

Supporting Information

Simplified Approach to Thermally Activated Delayed Fluorescence (TADF) Bipolar Host Polymers

Susanna V. Kunz, Cameron M. Cole, Steven C. Gauci, Felicia Zaar, Paul E. Shaw, Chandana Sampath Kumara
Ranasinghe, Thomas Baumann, Prashant Sonar, Soniya D. Yambem, Eva Blasco, Christopher-Barner-
Kowollik,* James P. Blinco*

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 (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.

Spin Coating

The polymer films were prepared by spin coating using a POLOS SPIN150i. 2 mg of each sample were dissolved in 200 μ l chloroform and stirred at room temperature for 1 hour. As substrates 10 x 45 mm rectangular quartz slides were first rinsed with *iso*-propanol and then treated in a plasma cleaner prior to spin coating. For every sample 150 μ L solution was distributed on the quartz substrate before the spinning process was started with a final spin speed of 2500 rpm which was held for 1 minute.

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 quartz slide.

Fluorescence Spectroscopy

The fluorescence of the polymer films spin-coated on the quartz substrates was measured with a Cary Eclipse Fluorescence Spectrometer with an excitation wavelength of 290 nm. Each sample was measured three times and the average of all three measurements was plotted after normalization.

Density Functional Theory Calculations

The DFT calculations of the HOMO and LUMO were performed with the software Gaussian 16 with the GaussView 6 interface using B3LYP / 6-31G* as the basis set. The calculations were run on the Tetralith cluster, provided by the National Supercomputer Centre at Linköping University.

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 x 6.5 mm²) 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*-Bu₄NPF₆) 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: HOMO (eV) = -5.1 eV - (E_{1/2ox} (vs Fc/Fc⁺)) where -5.1 eV is the HOMO energy of ferrocene and E_{1/2ox} (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 and HOMO value difference.

PLQY, TRPL and Temperature PL Procedure

The thin film solid-state absolute PLQYs were measured using the method described by Greenham et al.¹ The P3, P6 and P7 spin-coated thin were excited using a Kimmon 325 nm HeCd laser CW laser. During the measurement, the samples were kept in a SphereOptics integrating sphere under a nitrogen rich environment. A Newport 818-UV photodetector mounted to the integrating sphere was used to detect the photoluminescence, which was quantified using a KEITHLEY 2401 source meter. The reflectance and transmittance of the thin films were quantified using a Newport 1918-C optical power meter. The TRPL spectra and decay curves were measured using a custom-built spectrometer. [Sampath Ranasinghe, Organic Electronics 105, 106500, <https://doi.org/10.1016/j.orgel.2022.106500>] The set up included a ICCD camera (Andor iStar ICCD) (Hamamatsu, H10721-21) and photomultiplier tube connected to an oscilloscope (Teledyne WavePro ; 2Ghz, WavePro 7200A). Samples were kept at 300-77 K in a cryostat (Oxford Instruments; Optistat DN2 liquid N₂ cryostat) which cooled using liquid nitrogen. A pulsed laser (Opolette 355 LD; 10 ns, repetition rate 10 Hz, 10 μJ / Pulse, Nd:YAG) with an

excitation wavelength of 355 nm was used to excite the samples. To reduce the effects of scattered excitation on the emission, the emission was collected at a right angle through a 375 nm long pass filter.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry measurements were performed on a Q100 DSC V9.6 Build 290 from TA Instruments, measurements were cycled twice from 0 °C to 200 °C at 10 K 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 on a Jupiter STA 449F3 instrument STA 409 by Netzsch. The samples were run in open Al₂O₃ crucibles under nitrogen atmosphere at 50 mL min⁻¹ flow rate. The measurements were conducted with a heating rate of 10 K min⁻¹ in a range of 30-500 °C.

Fabrication Method for Hole Only Single Carrier Devices

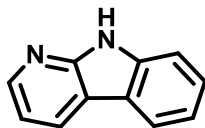
The single carrier devices were fabricated on an indium tin oxide (ITO) (Xin Yan Technology Ltd.) patterned substrate. Initially, the substrates were prepared by wiping with acetone before ultrasonicing in deionised water with lab detergent (Alconox). The substrates were then wiped with lab detergent in deionized water before sequential ultrasonication in deionised water, acetone and isopropanol with each step separated by drying with compressed air. Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) (Heraeus Clevis, AI 4083) was filtered with a 0.45 µm PVDF filter and spin-coated then annealing at 125°C for 20 minutes to produce a 30 nm film. The PEDOT:PSS coated substrates were then transferred into a low O₂ (<10 ppm) and H₂O (<0.1 ppm) environment. From here, a 5 mg ml⁻¹ solution of either **P3**, **P6** or **P7** in chloroform (Sigma-Aldrich, 288306) was spin coated at the required speed to yield an approximately 20 nm layer and annealed at 60°C for 10 minutes. Finally, Gold (Au) and Silver (Ag) (Sigma-Aldrich, 474711) were evaporated using masks (2 mm²) at a pressure under 10⁻⁶ mbar and to produce a ~20 nm Au film and a ~100 nm Ag film. Testing of these devices was performed using a semi-conductor analyser (Keysight, B1500A).

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 emitter methacrylate monomer **M1** was synthesized as previously reported.³ The carbazole methacrylate monomer **M2** was synthesized according to the literature.^{4,5}

9H-pyrido[2,3-b]indole (**1**)



The synthesis of **1** was based on a literature procedure.⁵

A mixture of 2,3-dichloropyridine (6.0 g, 40.54 mmol, 1.0 eq), aniline (4.07 ml, 44.60 mmol, 1.1 eq), palladium(II)acetate (0.46 g, 2.03 mmol, 0.05 eq), triphenylphosphine (1.06 g, 4.05 mmol, 0.1 eq), and sodium *tert*-butoxide (4.68 g, 48.65 mmol, 1.2 eq) in anhydrous *o*-xylene (100 ml) was sparged with nitrogen for 10 minutes and stirred at 120 °C for 3 hours. The reaction mixture was cooled to room temperature before adding palladium(II)acetate (0.46 g, 2.03 mmol, 0.05 eq), tricyclohexylphosphine tetrafluoroborate (1.0 g, 2.72 mmol, 0.10 eq), 1,8-diazabicyclo(5.4.0)undec-7-ene (12.10 ml, 81.09 mmol, 2.0 eq) and anhydrous DMAc (100 ml) to the reaction flask. The reaction mixture was sparged with nitrogen for 10 minutes and heated at 145 °C for 16 hours. The reaction mixture was concentrated *in vacuo* and the residue was dissolved in ethyl acetate. The mixture was washed with water, then brine, dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was purified by flash chromatography (silica, eluent: 1:1 cyclohexane:ethyl acetate) to give the desired product **1** as a light brown solid (yield: 3.44 g, 20.27 mmol, 50 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 10.07 (br s, 1H, NH), 8.50 (d, J = 4.5 Hz, 1H, Ar-H), 8.38 (d, J = 7.6 Hz, 1H, Ar-H), 8.08 (d, J = 7.8 Hz, 1H, Ar-H), 7.55 (d, J = 8.2 Hz, 1H, Ar-H), 7.51 (m, 1H, Ar-H), 7.30 (m, 1H, Ar-H), 7.23 (ddd, J = 7.6, 4.9, 0.9 Hz 1H, Ar-H).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 151.80, 144.91, 138.80, 129.08, 127.27, 121.20, 121.10, 120.41, 117.05, 115.43, 111.49.

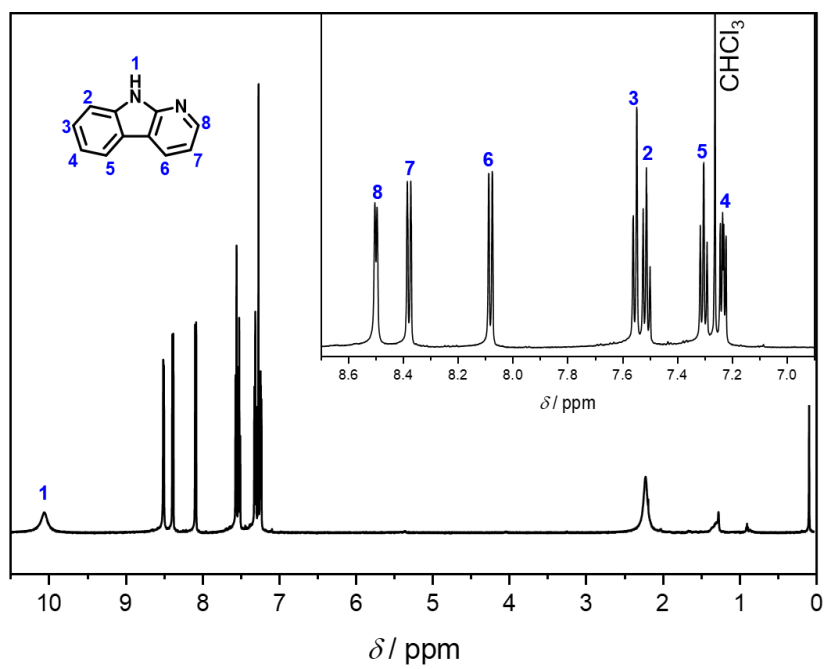


Figure S1: ¹H-NMR spectrum of **1** in CDCl₃ (600 MHz).

