQ), 1,5,7-triazabicyclo[4.4.0]dec-5—ene (Sigma Aldrich, 98 %), , *N*-Boc-ethylenediamine (Alfa Aesar, 98 %, may contain up to 5 % tert-butanol), acryloyl chloride (Alfa Aesar, 96 %, stabilized with 400 ppm phenothiazine), 2-ethyl-2-thiopseudourea hydrobromide (TCI, > 98.0 %), dimethylsulfoxide (DMSO, VWR, normapur, max. 0.025 % H₂O), sodium hydroxide (NaOH, Merck, ≥ 99.0 %), acetonitrile (CH₃CN, VWR, normapur), *N,N*-di-Boc-1*H*-pyrazole-1-carboxamide (Acros Organics, 98 %), magnesium sulfate anhydrous (VWR, 99.5 %), diethylether (VWR, normapur), trifluoroacetic acid (abcr, 99.5 %), 4,4'-azobis(4-cyanovaleric acid) (V501, Sigma Aldrich, ≥ 75 %), 2,2'-azobis(isobutyronitril) (AIBN, Sigma Aldrich, 98.0 %), 1,4-dioxane (Acros Organics, extra dry, AcroSeal, 99.8 %), 1,4-dioxane (Alfa Aesar, 99+ %, stabilized with ~5-10 ppm BHT), aluminiumoxide (Al₂O₃, Merck, 90 active basic), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (Sigma Aldrich, > 97.0 %), methyl-β-cyclodextrin (Cavasol W7 M, Wacker, > 95 %), 4-vinylbenzyl chloride (Sigma Aldrich), 90%), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimid (EDC, Sigma Aldrich, ≥ 97.0 %) were used without further purification.

Methylmethacrylate (MMA, Sigma Aldrich, 99 %, ≤ 30 ppm MEHQ as stabilizer), pentafluorophenyl methacrylate (TCI, > 97.0%) and pentafluorophenylacrylate (TCI, > 98.0 %) were passed through a basic Al₂O₃ – column to remove the stabilizer before using.

2-(Dodecylthiocarbonylthio)-2-methylpropionic acid (DMP) was synthesized according to a reported synthesis procedure.^[1]

B.2 Synthesis of guanidine-derivatives

B.2.1 2-Guanidinoethylmethacrylate (GEMA, G1)



Approach A:^[2] Under anhydrous conditions, 2.00 g of 2-aminoethylmethacrylate hydrochloride (0.0121 mol, 1.00 eq.) and 1.95 g 1*H*-Pyrazole-1-carboximidine hydrochloride (0.0133 mol, 1.10 eq.) were dissolved in 68 mL anhydrous EtOH. Then 6.5 mL diisopropylethylamine (0.0363 mol, 3.00 eq.) were added. The reaction mixture was stirred for 23 h at 54 °C. After cooling to ambient temperature, the residue was filtered off and the solvent was removed under reduced pressure. The yellow oil was purified via column chromatography (silica gel) using EtOH and EtOAc (1:1) as eluent. The fraction with the desired product (rf = 0.7) was recrystallized from EtOAc. For further purification a second column chromatography (silica gel) was conducted using DCM and MeOH (15:1) as eluent.

¹H NMR (500 MHz, D₂O) δ / ppm: 5.70 (s, 1H, CH₃-C_q-CH₂-CO-), 5.44 (s, 1H, CH₃-C_q-CH₂-CO-), 3.68 (m, 2H, -NH-CH₂-CH₂-O-), 3.38 (m, 2H, -NH-CH₂-CH₂-O-), 1.91 (s, 3H, CH₃-C_q-CO-O-).

Approach B:^[3] In a 100 mL two-neck round bottom flask, 1.59 g 2-aminoethylmethacrylate (9.6 mmol, 1.5 eq.) were dissolved in a mixture of 2.4 mL H₂O and 4.1 mL TEA (29.6 mmol, 4.6 eq.). The reaction mixture was stirred for 15 min at ambient temperature. 2.00 g *N,N*-di-Boc-1*H*-pyrazole-1-carboximidine (6.4 mmol, 1.0 eq.) were dissolved in 22 mL CH₃CN and added dropwise to the reaction mixture over 30 min. After 24 h, the reaction was stopped and the obtained white precipitate was filtered off. The organic layer was washed with H₂O (3 x 30 mL). Subsequently, the solvent was removed under reduced pressure and a beige solid was isolated (0.14 g, 0.3745 mmol, 6 %).

¹H NMR (500 MHz, CDCl₃) δ / ppm: 5.73 (s, 1H, CH₃-C_q-CH₂-), 5.35 (s, 1H, CH₃-C_q-CH₂-), 4.09 (s, 2H, -O-CH₂-CH₂-NH-), 3.44 (q, 2H, -O-CH₂-CH₂-NH-), 1.58 (s, 3H, CH₃-C_q-CH₂-), 1.48 (m, 18H, (CH₃)₃-C_q-O-CO-).

Approach C:^[4-5] In a 100 mL beaker 1.00 eq. 2-aminoethylmethacrylate hydrochloride was dissolved in deionized water (0.828 mmol / 1 mL). The pH was adjusted to pH = 11 with the addition of 50 wt % NaOH. In a separatory funnel the mixture was washed with CH₂Cl₂ and the organic layers were combined. Evaporating the solvent yielded 2-aminoethylmethacrylate (AEMA) as transparent, yellow oil.

Three experiments have been conducted to synthesize the AEMA with different volumes of CH₂Cl₂, the results are presented in Table S1.

Table S1: Volumes of the CH₂Cl₂ and the respective yields for the conducted experiments to obtain AEMA.

	V (CH ₂ Cl ₂) [mL]	m [g]	n [mmol]	Yield [%]
1	3 x 50	0.2524	1.954	16
2	5 x 50	0.5361	4.151	35
3	10 x 50	0.6319	4.890	38

For the second step, 0.88 eq. 2-ethyl-2-thiopseudourea hydrobromide were dissolved in CH₃CN (0.873 mmol / 1 mL) and 0.88 eq. of an organic base was added under an inert gas flow. 1.00 eq. of AEMA was added dropwise to the solution while stirring. To ensure everything is dissolved, 0.1 mL deionized water was added. The reaction mixture was stirred over night at ambient temperature. After evaporating the solvent, a turbid, yellow oil was obtained. The crude product was purified by column chromatography (silica gel) with either EtOH and EtOAc or DCM and MeOH as eluent (as shown in Table S2).

Table S2: Conditions for the experiments conducted for the synthesis of **G1C**.

	Base	Ratio 2-AEMA : 2E-2TPU : base	Reaction time [h]	Column chromatography	m [g] (isolated product)
1	TEA	1.00 : 0.88 : 0.88	20	EtOH : EtOAc 1:1	0.0423
2	TEA	1.00 : 0.88 : 0.88	40	DCM : MeOH 9:1	0.1157
3	TEA	1.00 : 1.20 : 1.05	21	-	1.0073
4	TBD	1.00 : 0.88 : 0.88	20	DCM : MeOH 9:1	0.0799

¹H NMR (500MHz, D₂O) δ / ppm: 5.71 (s, 1H, CH₃-C_q-CH₂-), 5.44 (s, 1H, CH₃-C_q-CH₂-), 3.63 (m, 2H, -CO-O-CH₂-CH₂-NH-), 3.10 (m, 2H, -CO-O-CH₂-CH₂-NH-), 1.91 (s, 3H, CH₃-C_q-CO-O-).

For the synthesis of 2-ethyl-2-thiopseudourea hydrobromide, 1.00 g thiourea (13.137 mmol, 1.00 eq.) were dissolved in 25 mL EtOH. In order to dissolve the thiourea completely, the reaction mixture was heated up to 60°C. Subsequently 1.49 g bromoethan (13.663 mmol, 1.04 eq.) were added. The solution was refluxed for additional 15 h at 80°C. After cooling the reaction mixture to ambient temperature the solvent was evaporated. The product was purified by recrystallization from MeOH yielding a white solid (2.1209 g, 11.459 mmol, 87 %).

¹H NMR (500 MHz, DMSO) δ / ppm: 3.16 (q, 2H, CH₃-CH₂-S-), 1.24 (s, 3H, CH₃-CH₂-S-).

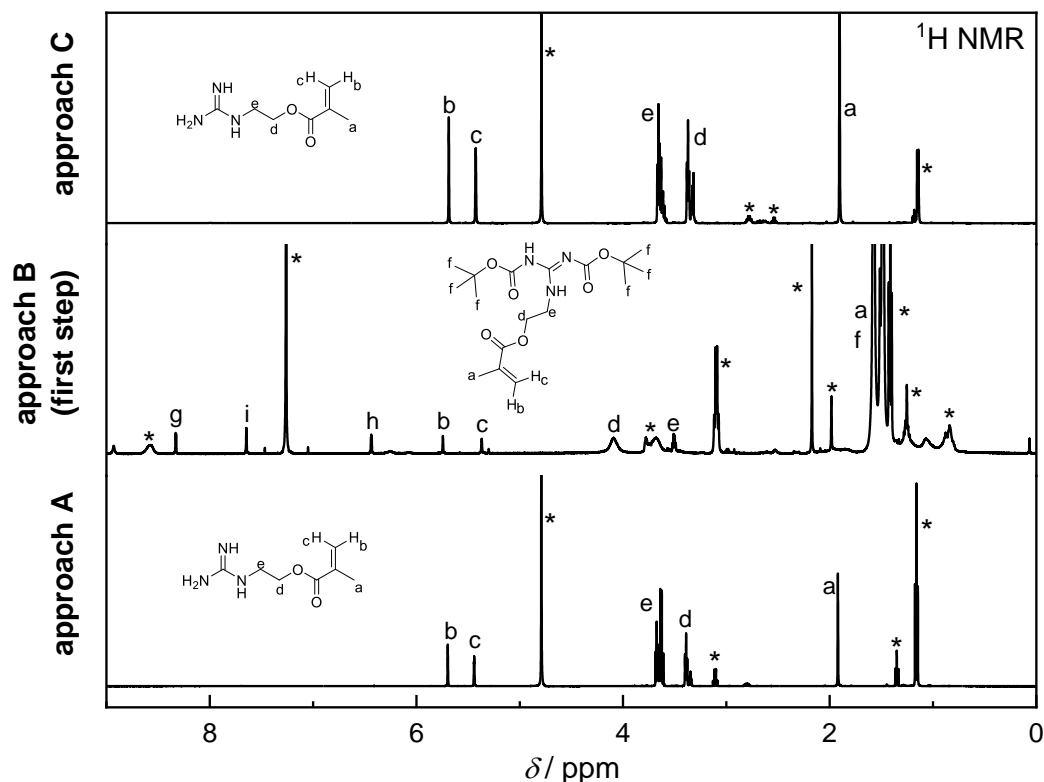
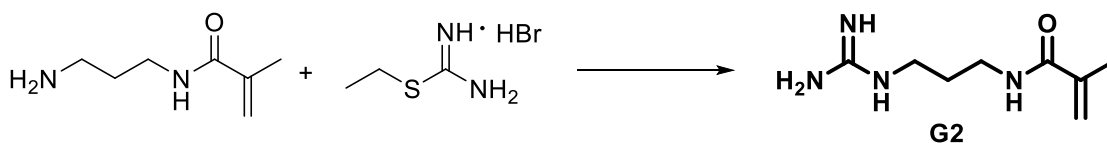


Figure S7: ^1H NMR (500 MHz) spectra of **G1**, approach A–C. The spectra of approach A and C were recorded in D_2O , the spectrum of approach B in CDCl_3 . All spectra were recorded at ambient temperature.

