

Supporting Information

Emissive Semi-Interpenetrating Polymer Networks for Ink-Jet Printed Multilayer OLEDs

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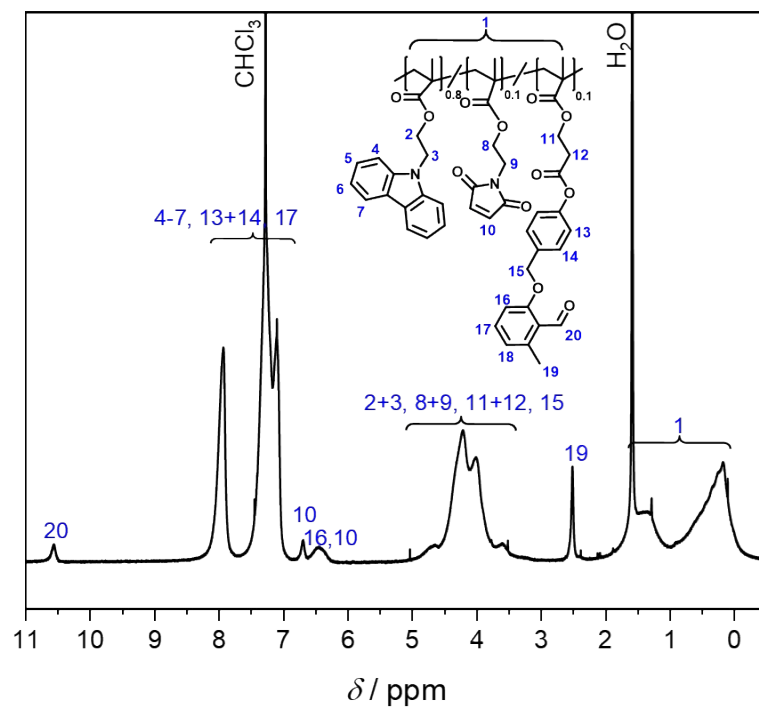


Figure S1: $^1\text{H-NMR}$ spectrum of **PC1** in CDCl_3 (600 MHz).

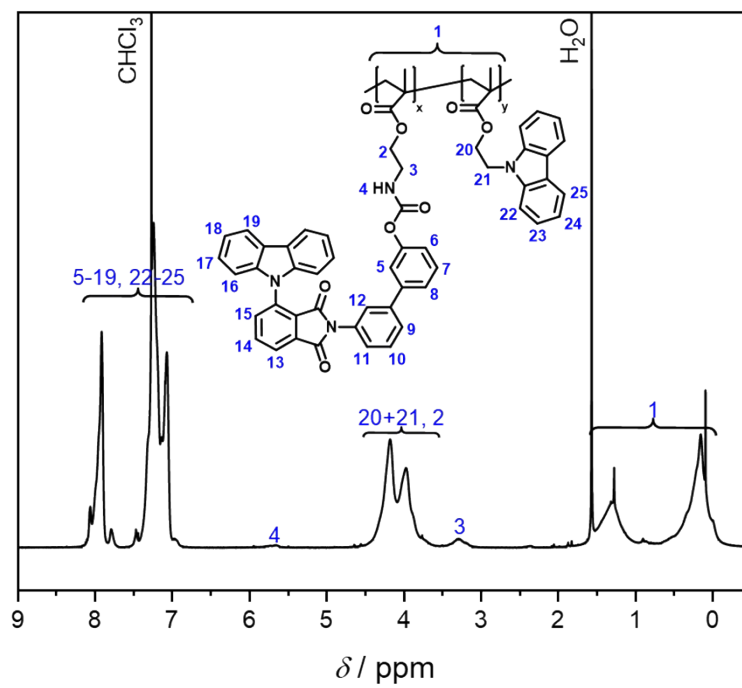


Figure S2: $^1\text{H-NMR}$ spectrum of **PE5** in CDCl_3 (600 MHz).

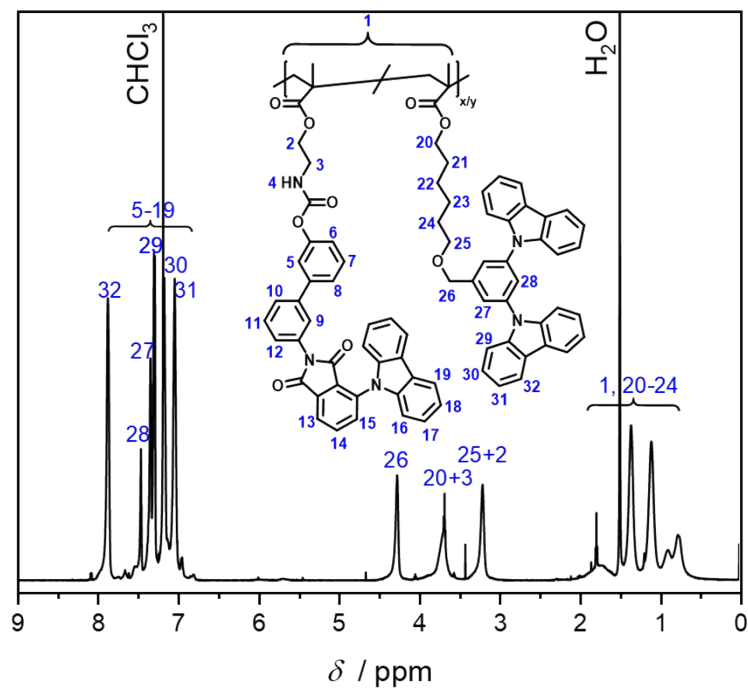


Figure S3: $^1\text{H-NMR}$ spectrum of **PE7** in CDCl_3 (600 MHz).

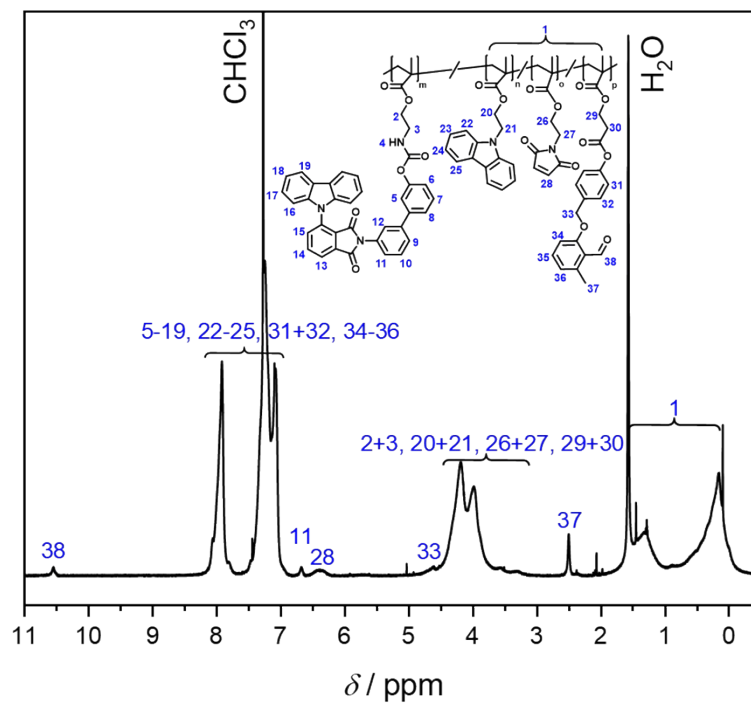


Figure S4: $^1\text{H-NMR}$ spectrum of **PCE8** in CDCl_3 (600 MHz).

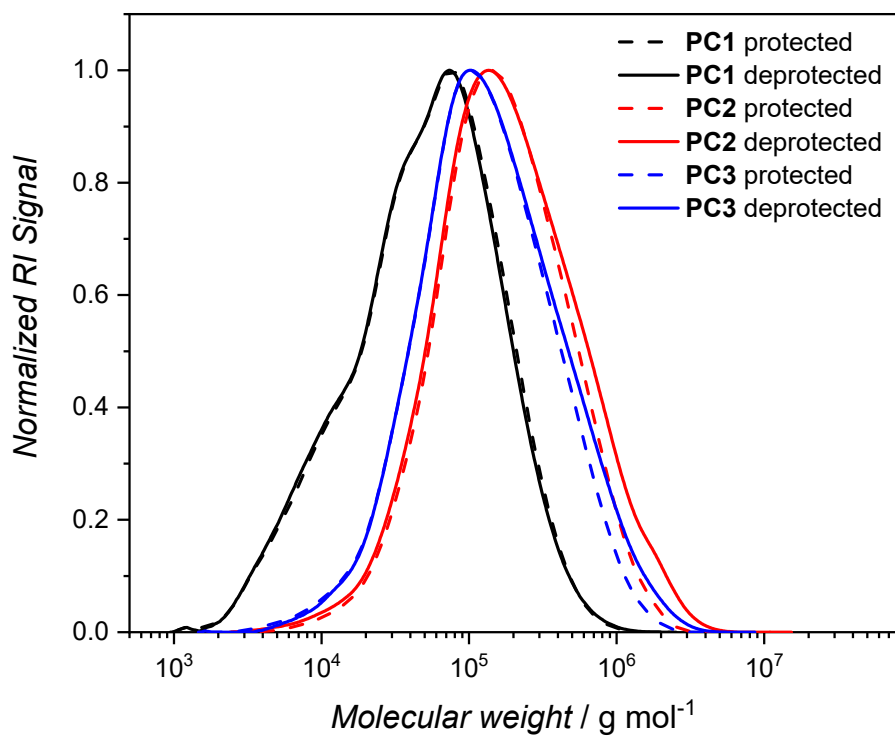


Figure S5: Size exclusion chromatograms of **PC1-3** before (dashed) and after (straight) maleimide deprotection (THF, PMMA calibration).