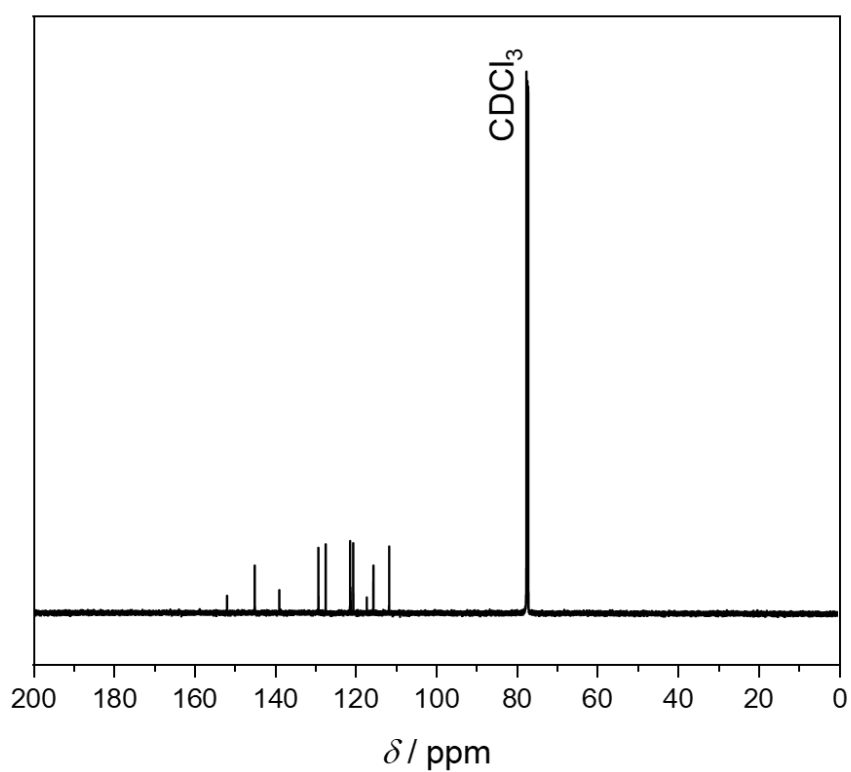
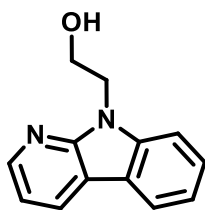


Figure S2: ¹³C-NMR spectrum of **1** in CDCl₃ (151 MHz).

2-(9H-pyrido[2,3-b]indol-9-yl)ethan-1-ol (2)



A mixture of **1** (1.95 g, 11.6 mmol, 1.0 eq) and KOH powder (3.26 g, 58.1 mmol, 5.0 eq) in anhydrous DMF (29 mL) was placed under argon atmosphere and stirred at room temperature for 1 hour. Then 2-bromoethanol (2.29 g, 1.30 mL, 18.3 mmol, 1.5 eq) was added dropwise and the reaction mixture was stirred at 40 °C for 24 hours. Ethyl acetate was added to the mixture which was washed with saturated ammonium chloride solution, water, then brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, eluent: 1:1 cyclohexane:ethyl acetate) to give the desired product **2** as a colourless solid (1.53 g, 7.21 mmol, 62 %). **¹H-NMR (600 MHz, CDCl₃):** δ (ppm) = 8.44 (dd, J = 5.0, 1.6 Hz, 1H, Ar-**H**), 8.37 (dd, J = 7.6, 1.6 Hz, 1H, Ar-**H**), 8.09 (d, J = 7.6 Hz, 1H, Ar-**H**), 7.55 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H, Ar-**H**), 7.50 (d, J = 8.3 Hz, 1H, Ar-**H**), 7.32 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H, Ar-**H**), 7.22 (dd, J = 7.6, 5.0 Hz, 1H, Ar-**H**), 4.61 (t, J = 4.8 Hz, 2H, N-CH₂-CH₂), 4.14 (t, J = 4.8 Hz, 2H, N-CH₂), 1.82 (br s, 1H, OH).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 151.80, 140.09, 128.86, 127.19, 121.26, 120.62, 120.36, 116.64, 115.41, 109.37, 62.52, 46.10.

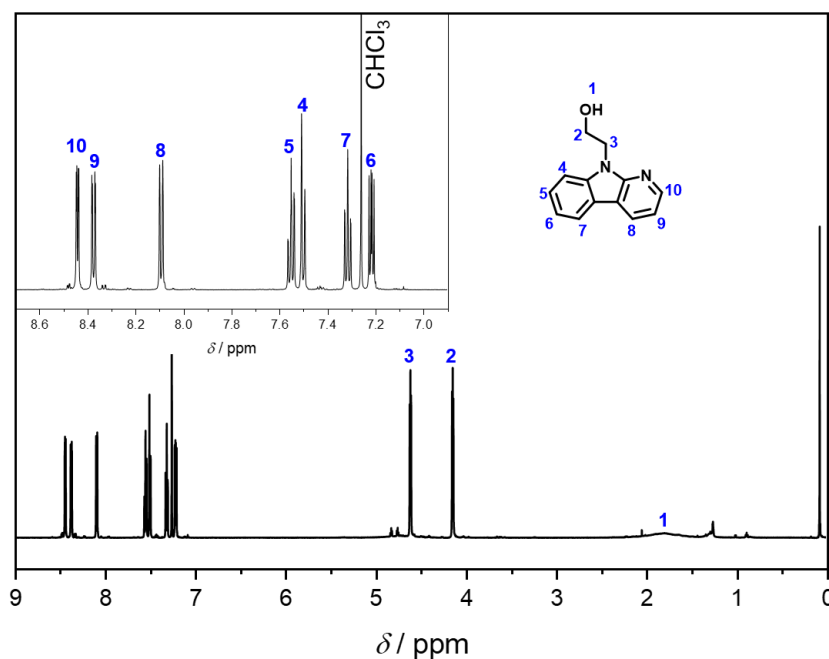


Figure S3: ¹H-NMR spectrum of **2** in CDCl₃ (600 MHz).

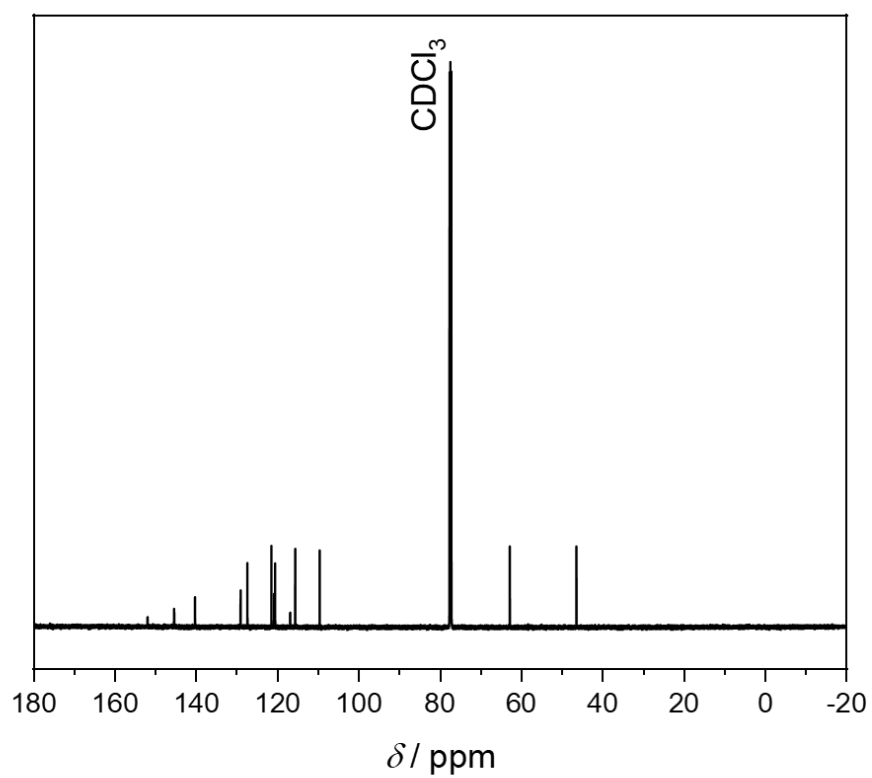
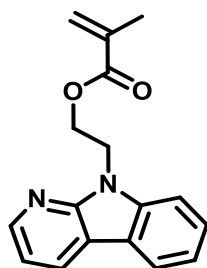


Figure S4: ^{13}C -NMR spectrum of **2** in CDCl_3 (151 MHz).