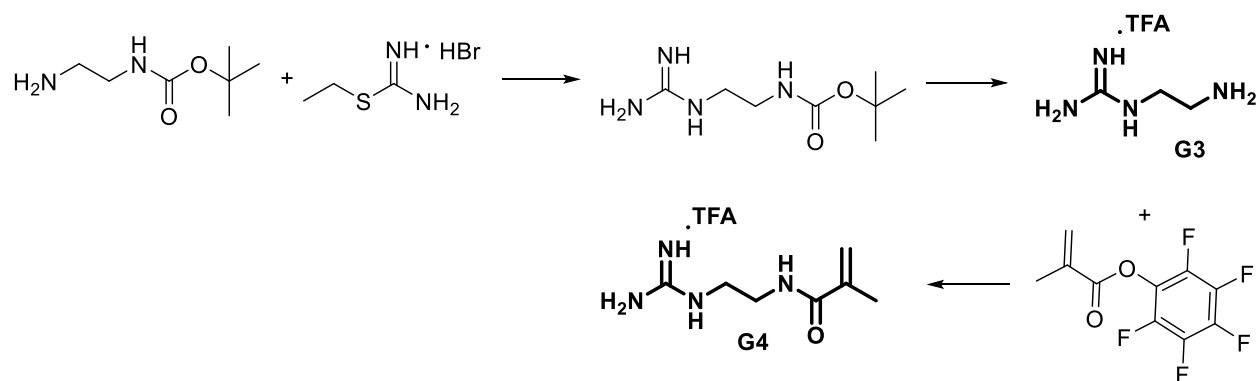
B.2.2 Guanidinopropylmethacrylamide (GPMA, **G2**)^[4]



To a solution of 1.92 g 2-ethyl-2-thiopseudourea (10.348 mmol, 0.88 eq.) and 1.43 TEA (10.348 mmol, 0.88 eq.) in 10 mL CH_3CN , 1.67 g *N*-(3-aminopropyl)methacrylamide (11.759 mmol, 1.00 eq.) were added slowly. In order to completely dissolve the reactants, additionally 2 mL dist. H_2O were added. The reaction mixture was stirred at ambient temperature for 21 h. By evaporating the solvent, a white-yellow oil was isolated, which was dissolved in H_2O and washed with DCM (4 x 50 mL). The solvent was evaporated, and a yellow oil was obtained. Further purification was conducted *via* recrystallization from EtOAc, followed by a column chromatography (silica gel, EtOAc / EtOH in a ratio 1:1 as eluent). The isolated product was dried under high vacuum for 3 days. In addition, a vacuum distillation ($8.2 \cdot 10^{-1}$ mbar) up to 190°C was carried out. Finally, a small amount of a yellow oil was obtained (0.26 g, 1.413 mmol, 12 %).

^1H NMR (500 MHz, D_2O) δ / ppm: 5.67 (s, 1H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$), 5.43 (s, 1H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$), 3.32 (t, 2H, $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-}$), 3.22 (t, 2H, $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-}$), 1.92 (s, 3H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$), 1.81 (quin, 2H, $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH-}$).

B.2.3 Guanidinoethylmethacrylamide (GEMAA, **G4**)^[4, 6]



In a 15 mL round bottom flask, 1.16 g 2-ethyl-2-thiopseudourea (6.242 mmol, 1.00 eq.) were dissolved in 4.7 mL CH₃CN and 0.5 mL distilled water. Once everything was completely dissolved, 0.92 mL TEA (6.554 mmol, 1.05 eq.) were added. Subsequently, 1.00 mL *tert*-butyl (2-aminoethyl)carbamate (6.242 mmol, 1.00 eq.) were added, and the reaction mixture was stirred for 20 h at ambient temperature. The solvent was evaporated, and a yellow sticky material was isolated (1.97 g, 9.739 mmol). For the deprotection, the obtained material (1.97 g, 9.739 mmol, 1.00 eq.) was dissolved in 25 mL DCM. Under vigorous stirring, 16 mL TFA (23.84 g, 0.209 mmol, 2147 eq.) were slowly added in a dropwise manner. The clear, yellow solution was stirred for additional 18 h at ambient temperature. Once the solvent was removed under reduced pressure, the residue was dissolved in 20 mL H₂O and was washed with DCM (3 x 20 mL). The solvent of the aqueous layer was evaporated and a yellow sticky material, 2-aminoethylguanidine (**G3**), was isolated (1.98 g). In the last step, 1.98 g of **G3** (19.366 mmol, 1.00 eq.) were dissolved in 20 mL dry DMF under anhydrous conditions. To the clear yellow solution 6.7 mL TEA (48.415 mmol, 2.50 eq.) were added. Subsequently, 3.5 mL pentafluorophenyl methacrylate (19.366 mmol, 1.00 eq.) were added dropwise to the reaction mixture. The mixture was stirred for 18.5 h at ambient temperature. After evaporating the solvent, the residue was dissolved in 1 mL MeOH and precipitated into 100 mL cold Et₂O. The precipitate was collected by centrifugation and an orange / brown material was isolated (0.41 g, 2.4224 mmol, 12 %).

¹H NMR (500 MHz, D₂O) δ / ppm: 5.68 (s, 1H, CH₃-C_q-CH₂-), 5.45 (s, 1H, CH₃-C_q-CH₂-), 3.44 (m, 2H, -NH-CH₂-CH₂-NH-CO-), 3.36 (m, 2H, -NH-CH₂-CH₂-NH-CO-), 1.91 (s, 3H, CH₃-C_q-CH₂-).

¹⁹F NMR (471 MHz, D₂O) δ / ppm: -75.84 (s, 1F, F₃C-CO-OH), -164.32 (s, 2F, F_{ortho}), -166.52 (s, 1F, F_{para}), -173.07 (s, 2F, F_{meta}).

The reaction was repeated several times by altering the amount of TEA or the base (as depicted in Table S3). Alternatively to TEA, pyridine and TBD were tested as base. The ¹H and ¹³C NMR spectra of the products resulting from these reactions were quite similar and showed many impurities.

Table S3: Reaction conditions for the experiments conducted to synthesize **G3**.

	Base	Eq. of base	Reaction time	Yield [%]
1	TEA	2.5 / 1.1	18.5h / 17h	12 / 23
2	Pyridine	1.1	17h	23
3	TBD	1.1	17h	40

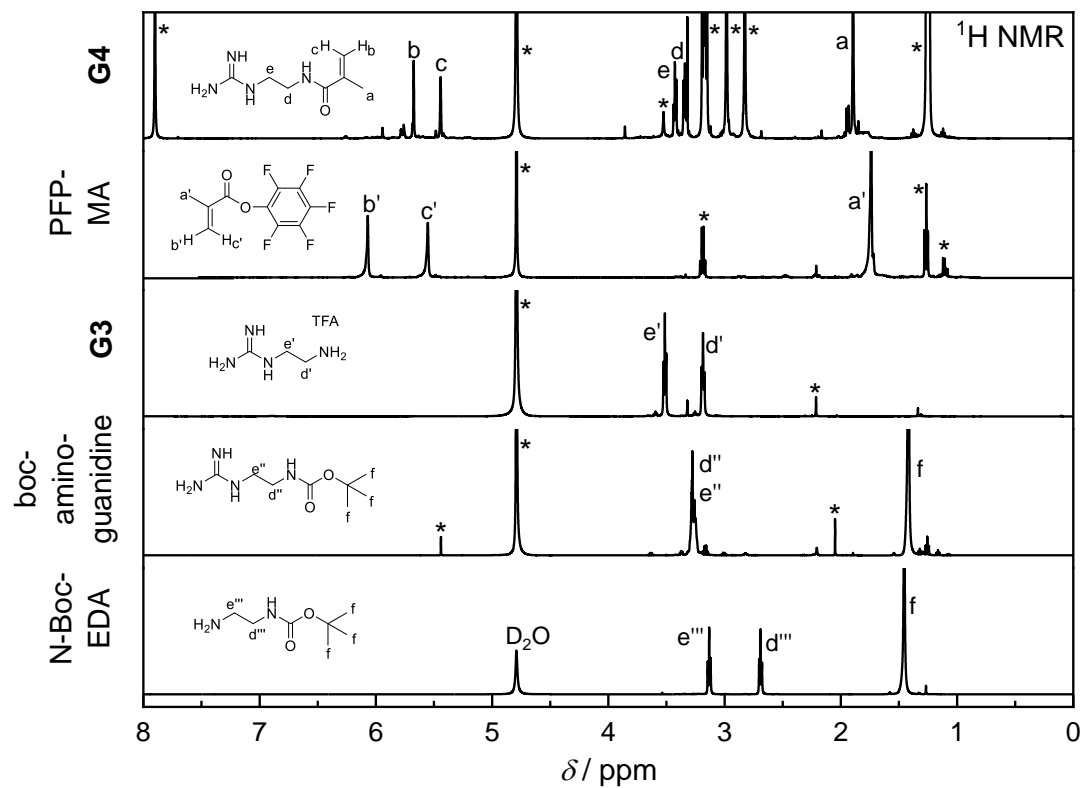


Figure S8: ^1H NMR (500 MHz) spectra of **G3** and **G4** compared with the spectra of the starting materials N-Boc-EDA and PFPMA. All spectra were recorded in D_2O at ambient temperature.

