# Light-Induced Cross-linking and Post-cross-linking Modification of Polyglycidol

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## Experimental

**Materials.** Phenyl chloroformate (>97%, Fluka), pyridine (99.5%, dry over molecular sieve, Acros Organics), dichloromethane (99.8%, anhydrous, Sigma-Aldrich), 3-(dimethylamino)-1-propylamine (99%, Acros Organics), tetrahydrofuran (99.8%, extra dry, stabilizer free, Acros Organics), camphorquinone (99%, Acros Organics), *N*,*N*-dimethylformamide (99.8%, VWR), methyl iodide (99%, Sigma-Aldrich), 1-iodooctane (>97%, TCI), triethylene glycol monomethyl ether (95%, Sigma-Aldrich) and 1H, 1H, 2H, 2H-heptadecafluorodecyl iodide (>98%, TCI) were used as received.

Ethoxyethyl glycidyl ether (EEGE) was synthesized from 2,3-epoxypropan-1-ol (glycidol) and ethyl vinyl ether according to *Fitton* et al.[1], purified by distillation, and stored under a nitrogen atmosphere over molecular sieve (3 A).

1-Iodo-3,6,9-trioxadecane was synthesized from the corresponding tosylate by reaction with sodium iodide.[2] The tosylate was prepared according to literature from tri(ethylene glycol) monomethyl ether and tosyl chloride.[3]

Water-sensitive reactions were carried out in a nitrogen atmosphere. Nitrogen (Linde 5.0) was passed over molecular sieve (4 Å) and finely distributed potassium on aluminum oxide.

**Measurements.** $^{1}$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DPX-400 FT-NMR spectrometer at 400 and 101 MHz, respectively. Chloroform ($CDCl_3$) and deuterated dimethyl

sulfoxide (DMSO-$d_6$) were used as solvents. The residual solvent signal was used as internal standard. Coupling constants $\boldsymbol{J_{xy}}$ are given in Hz.

FTIR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR spectrometer at 25 °C. The samples were prepared as KBr pellets and scanned over a range of 400-4000 $cm^{-1}$.

DSC measurements were performed on a Netzsch DSC 204 differential scanning calorimeter under a nitrogen atmosphere. Samples were prepared in perforated closed aluminum pans using 5 mg of the sample. The sample was heated and cooled with a rate of 10 °C · $min^{-1}$ in various temperature ranges. The heat flow was measured as a function of the temperature. Transitions were reported during the second heating cycle.

Molecular weights ($M_{n,SEC}$) and molecular weight distributions ($Đ$) were determined by size exclusion chromatography (SEC). SEC with DMF (HPLC grade, VWR) as eluent was performed using an Agilent 1100 system equipped with a dual RI-/Visco detector (ETA-2020, WGE). The eluent contained 1 g · $L^{-1}$ LiBr (≥99%, Aldrich). The sample solvent contained traces of distilled water as internal standard. One pre-column (8x50 mm) and four GRAM gel columns (8x300 mm, Polymer Standards Service) were applied at a flow rate of 1.0 mL · $min^{-1}$ at 40 °C. The diameter of the gel particles measured 10 µm, the nominal pore widths were 30, 100, 1000 and 3000 Å. Calibration was achieved using narrowly distributed poly(methyl methacrylate) standards (Polymer Standards Service). Results were evaluated using the PSS WinGPC UniChrom software (Version 8.1.1).

Dynamic light scattering was performed on an ALV system equipped with a helium-neon laser (633 nm, 35 mW, JDS Uniphase), a goniometer (CGS-8F, ALV), two avalanche photodiodes (SPCM-CD2969, Perkin Elmer), a light scattering electronics unit (LSE-5003, ALV), a digital hardware correlator (ALV 5000), an external programmable thermostate (Julabo F32) and an index-match bath filled with toluene. All measurements were recorded pseudo cross-correlated at room temperature.

Zeta potential measurements were performed on a Zetasizer Nano ZS (Malvern Instruments) at room temperature using folded capillary cells.

XPS measurements were performed using a K-Alpha+ XPS spectrometer (Thermo Fisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Avantage software is described elsewhere.[4]All samples were analyzed using a microfocused, monochromated Al Kα X-ray source (30-400 µm spot size). The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: +/- 0.2 eV). The analyzer transmission function,

Scofield sensitivity factors[5], and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism.[6] All spectra were referenced to the C 1s peak of hydrocarbon at 285.0 eV binding energy controlled by means of the well-known photoelectron peaks of metallic Cu, Ag, and Au.

Dialysis was performed in methanol and water using Biotech CE Tubing (MWCO: 100-500 D, 3.1 mL · $cm^{-1}$, Spectrumlabs) and Biotech RC Tubing (MWCO: 8-10 kD, 3.3 mL· $cm^{-1}$, Spectrumlabs), respectively. The membrane was washed for 15 min in water before use to remove the sodium azide solution.

Polymer films were prepared on Si-wafers by evaporation of water from the aqueous dispersions at 50 °C in vacuo.

**Syntheses.** Poly(ethoxyethyl glycidyl ether) (P(EEGE)) and polyglycidol (PG) (**1**) were synthesized according to literature.[7] The results of the chemical analyses for $PG_{27}$ are summarized in Figure S1-3.