2-(9H-pyrido[2,3-b]indol-9-yl)ethyl methacrylate (M3)



A solution of **2** (0.58 g, 2.75 mmol, 1.0 eq) in DCM was placed under nitrogen atmosphere and stirred at room temperature for 10 minutes. The solution was cooled to 0 °C, after which triethylamine (0.96 ml, 6.88 mmol, 2.0 eq) was added dropwise and the reaction mixture was stirred for 30 minutes. Subsequently, methacryloyl chloride (0.34 ml, 3.44 mmol, 1.25 eq) was slowly added and the reaction mixture was stirred at room temperature for 2 hours. The mixture was diluted with DCM, washed with water, then brine, dried over anhydrous MgSO₄ and filtered over neutral aluminium oxide. The solvent was removed *in vacuo* to give the desired product **M3** as a colourless solid (0.65 g, 2.32 mmol, 84 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.49 (dd, J = 4.9, 1.6 Hz, 1H, Ar-**H**), 8.33 (dd, J = 7.6, 1.6 Hz, 1H, Ar-**H**), 8.08 (d, J = 7.8 Hz, 1H, Ar-**H**), 7.56 - 7.49 (m, 2H, Ar-**H**), 7.29 (dd, J = 7.6, 4.9 Hz, 1H, Ar-**H**), 7.19 (dd, J = 7.6, 4.9 Hz, 1H, Ar-**H**), 5.90 (s, 1H, CH₃-C-**CH**₂), 5.45 (s, 1H, CH₃-C-**CH**₂), 4.81 (t, J = 5.7 Hz, 2H, O-**CH**₂), 4.60 (t, J = 5.7 Hz, 2H, N-**CH**₂), 1.77 (s, 3H, **CH**₃).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 167.33, 151.55, 146.03, 139.86, 135.92, 128.27, 126.86, 126.16, 121.14, 120.63, 120.13, 116.17, 115.46, 109.48, 62.84, 40.36, 18.28.

LC-MS (m/z for [MH]⁺): calculated: 281.1285, found 281.1280.

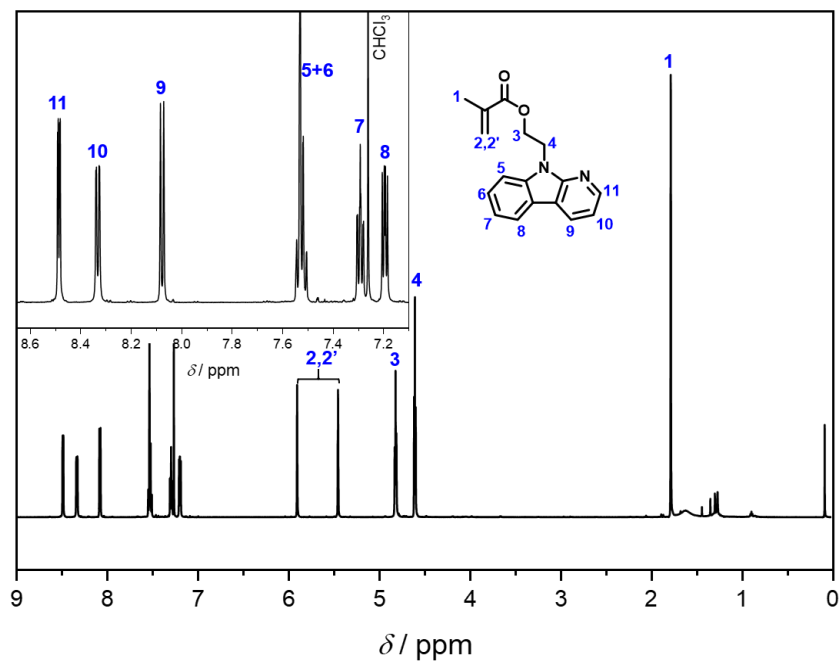


Figure S5: $^1\text{H-NMR}$ spectrum of **M3** in CDCl_3 (600 MHz).

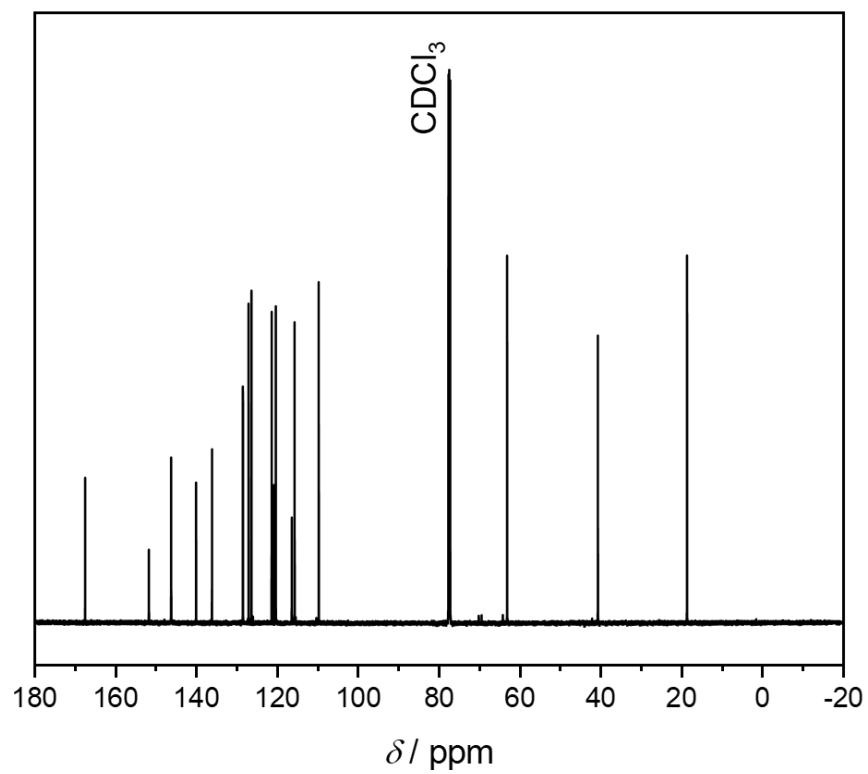
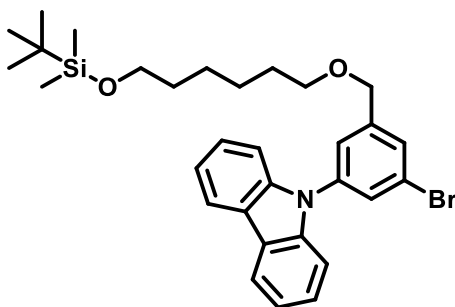


Figure S6: $^{13}\text{C-NMR}$ spectrum of **M3** in CDCl_3 (151 MHz).