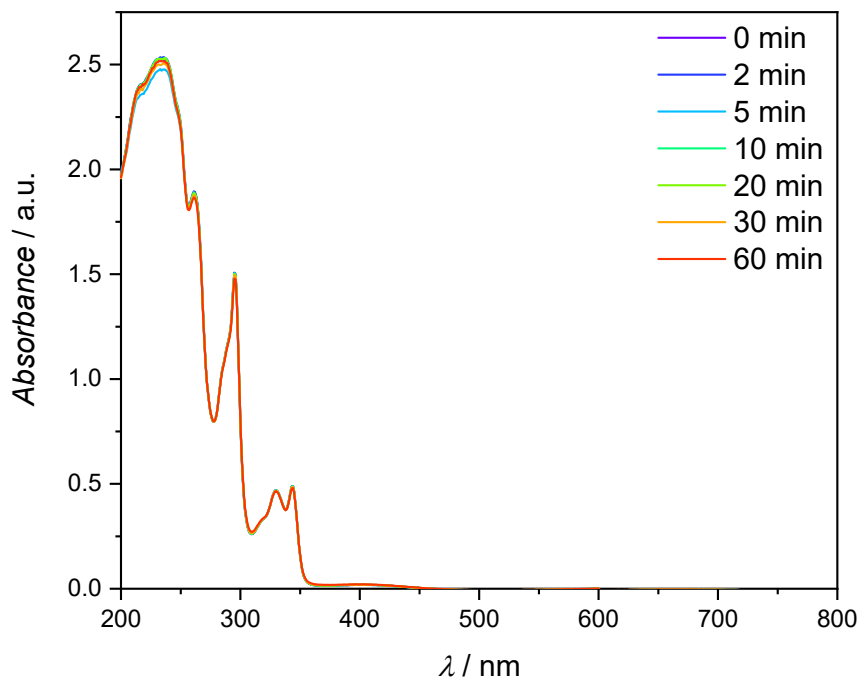


Figure S6: UV-Vis absorbance of PE6 upon irradiation at 365 nm.

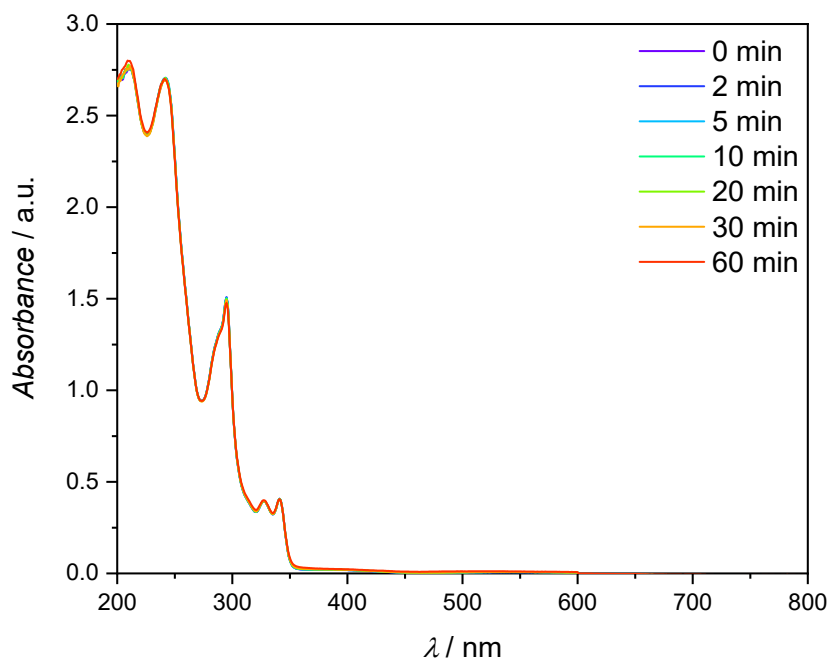


Figure S7: UV-Vis absorbance of PE7 upon irradiation at 365 nm.

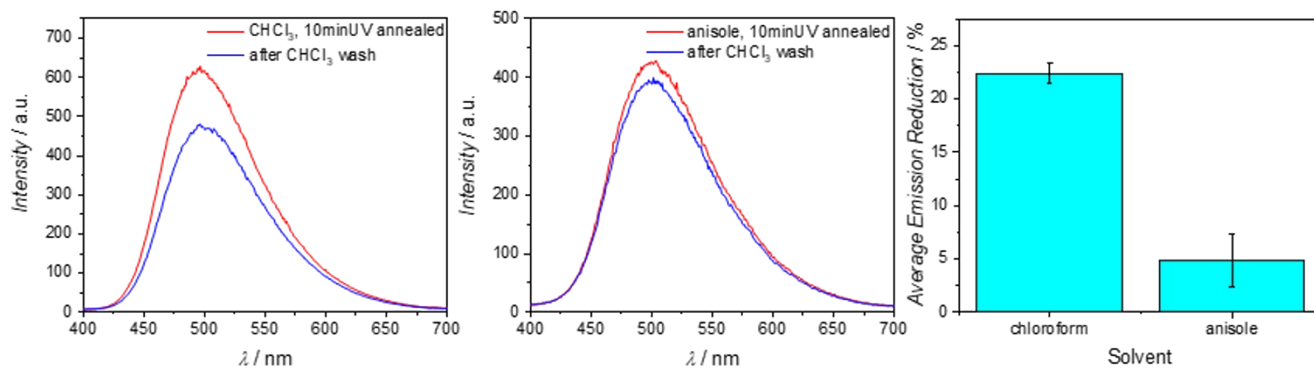


Figure S8: Photoluminescence of cross-linked blends of 1:1 **PC2:PE6** spin coated from a CHCl₃ (left) or anisole (middle) solution before and after the solvent wash. Right: Average reduction of the photoluminescence after the solvent wash.

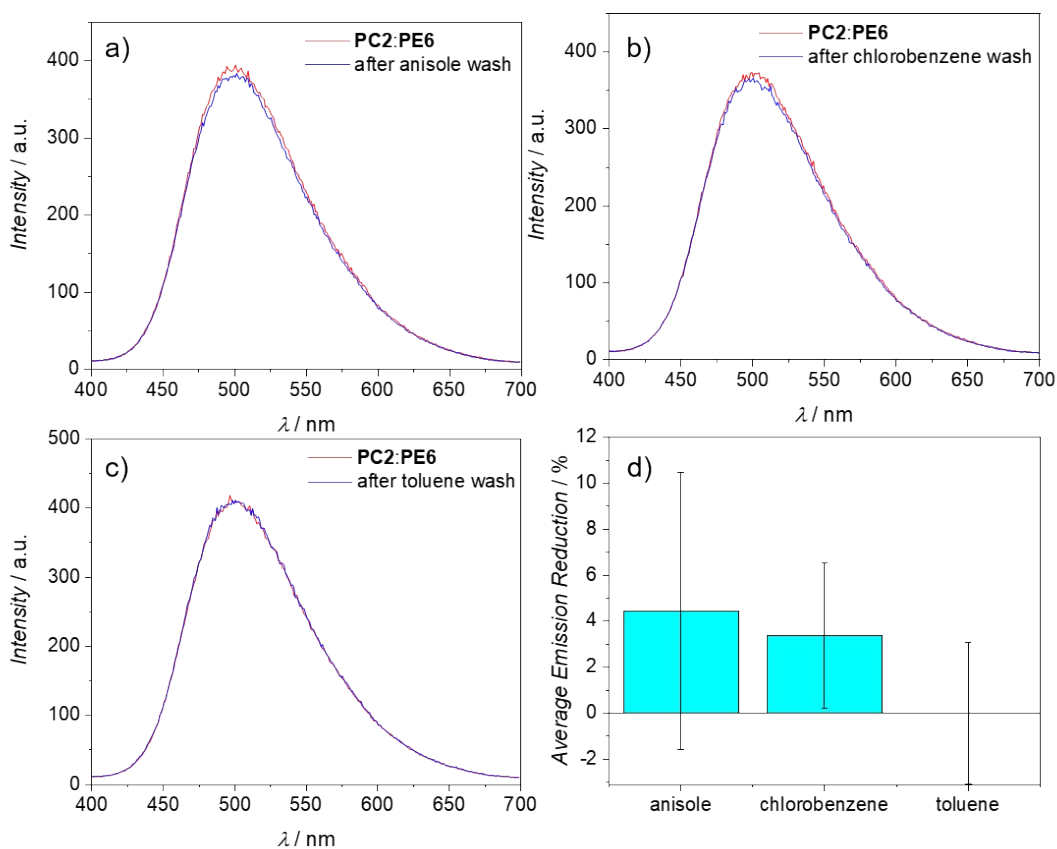


Figure S9: Photoluminescence of cross-linked blends of 1:1 **PC2:PE6** washed with anisole (a), chlorobenzene (b) and toluene (c). d) Average reduction of the photoluminescence intensity after the solvent wash.