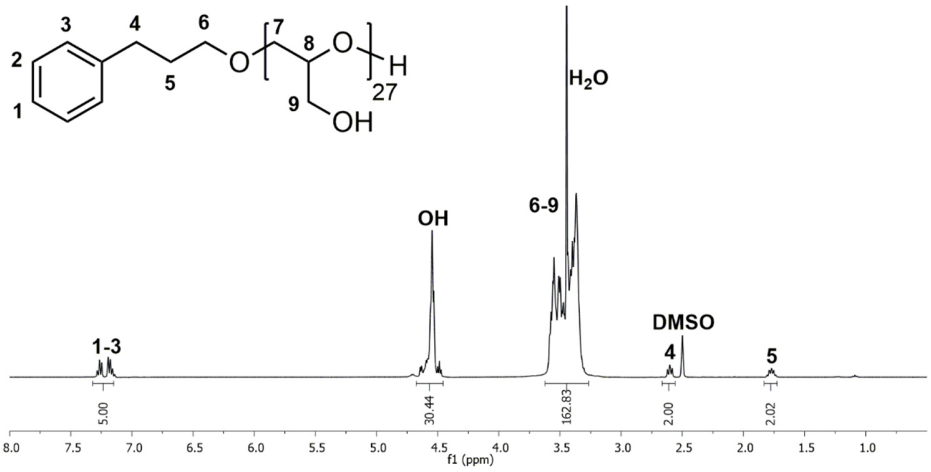


**Figure S1:** $^1$H NMR spectrum of $PG_{27}$ (**1**) measured in DMSO-$d_6$.

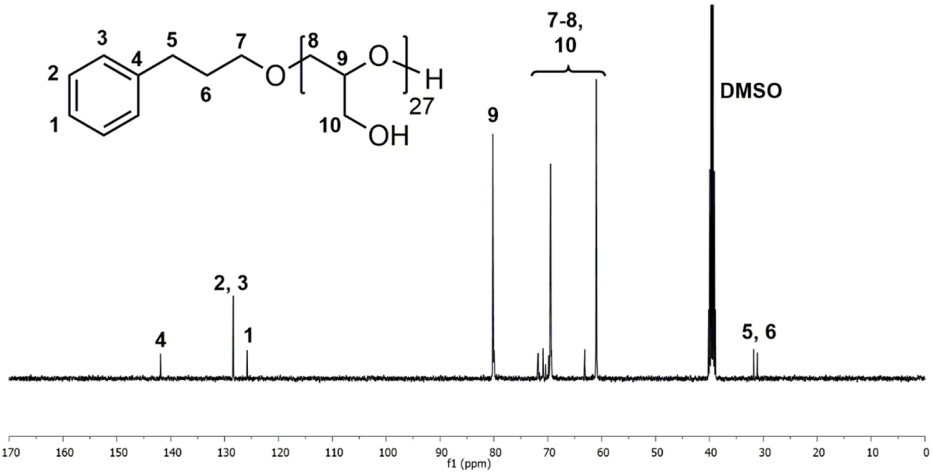


**Figure S2:** $^{13}$C NMR spectrum of $PG_{27}$ (**1**) measured in DMSO-$d_6$.

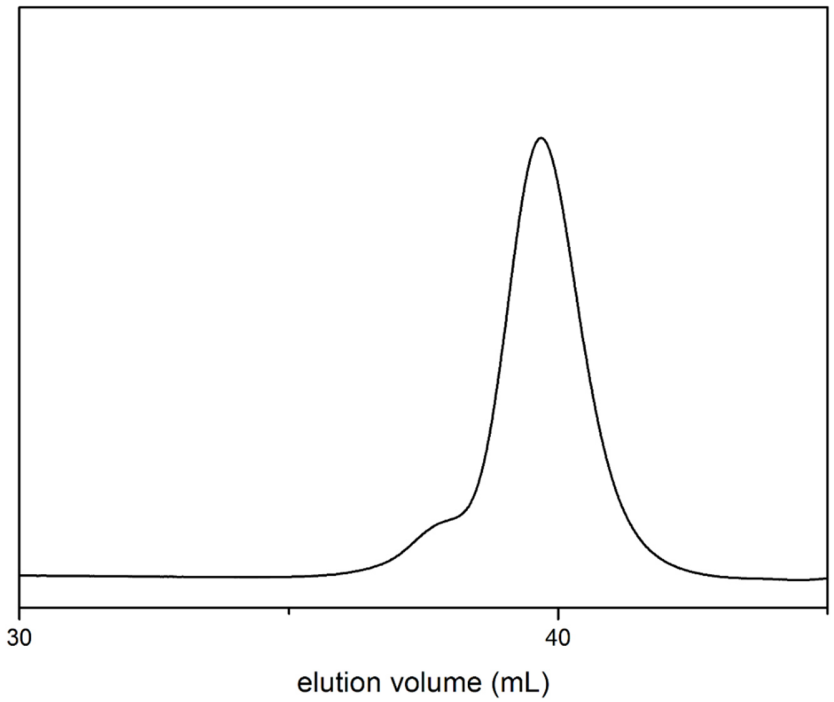


**Figure S3:** DMF-SEC traces of $PG_{27}$ (**1**).

**Poly(glycidyl phenyl carbonate), $P(G^{PC})_{27}$ (2).** Polyglycidol ($PG_{27}$) (**1**) (2.018 g, 27.24 mmol OH) was dissolved in pyridine (18.87 mL) and a solution of phenyl chloroformate (4.692 g, 29.97 mmol) in dichloromethane (17.50 mL) was added in 30 min at 0 °C using a syringe pump. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. The precipitate

was removed by filtration. The solution was washed with water (15 mL), 1 M HCl solution (aq.) (3 · 15 mL) and sat. NaCl solution (aq.). The organic phase was dried over $Na_2SO_4$, filtrated and the solvent removed under reduced pressure. Precipitation in methanol gave $P(G^{PC})_{27}$ (**2**) as a brown viscous liquid (3.629 g, 69%). $M_{n,\,NMR}$ = 5243 g · mol$^{-1}$, $M_{n,\,SEC}$ = 4400 g · mol$^{-1}$, $Đ$ = 1.15.

**$^1$H NMR (400 MHz, $CDCl_3$) (2):** δ = 1.82–1.92 (m, $ArCH_2\mathit{CH_2}$), 2.66 (t, 2H, $^3J_{HH}$ = 7.7 Hz $Ar\mathit{CH_2}CH_2$), 3.48–3.93 (m, $ArCH_2CH_2\mathit{CH_2}$, $O\mathit{CH_2CH}(CH_2OC{=}OOPh)O$), 4.15–4.48 (m, $OCH_2CH(\mathit{CH_2}OC{=}OOPh)O$), 7.05–7.39 (m, $\mathit{Ar}CH_2CH_2$, $(OC{=}OO\mathit{Ph})O$) ppm.

**$^{13}$C NMR (101 MHz, $CDCl_3$) (2):** δ = 31.2 ($ArCH_2\mathit{CH_2}$), 32.3 ($Ar\mathit{CH_2}CH_2$), 67.7–69.4 $ArCH_2CH_2\mathit{CH_2}$, $O\mathit{CH_2CH}(CH_2OC{=}OOPh)O$), 77.4 ($OCH_2CH(\mathit{CH_2}OC{=}OOPh)O$), 121.0 $(OC{=}OO\mathit{Ph})O$), 126.1 (*Ar*, $OC{=}OO\mathit{Ph})O$), 128.4 (*Ar*), 128.5 (*Ar*), 129.6 $(OC{=}OO\mathit{Ph})O$), 141.8 (*Ar*), 151.1 $(OC{=}OO\mathit{Ph})O$), 153.6 $(O\mathit{C}{=}OOPh)O$) ppm.