9-(3-bromo-5-(((6-((tert-butyl)dimethylsilyl)oxy)hexyl)oxy)methyl)phenyl)-9H-carbazole (5)



Tert-butyl((6-((3,5-dibromobenzyl)oxy)hexyl)oxy)dimethylsilane **3** (1 g, 2.08 mmol, 1.0 eq) was dissolved in anhydrous dioxane (5 mL) and degassed with argon for 5 minutes. The solution was transferred to a Schlenk tube containing carbazole (69.2 mg, 0.42 mmol, 0.2 eq), copper(I) iodide (39.6 mg, 0.21 mmol, 0.1 eq) and K₃PO₄ (1.76 g, 8.33 mmol, 4.0 eq) under argon atmosphere before degassed dioxane (25 mL) and *trans*-1,2-diaminocyclohexane (50.0 μL, 0.42 mmol, 0.2 eq) were added. The reaction mixture was placed in an oil bath at 100 °C and stirred for 22 hours. Another portion of carbazole (69.2 mg, 0.42 mmol, 0.2 eq) and CuI (39.6 mg, 0.21 mmol, 0.1 eq) were added and the mixture stirred at 100 °C for another 22 hours. The mixture was filtered over neutral aluminium oxide, diluted with ethyl acetate and washed with brine. The organic phase was dried over anhydrous MgSO₄ 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 **5** as a colourless oil (330 mg, 0.58 mmol, 28 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.14 (d, 2H, Ar-*H*), 7.66 (t, 1H, Ar-*H*), 7.60 (t, 1H, Ar-*H*), 7.51 (t, 1H, Ar-*H*), 7.43 (m, 4H, Ar-*H*), 7.31 (m, 2H, Ar-*H*), 7.31 (m, 2H, Ar-*H*), 4.60 (s, 2H, C-*CH*₂), 3.61 (t, 2H, Si-O-*CH*₂), 3.55 (t, 2H, C-*CH*₂-O-*CH*₂), 1.67 (m, 2H, Si-O-*CH*₂-*CH*₂), 1.54 (m, 2H, O-*CH*₂-*CH*₂), 1.40 (m, 4H, Si-O-*CH*₂-*CH*₂-*CH*₂, O-*CH*₂-*CH*₂-*CH*₂), 0.90 (s, 9H, C-*CH*₃), 0.05 (s, 6H, Si-*CH*₃).
¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 142.85, 140.53, 139.04, 129.22, 128.89, 126.10, 124.46, 123.53, 123.17, 120.38, 120.32, 109.68, 71.65, 71.08, 63.16, 32.79, 29.73, 26.02, 25.98, 25.69, 18.37, -5.25.

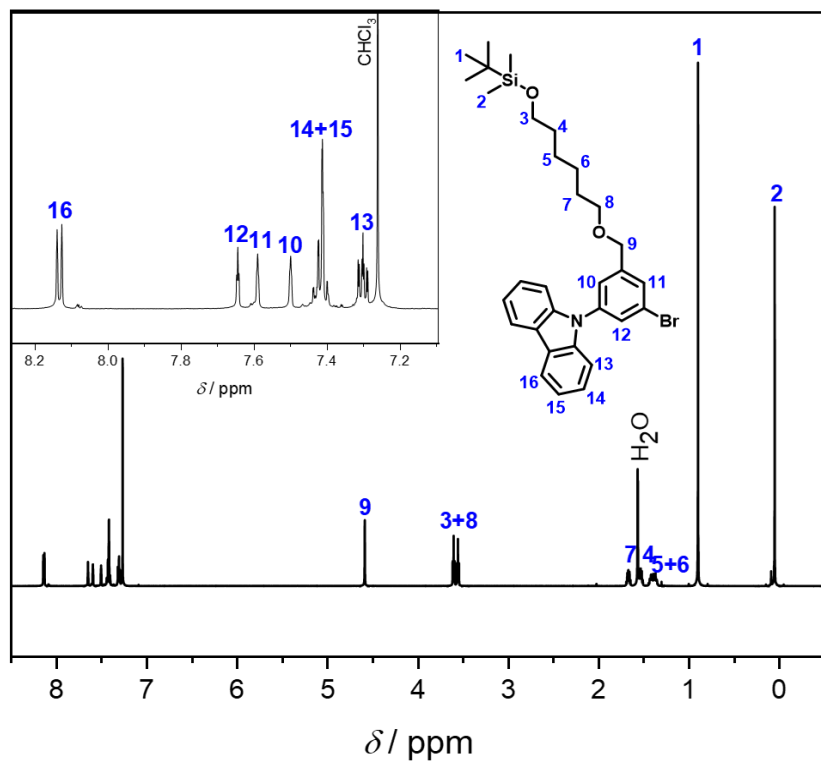


Figure S7: $^1\text{H-NMR}$ spectrum of **5** (CDCl_3 , 600 MHz).

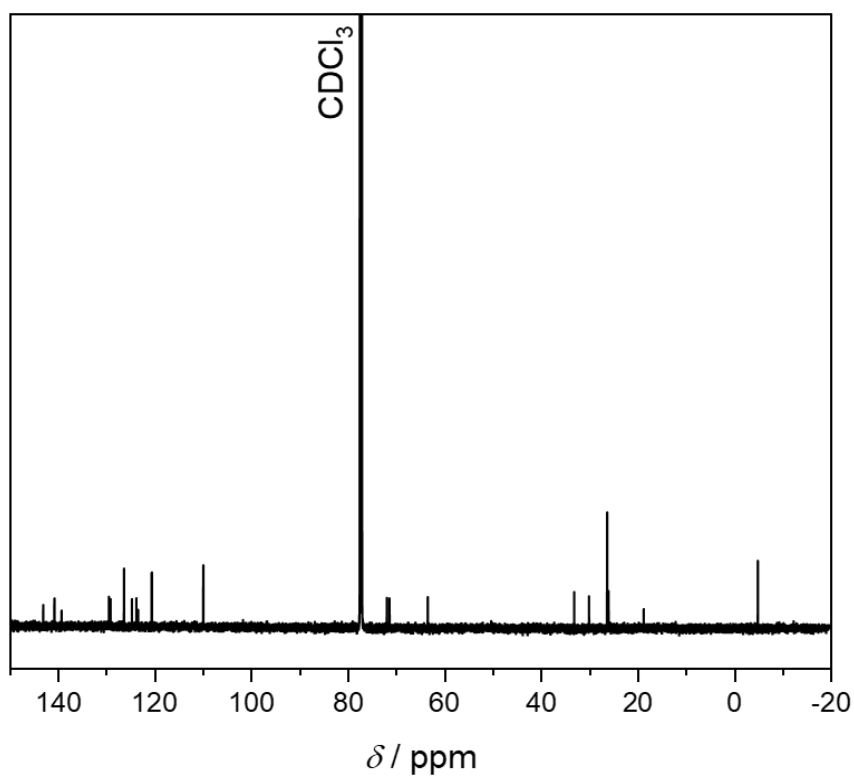
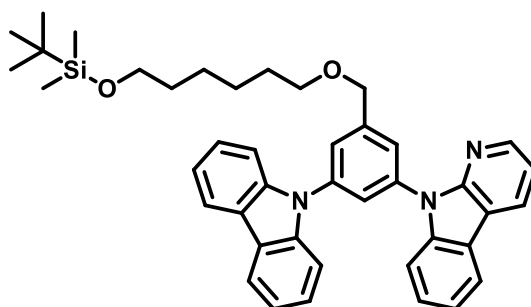


Figure S8: $^{13}\text{C-NMR}$ spectrum of **5** in CDCl_3 (151 MHz).

9-(3-(((6-((tert-butyl)dimethylsilyloxy)hexyl)oxy)methyl)phenyl)-9H-pyrido[2,3-b]indole (6)



9-(3-bromo-5-(((6-((tert-butyl)dimethylsilyloxy)hexyl)oxy)methyl)phenyl)-9H-carbazole **5** (300 mg, 0.52 mmol, 1.0 eq), α -carboline **1** (178.1 mg, 1.06 mmol, 2 eq), copper(I) iodide (50.4 mg, 0.26 mmol, 0.5 eq), and K_3PO_4 (449.5 mg, 2.1 mmol, 4.0 eq) were placed under argon atmosphere and dissolved in degassed, anhydrous dioxane (2.65 mL) before *trans*-1,2-diaminocyclohexane (63.5 μ L, 0.53 mmol, 1 eq) was added. The reaction mixture was stirred at 100 °C for 23 hours and additional portions of copper(I) iodide (50.4 mg, 0.26 mmol, 0.5 eq), α -carboline **1** (178.1 mg, 1.06 mmol, 2 eq), and *trans*-1,2-diaminocyclohexane (63.5 μ L, 0.53 mmol, 1 eq) were added. The mixture stirred at 100 °C for another 39 hours before it was filtered over neutral aluminium oxide, diluted with ethyl acetate and washed with brine. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica, eluent: gradient cyclohexane:ethyl acetate 98:2 to 9:1) to give the desired product **6** as a colourless oil (153 mg, 0.23 mmol, 44 %).

1H -NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.54 (s, 1H, Ar-*H*), 8.40 (d, 1H, Ar-*H*), 8.17 (d, 2H, Ar-*H*), 8.14 (d, 1H, Ar-*H*), 7.90 (s, 1H, Ar-*H*), 7.80 (s, 1H, Ar-*H*), 7.72 (m, 1H, Ar-*H*), 7.72 (m, 1H, Ar-*H*), 7.68 (m, 1H, Ar-*H*), 7.53 (m, 2H, Ar-*H*), 7.47 (m, 2H, Ar-*H*), 7.37 (m, 1H, Ar-*H*), 7.33 (m, 2H, Ar-*H*), 7.29 (m, 1H, Ar-*H*), 4.76 (s, 2H, C- CH_2), 3.64 (t, 2H, Si-O- CH_2), 3.60 (t, 2H, C- CH_2 -O- CH_2), 1.70 (m, 2H, Si-O- CH_2 - CH_2), 1.53 (m, 2H, O- CH_2 - CH_2), 1.40 (m, 4H, Si-O- CH_2 - CH_2 - CH_2 , O- CH_2 - CH_2 - CH_2), 0.90 (s, 9H, C- CH_3), 0.05 (s, 6H, Si- CH_3).