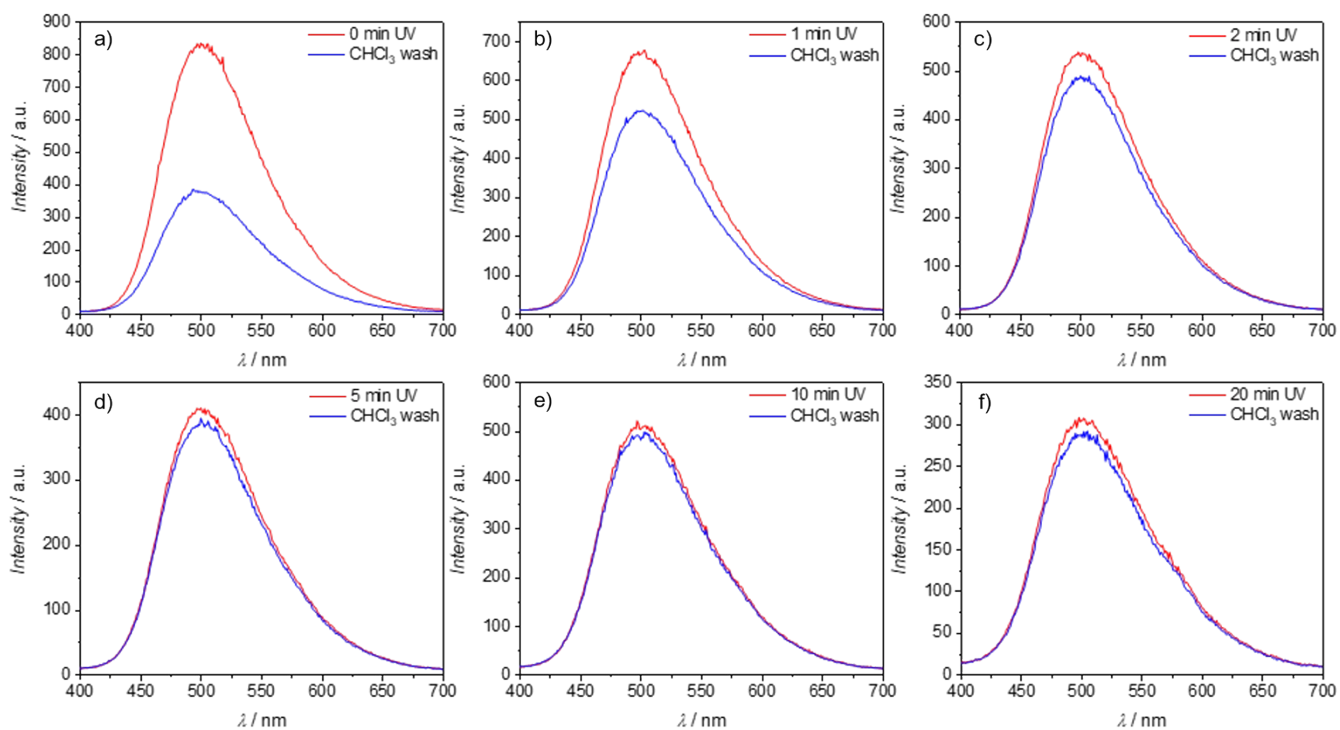


Figure S10: Photoluminescence of blends of 1:1 **PC2:PE6**, irradiated for a) 0 min, b) 1 min, c) 2 min, d) 5 min, e) 10 min, f) 20 min at 365nm (red) and after a chloroform wash (blue).

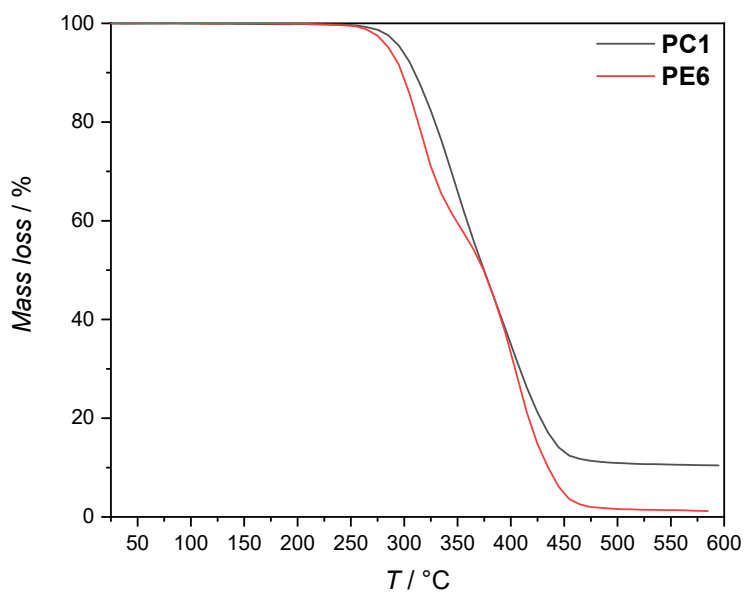


Figure S11: Thermogravimetric analysis of **PC1** and **PE6** under nitrogen atmosphere (heating rate 10 K/min).

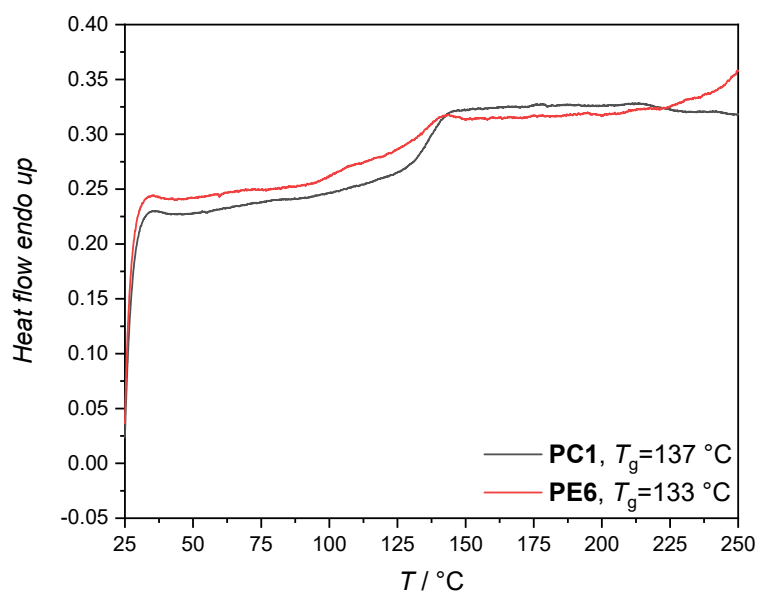


Figure S12: Differential Scanning Calorimetry of **PC1** and **PE6** under nitrogen atmosphere (heating rate 10 K/min).

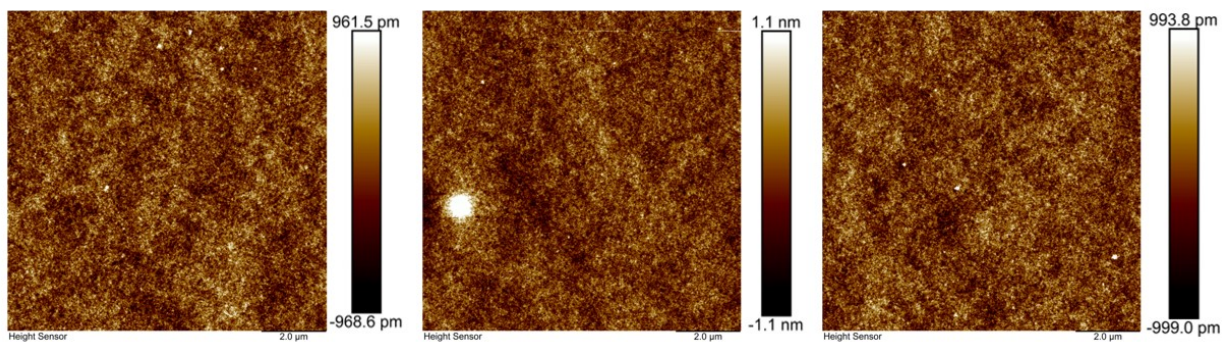


Figure S13: AFM height image of **PC1:PE6** blend (1:1) before irradiation (10 x 10 μm , Scan rate 1 Hz).

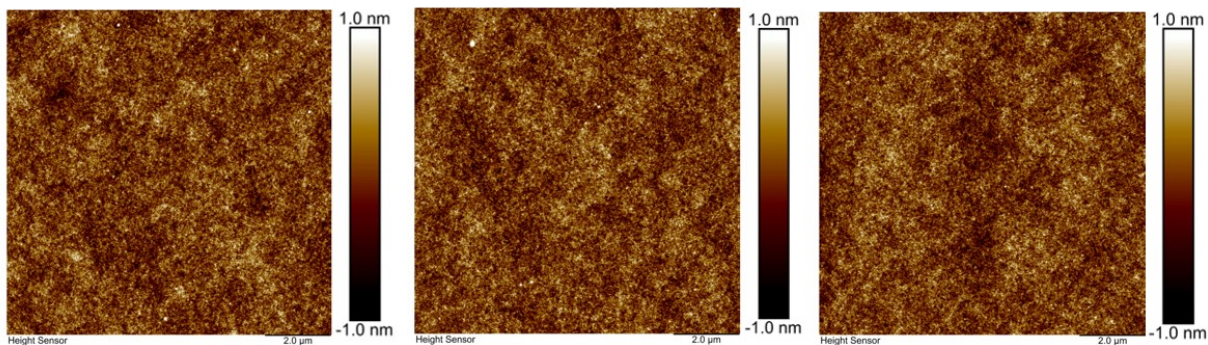


Figure S14: AFM height image of **PC1:PE6** blend (1:1) after 10 minutes irradiation at 365 nm (10 x 10 μm , Scan rate 1 Hz).

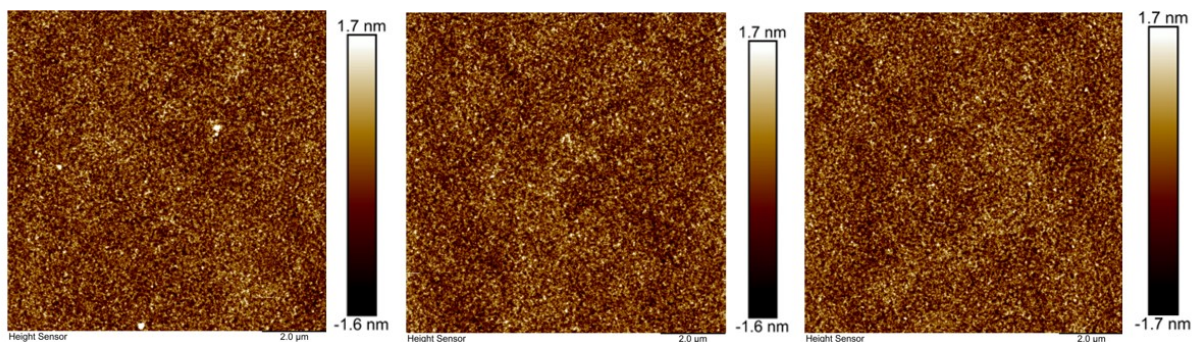


Figure S15: AFM height image of irradiated **PC1:PE6** blend (1:1) after chloroform wash (10 x 10 μm , Scan rate 1 Hz).