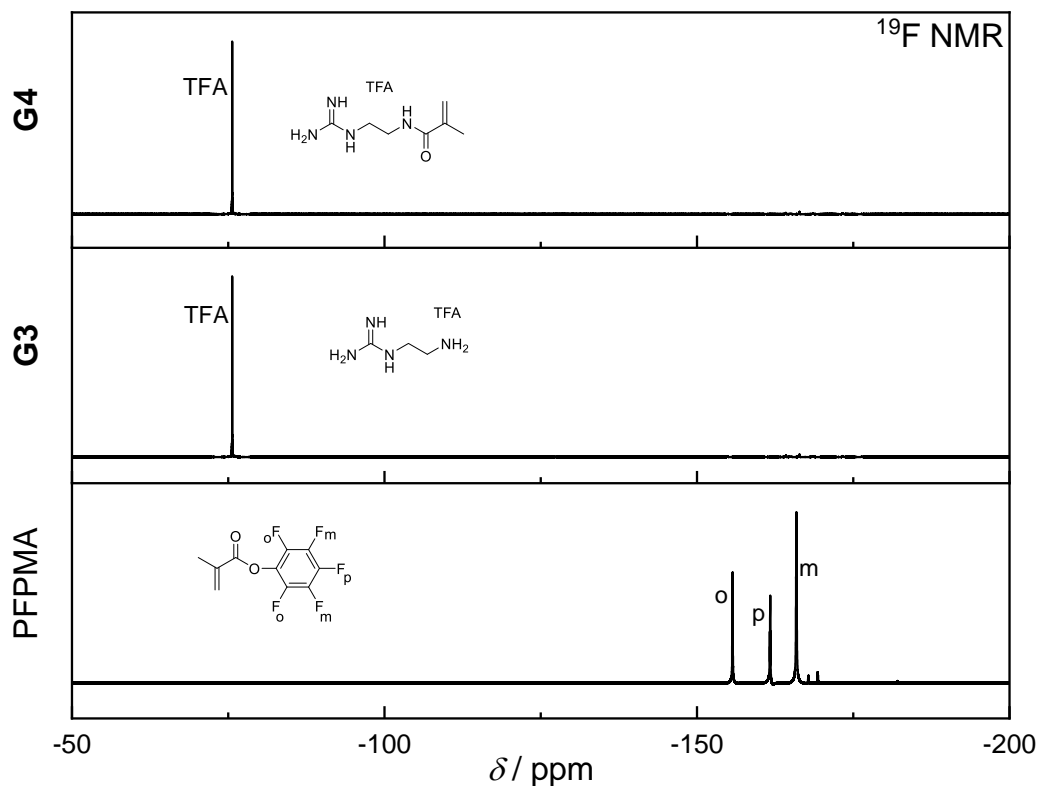
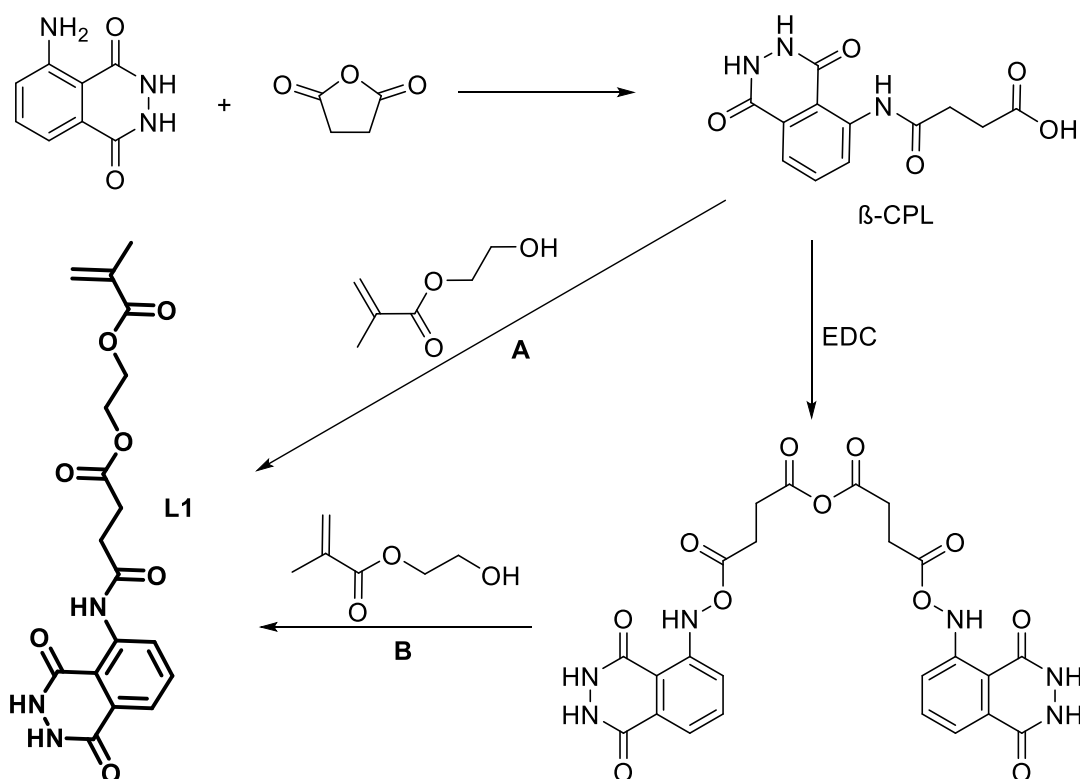


Figure S9: ^{19}F NMR spectra of **G3** and **G4** in D_2O recorded at ambient temperature.

B.3 Synthesis of luminol derivatives

B.3.1 2-(methacryloyloxy)ethyl 4-((1,2,3,4-tetrahydrophthalazin-5-yl)amino)-4-oxobutanoate (L1)^[7-8]



For the synthesis of β -CPL, 0.50 g luminol (2.822 mmol, 1.00 eq.) and 0.57 g succinic anhydride (5.644 mmol, 2.00 eq.) were dissolved in 12 mL dry DMF under anhydrous conditions. After adding 0.30 mL pyridine, the reaction mixture was heated to 60°C. The reaction was stopped after 20 h and the reaction mixture was poured into a mixture of ice and 55 mL 0.8 M HCl. Subsequently, the precipitate was filtered off, washed with H₂O and MeOH. The obtained pale white / yellow solid was dissolved in 40 mL DMF and the product was extracted with NaHCO₃ (3 x 20 mL). The combined aqueous layers were acidified with HCl in ice until pH = 1 was adjusted. A white colloidal material precipitated which was collected by centrifugation.

¹H NMR (500 MHz, DMF) δ / ppm: 7.92 (m, 1H, *H*_{arom.}), 7.70 (m, 1H, -CO-C_q-CH_{arom.}), 7.50 (m, 1H, -NH-C_q-CH_{arom.}), 3.41 (s, 2H, HO-CO-CH₂-CH₂-), 3.14 (m, 2H, HO-CO-CH₂-CH₂-).

The reaction was repeated with a slightly modified procedure:

Under anhydrous conditions, 0.25 g luminol (1.4112 mmol, 1.00 eq.) and 0.21 g succinic anhydride (2.1168 mmol, 1.5 eq.) were dissolved in 6 mL dry DMF. After adding 2 mL pyridine, the reaction mixture was stirred for 24 h at 60°C. The reaction mixture was poured into a mixture of ice and 23 mL 0.8 M HCl. A yellow residue was collected by centrifugation, which was dried after decantation under reduced pressure. The residue was dissolved in NaHCO₃ and acidified with HCl. For nothing precipitated, the solvent was evaporated. The residue was dissolved in H₂O and the product was extracted with DCM (5 x 50 mL). Evaporating the solvent yielded a yellow oil (4.13 g) and a beige residue (2.06 g). Although the characteristic resonances of the β -CPL protons could be assigned in the ¹H NMR spectra, there were still

too many impurities present to enable the subsequent reaction with the 2-hydroxyethyl methacrylate (approach A).

In a second approach (B), 0.25 g luminol (1.406 mmol, 1.0 eq.), 0.17 g succinic anhydride (1.687 mmol, 1.2 eq.) and 0.035 g DMAP (0.281 mmol, 0.2 eq.) were dissolved in 4 mL dry DCM. Under anhydrous conditions After 24 h 0.29 g EDC (1.476 mmol, 1.05 eq.) were added and the reaction mixture was stirred for additional 42 h at ambient temperature. The reaction mixture was washed with 0.8 M HCl (pH = 2) (2 x 6 mL) and H₂O (3 x 6 mL). Centrifugation of the organic layer isolated a beige solid (0.1593 g). Unfortunately, the NMR spectrum still showed similar impurities as in approach A.