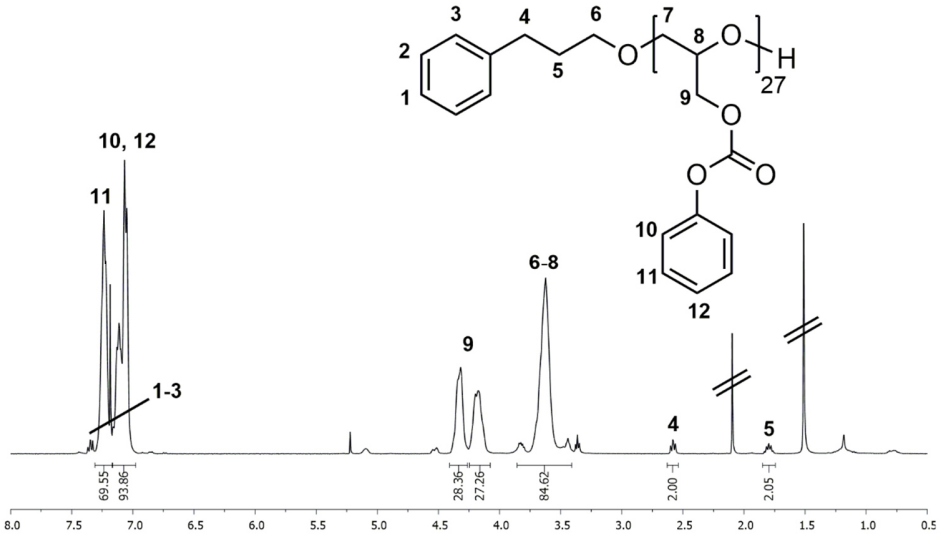


**Figure S4:** $^1$H NMR spectrum of $P(G^{PC})_{27}$ (**2**) measured in $CDCl_3$.

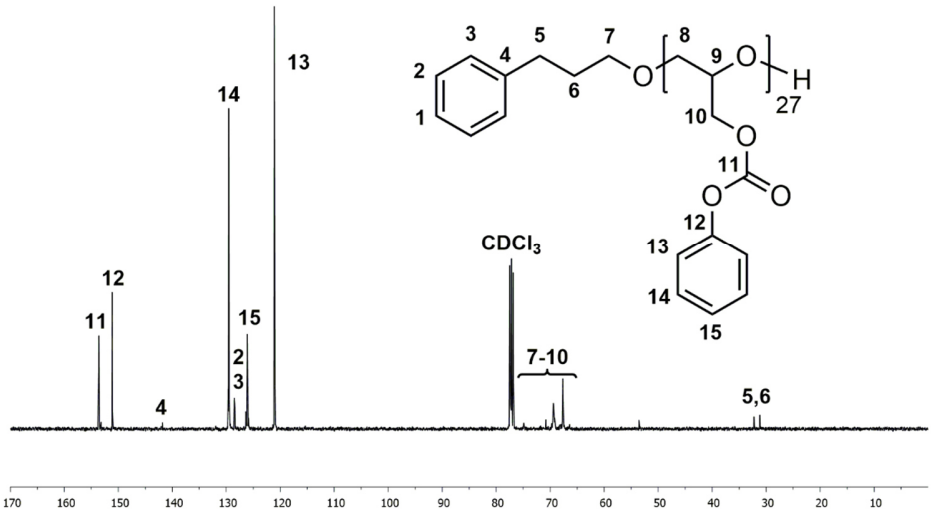


**Figure S5:** $^{13}C$ NMR spectrum of $P(G^{PC})_{27}$ (**2**) measured in $CDCl_3$.

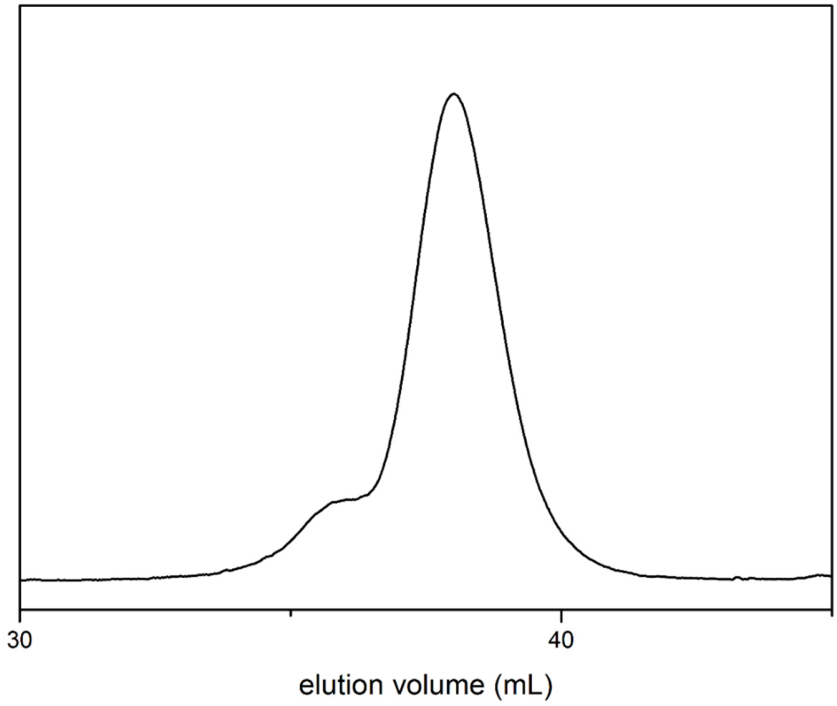


**Figure S6:** DMF-SEC traces of $P(G^{PC})_{27}$ (**2**).

**Poly(3-(dimethylamino)-1-propyl glycidyl carbamate), $P(G^{DMAPA})_{27}$ (3).** $P(G^{PC})_{27}$ (**2**) (1.422 g, 7.32 mmol carbonate) was dissolved in tetrahydrofuran (18.0 mL) and a solution of 3-(dimethylamino)-1-propylamine (DMAPA) (0.436 g, 4.27 mmol) in tetrahydrofuran (10.0 mL) was added in 1 h at 0 °C using a syringe pump. The reaction was allowed to warm to room

temperature and stirred for 42 h. The solvent was removed under reduced pressure and the polymer purified by dialysis in methanol. $P(G^{DMAPA})_{27}$ (**3**) was obtained as a slightly yellow, viscous liquid (1.194, 81%) $M_{n,\,NMR}$ = 5461 g · mol$^{-1}$, $M_{n,\,SEC}$ = 6200 g · mol$^{-1}$, $Đ$ = 1.21.

**$^{1}$H NMR (400 MHz, $CDCl_3$) (3):** δ = 1.51–1.67 (m, $NHCH_2\mathit{CH_2}CH_2N(CH_3)_2$), 1.77–1.86 (m, $ArCH_2\mathit{CH_2}$), 2.14 (s, $NHCH_2CH_2CH_2N(\mathit{CH_3})_2$), 2.25 (t, 2H, $^{3}J_{HH}$ = 7.0 Hz, $NHCH_2CH_2\mathit{CH_2}N(CH_3)_2$), 2.60 (t, $^{3}J_{HH}$ = 7.6 Hz, $Ar\mathit{CH_2}CH_2$), 3.04–3.19 (m, $NH\mathit{CH_2}CH_2CH_2N(CH_3)_2$), 3.46–3.70 (m, $ArCH_2CH_2\mathit{CH_2}$, $O\mathit{CH_2CH}(CH_2OC{=}ONHR)O$), 3.88–4.27 (m, $OCH_2CH(\mathit{CH_2}OC{=}ONHR)O$), 5.83–6.34 (m, NH), 7.06–7.24 (m, $\mathit{Ar}CH_2CH_2$) ppm.

**$^{13}$C NMR (101 MHz, $CDCl_3$) (3):** δ = 27.5 ($NHCH_2\mathit{CH_2}CH_2N(CH_3)_2$, 31.2 ($ArCH_2\mathit{CH_2}$), 32.2 ($Ar\mathit{CH_2}CH_2$), 39.7 ($NH\mathit{CH_2}CH_2CH_2N(CH_3)_2$), 45.4 ($NHCH_2CH_2CH_2N(\mathit{CH_3})_2$), 57.5 ($NHCH_2CH_2\mathit{CH_2}N(CH_3)_2$), 64.3–69.9 ($ArCH_2CH_2\mathit{CH_2}$, $O\mathit{CH_2CH}(CH_2OC{=}ONHR)O$), 77.9 ($OCH_2CH(\mathit{CH_2}OC{=}ONHR)O$), 125.8 (*Ar*), 128.3 (*Ar*), 128.5 (*Ar*), 141.9 (*Ar*), 156.7 ($OCH_2CH(CH_2O\mathit{C}{=}ONHR)O$) ppm.