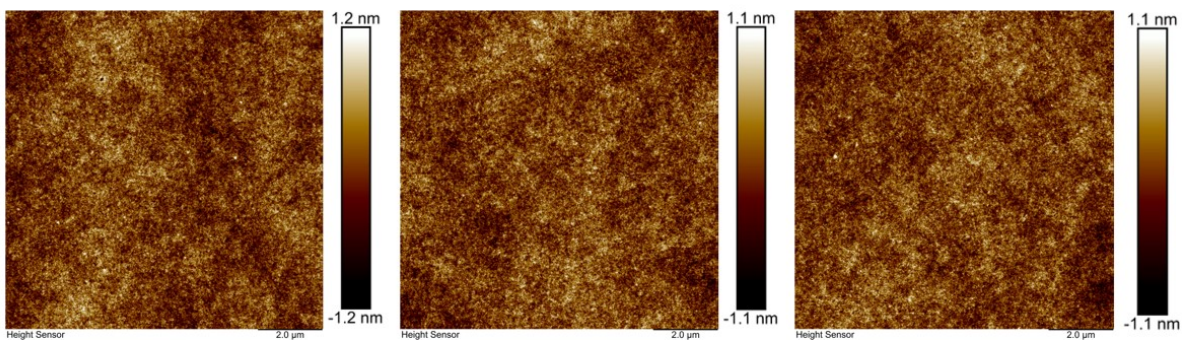


Figure S16: AFM height image of **PCE8** before irradiation (10 x 10 μm, Scan rate 1 Hz).

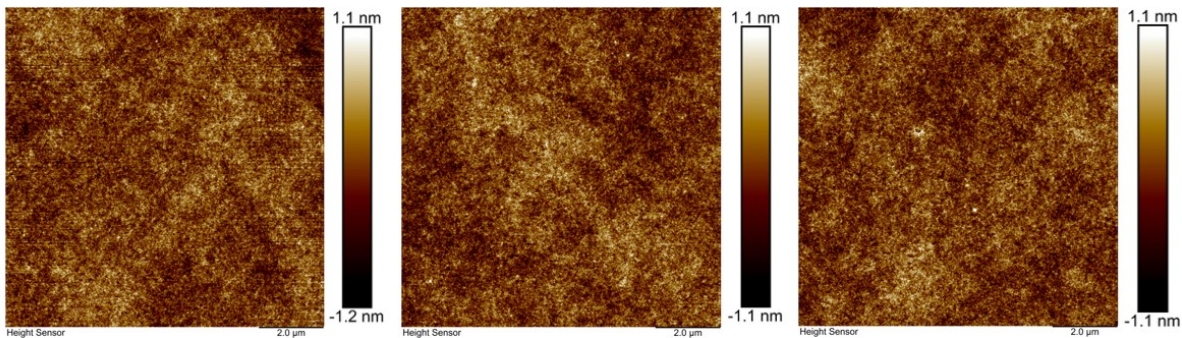


Figure S17: AFM height image of **PCE8** after 10 minutes irradiation at 365 nm (10 x 10 μm, Scan rate 1 Hz).

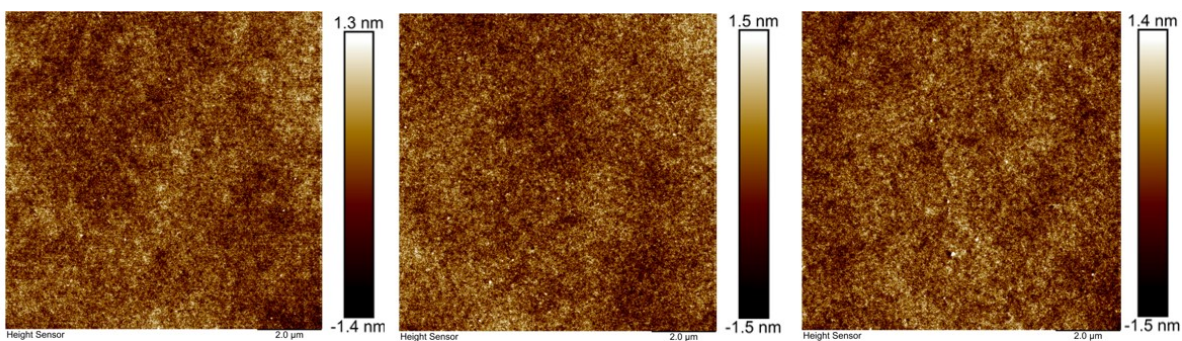


Figure S18: AFM height image of irradiated **PCE8** after chloroform wash (10 x 10 μm, Scan rate 1 Hz).

Table S1. Film thickness of the polymer blend **PC1:PE6** determined by Dektak stylus profilometry pre and post UV irradiation as well as after solvent treatment.

sample	film thickness / nm
before crosslinking	25.9 ± 2.4
after 10 min UV	25.7 ± 1.7
after CHCl ₃ wash	24.8 ± 4.3

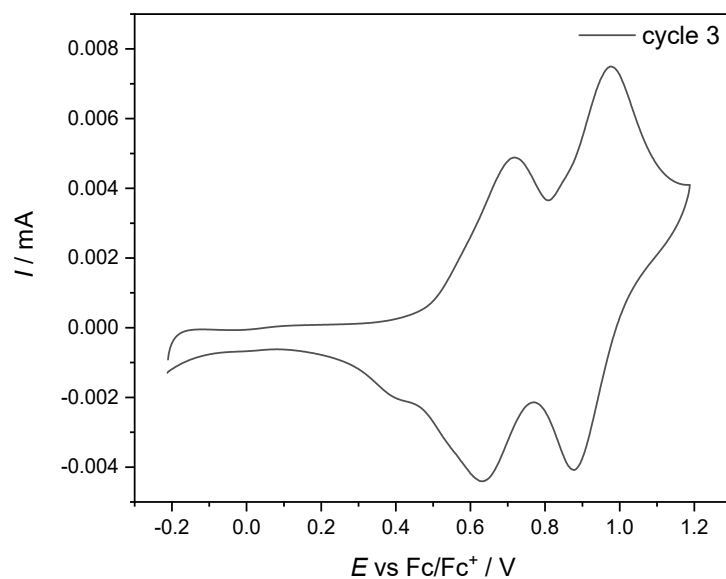


Figure S19: Cyclic voltammogram of a homopolymer of **M5** 1 mM in anhydrous DCM (0.1 M $n\text{Bu}_4\text{NPF}_6$ as electrolyte, Scan rate 100 mVs^{-1} , working electrode: platinum).

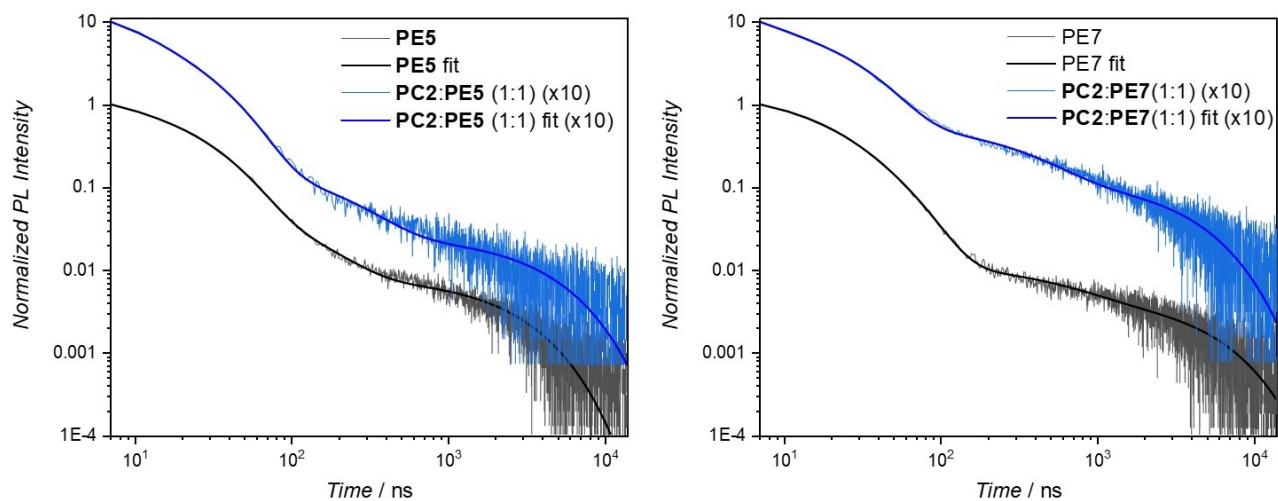


Figure S20: TRPL decay curves of **PE5** and cross-linked **PC2:PE5** (left) and **PE7** and cross-linked **PC2:PE7** (right) with the fits to the TRPL curves (red and green lines). **PC2:PE5** and **PC2:PE7** TRPL data is multiplied by for clarity.

Methods

¹H-NMR-Spectroscopy:

¹H-NMR spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (¹H: 600.13 MHz, ¹³C: 150.90 MHz). Resonances are reported in parts per million (ppm) relative to tetramethylsilane (TMS). The δ -scale was calibrated to the respective solvent signal of CHCl₃ for ¹H spectra and for ¹³C spectra on the middle signal of the CDCl₃ triplet.

Size Exclusion Chromatography (THF SEC):

The SEC measurements were conducted on a PSS SECurity2 system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8 x 150 mm x 5 μ m Pre-column, 8 x 300 mm 5 μ m Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL min⁻¹. Narrow disperse linear poly(methyl methacrylate) (M_n : 202 g mol⁻¹ to 2.2·10⁶ g mol⁻¹) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 μ m PTFE membrane filters. Molecular weight and dispersity analysis were performed in PSS WinGPC UniChrom software (version 8.2).

Flash Chromatography:

Flash chromatography was performed on an Interchim XS420+ flash chromatography system consisting of a SP-in-line filter 20 μ m and a UV-Vis detector (200-800 nm) connected via a flow splitter (Interchim Split ELSD F04590). The separations were performed using an Interchim dry load column (dryload on celite 565) and an Interchim Puriflash Silica HP 30 μ m column.