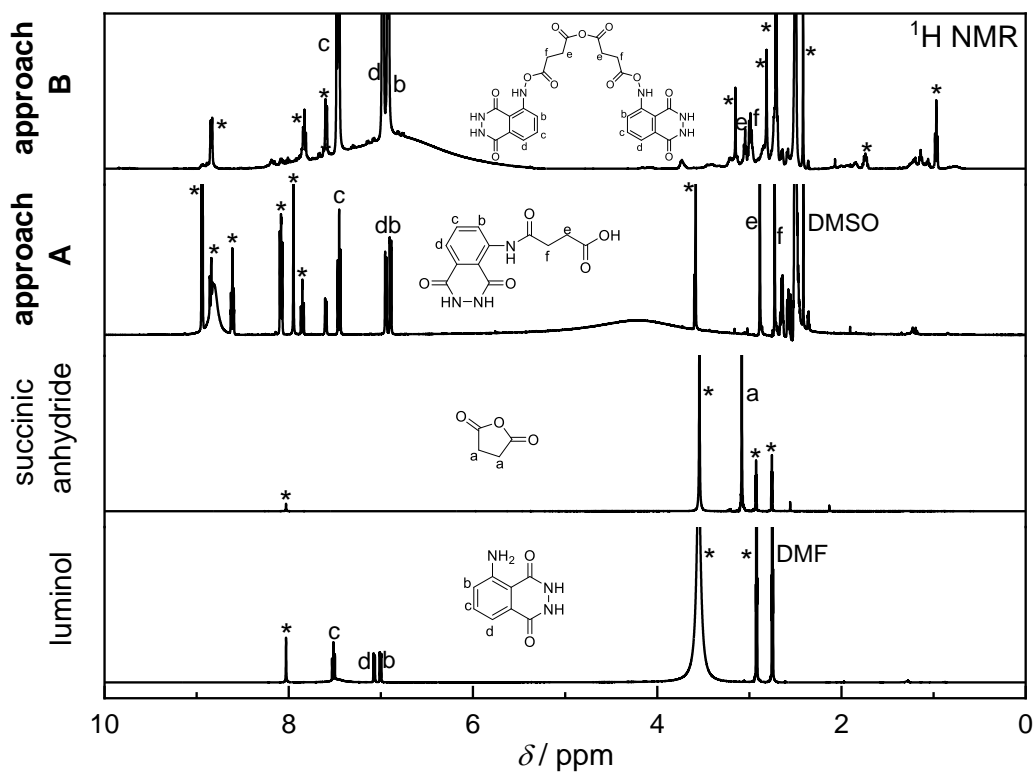
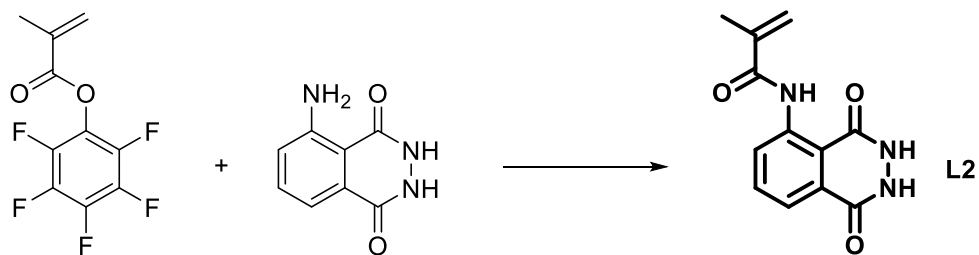


Figure S10: ¹H NMR (500 MHz) spectra of **L1**, approach A and B in comparison to the starting materials. The spectra were recorded in DMSO-d₆ and DMF-d₇ at ambient temperature.

B.3.2 N-(1,4-dioxo-1,2,3,4-tetrahydrophthalazin-5-yl)methacrylamine (**L2**)^[6]

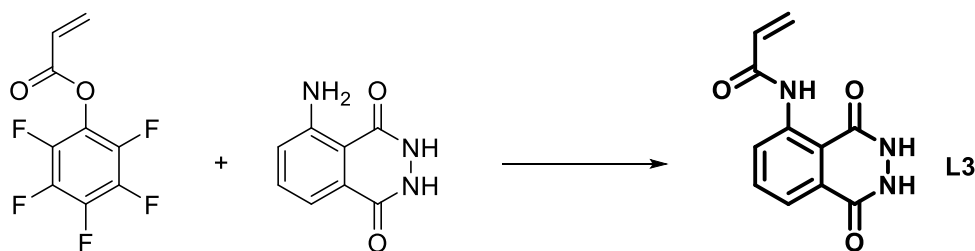


Under anhydrous conditions, 7 mg luminol (0.0397 mmol, 1.00 eq.) were dissolved in 45 mL dry DMF and 13.8 mL TEA (0.0993 mmol, 2.5 eq.). Subsequently, 7.2 mL pentafluorophenylmethacrylate (0.0397 mmol,

1.00 eq.) were added and the reaction mixture was stirred for 22 h at ambient temperature. Due to the small amount, no further purification was conducted after evaporating the solvent.

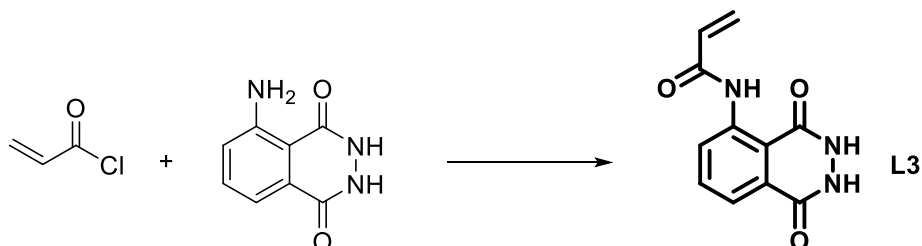
^1H NMR (500 MHz, DMSO) δ / ppm: 7.44 (m, 1H, $H_{\text{arom.}}$), 6.94 (m, 1H, $H_{\text{arom.}}$), 6.87 (m, 1H, $H_{\text{arom.}}$), 6.40 (s, 1H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$), 6.08 (s, 1H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$), 2.08 (s, 3H, $\text{CH}_3\text{-C}_q\text{-CH}_2\text{-}$).

B.3.3 N-(1,4-dioxo-1,2,3,4-tetrahydrophthalazin-5-yl)acrylamine (L3)^[6]



Approach A: Under anhydrous conditions, 0.027 g luminol (0.152 mmol, 1.00 eq.) were dissolved in 0.33 mL dry DMF. Then 0.011 mL TEA (0.076 mmol, 0.50 eq.) were added. After the addition of 0.025 mL pentafluorophenylacrylate (0.152 mmol, 1.00 eq.) to the turbid beige colored reaction mixture, everything got dissolved and the clear yellow solution was stirred for 20 h at ambient temperature. The yellow residue was filtered off and the solvent from the filtrate was evaporated, resulting in an orange residue (0.020 g, 0.087 mmol, 6 %).

The NMR analysis revealed that the desired product was not obtained, therefore the reaction was repeated with a different synthesis strategy:^[9]



Approach B: Under anhydrous conditions, 0.50 g luminol (2.8229 mmol, 1.00 eq.) were dissolved in 10.1 mL dry DMF. After addition of 0.23 mL pyridine (2.7664 mmol, 0.98 eq.) the reaction mixture was cooled to 0°C. Then 0.26 mL acryloyl chloride (3.1052 mmol, 1.10 eq.) were added slowly in a dropwise manner. The reaction mixture was stirred for 1 h at 0°C and additional 22 h at ambient temperature. Slowly, 20 mL water were added and the mixture was put in the fridge for 45 min. Subsequently, the reaction mixture was centrifuged and a yellow jelly-like material was obtained. The material was washed with water, until the filtrate was almost colorless. After drying the material under reduced pressure a yellow solid was isolated (0.045 g, 0.1935 mmol, 7 %).

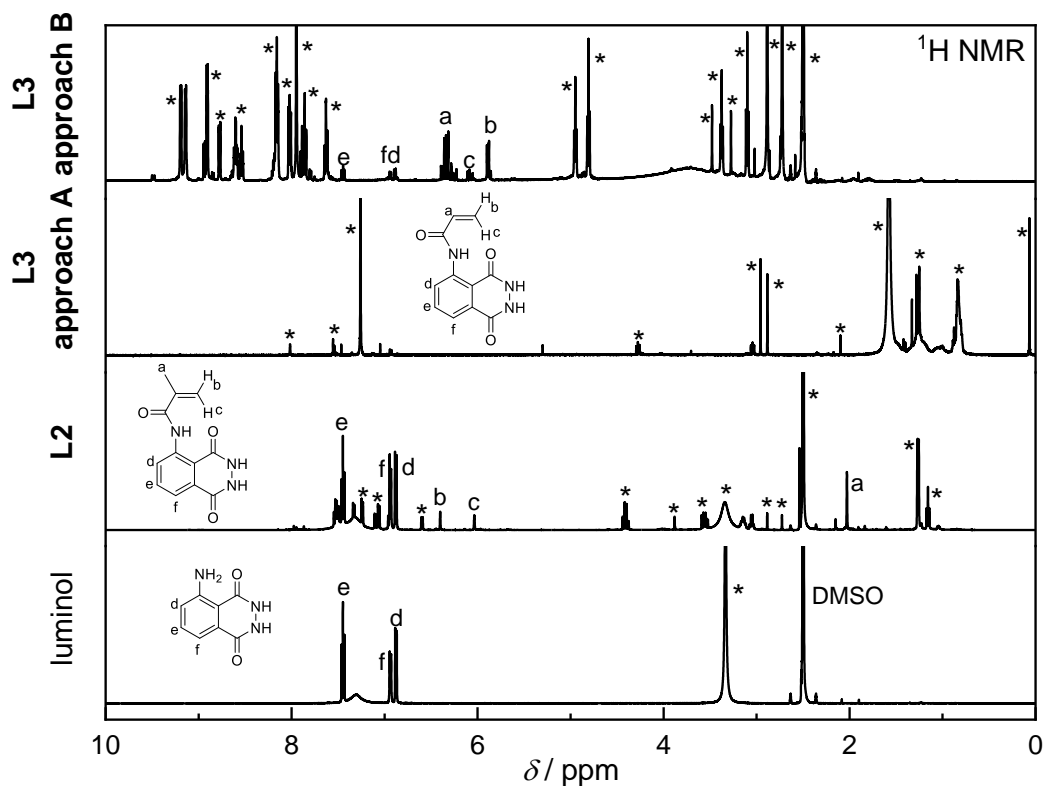
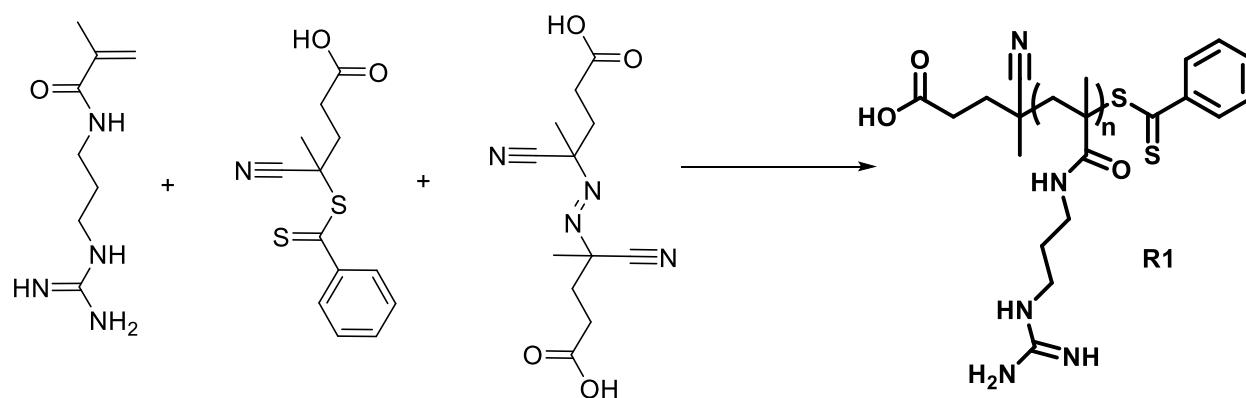


Figure S11: ^1H NMR (500 MHz) spectra of luminol, **L2** and **L3** (approach A and B). All spectra were recorded in DMSO at ambient temperature.