**FTIR (3):** $\upsilon_{max}$ = 3322 (w), 2923 (m), 2853 (m), 2816 (w), 2765 (w), 1690 (s), 1537 (m), 1461 (m), 1255 (s), 1138 (m), 1039 (m), 849 (w), 780 (w) cm$^{-1}$.

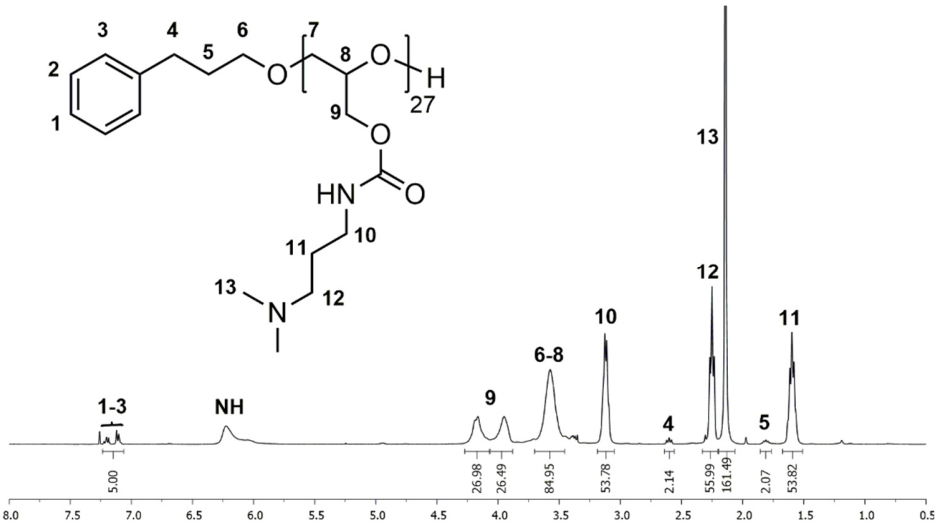


**Figure S7:** $^{1}$H NMR spectrum of $P(G^{DMAPA})_{27}$ (**3**) measured in $CDCl_3$.

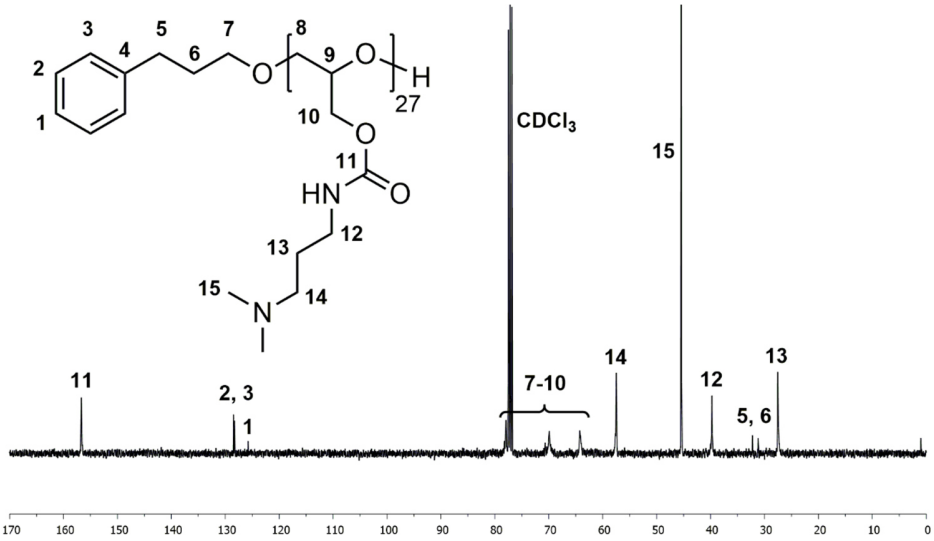


**Figure S8:** $^{13}C$ NMR spectrum of $P(G^{DMAPA})_{27}$ (**3**) measured in $CDCl_3$.

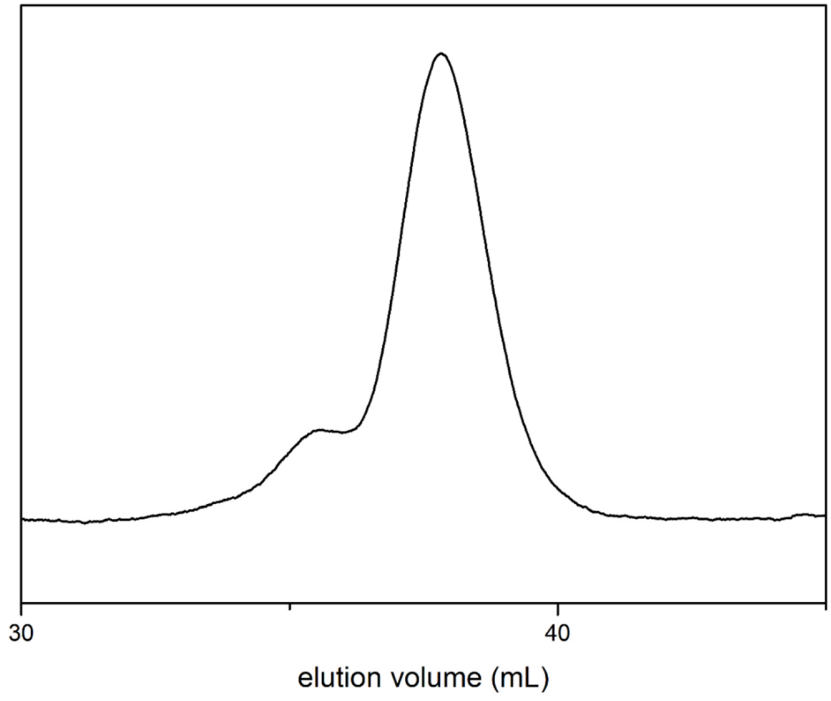


**Figure S9:** DMF-SEC traces of $P(G^{DMAPA})_{27}$ (**3**).

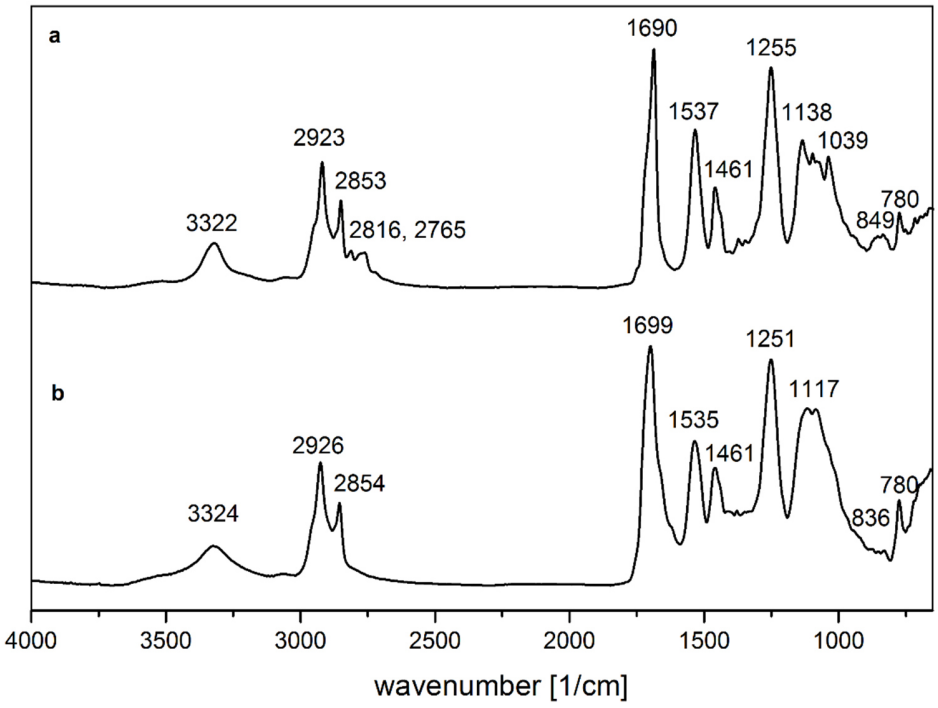


**Figure S10:** FTIR spectra of $P(G^{DMAPA})_{27}$ (**3**) (**a**) and $[P(G^{DMAPA})_{27}]_X$ (**4**) (**b**).

**Light-promoted cross-linking of $P(G^{DMAPA})_{27}$ (3).** $P(G^{DMAPA})_{27}$ (**3**) (0.336 g, 1.66 mmol $-NMe_2$) was dissolved in *N*,*N*-dimethylformamide (12 mL) and camphorquinone (0.276 g, 1.66 mmol) was added. The mixture was irradiated for 20 h with a 25 W solarium lamp emitting light at 400–500 nm at room temperature. The polymer was purified by dialysis in methanol followed by dialysis in water. The cross-linked product $[P(G^{DMAPA})_{27}]_X$ (**4**) was obtained as an opaque, aqueous dispersion.

**FTIR (4) :** $\upsilon_{max}$ = 3324 (w), 2926 (m), 2854 (m), 1699 (s), 1535 (m), 1461 (m), 1251 (s), 1117 (m), 1076 (m), 836 (w), 780 (w) $cm^{-1}$

**Determination of camphorquinone concentration by UV/VIS spectroscopy**

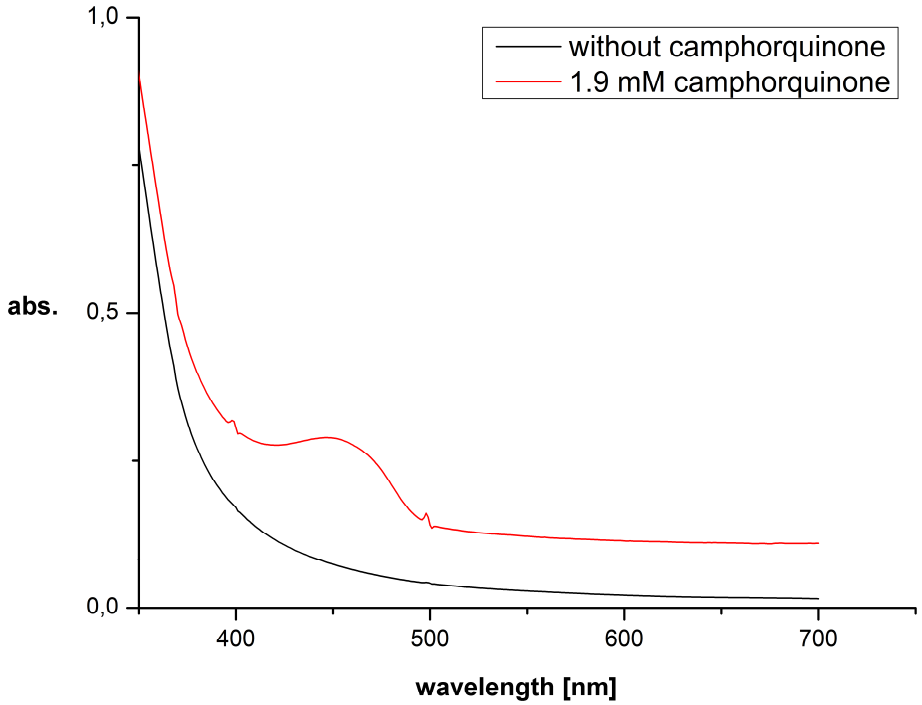


**Figure S11:** UV/Vis spectra of $[P(G^{DMAPA})_{27}]_X$ (**4**) (black) after dialysis in methanol and after addition of 1% of the amount of camphorquinone used during the reaction (red).

**Quaternization of $[P(G^{DMAPA})_{27}]_X$ (4) with MeI.