Differential Scanning Calorimetry (DSC):

Differential Scanning Calorimetry was done with a Q100 DSC V9.6 Build 290 from TA Instruments, measurements were cycled twice from 30 °C to 150 °C at 10 °C min⁻¹. A nitrogen sample purge flow of 50 mL min⁻¹ was utilized. The T_g was determined at the point of inflection via TA Instruments Universal Analysis 2000 software (version 4.2E).

Thermogravimetric Analysis (TGA):

Thermogravimetric measurements were performed by E. Graham on a Jupiter STA 449F3 instrument STA 409 by Netzsch. The samples were run in open Al_2O_3 crucibles under inert (nitrogen) atmosphere at 50 mL min^{-1} flow rate. The measurements were conducted with a heating rate of 10 K/min in a range of $25\text{-}580 \text{ }^\circ\text{C}$.

Spin Coating:

The film preparation was carried out using a POLOS SPIN150i. The polymers were mixed in the respective mass ratio, dissolved in anisole to give a solution with a concentration of 15 mg mL^{-1} and stirred at room temperature for 1 hour. The glass substrates were rinsed with *iso*-propanol and treated in a plasma cleaner prior to spin coating. For every sample $150 \text{ } \mu\text{L}$ solution was dispensed on the glass substrate before the spinning process was started with a final spin speed of 2500 rpm for 1 minute.

Photo-cross-linking and Solvent Resistance Tests/Fluorescence Measurements:

The spin-coated polymer films were irradiated with a 1.45 W LED centered around 365 nm for 10 minutes unless stated otherwise. The distance between the sample and the LED was 2 cm (Figure S19). After the irradiation, the films were annealed at $150 \text{ }^\circ\text{C}$ when anisole was used and at $60 \text{ }^\circ\text{C}$ when chloroform was used. The solvent wash was performed by adding $150 \text{ } \mu\text{L}$ chloroform on the polymer film and spin coating the sample at 2500 rpm for 1 minute.



Figure S21: Experimental setup for irradiation with LED ($\lambda = 365 \text{ nm}$) with variable power source in photoreactor.

The fluorescence of the polymer films on the glass substrates was measured with a Cary Eclipse Fluorescence Spectrometer with an excitation wavelength of 290 nm . Each sample was measured on three different spots to determine the average fluorescence intensity (area under the curve) and the standard deviation.

Attenuated Total Reflection Infrared (ATR-IR) Spectroscopy:

Samples were collected on a Thermo Nicolet iS50 FTIR equipped with a single bounce diamond ATR cell. Each spectrum comprised 256 coadded scans with a resolution of 4 cm^{-1} using a $100\text{ }\mu\text{m}$ aperture and a detector gain of 4.

Atomic Force Microscopy (AFM):

A Bruker Dimension Icon Atomic Force Microscope was used to record topographical images as well as the surface roughness with a Scanasyst-Air (Bruker, Billerica, USA) AFM cantilever (typical resonant frequency of 70 kHz and force constant of 0.4 N m^{-1}) in PeakForce Tapping mode (in air). The surface roughness (root mean square (RMS)) was determined on a surface area of $10 \times 10\text{ }\mu\text{m}^2$. The data was evaluated with NanoScope Analysis 2.0 software.

UV-Vis Spectroscopy:

UV-Vis spectra were recorded on a Shimadzu UV-2700 spectrophotometer. Samples were prepared by spin coating from a 10 wt% solution in anisole (3400 rpm, 1 minute) on a glass cover slide.

Cyclic Voltammetry:

Cyclic voltammetry (CV) was performed on a SP-150 Biologic Potentiostat with the ECLab Software. The CV cell for the oxidation potential measurements consisted of a platinum working electrode, a Pt sheet counter electrode ($6.5 \times 6.5\text{ mm}^2$) and a Pt coil reference electrode and the analyte was measured in DCM. All measurements were carried out under argon atmosphere, using anhydrous DCM. Tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) was used as a supporting electrolyte and the scan rate was 100 mVs^{-1} . Ferrocene was used as an internal standard, the oxidation can be converted into the HOMO energies versus vacuum level using the following expressions: $\text{HOMO (eV)} = -5.1\text{ eV} - (E_{1/2\text{ox}} \text{ (vs Fc/Fc}^+))$ where -5.1 eV is the HOMO energy of ferrocene and $E_{1/2\text{ox}} \text{ (vs Fc/Fc}^+)$ define the average potential between the minimum and maximum values of the voltammogram (half wave potential). The LUMO value was determined from the optical band gap.

Time Resolved Photoluminescence:

The samples were prepared by spin-coating a 10 wt% solution of **PE5**, **PC2:PE5** (1:1) and **PE7**, **PC2:PE7** (1:1) in anisole on a quartz glass slide (spin speed of 3400 rpm, 1 min). The time resolved photoluminescence measurements were achieved through time-correlated single photon counting (TCSPC) using a Fluorolog steady state and lifetime modular spectrometer (Horiba). A pulsed LED emitting at 372 nm was used to photo-excite the

samples and the photoluminescence was measured at 500 nm, which corresponds to the peak emission wavelength. An optical filter was included to prevent the scattered excitation from reaching the detector. The sample was stored under vacuum for the duration of the measurements ($\sim 10^{-4}$ mbar) to prevent quenching of the triplet excitons by oxygen. The TRPL data in Figure S20 was fitted using a sum of four exponentials.

Ink-Jet Printing:

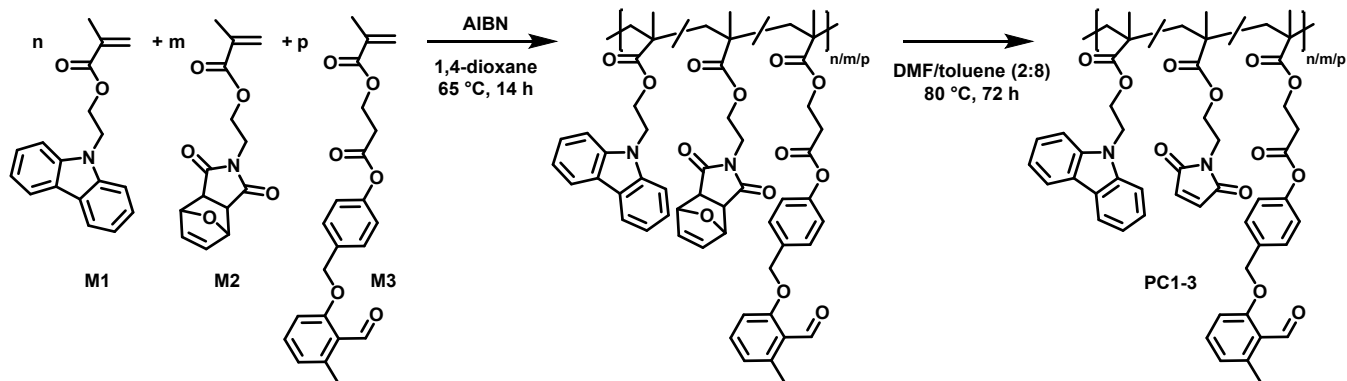
The koala film was printed using a piezoelectric, drop on demand ink jet printer JetLab 4XL by MicroFab. A 50 μm printing nozzle was used along with a standard trapezoidal waveform to produce the film. The print head was heated to 30 °C to maintain a constant printing temperature and the print bed was set to 50 °C. The used polymer ink was prepared by dissolving **PC2** and **PE6** in a mixture of anisole and propylene carbonate (vol% 95:5) (15 mg mL⁻¹) and filtering the solution prior to the printing process.

Materials:

All chemicals were purchased from Acros, Sigma-Aldrich, Fisher Chemicals, Ajax Finechemicals or Chem Supply Pty Ltd and used without further purification unless specified. Methyl methacrylate, THF and 1,4-dioxane were passed over basic alumina to remove inhibitor or peroxide residues prior to polymerization. Commercial methacryloyl chloride was distilled at high vacuum and room temperature and stored at -18 °C. Commercial carbazole was recrystallized from hot acetone prior to use. The TADF emitter was provided by the project partner Cynora GmbH.

The carbazole methacrylate monomer **M1** was synthesized according to the literature.^{1,2} The furan protected maleimide methacrylate monomer **M2** was obtained as described in reference³ and the *o*-methylbenzaldehyde methacrylate monomer **M3** was synthesized according to reference⁴. The emitter methacrylate monomer **M4** was synthesized as previously reported.⁵

Example of a Polymerization and Deprotection Procedure for the Photo-cross-linkable Copolymer (PC1-3).



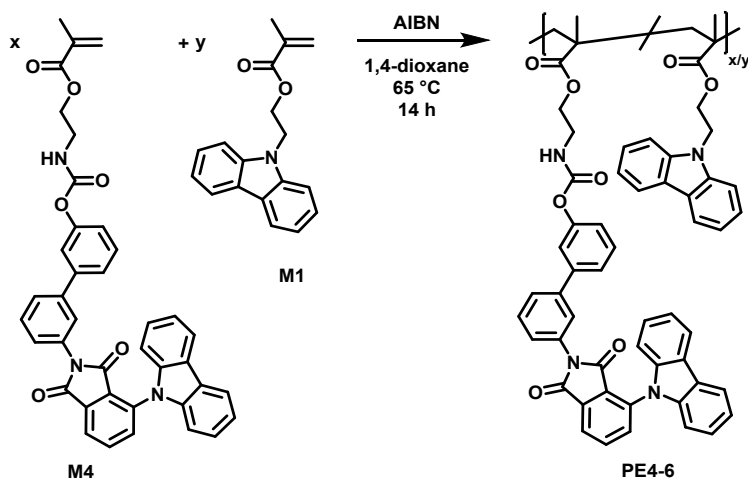
PC2: 1,4-Dioxane was passed over basic alumina prior to utilization and degassed by purging with argon for 30 min. 9H-Carbazole-9-ethyl methacrylate **M1** (408.3 mg, 1.46 mmol, 80 eq.), 2-(methacryloyloxy)ethyl 4-((2-formyl-3-methyl-phenoxy)-methyl)-benzoate **M3** (69.9 mg, 0.18 mmol, 10 eq.), furan protected maleimide methacrylate **M2** (50.7 mg, 0.18 mmol, 10 eq.) and AIBN (0.3 mg, 0.002 mmol, 0.1 eq.) were carefully weighed in a dry headspace vial and sealed airtight. The vial was evacuated and flushed with argon three times before previously degassed 1,4-dioxane (3.7 mL) was added. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C. The conversion was monitored via ¹H-NMR-spectroscopy and the polymerization was stopped after about 35 % conversion by opening to oxygen and cooling the mixture to -18 °C. The polymer subsequently was precipitated from ice-cold methanol and the colourless polymer was dried in vacuo (yield: 157 mg, 30 %).