^{13}C -NMR (151 MHz, $CDCl_3$): δ (ppm) = 151.61, 142.44, 140.57, 139.67, 138.89, 137.67, 128.53, 127.22, 126.09, 124.46, 124.35, 124.20, 123.61, 121.16, 121.12, 121.07, 120.34, 120.23, 116.65, 116.48, 110.47, 110.12, 72.18, 71.13, 63.19, 32.83, 29.83, 26.95, 26.09, 26.00, 25.75, 18.38, -5.24.

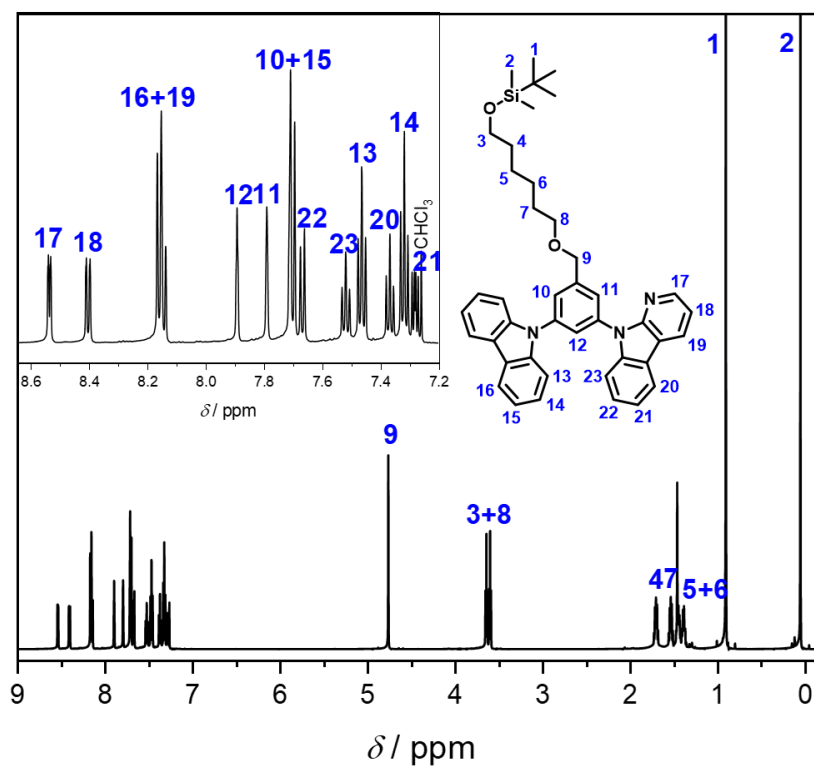


Figure S9: $^1\text{H-NMR}$ spectrum of **6** in CDCl_3 (600 MHz).

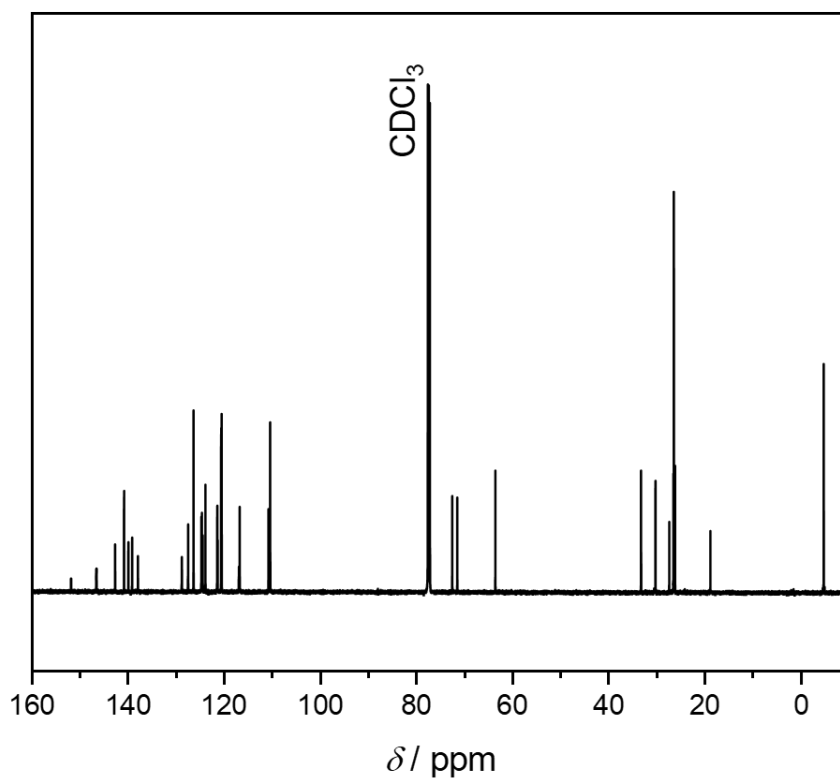
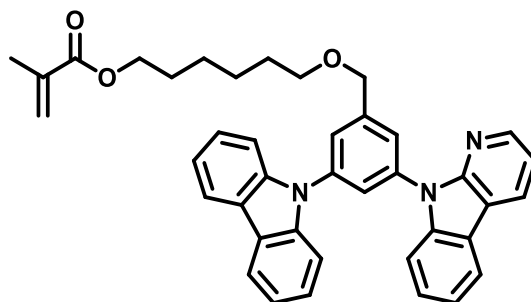


Figure S10: $^{13}\text{C-NMR}$ spectrum of **6** in CDCl_3 (151 MHz).

6-((3-(9H-carbazol-9-yl)-5-(9H-pyrido[2,3-b]indol-9-yl)benzyl)oxy)hexyl methacrylate (M5)



6 (0.17 g, 0.26 mmol, 1.0 eq) was dissolved in anhydrous THF (2.6 mL) and tetrabutylammonium fluoride (1 M in THF, 94.5 mg, 0.1 mL, 0.39 mmol, 1.5 eq) was added dropwise. The solution turned pale yellow and was stirred at room temperature overnight. Methanol was added 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 1:1) to give the desired product as a colourless solid (110 mg, 0.2 mmol, 78%).

The deprotected alcohol (110 mg, 0.2 mmol, 1.0 eq) was dissolved in anhydrous DCM (0.7 mL) under argon atmosphere and triethylamine (31 mg, 43 μ L, 0.3 mmol, 1.5 eq) was added. The solution was stirred at room temperature for 1 hour before it was cooled to 0 °C and methacryloyl chloride (27.7 mg, 26 μ L, 0.27 mmol, 1.3 eq) was added dropwise. The reaction mixture was stirred at 0 °C for 5 hours. Another portion of methacryloyl chloride (6.4 mg, 6 μ L, 0.06 mmol, 0.3 eq) was added and the reaction was stirred overnight at room temperature. Water was added and the mixture was diluted with DCM, washed with water and brine, dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue was filtered over neutral alumina to give the desired product **M5** as a colourless oil (105 mg, 0.17 mmol, 85 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.52 (m, 1H, Ar-*H*), 8.40 (d, 1H, Ar-*H*), 8.15 (m, 2H, Ar-*H*), 8.15 (m, 1H, Ar-*H*), 7.88 (s, 1H, Ar-*H*), 7.78 (s, 1H, Ar-*H*), 7.72 (m, 1H, Ar-*H*), 7.68 (m, 1H, Ar-*H*), 7.66 (m, 1H, O-CH₂-C-*CH*), 7.51 (m, 1H, Ar-*H*), 7.45 (m, 1H, Ar-*H*), 7.36 (m, 1H, Ar-*H*), 7.30 (m, 1H, Ar-*H*), 7.30 (m, 1H, Ar-*H*), 6.07 (s, 1H, CH₃-C-*CH*₂), 5.52 (s, 1H, CH₃-C-*CH*₂), 4.74 (s, 2H, C-*CH*₂), 4.11 (t, 2H, C-O-*CH*₂), 3.62 (t, 2H, CH₂-O-*CH*₂), 1.92 (s, 3H, CH₃), 1.67 (m, 2H, O-C-O-CH₂-*CH*₂), 1.67 (m, 4H, O-CH₂-*CH*₂), 1.43 (m, 4H, O-C-O-CH₂-CH₂-*CH*₂, O-CH₂-CH₂-*CH*₂).