B.4 RAFT-Polymers

B.4.1 Guanidinopropylmethacrylamide-Macro-CTA **R1**^[4]

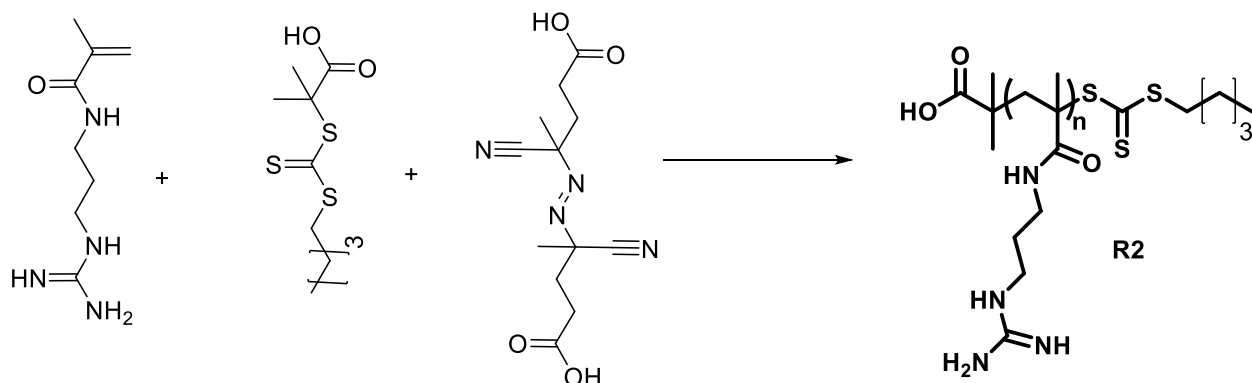


Under anhydrous conditions, 0.11 g guanidinopropylmethacrylamide (0.5931 mmol, 1.00 eq.) were dissolved in 0.9 mL acetate buffer. In a separate round bottom flask under inert atmosphere, 1.5 mg 4-cyano-4-((phenylcarbonothioyl)thio)pentanoic acid (0.0054 mmol, 0.009 eq.) and 0.3 mg V-501 (0.0012 mmol, 0.002 eq.) were dissolved in 0.1 mL MeOH. After addition of the MeOH – solution, the reaction mixture was purged with N_2 for 1 h. Subsequently, the reaction mixture was put in a preheated oil bath at 70°C . After 21 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated.

The residue was dissolved in a small amount of MeOH and was precipitated into ice cold Et₂O, yielding a pink solid.

¹H NMR (500 MHz, D₂O) δ / ppm: 5.67 (s, 1H, CH₃-C_q-CH₂-), 5.43 (s, 1H, CH₃-C_q-CH₂-), 3.32 (t, 2H, H₂N-CH₂-CH₂-CH₂-NH-), 3.22 (t, 2H, H₂N-CH₂-CH₂-CH₂-NH-), 1.92 (s, 3H, CH₃-C_q-CH₂-), 1.81 (quin, 2H, H₂N-CH₂-CH₂-CH₂-NH-).

B.4.2 Guanidinopropylmethacrylamide-Macro-CTA R2^[4]

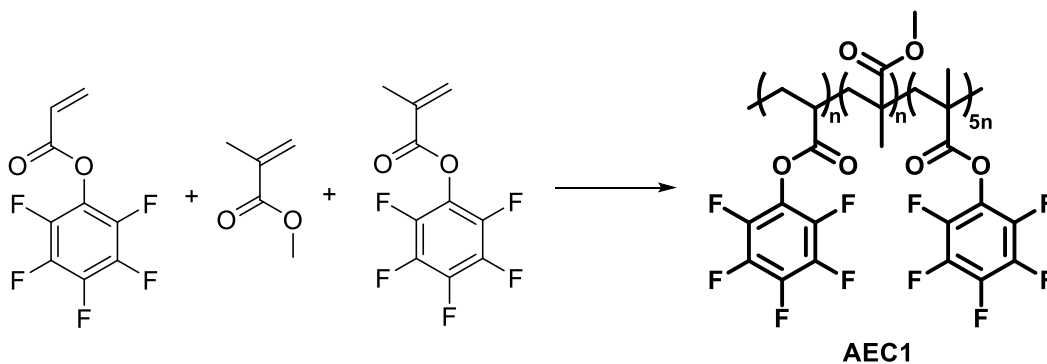


Under anhydrous conditions, 0.12 g guanidinopropylmethacrylamide (0.655 mmol, 1.00 eq.) were dissolved in a mixture of 1 mL acetate buffer and 2 drops of MeOH. In a separate round bottom flask under inert atmosphere, 2.2 mg DMP (0.006 mmol, 0.009 eq.) and 0.3 mg V-501 (0.0012 mmol, 0.002 eq.) were dissolved in 0.1 mL MeOH prior addition to the reaction mixture. The reaction mixture was purged with N₂ for 30 min. Subsequently, the reaction mixture was put in a preheated oil bath at 70°C. After 22 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated. The residue was dissolved in a small amount of MeOH and precipitated into ice cold Et₂O. A white solid was isolated.

¹H NMR (500 MHz, D₂O) δ / ppm: 5.67 (s, 1H, CH₃-C_q-CH₂-), 5.43 (s, 1H, CH₃-C_q-CH₂-), 3.32 (t, 2H, H₂N-CH₂-CH₂-CH₂-NH-), 3.22 (t, 2H, H₂N-CH₂-CH₂-CH₂-NH-), 1.92 (s, 3H, CH₃-C_q-CH₂-), 1.81 (quin, 2H, H₂N-CH₂-CH₂-CH₂-NH-).

B.5 Active Ester Copolymers

B.5.1 Copolymer AEC1



Under anhydrous conditions, 0.50 g pentafluorophenylmethacrylate (1.984 mmol, 5.00 eq.), 0.0945 g pentafluorophenylacrylate (0.397 mmol, 1.00 eq.) and 0.0397 g methylmethacrylate (0.397 mmol, 1.00

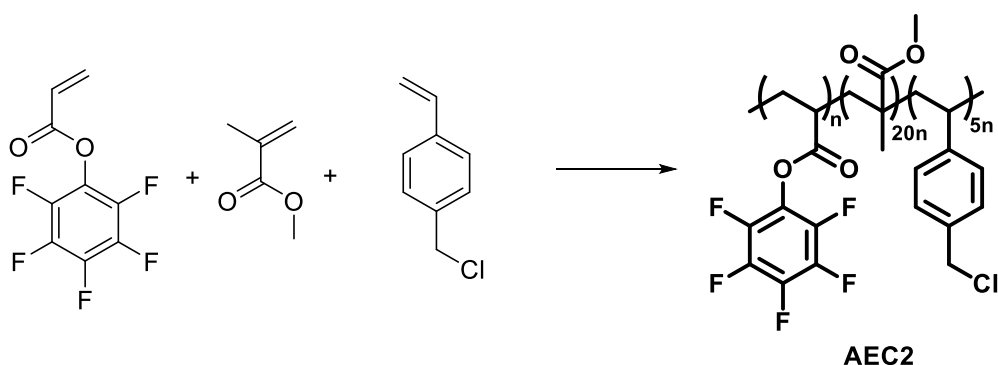
eq.) were dissolved in 4 mL dry 1,4-dioxane. 4 mg AIBN were dissolved in 4 mL dry 1,4-dioxane and were added to the reaction mixture. The reaction mixture was purged with N₂ for 1 h before being put in a preheated oil bath at 90°C. After 17 h, the reaction was stopped and the reaction mixture was cooled to ambient temperature. The solvent was evaporated and the residue was precipitated into ice cold MeOH, yielding a white solid (**AEC1**, 0.18 g).

SEC (THF): $M_n = 7\,720\text{ g mol}^{-1}$, $M_w = 12\,100\text{ g mol}^{-1}$, $\mathcal{D} = 1.57$

¹H NMR (500 MHz, CDCl₃) δ / ppm: 3.60 (m, 3H, $\text{CH}_3\text{-O-CO-}$), 2.37 – 0.78 (m, 13H, $(-\text{CH}_2\text{-C}_q)_n(-\text{CH}_2\text{-C}_q)_m(-\text{CH}_2\text{-CH})_o$, $-\text{CO-C}_q\text{-CH}_3$).

¹⁹F NMR (471 MHz, CDCl₃) δ / ppm: -152.14 (m, 2F, E_{ortho}), -157.47 (m, 1F, E_{para}), -162.02 (m, 2F, E_{meta}).

B.5.2 Copolymer **AEC2**



Under anhydrous conditions, 0.7631 g 4-vinyl benzylchloride (5.0 mmol, 5.00 eq.), 0.2381 g pentafluorophenylacrylate (1.0 mmol, 1.00 eq.) and 2.0040 g methylmethacrylate (20.0 mmol, 20.00 eq.) were dissolved in 10 mL dry 1,4-dioxane. 9.9 mg AIBN (0.06 mmol, 0.06 eq.) were dissolved in 10 mL dry 1,4-dioxane and were added to the reaction mixture. The reaction mixture was purged with N₂ for 1 h before being put in a preheated oil bath at 90°C. After 17 h, the reaction was stopped and the reaction mixture was cooled to ambient temperature. The solvent was evaporated and the residue was precipitated into ice cold MeOH, yielding a white solid (**AEC2**, 2.8474 g).