The polymer (147 mg) was dissolved in anhydrous DMF (30 mL) and toluene (120 mL) was added. The polymer solution was heated at 80 °C for 72 h. The solvent was removed under reduced pressure and the polymer precipitated from ice-cold methanol, filtrated and subsequently dried in vacuo (yield: 101 mg, 69 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 10.54 (s, 1H, C=O-*H*), 8.10 - 7.81 (s, 21H, Ar-*H*), 7.46 - 7.14 (s, 46H, Ar-*H*, CHCl₃), 7.14 - 6.98 (s, 16H, Ar-*H*), 6.67 (s, 1H, Ar-*H*), 6.44 (br s, 2H, CH=CH), 4.92 - 4.52, (br s, 2H, CH₂-O), 4.52 - 4.07 (s, 22H, CH₂-O), 4.07 - 3.70 (m, 17H, CH₂-O), 2.48 (s, 3H, Ar-CH₃), 1.73 - 0.89 (m, 83H, aliphatic-CH₂/CH₃, H₂O), 0.89 - -0.29 (m, 36H, aliphatic-CH₂/CH₃).

Polymer	Eq. (M1)	Eq. (M2 and M3)	Eq. (M4)	Eq. (AIBN)
PC1	80	10	0	1
PC3	70	15	0	0.1
PCE8	87	5	3	2

Example of a Polymerization Procedure for the Emissive Copolymer (PE4-6).

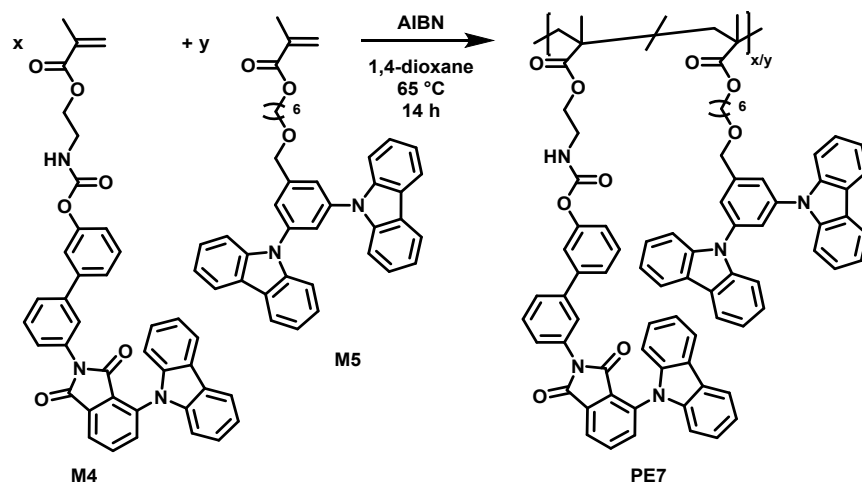


PE6: 1,4-Dioxane was passed over basic alumina prior to utilization and degassed by purging with argon for 30 min. The emitter carbamate methacrylate **MX** (24.7 mg, 0.038 mmol, 6.4 eq.), 9H-carbazole-9-ethyl methacrylate **MX** (159.3 mg, 0.570 mmol, 93.6 eq.) and AIBN (0.2 mg, 0.001 mmol, 0.2 eq.) were carefully weighed in a dry headspace vial and sealed airtight. The vial was evacuated and flushed with argon three times before previously degassed 1,4-dioxane (0.7 mL) was added. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C for 14 h. The polymerization was quenched by opening to oxygen and cooling the mixture to -18 °C. Afterwards, the polymer was precipitated from ice-cold methanol. After filtration the yellow polymer was dried in vacuo (yield: 78%).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.19 – 7.82 (m, 20H, Ar-*H*), 7.78 (s, 2H, Ar-*H*), 7.46 (s, 1H, Ar-*H*), 7.25 (d, J = 16.7 Hz, 44H, CHCl₃, Ar-*H*), 7.08 (d, J = 21.7 Hz, 17H, Ar-*H*), 6.97 (s, 1H, Ar-*H*), 5.89 – 5.53 (m, 1H, C=ON*H*), 4.17 (s, 20H, O-CH₂, N-CH₂), 3.96 (s, 18H, O-CH₂), 3.34 (s, 2H, NH-CH₂), 1.56 – 1.01 (s, 16H, H₂O, aliphatic-CH₂/CH₃), 0.59 – -0.17 (m, 31H, aliphatic-CH₂/CH₃).

Polymer	Eq. (AIBN)
PE4	4
PE5	1

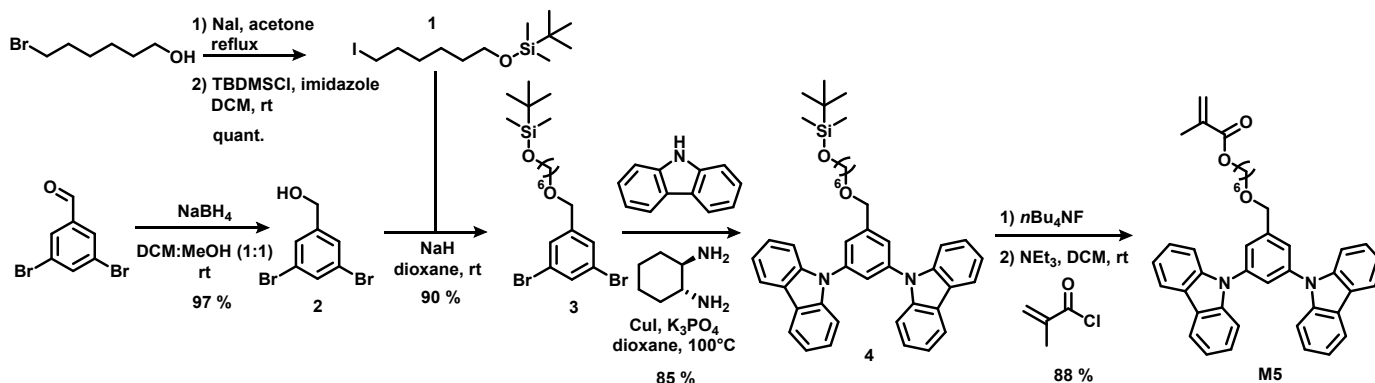
Polymerization Procedure for the Emissive Copolymer (PE7).



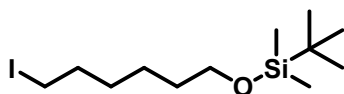
1,4-Dioxane was passed over basic alumina prior to utilization and degassed by purging with argon for 30 min. The emitter carbamate methacrylate **M4** (24.6 mg, 0.039 mmol, 12.7 eq.) and **M5** (161.3 mg, 0.266 mmol, 87.3 eq.) were carefully weighed in a dry headspace vial and sealed airtight. The vial was evacuated and flushed with argon three times before previously degassed 1,4-dioxane (0.9 mL) was added. An AIBN stock solution (1 mg mL⁻¹ in 1,4-dioxane, 0.05 mg, 0.0003 mmol, 0.1 eq.) was added to the monomer solution. The polymerization mixture was then placed in a preheated oil bath and stirred at 65 °C for 14 h. The polymerization was quenched by opening to oxygen and cooling the mixture to -18 °C. Afterwards, the polymer was precipitated from ice-cold methanol. After filtration the yellow polymer was dried in vacuo (yield: 126 mg, 68%).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 7.95 (s, 29H, Ar-**H**), 7.78 – 7.67 (m, 1H, Ar-**H**), 7.54 (d, $J = 7.7$ Hz, 10H, Ar-**H**), 7.50 – 7.31 (m, 43H, Ar-**H**), 7.25 (s, 41H, CHCl₃, Ar-**H**), 7.12 (s, 32H, Ar-**H**), 7.03 (d, $J = 7.8$ Hz, 2H, Ar-**H**), 6.88 (s, 1H, Ar-**H**), 4.34 (s, 13H, Ar-CH₂-O), 4.01 – 3.62 (m, 16H, CH₂-O, NH-CH₂), 3.28 (s, 15H, CH₂-O), 2.09 – 1.62 (m, 12H, CH₂-CH₂), 1.52 – 1.29 (m, 29H, aliphatic-CH₂/CH₃), 1.17 (s, 30H, aliphatic-CH₂/CH₃), 0.84 (s, 23H, CH₂-CH₂).

Synthesis route for mCP methacrylate (M5):



((6-Iodohexyl)oxy)(*tert*-butyl)dimethylsilane (**1**)



6-Chlorohexan-1-ol (4.0 g, 3.91 mL, 29.3 mmol, 1.0 eq) and sodium iodide (13.2 g, 87.8 mmol, 3.0 eq) were dissolved in acetone (17.6 mL), refluxed for 8 hours and stirred at room temperature overnight. Subsequently, ethyl acetate was added to the reaction mixture which was washed with H₂O and brine. The organic phase was dried over MgSO₄ and the solvent was removed under reduced pressure to yield a brownish liquid (6.56 g, 28.78 mmol, 97 %).