** Methyl iodide (0.026 g, 0.178 mmol) was added to an aqueous dispersion of **5** (4.5 mg · $mL^{-1}$, 22 µmol · $mL^{-1}$ -$NR_3$) and the mixture was stirred for 24 h at 40 °C. The product was purified by dialysis in water. $[P(G^{TMAPA})_{27}]_X$ (**5**) (TMAPA: 3-(trimethylamino)-1-propylamine) was obtained as an opaque, aqueous dispersion.

**Quaternization of $[P(G^{DMAPA})_{27}]_X$ (4) with 1-iodooctane.** Without the purification step a solution of $[P(G^{DMAPA})_{27}]_X$ (**4**) in DMF (28 mg · $mL^{-1}$, 138 µmol · $mL^{-1}$ -$NR_3$) was reacted with 1-iodooctane (0.199 g, 0.830 mmol) for 20 h at 100 °C. The polymer was purified by dialysis in methanol followed by dialysis in water. $[P(G^{ODMAPA})_{27}]_X$ (**6**) (ODMAPA: 3-(octyldimethylamino)-1-propylamine) was obtained as an opaque, aqueous dispersion.

**Quaternization of $[P(G^{DMAPA})_{27}]_X$ (4) with 1-iodo-3,6,9-trioxadecane.** Without the purification step a solution of $[P(G^{DMAPA})_{27}]_X$ (**4**) in DMF (28 mg · $mL^{-1}$, 138 µmol · $mL^{-1}$ -$NR_3$) was reacted

with 1-iodo-3,6,9-trioxadecane (0.228 g, 0.830 mmol) for 20 h at 100 °C. The polymer was purified by dialysis in methanol followed by dialysis in water. $[P(G^{PDMAPA})_{27}]_X$ (**7**) (PDMAPA: 3-(PEG-dimethylamino)-1-propylamine) was obtained as an opaque, aqueous dispersion.

**Quaternization of $[P(G^{DMAPA})_{27}]_X$ (4) with 1H, 1H, 2H, 2H-heptadecafluorodecyl iodide.** Without the purification step a solution of $[P(G^{DMAPA})_{27}]_X$ (**4**) in DMF (28 mg · $mL^{-1}$, 138 µmol · $mL^{-1}$ $-NR_3$) was reacted with 1H, 1H, 2H, 2H-heptadecafluorodecyl iodide (0.476 g, 0.830 mmol) for 20 h at 100 °C. The polymer was purified by dialysis in methanol followed by dialysis in water. $[P(G^{FDMAPA})_{27}]_X$ (**8**) (FDMAPA: fluorinated 3-(dimethylamino)-1-propylamine) was obtained as an opaque, aqueous dispersion.