¹³C-NMR (151 MHz, CDCl₃): δ (ppm) = 151.74, 146.51, 142.33, 140.51, 139.62, 138.88, 137.74, 136.46, 128.37, 127.15, 126.07, 125.12, 124.48, 124.31, 124.10, 123.6, 121.11, 120.63, 120.34, 210.22, 116.5, 110.42, 110.09, 72.16, 70.92, 64.67, 29.68, 28.54, 26.91, 25.93, 18.34.

LC-MS (m/z for [MH]⁺): calculated: 608.2908, found 608.2909.

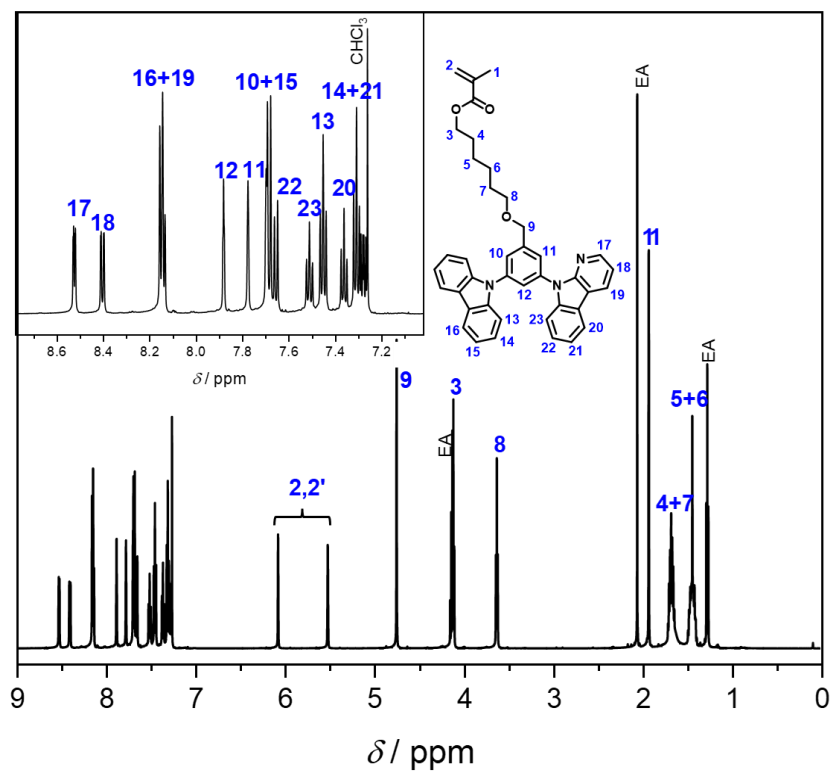


Figure S11: $^1\text{H-NMR}$ spectrum of **M5** in CDCl_3 (600 MHz).

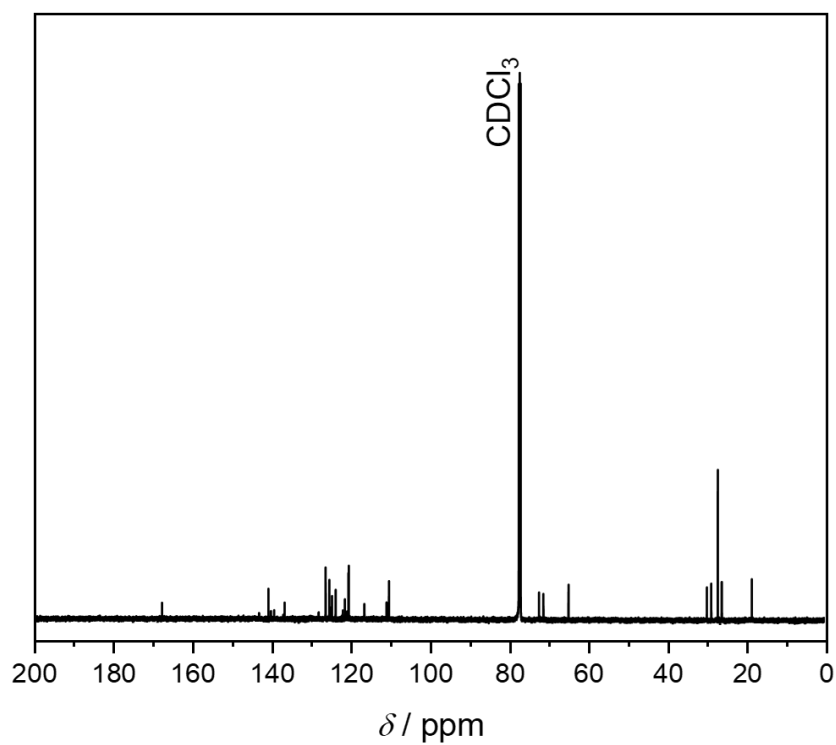
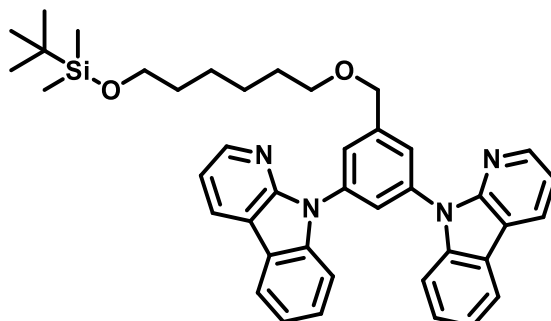


Figure S12: $^{13}\text{C-NMR}$ spectrum of **M5** in CDCl_3 (151 MHz).

9,9'-(5-(((6-((tert-butyldimethylsilyl)oxy)hexyl)oxy)methyl)-1,3-phenylene)bis(9H-pyrido[2,3-b]indole) (7)



Tert-butyl((6-((3,5-dibromobenzyl)oxy)hexyl)oxy)dimethylsilane **3** (806 mg, 1.68 mmol, 1.0 eq) was dissolved in anhydrous dioxane (8.4 mL) and degassed with argon for 20 minutes. The solution was transferred to a Schlenk tube containing α -carboline (592.7 mg, 3.52 mmol, 2.1 eq), copper(I) iodide (159.8 mg, 0.84 mmol, 0.5 eq) and K_3PO_4 (1.42 g, 6.71 mmol, 4.0 eq) under argon atmosphere before *trans*-1,2-diaminocyclohexane (134.1 mg, 0.14 ml, 1.17 mmol, 0.7 eq) were added. The reaction mixture was placed in an oil bath at 100 °C. After 18 hours additional portions of copper(I) iodide (319.6 mg, 1.68 mmol, 1 eq) and *trans*-1,2-diaminocyclohexane (268 mg, 0.28 ml, 2.25 mmol, 1.4 eq) were added and the mixture was stirred at 100 °C for another 24h. 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 95:5 to 90:10) to give the desired product **7** as a colourless oil (680 g, 1.03 mmol, 62 %).

1H -NMR (600 MHz, $CDCl_3$): δ (ppm) = 8.50 (dd, J = 4.8, 1.6 Hz, 2H, Ar-**H**), 8.38 (ddd, J = 7.6, 1.6, 0.8 Hz, 2H, Ar-**H**), 8.15 – 8.10 (m, 2H, Ar-**H**), 7.98 (t, J = 2.0 Hz, 1H, Ar-**H**), 7.84 – 7.77 (m, 4H, Ar-**H**), 7.54 – 7.49 (m, 2H, Ar-**H**), 7.37 – 7.32 (m, 2H, Ar-**H**), 7.26 (t, J = 0.7 Hz, 2H, Ar-**H**), 4.75 (s, 2H, C-O-**CH**₂), 3.59 (t, J = 6.6 Hz, 2H, O-**CH**₂), 3.55 (t, J = 6.6 Hz, 2H, O-**CH**₂), 1.64 (dt, J = 14.8, 6.7 Hz, 2H, O-CH₂-**CH**₂), 1.51 – 1.44 (m, 2H, O-CH₂-**CH**₂), 1.40 – 1.28 (m, 4H, O-CH₂-CH₂-**CH**₂), 0.85 (s, 9H, Si-C-**CH**₃), 0.01 (s, 6H, Si-**CH**₃).

^{13}C -NMR (151 MHz, $CDCl_3$): δ (ppm) = 139.78, 137.15, 127.27, 124.40, 121.12, 120.95, 116.34, 110.99, 72.20, 70.97, 70.72, 63.19, 32.81, 32.65, 29.82, 29.67, 26.93, 26.05, 25.97, 25.72, 25.65, 25.51, 18.36, -3.57, -5.27.