The obtained 6-iodohexan-1-ol was dissolved in anhydrous DCM (26.2 ml) and imidazole (2.94 g, 43.1 mmol, 1.5 eq) was added slowly. The reaction mixture was stirred at room temperature for 15 minutes before *tert*-butyldimethylsilyl chloride (4.77 g, 31.64 mmol, 1.1 eq) was added. The reaction mixture was stirred at room temperature overnight. The white precipitate was filtered off and the filtrate was diluted with DCM, washed with water, then brine and dried over MgSO₄. The solvent was removed under reduced pressure and the desired product **1** was obtained as a colourless liquid (9.63 g, 28.13 mmol, 98 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 3.61 (t, 2H, O-CH₂), 3.41 (t, 2H, Br-CH₂), 1.87 (m, 2H, O-CH₂-CH₂), 1.52 (m, 2H, Br-CH₂-CH₂), 1.45 (m, 2H, O-CH₂-CH₂-CH₂), 1.36 (m, 2H, Br-CH₂-CH₂-CH₂), 0.90 (s, 9H, C-CH₃), 0.05 (s, 6H, Si-CH₃).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 63.03, 33.55, 32.60, 30.31, 25.99, 24.81, 18.38, 7.13, -5.25.

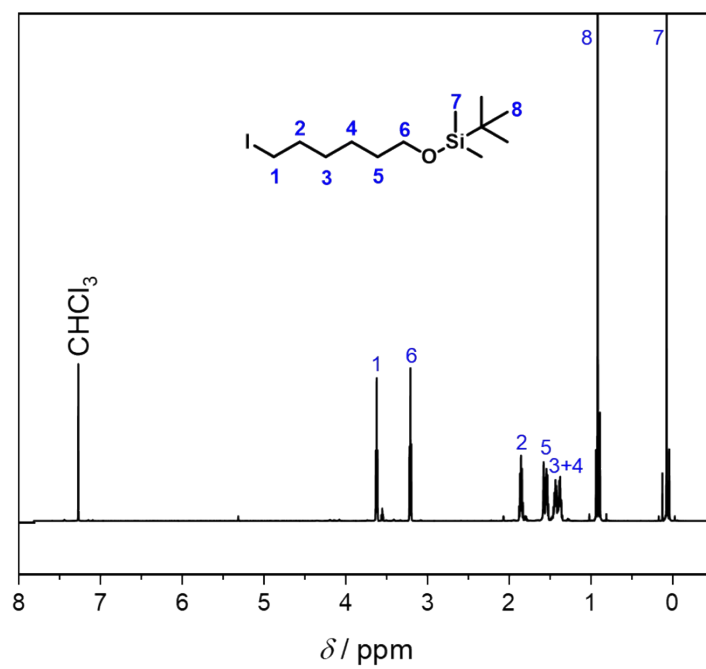
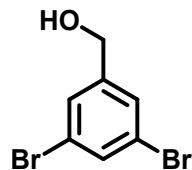


Figure S22: ¹H-NMR spectrum of ((6-iodohexyl)oxy)(tert-butyl)dimethylsilane (**1**) in CDCl₃ (600 MHz).

3,5-Dibromophenyl-methanol (**2**)



3,5-Dibromobenzaldehyde (5.0 g, 18.95 mmol, 1.0 eq) was dissolved in DCM (65 ml) and MeOH (65 ml) and sodium borohydride (0.72 g, 18.95 mmol, 1.0 eq) was slowly added and the reaction mixture was stirred at room temperature for 3 hours. The mixture was diluted with DCM, washed with water, then brine, dried over MgSO₄ and the solvent was removed *in vacuo* to give the desired product **2** as a white solid (4.88 g, 18.36 mmol, 97 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 7.58 (t, 1H, CH₂-C-CH-C-CH), 7.46 (d, 2H, CH₂-C-CH), 4.67 (s, 2H, OH-CH₂).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 144.66, 133.08, 128.41, 123.06, 63.75.

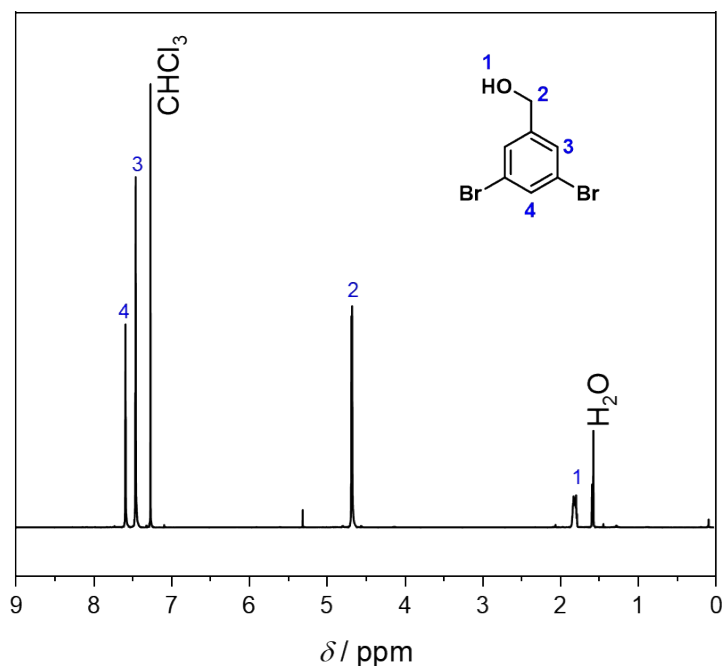
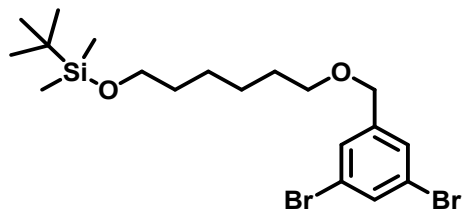


Figure S23: ¹H-NMR spectrum of 3,5-dibromophenyl-methanol (**2**) in CDCl₃ (600 MHz).

***tert*-Butyl((6-((3,5-dibromobenzyl)oxy)hexyl)oxy)dimethylsilane (3)**



Under argon atmosphere, 3,5-dibromophenyl-methanol **2** (4.84 g, 18.2 mmol, 1.0 eq) was dissolved in anhydrous 1,4-dioxane (36 mL) and sodium hydride (60 % in mineral oil, 1.53 g, 63.7 mmol, 3.5 eq) was added portion wise. The mixture was stirred at room temperature for 10 minutes before heating to 50 °C for 1 hour. After cooling the mixture to room temperature, a solution of ((6-iodohexyl)oxy)(*tert*-butyl)dimethylsilane **1** (7.47 g, 21.8 mmol, 1.2 eq) in 1,4-dioxane (8 mL) was added dropwise and the reaction was stirred at room temperature for 24 hours. Another portion of **1** (2.45 g, 7.19 mmol, 0.4 eq.) in 1,4-dioxane (6 mL) was added and the mixture stirred at room temperature for another 18 hours. Subsequently, the reaction mixture was cooled to 0 °C and quenched with MeOH, diluted with ethyl acetate, washed with water and brine and dried over anhydrous MgSO₄. The mixture was concentrated *in vacuo* and the residue was purified by flash chromatography (silica, eluent: cyclohexane) to give the desired product **3** as a colorless liquid (5.93 g, 12.34 mmol, 68 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 7.57 (t, 1H, CH₂-C-CH-C-CH), 7.41 (m, 2H, CH₂-C-CH), 4.43 (s, 2H, C-CH₂), 3.61 (t, 2H, Si-O-CH₂), 3.46 (t, 2H, C-CH₂-O-CH₂), 1.63 (m, 2H, Si-O-CH₂-CH₂), 1.53 (m, 2H, O-CH₂-CH₂), 1.37 (m, 4H, Si-O-CH₂-CH₂-CH₂, O-CH₂-CH₂-CH₂), 0.90 (s, 9H, C-CH₃), 0.05 (s, 6H, Si-CH₃).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 142.83, 132.98, 129.69, 129.03, 122.91, 71.28, 70.94, 70.83, 63.18, 32.79, 32.08, 29.67, 25.99, 25.96, 25.66, 25.31, 18.38, -3.57, -5.24.

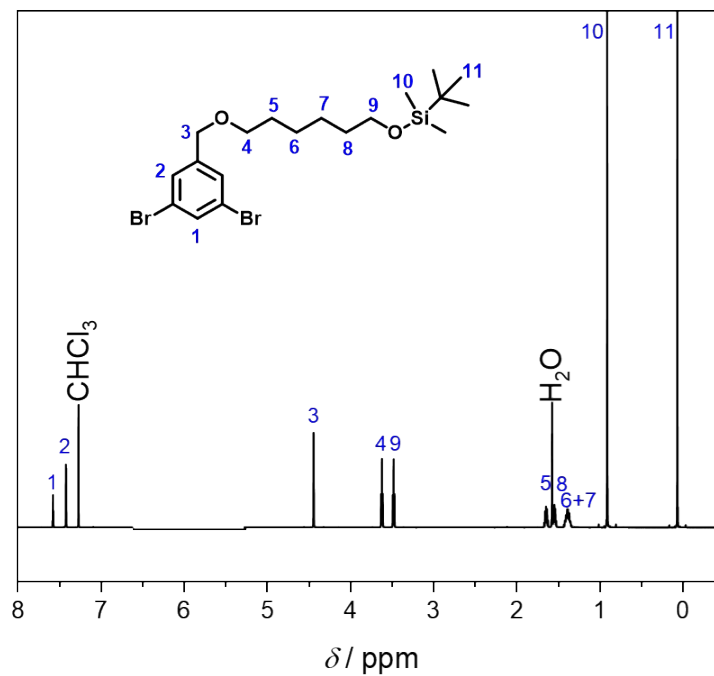
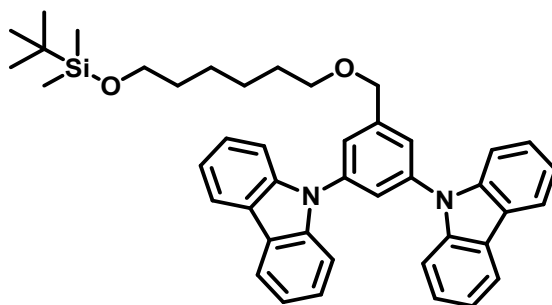


Figure S24: ¹H-NMR spectrum of tert-butyl((6-((3,5-dibromobenzyl)oxy)hexyl)oxy)dimethylsilane (**3**) in CDCl₃ (600 MHz).