## DSC measurements

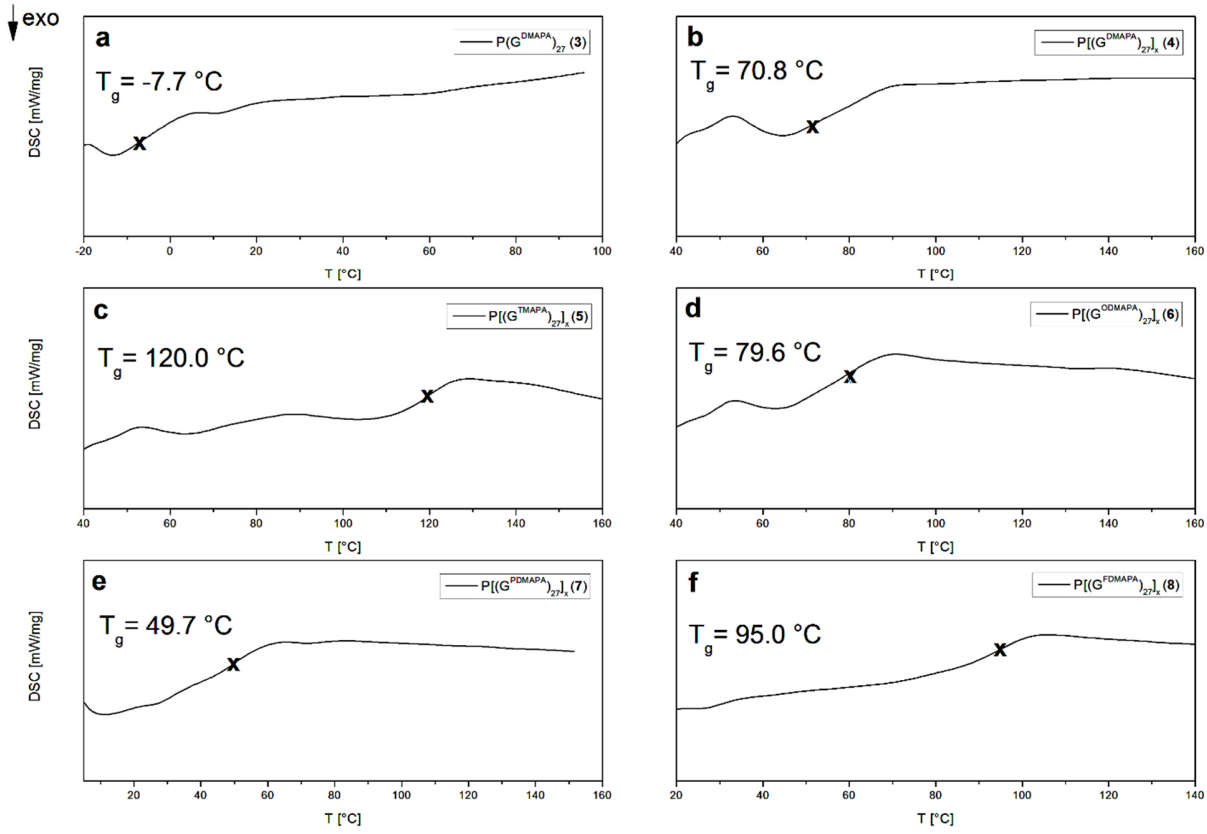


**Figure S12:** DSC curves of the second heating cycle of $P(G^{DMAPA})_{27}$ (**3**) (a), $P[(G^{DMAPA})_{27}]_X$ (**4**) (b), $P[(G^{TMAPA})_{27}]_X$ (**5**) (c), $P[(G^{ODMAPA})_{27}]_X$ (**6**) (d), $P[(G^{PDMAPA})_{27}]_X$ (**7**) (e) and $P[(G^{FDMAPA})_{27}]_X$ (**8**) (f).

## XPS measurements

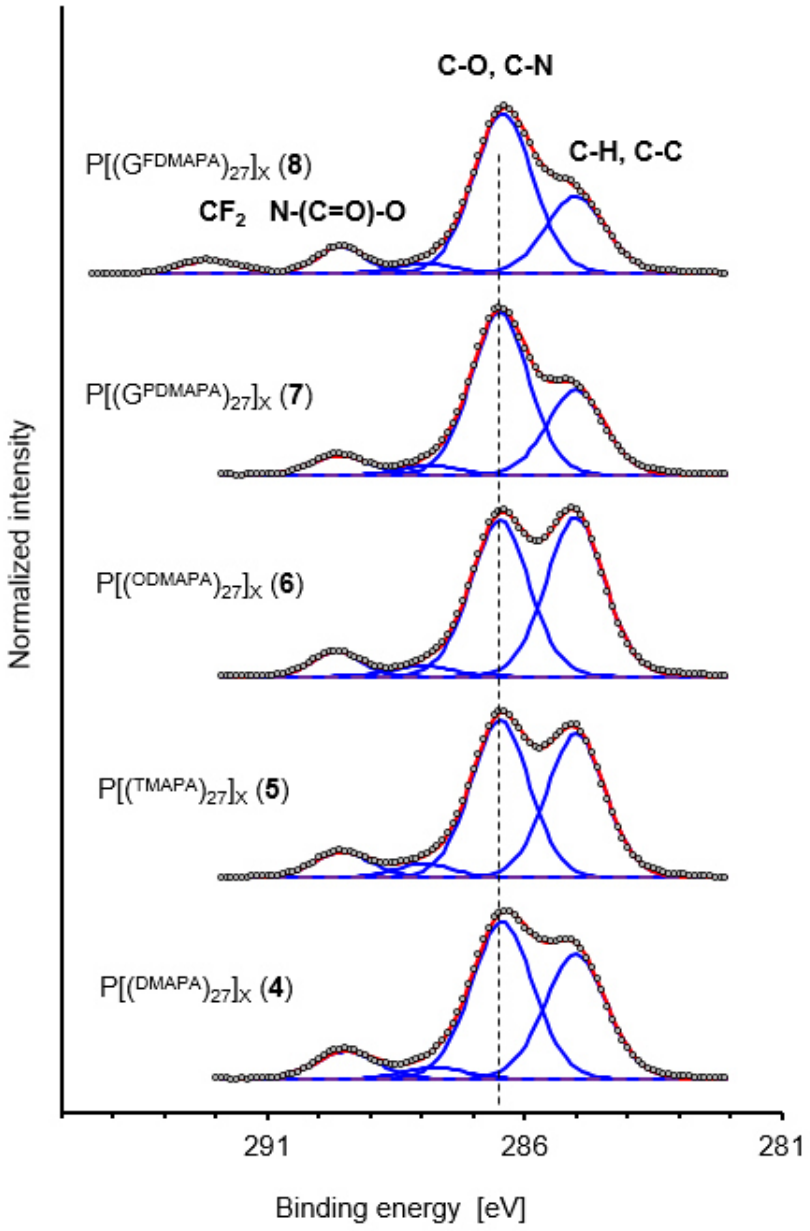


**Figure S13:** High-resolution XPS spectra of the C 1s region of P[($G^{DMAPA}$)$_{27}$]$_X$ (**4**), P[($G^{TMAPA}$)$_{27}$]$_X$ (**5**), P[($G^{ODMAPA}$)$_{27}$]$_X$ (**6**), P[($G^{PDMAPA}$)$_{27}$]$_X$ (**7**) and P[($G^{FDMAPA}$)$_{27}$]$_X$ (**8**).