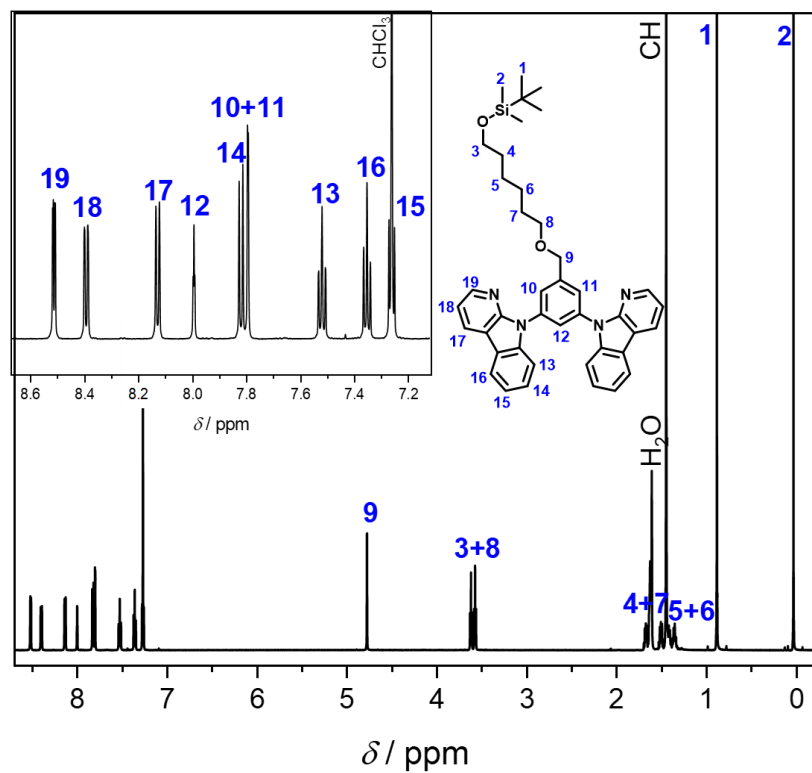


Figure S13: $^1\text{H-NMR}$ spectrum of **7** in CDCl_3 (600 MHz).

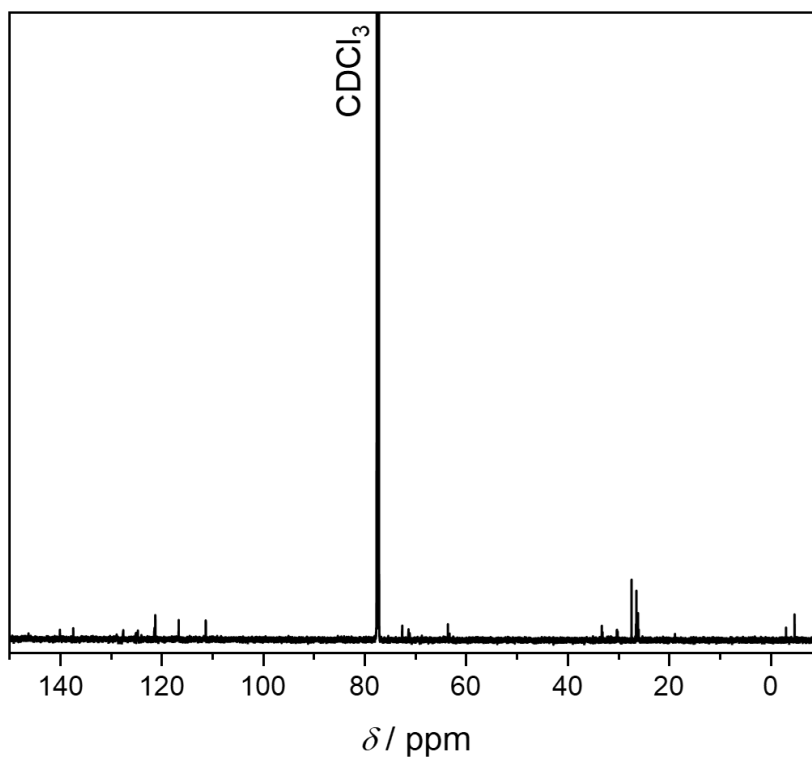
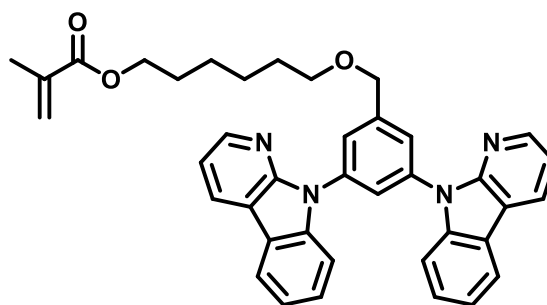


Figure S14: $^{13}\text{C-NMR}$ spectrum of **7** in CDCl_3 (151 MHz).

6-((3,5-bis(9H-pyrido[2,3-b]indol-9-yl)benzyl)oxy)hexyl methacrylate (M6)



7 (650 mg, 0.99 mmol, 1.0 eq) was dissolved in anhydrous THF (10 mL) and tetrabutylammonium fluoride (1 M in THF, 0.36 g, 0.40 mL, 1.5 mmol, 1.5 eq) was added dropwise. The solution turned pale yellow and 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 2:8) to give the desired product as a colourless solid (502 mg, 0.93 mmol, 94%).

The deprotected alcohol (502 mg, 0.93 mmol, 1.0 eq) was dissolved in anhydrous DCM (1.9 mL) under argon atmosphere and triethylamine (0.14 g, 0.19 mL, 1.4 mmol, 1.5 eq) was added. The solution was stirred at room temperature for 1 hour before it was cooled to 0 °C and methacryloyl chloride (0.12 g, 0.11 mL, 1.1 mmol, 1.2 eq) was added dropwise. The reaction mixture was stirred overnight at 0 °C and slowly warmed up to room temperature. Another portion of triethylamine (75.2 mg, 0.10 mL, 0.74 mmol, 0.8 eq) and methacryloyl chloride (48.5 mg, 45.4 μ L, 0.46 mmol, 0.5 eq) was added and the mixture was stirred overnight. Methanol was added and the mixture was diluted with DCM, washed with brine, dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (silica, eluent: gradient cyclohexane:ethyl acetate 8:2 to 2:8) to give the desired product **M6** as a colourless oil (512 mg, 0.84 mmol, 91 %).

$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ (ppm) = 8.53 (dd, $J = 4.9, 1.5$ Hz, 2H, Ar-**H**), 8.41 (dd, $J = 7.7, 1.5$ Hz, 2H, Ar-**H**), 8.13 (dd, $J = 7.8, 1.2$ Hz, 2H, Ar-**H**), 7.99 (d, $J = 2.0$ Hz, 1H, Ar-**H**), 7.86 – 7.78 (m, 4H, Ar-**H**), 7.56 – 7.50 (m, 2H, Ar-**H**), 7.36 (t, $J = 7.5$ Hz, 2H, Ar-**H**), 7.28 (dd, $J = 7.7, 4.9$ Hz, 2H, Ar-**H**), 6.06 (s, 1H, $\text{CH}_2=\text{CH}$), 5.51 (q, $J = 1.7$ Hz, 1H, $\text{CH}_2=\text{CH}$), 4.78 (s, 2H, C- $\text{CH}_2\text{-O}$), 4.10 (q, $J = 7.1, 6.6$ Hz, 2H, O- CH_2), 3.61 (t, $J = 6.5$ Hz, 2H, O- CH_2), 1.93 – 1.89 (m, 3H, CH_3), 1.65 (dp, $J = 13.9, 6.8$ Hz, 4H, O- $\text{CH}_2\text{-CH}_2$), 1.48 – 1.35 (m, 4H, O- $\text{CH}_2\text{-CH}_2\text{-CH}_2$).

$^{13}\text{C-NMR}$ (151 MHz, CDCl_3): δ (ppm) = 139.94, 137.25, 136.64, 127.49, 125.30, 124.97, 124.67, 121.35, 121.12, 121.05, 116.48, 111.15, 72.35, 70.96, 64.84, 29.84, 28.72, 26.07, 18.47.

LC-MS (m/z for $[\text{MH}]^+$): calculated: 609.2821, found 609.2846.