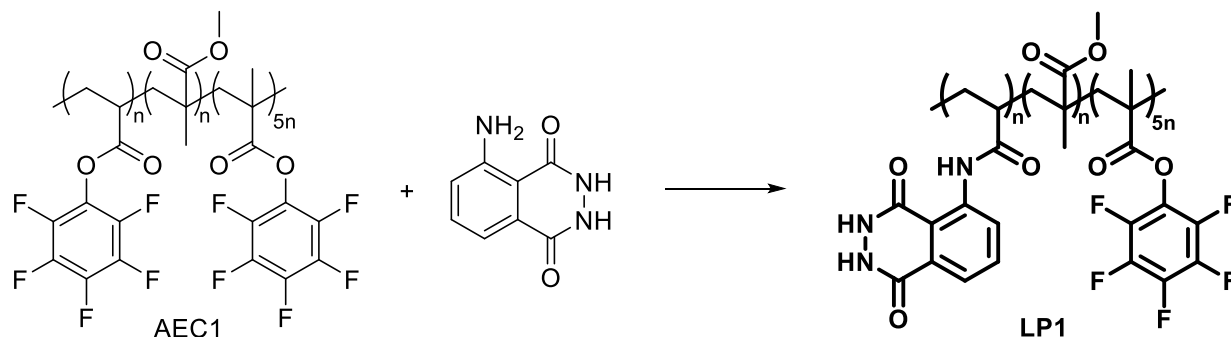
SEC (THF): $M_n = 14\,600\text{ g mol}^{-1}$, $M_w = 23\,700\text{ g mol}^{-1}$, $\mathcal{D} = 1.62$

¹H NMR (400 MHz, CDCl₃) δ / ppm: 7.23 (m, 2H, $H_{arom.}$), 7.01 (m, 2H, $H_{arom.}$), 4.50 (m, 2H, $-\text{C}_q\text{-CH}_2\text{-Cl}$), 3.54 (m, 3H, $-\text{CO-O-CH}_3$), 1.80 (m, 2H, $(-\text{CH}_2\text{-CH})_n(-\text{CH}_2\text{-C}_q)_m(-\text{CH}_2\text{-CH})_o$), 1.23-0.45 (m, 9H, $\text{CH}_3\text{-C}_q$, $(-\text{CH}_2\text{-CH})_n(-\text{CH}_2\text{-C}_q)_m(-\text{CH}_2\text{-CH})_o$).

¹⁹F NMR (376 MHz, CDCl₃) δ / ppm: -152.08 (s, 2F, E_{ortho}), -157.64 (s, 1F, E_{para}), -162.07 (s, 2F, E_{meta}).

B.6 Luminol-Polymers^[10]

B.6.1 Luminol-Polymer **LP1**



Under anhydrous conditions, 0.3384 g **AEC1** (0.2118 mmol of the pentafluorophenylacrylate moiety, 1.00 eq.) were dissolved in 4 mL dry 1,4-dioxane. In a separate round bottom flask, 0.0938 g luminol (0.0938 mmol, 2.50 eq. with respect to the pentafluorophenylacrylate moiety of the polymer backbone) and 0.15 mL TEA (0.1072 g, 1.0590 mmol, 5.00 eq. with respect to the pentafluorophenylacrylate moiety of the polymer backbone) were dissolved in 2 mL dry DMSO, also under anhydrous conditions. The luminol – mixture was added to the dissolved polymer mixture and the reaction mixture was put in a preheated oil bath at 50°C. After 24 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated. Precipitation into ice cold MeOH yielded a yellow solid (**LP1**, 0.3182 g).

¹H NMR (500 MHz, DMF) δ / ppm: 12.06 (s, 2H, $-\text{CO}-\text{NH}-\text{NH}-\text{CO}-$), 11.25 (s, 1H, $-\text{CO}-\text{NH}-\text{C}_q-$), 7.47 (m, 1H, $H_{\text{arom.}}$), 6.93 (m, 1H, $H_{\text{arom.}}$), 6.89 (m, 1H, $H_{\text{arom.}}$), 3.57 (m, 3H, $\text{CH}_3-\text{O}-\text{CO}-$), 2.36 – 1.08 (m, 13H, $-(\text{CH}_2-\text{C}_q)_m-$ (CH_2-C_q)_n- $(\text{CH}_2-\text{CH})_o-$, $\text{CH}_3-\text{C}_q-\text{CO}-\text{O}-$).

¹⁹F NMR (471 MHz, DMSO) δ / ppm: -152.32 (m, 2F, E_{ortho}), -157.49 (m, 1F, E_{para}), -162.40 (m, 2F, E_{meta}).

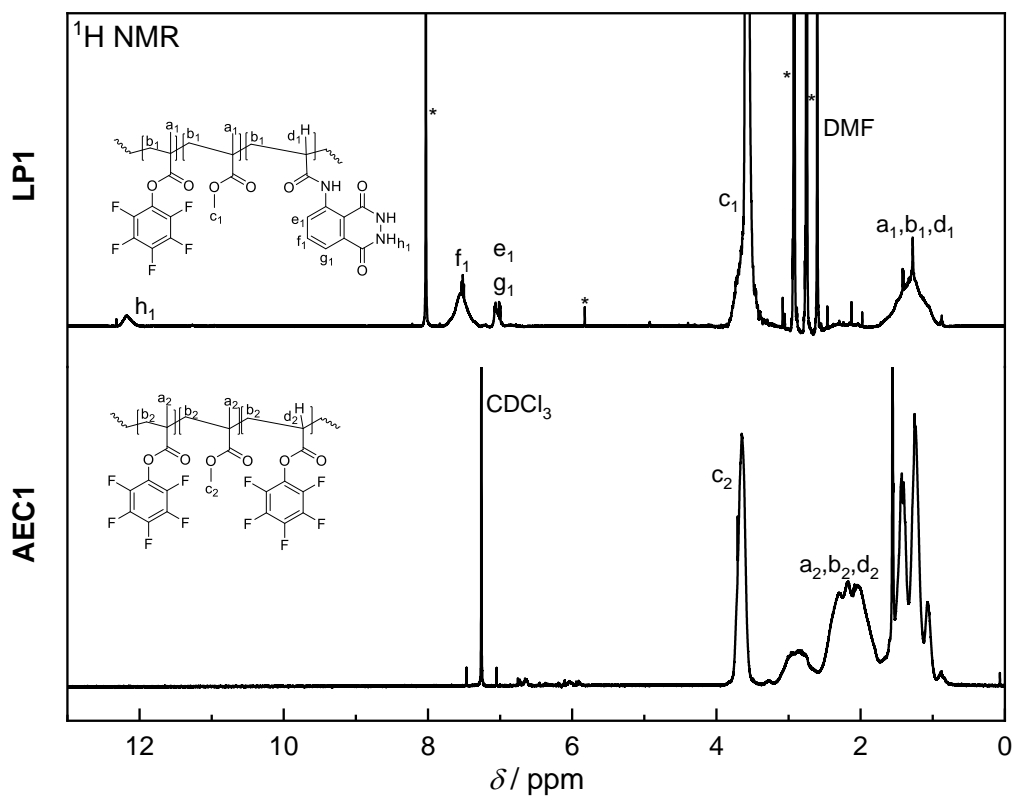


Figure S12: ^1H NMR (500 MHz) spectra of AEC1 in CDCl_3 and of LP1 in DMF, recorded at ambient temperature.

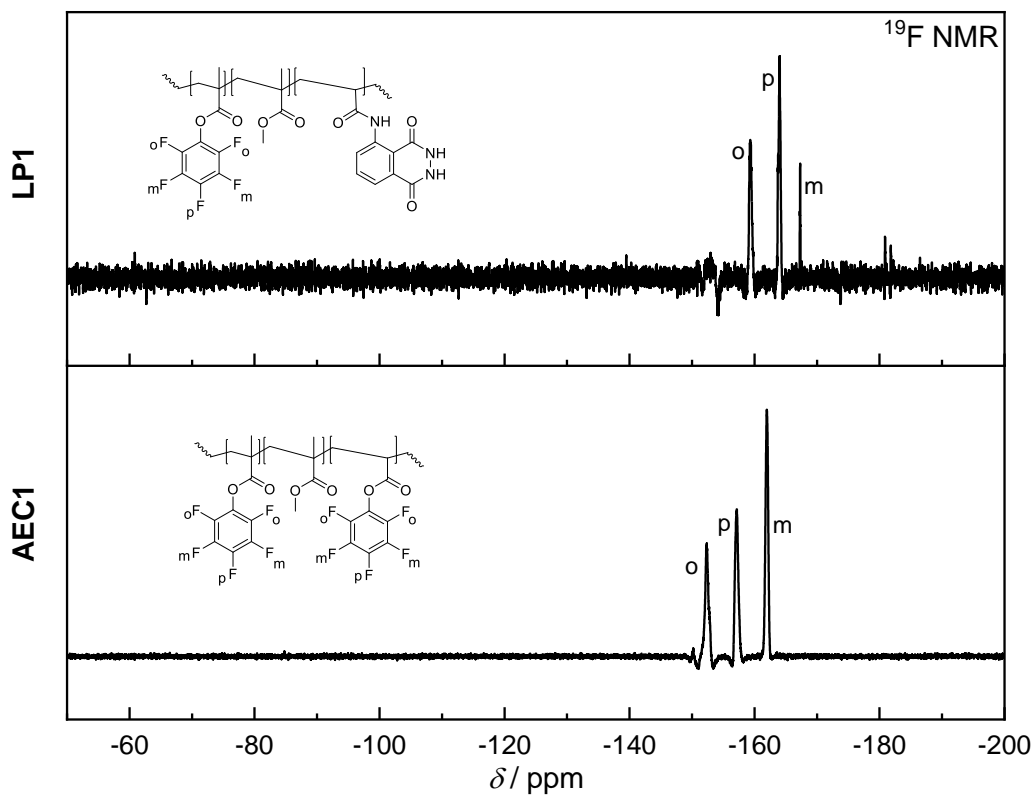
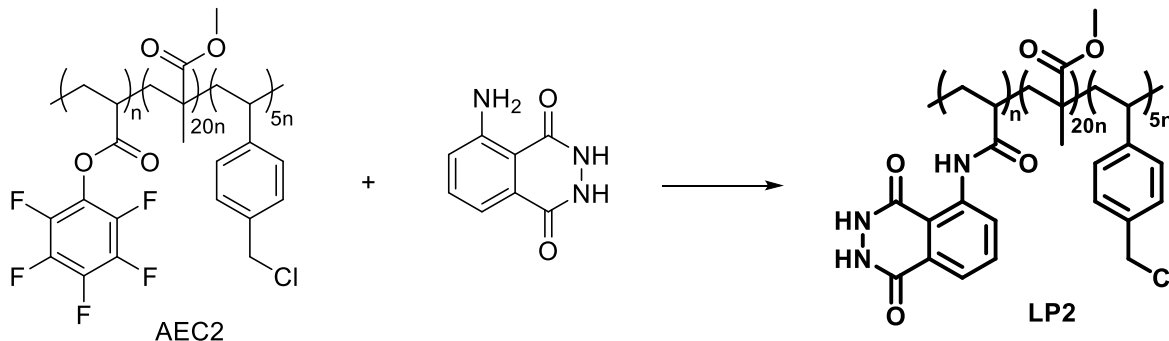