9,9'-(5-(((6-((*tert*-Butyldimethylsilyl)oxy)hexyl)oxy)methyl)-1,3-phenylene)bis(9H-carbazole) (4)



Tert-butyl((6-((3,5-dibromobenzyl)oxy)hexyl)oxy)dimethylsilane **3** (2 g, 4.16 mmol, 1.0 eq) was dissolved in anhydrous 1,4-dioxane (5 mL) and degassed with argon for 5 minutes. The solution was transferred to a Schlenk tube containing carbazole (1.74 g, 12.5 mmol, 2.5 eq), copper(I) iodide (397 mg, 2.1 mmol, 0.5 eq) and K_3PO_4 (3.53 g, 16.7 mmol, 4.0 eq) under argon atmosphere before degassed 1,4-dioxane (21 mL) and *trans*-1,2-diaminocyclohexane (333 mg, 0.35 ml, 2.9 mmol, 0.7 eq) were added. The reaction mixture was placed in an oil bath at 100 °C and stirred for 18 hours. The reaction mixture was filtered over neutral aluminium oxide, diluted with ethyl acetate and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, eluent: gradient cyclohexane:ethyl acetate 100:0 to 95:5) to give the desired product **4** as a colourless oil (2.318 g, 3.55 mmol, 85 %).

1H -NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.16 (ddd, J = 7.8, 1.3, 0.7 Hz, 4H, *H*-Ar), 7.73 (t, J = 2.0 Hz, 1H, *H*-Ar), 7.69 (dd, J = 1.7, 1.0 Hz, 2H, *H*-Ar), 7.54 (dt, J = 8.3, 0.9 Hz, 4H, *H*-Ar), 7.48 – 7.41 (m, 4H, *H*-Ar), 7.31 (ddd, J = 8.0, 7.1, 1.0 Hz, 4H, *H*-Ar), 4.73 (s, 2H, C- CH_2 -O), 3.63 (t, J = 6.6 Hz, 2H, C- CH_2 -O- CH_2), 3.58 (t, J = 6.6 Hz, 2H, Si-O- CH_2), 1.72-1.65 (m, 2H, O- CH_2 - CH_2), 1.55 – 1.47 (m, 2H, Si-O- CH_2 - CH_2), 1.46 – 1.39 (m, 2H, O- CH_2 - CH_2 - CH_2), 1.39-1.33 (m, 2H, Si-O- CH_2 - CH_2 - CH_2), 0.87 (s, 9H, C- CH_3), 0.05 (s, 6H, Si- CH_3).

^{13}C -NMR (151 MHz, $CDCl_3$): δ (ppm) = 142.92, 140.57, 139.33, 126.14, 124.42, 124.02, 123.60, 120.44, 120.31, 109.76, 72.05, 71.24, 63.16, 32.80, 29.79, 26.08, 26.00, 25.98, 25.72, 18.36, -5.26.

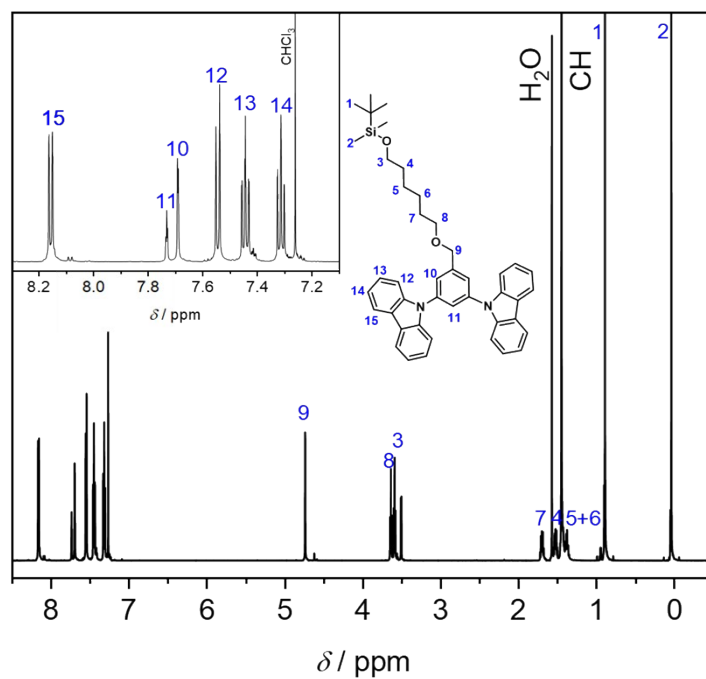
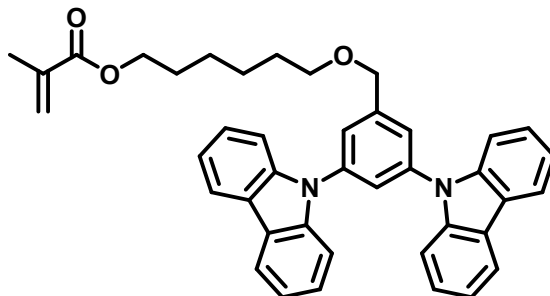


Figure S25: ¹H-NMR spectrum of 9,9'-(5-(((6-((tert-butyl dimethylsilyl)oxy)hexyl)oxy)methyl)-1,3-phenylene)bis(9H-carbazole) (**4**) in CDCl₃ (600 MHz, CH=cyclohexane).

6-((3,5-Di(9H-carbazol-9-yl)benzyl)oxy)hexyl methacrylate (M5)



4 (1.18 g, 1.8 mmol, 1.0 eq) was dissolved in anhydrous THF (18.1 mL) and tetrabutylammonium fluoride (1 M in THF, 0.44 g, 0.49 mL, 0.1.8 mmol, 1 eq) was added dropwise. The solution turned pale yellow and was stirred at room temperature for 3 hours. Another portion of tetrabutylammonium fluoride (1 M in THF, 0.44 g, 0.49 mL, 0.1.8 mmol, 1 eq) was added and the solution was stirred at room temperature overnight. Upon addition of methanol the solution turned colourless and the solution was filtered over a short silica plug and washed with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, eluent: gradient cyclohexane:ethyl acetate 95:5 to 6:4) to give the desired product as a colourless solid (957 mg, 1.78 mmol, 98%).

The deprotected alcohol (957 g, 1.8 mmol, 1.0 eq) was dissolved in anhydrous DCM (3.6 mL) under argon atmosphere and triethylamine (0.27 g, 0.37 mL, 2.7 mmol, 1.5 eq) was added. The solution was stirred at room temperature for 30 minutes before it was cooled to 0 °C and methacryloyl chloride (0.22 g, 0.21 mL, 2.1 mmol, 1.2 eq) was added dropwise. The reaction mixture was stirred overnight at 0 °C and slowly warmed up to room temperature. Water was added and the mixture was diluted with DCM, washed with brine, dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica, eluent: gradient cyclohexane:ethyl acetate 95:5 to 9:1) to give the desired product **M5** as a colourless oil (945 mg, 1.55 mmol, 88 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.16 (dt, J = 7.7, 1.0 Hz, 4H, *H*-Ar), 7.73 (t, J = 2.0 Hz, 1H, *H*-Ar), 7.69 (d, J = 1.9 Hz, 2H, *H*-Ar), 7.54 (dt, J = 8.2, 0.9 Hz, 4H, *H*-Ar), 7.44 (ddd, J = 8.3, 7.1, 1.3 Hz, 4H, *H*-Ar), 7.31 (ddd, J = 8.0, 7.2, 1.0 Hz, 4H, *H*-Ar), 6.07 (dq, J = 2.0, 1.0 Hz, 1H, CH₃-C-CH₂), 5.52 (p, J = 1.6 Hz, 1H, CH₃-C-CH₂), 4.73 (s, 2H, C-CH₂-O), 4.12 (t, J = 6.6 Hz, 2H, C=O-O-CH₂), 3.63 (t, J = 6.5 Hz, 2H, C-O-CH₂), 1.92 (dd, J = 1.6, 1.0 Hz, 3H, CH₃), 1.68 (ddt, J = 16.8, 14.6, 6.7 Hz, 4H, O-C-O-CH₂-CH₂), 1.50 – 1.37 (m, 4H, O-CH₂-CH₂-CH₂).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 167.43, 142.79, 140.49, 139.27, 136.43, 126.06, 125.11, 124.33, 123.98, 123.53, 120.38, 120.25, 109.67, 72.00, 71.02, 64.58, 29.61, 28.51, 25.88, 25.83, 18.26.

ESI-MS (m/z for [MH]⁺): calculated: 607.2955, found 607.2946.

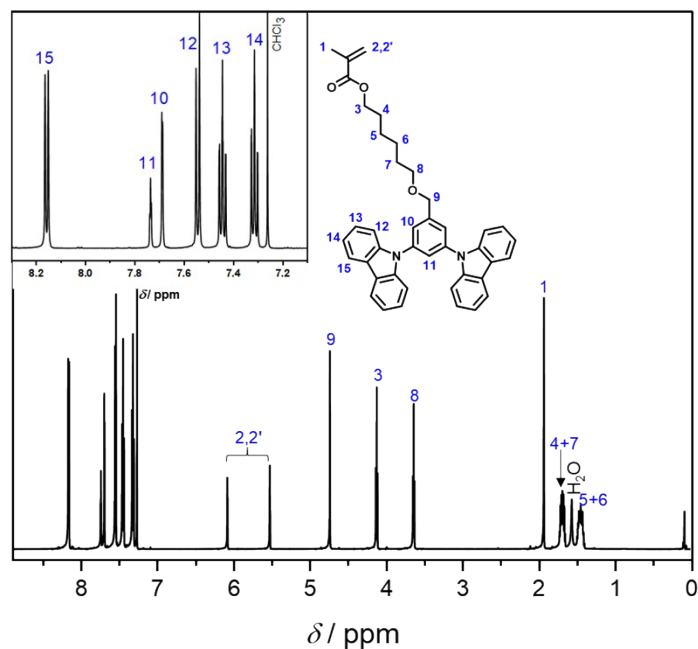


Figure S26: ^1H -NMR spectrum of **M5** in CDCl_3 (600 MHz).

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