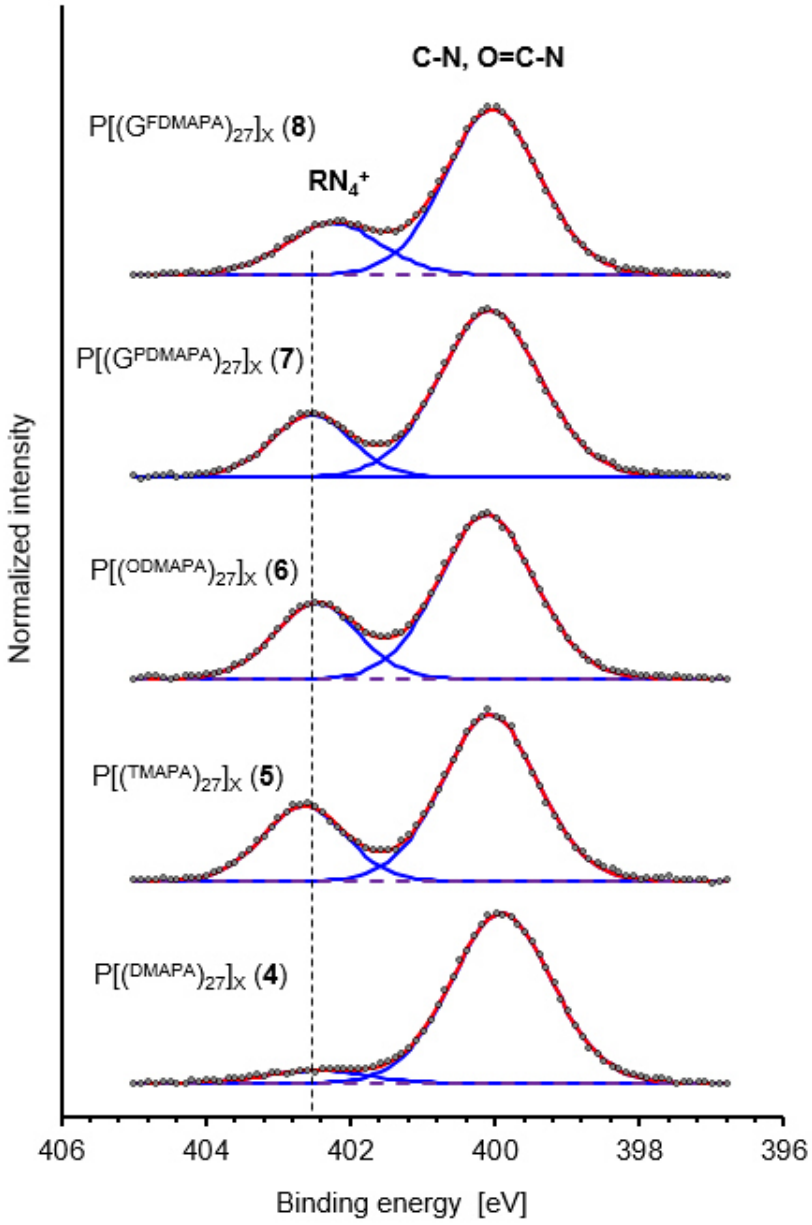


**Figure S14:** High-resolution XPS spectra of the N 1s region of $P[(G^{DMAPA})_{27}]_X$ (**4**), $P[(G^{TMAPA})_{27}]_X$ (**5**), $P[(G^{ODMAPA})_{27}]_X$ (**6**), $P[(G^{PDMAPA})_{27}]_X$ (**7**) and $P[(G^{FDMAPA})_{27}]_X$ (**8**).

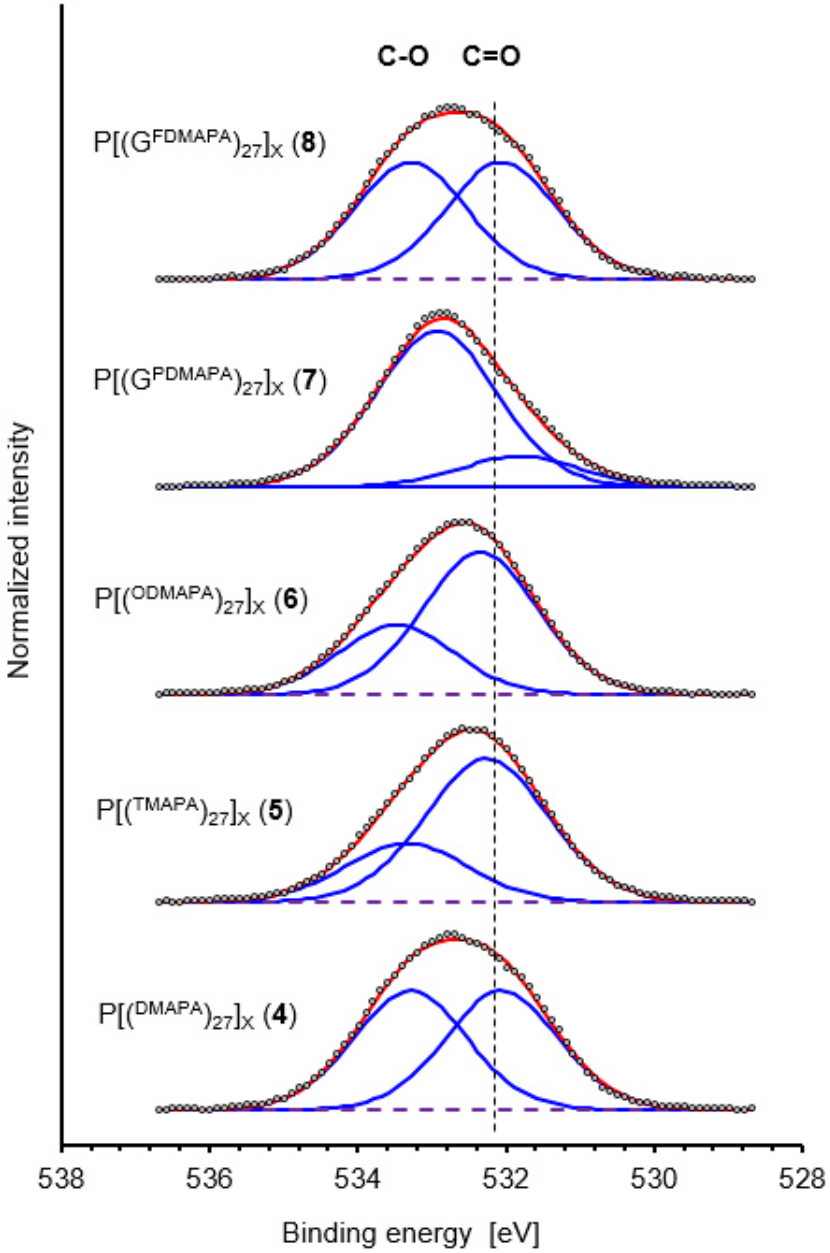


**Figure S15:** High-resolution XPS spectra of the O 1s region of $P[(G^{DMAPA})_{27}]_X$ (**4**), $P[(G^{TMAPA})_{27}]_X$ (**5**), $P[(G^{ODMAPA})_{27}]_X$ (**6**), $P[(G^{PDMAPA})_{27}]_X$ (**7**) and $P[(G^{FDMAPA})_{27}]_X$ (**8**).