Figure S13: ^{19}F NMR spectra of AEC1 (CDCl_3) and LP1 (DMF) at ambient temperature.

B.6.2 Luminol-Polymer LP2



Under anhydrous conditions, 0.5 g **AEC2** (0.1608 mmol of the PFPA-moiety, 1.00 eq.) were dissolved in 1.7 mL dry 1,4-dioxane. In a separate round bottom flask, 0.0285 g luminol (0.1608 mmol, 1.00 eq. with respect to the PFPA moiety of the polymer backbone) and 0.045 mL TEA (0.0325 g, 0.3216 mmol, 2.00 eq.) were dissolved in 0.9 mL dry DMSO under N_2 . The luminol-mixture was added to the dissolved polymer mixture and the reaction mixture was put in a preheated oil bath at 50°C. After 21 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated. Precipitation into ice cold MeOH yielded **LP2** as a light yellow solid (0.4226 g).

1H NMR (400 MHz, DMSO) δ / ppm: 11.28 (m, 2H, $-CO-NH-$), 7.45 (m, 1H, $H_{arom.}$), 7.29 (m, 2H, $H_{arom.}$), 7.04 (m, 3H, $H_{arom.}$, $-CO-NH-$), 6.91 (m, 1H, $H_{arom.}$), 6.84 (m, 1H, $H_{arom.}$), 4.69 (m, 2H, $-C_q-CH_2-Cl$), 3.47 (m, 3H, $-CO-O-CH_3$), 1.74 (m, 2H, $(-CH_2-CH)_n(-CH_2-C_q)_m(-CH_2-CH)_o$), 1.35-0.39 (m, 9H, $, CH_3-C_q-, (-CH_2-CH)_n(-CH_2-C_q)_m(-CH_2-CH)_o$).

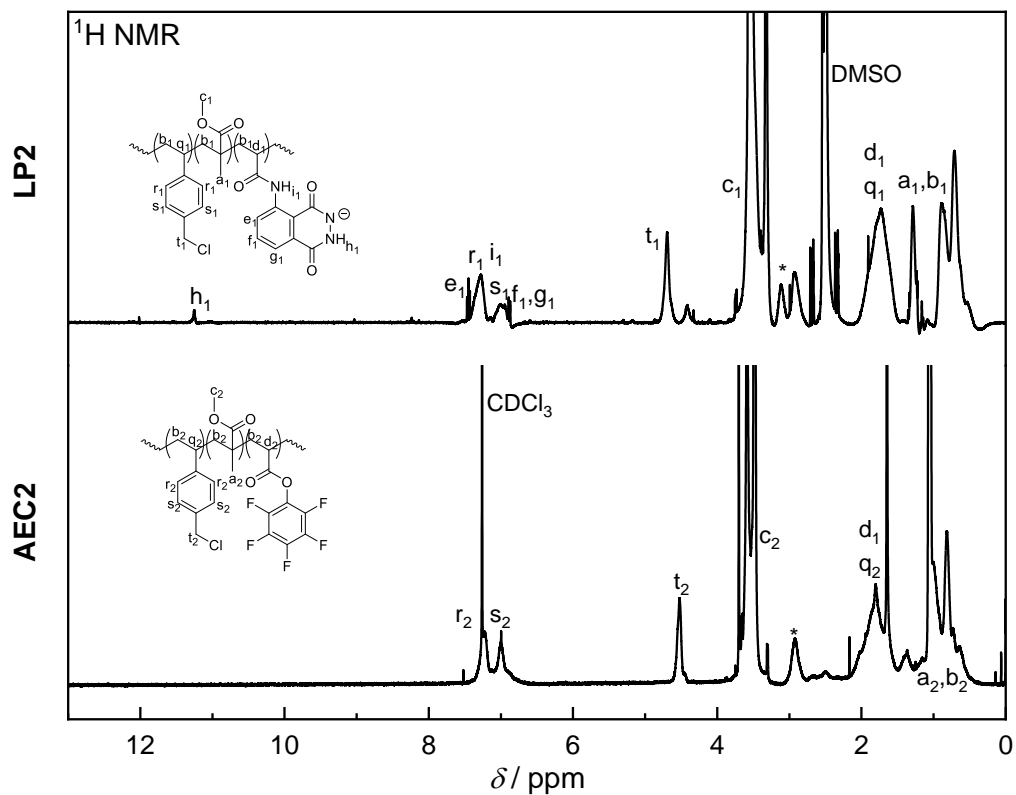


Figure S14: ¹H NMR (400 MHz) spectra of **AEC2** in CDCl₃ and of **LP2** in DMSO. All spectra recorded at ambient temperature.

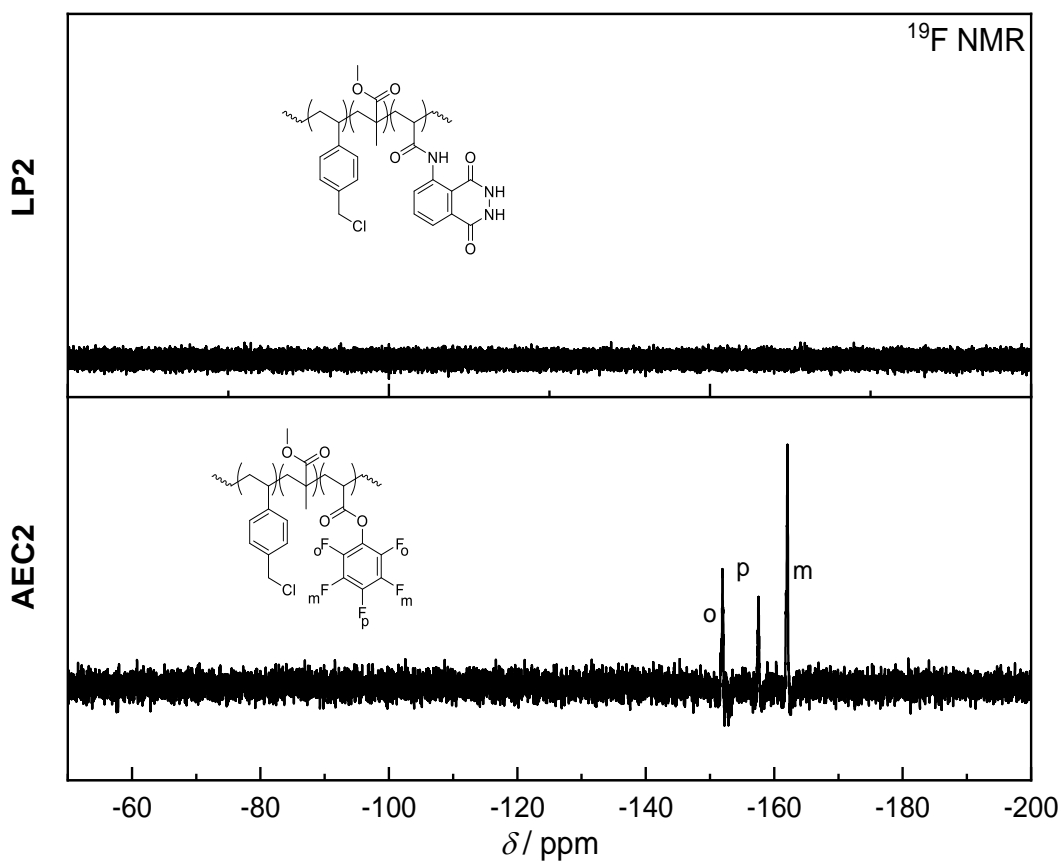
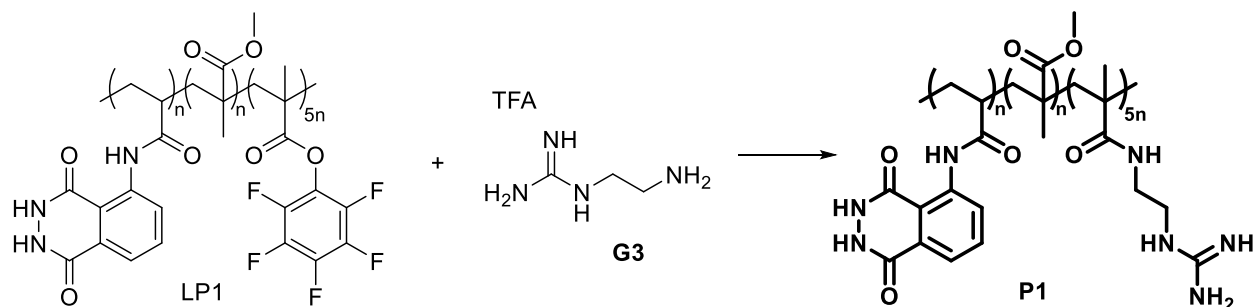


Figure S15: ¹⁹F NMR spectra of **AEC2** in CDCl₃ and of **LP2** in DMSO. All spectra were recorded at ambient temperature.

B.7 Luminol-Superbase-Polymers^[10]

B.7.1 Luminol-guanidine-polymer **P1**

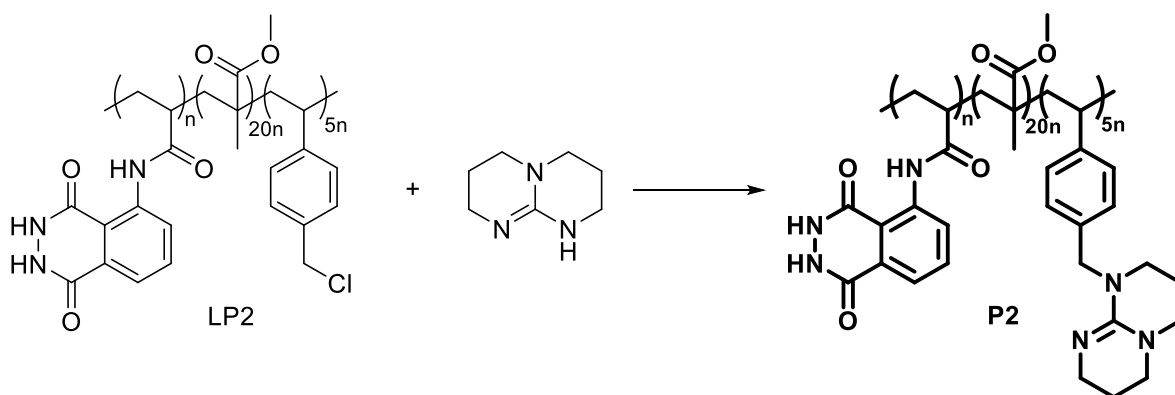


Under anhydrous conditions, 0.3182 g **LP1** (1.0330 mmol of the PFPA-moiety, 1.00 eq.) were dissolved in 7.17 mL dry 1,4-dioxane. In a separate round bottom flask, 0.5274 g **G3** (5.1650 mmol, 5.00 eq. with respect to the PFPA moiety of the polymer backbone) and 0.72 mL TEA (0.5226 g, 5.1650 mmol, 5.00 eq.) were dissolved in 3.6 mL dry DMSO under N_2 . The **G3**-mixture was added to the dissolved polymer mixture and the reaction mixture was put in a preheated oil bath at 50°C. After 23 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated. Precipitation into ice cold Et_2O yielded **P1** as yellow solid (0.2335 g).

1H NMR (500 MHz, DMF) δ / ppm: 12.16 (m, 2H, $-CO-NH-$), 8.20 (m, 2H, $-CO-NH-CH_2-$, $H_{arom.}$), 7.78 (m, 3H, $-CO-NH-C_q$, $-CH-NH_2$), 7.50 (m, 1H, $H_{arom.}$), 7.07 (m, 1H, $H_{arom.}$), 7.00 (m, 2H, $-NH-CH-NH_2$), 4.14 (m, 1H, $-CH_2-NH-CH-$), 3.86-2.98 (m, 7H, $-NH-CH_2-CH_2-NH-$, $-CO-O-CH_3$), 2.91-2.67 (m, 1H, $(CH_2-CH)_n$), 1.58-0.78 (m, 9H, $(-CH_2-CH)_m(-CH_2-C_q)_n$, $-CO-C_q-CH_3$).

^{19}F NMR (471 MHz, DMF) δ / ppm: -75 (s, 3F, **TFA**).

B.7.2 Luminol-TBD-polymer **P2**



Under anhydrous conditions, 0.4226 g **LP2** (0.1359 mmol of the PFPA-moiety, 1.00 eq.) were dissolved in 1.7 mL dry 1,4-dioxane. In a separate round bottom flask, 0.0946 g TBD (0.6795 mmol, 5.00 eq. with respect to the PFPA moiety of the polymer backbone) and 0.038 mL TEA (0.0275 g, 0.2718 mmol, 5.00 eq.) were dissolved in 0.9 mL dry DMSO under N_2 . The TBD-mixture was added to the dissolved polymer mixture and the reaction mixture was put in a preheated oil bath at 50°C. After 20 h, the reaction mixture was cooled to ambient temperature and the solvent was evaporated. Precipitation into ice cold Et_2O yielded **P2** as a yellow solid (0.4067 g).

^1H NMR (400 MHz, DMSO) δ / ppm: 8.52 (m, 1H, $-\text{CH}_2-\text{NH}-\text{CH}-$), 7.33 (m, 1H, $H_{\text{arom.}}$), 7.14 (m, 2H, $-\text{CO}-\text{NH}-$), 7.01 (m, 3H, $H_{\text{arom.}}$), 6.74 (m, 3H, $H_{\text{arom.}}$), 6.10 (s, 2H, $-\text{C}_q-\text{CH}_2-\text{N}_t-$), 3.47 (m, 3H, $\text{CH}_3-\text{O}-\text{CO}-$), 3.26 (m, 8H, $-\text{N}_t-\text{CH}_2-\text{CH}_2-$), 1.91-1.18 (m, 2H, $(-\text{CH}_2-\text{CH})_n(-\text{CH}_2-\text{C}_q)_m(-\text{CH}_2-\text{CH})_o$), 1.11-0.49 (m, 9H, CH_3-C_q- , $(-\text{CH}_2-\text{CH})_n(-\text{CH}_2-\text{C}_q)_m(-\text{CH}_2-\text{CH})_o$).

B.8 Host-Guest-Complexes **C1** and **C2**

For the formation of the supramolecular complexes **C1** and the **C2**, the respective polymer **P1** or **P2** (1.0 eq., 0.02 g mL^{-1}) was dissolved in the solvent (DMF, DMSO). After complete dissolving, the host-molecule Me- β -CD (5.2 eq.) was added. The solution was stirred at room temperature for 1h.

C Measurements and analytical methods

C.1 Nuclear magnetic resonance (NMR) spectroscopy

The NMR spectra were recorded on Bruker Avance 400 MHz. Spectra were referenced on residual solvent signal according to Nudelman et al^[41]: 2.50 ppm for DMSO- d_6 , 2.75 ppm for DMF- d_7 and 4.79 for D_2O . The deuterated solvents were purchased from Euriso-TOP and used without further purification.

C.2 Nuclear Overhauser effect spectroscopy (NOESY)

The NOESY NMR spectra are recorded either on Bruker Avance II+ 600 MHz spectrometer equipped with a 5 mm BBI inversely detected $^1\text{H}, ^{31}\text{P}-^{109}\text{Ag}$ double resonance probehead with actively shielded z-gradient, on Bruker Avance III 600 MHz spectrometer with a 5 mm CPTCI inversely detected $^1\text{H}, ^{13}\text{C}, ^{15}\text{N}$ triple resonance cryogenically cooled probehead with actively shielded z-gradient or on Bruker Avance III 600 MHz spectrometer with a 5 mm TBI inversely detected $^1\text{H}, ^{31}\text{P}-^{109}\text{Ag}, ^{13}\text{C}$ double resonance probehead with actively shielded z-gradient. The respective frequencies are 600.19 MHz and 599.70 MHz and 600.19 MHz for proton frequency. The temperature is controlled with Bruker VT-unit or a Bruker Smart VT-Unit. The used NOESY pulse sequences are implemented in the spectrometer manufacturer software and are based on publications of Wagner^[12] and Thrippleton.^[13]

C.3 Dynamic light scattering (DLS)

The apparent hydrodynamic diameters ($D_{h,app}$) were determined at 20 °C by means of a dynamic light scattering (DLS) analysis using a Zetasizer Nano ZS light scattering apparatus (Malvern Instruments, UK) equipped with He-Ne laser (at a wavelength of 633 nm, 4 mW). The Nano ZS instrument incorporates a non-invasive backscattering (NIBS) optic with a detection angle of 173°. The polymer solutions were prepared in DMF ($c = 1 \text{ mg mL}^{-1}$) and were subsequently filtered into disposable micro cuvettes. The prepared samples were stabilized prior to DLS analysis at an ambient temperature. All values of the apparent hydrodynamic diameter for each polymer mixture were averaged over three measurements (14 runs/measurement), and were automatically provided by the instrument using a cumulative analysis.

C.4 Ultraviolet-visible (UV/Vis) spectroscopy

The absorbance spectra were recorded on a Cary 100 UV-Visible Spectrometer (Agilent Technologies, USA) possessing a tungsten halogen light source (190 to 900 nm, accuracy $\pm 2 \text{ nm}$) and a R928 PMT detector. For the measurement, the polymers were dissolved in DMSO or DMF ($c = 3.25 \cdot 10^{-6} \text{ mmol mL}^{-1}$). The H_2O_2 (1 mol L^{-1}) was directly added to the quartz cuvette and the sample was analyzed immediately in the range from 250 to 500 nm. The absorbance of the polymers **P1** and **P2** were normalized to 1, all other

absorbances were referred to the absorbances of **P1** or **P2**, respectively. The samples were baseline corrected with respect to the pure solvent.

C.5 Chemiluminescence (CL) measurements

Chemiluminescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer in the Bio-/Chemiluminescence mode. The CL emission intensity was recorded in dependence on the wavelength from 300 to 800 nm (scan rate = 600 nm min⁻¹, averaging time = 0.1 s, emission slit = 5.0 nm, detector voltage = 800 V) with a concentration of 3.25*10⁻⁴ mmol mL⁻¹. The intensity of **C2** was normalized to 1, the intensity of **C1** was referred to the intensity of **C2**.

C.6 Size exclusion chromatography (SEC)

The apparent number average molar mass (M_n) and the molar mass distribution [Đ (dispersity index) = M_w/M_n] values of the polymers were determined using a size exclusion chromatography (SEC) system equipped with Shimadzu LC20AD pump, Wyatt Optilab rEX refractive index detector and four PLgel 5μ Mixed-C columns. The characterization was performed at 30 °C in THF with a flow rate of 1 mL·min⁻¹. The molecular weight calibration was based on sixteen narrow molecular weight linear polystyrene standards from Polymer Laboratories.

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