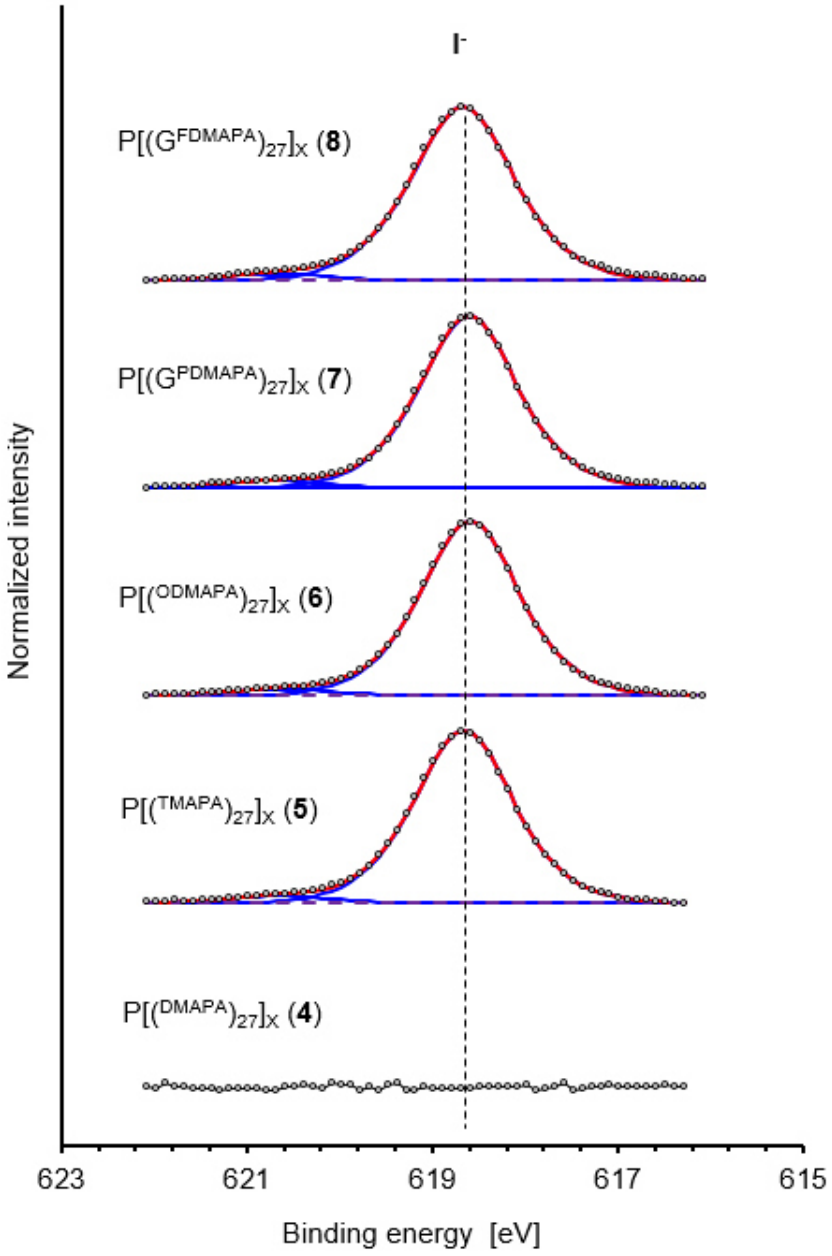


**Figure S16:** High-resolution XPS spectra of the I $3d_{5/2}$ region of $P[(G^{DMAPA})_{27}]_X$ (**4**), $P[(G^{TMAPA})_{27}]_X$ (**5**), $P[(G^{ODMAPA})_{27}]_X$ (**6**), $P[(G^{PDMAPA})_{27}]_X$ (**7**) and $P[(G^{FDMAPA})_{27}]_X$ (**8**).

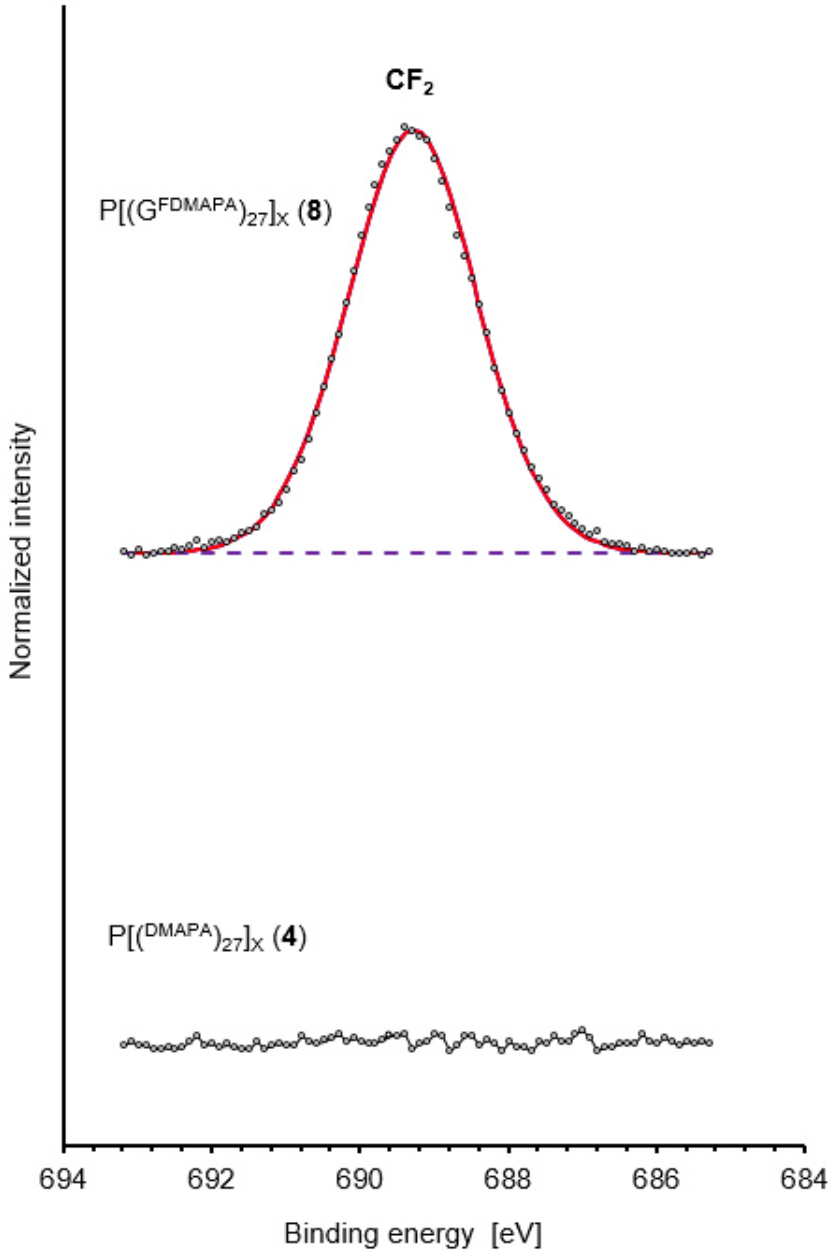


**Figure S17:** High-resolution XPS spectra of the F 1s region of P[($G^{DMAPA}$)$_{27}$]$_X$ (**4**) and P[($G^{FDMAPA}$)$_{27}$]$_X$ (**8**).

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