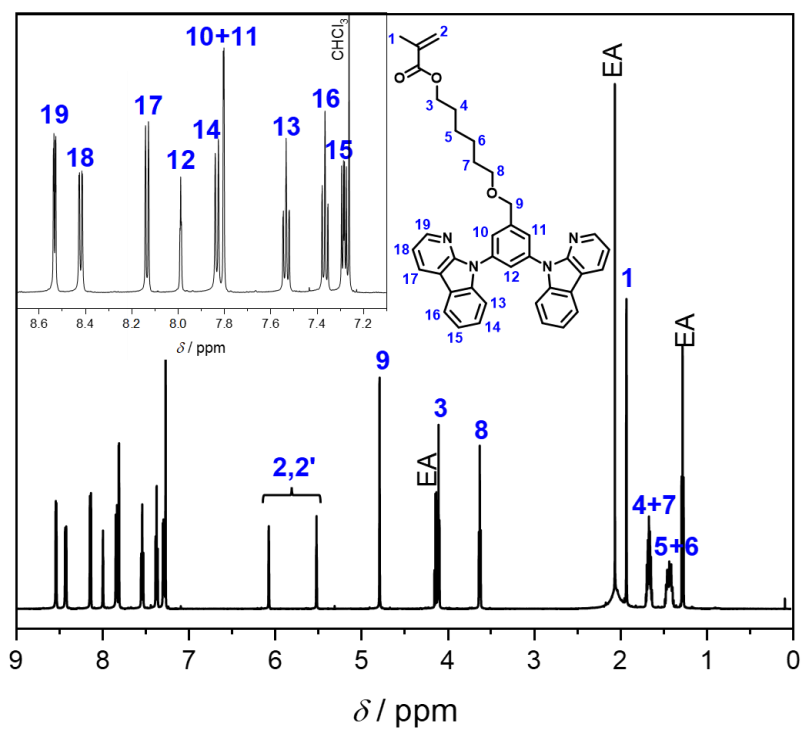


Figure S15: $^1\text{H-NMR}$ spectrum of **M6** in CDCl_3 (600 MHz).

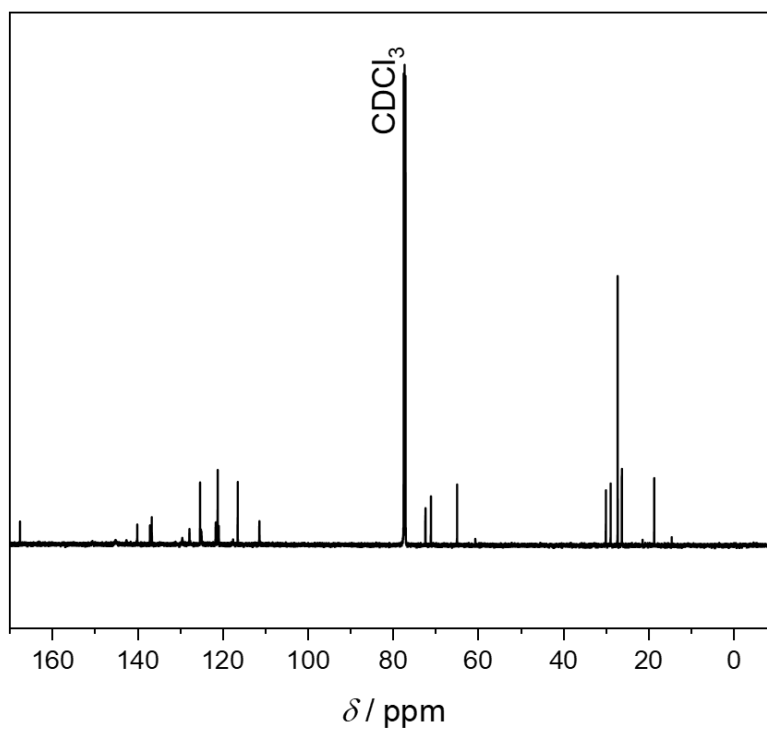
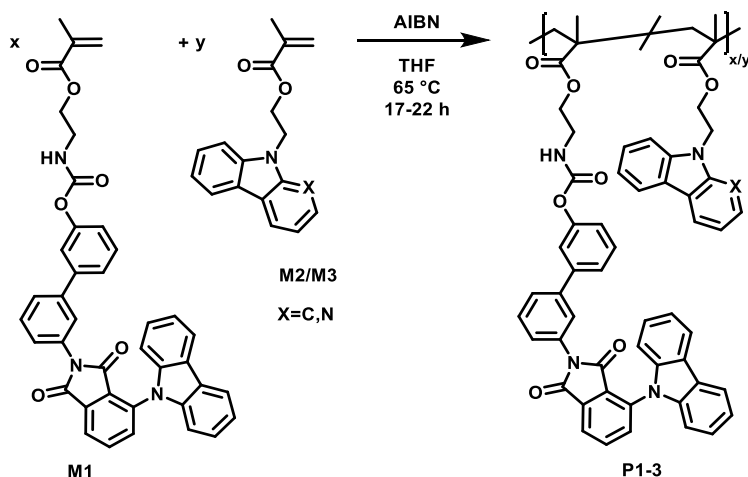


Figure S16: $^{13}\text{C-NMR}$ spectrum of **M6** in CDCl_3 (151 MHz).

Example of a Polymerization Procedure (P1-3).



P2: Prior to utilization, anhydrous THF was passed over basic alumina and degassed by argon purge for 30 min. AIBN (0.4 mg, 0.002 mmol, 0.2 eq.), the TADF emitter methacrylate **M1** (49.4 mg, 0.07 mmol, 6.38 eq.) and the 9H-carboline-9-ethyl methacrylate **M3** (319.6, 1.14 mmol, 93.6 eq.) were carefully weighed in a dry headspace vial. The sealed vial was evacuated and backfilled with argon three times before degassed THF (1.4 mL) was added. The mixture was stirred at room temperature to dissolve and subsequently placed in an oil bath at 65°C to start the polymerization. After 22 h, the vial was opened to air and cooled in an ice bath. The polymer was precipitated from ice-cold methanol, filtered and dried *in vacuo* to yield a pale yellow powder (311 mg, 84 %).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.49-8.26 (m, 1H, Ar-*H*), 8.25-8.01 (m, 1H, Ar-*H*), 8.01-7.71 (m, 1H, Ar-*H*), 7.50-7.19 (m, 4H, Ar-*H*, CHCl₃), 7.19-7.03 (m, 1H, Ar-*H*), 7.03-6.85 (m, 1H, Ar-*H*), 4.49 (s, 2H, O-CH₂, N-CH₂), 4.10 (s, 2H, O-CH₂), 3.37 (s, 0.14H, NH-CH₂), 2.35-1.58 (m, 2H, CH₂/CH₃), 1.58-0.85 (m, 2H, CH₂/CH₃), 0.64- -0.35 (m, 4H, CH₂/CH₃).

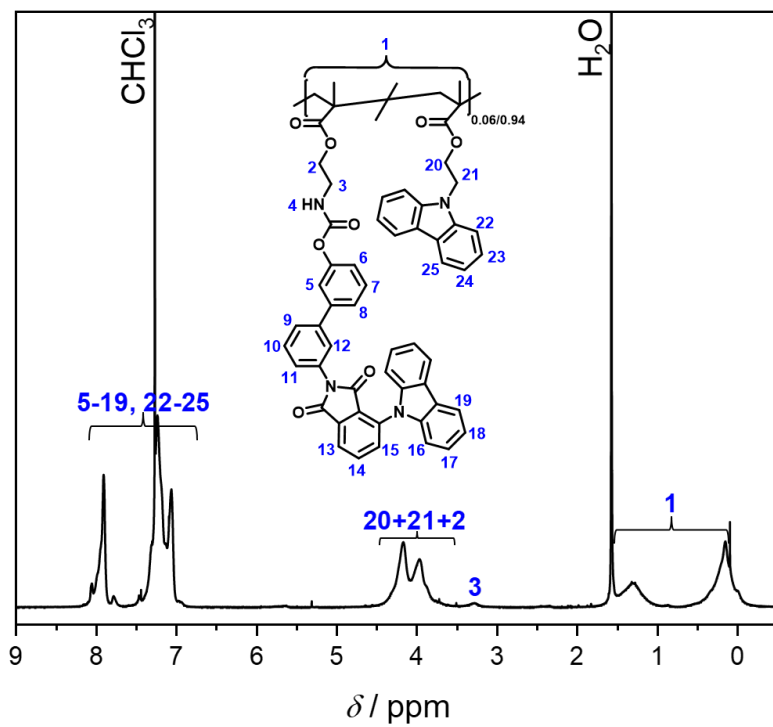


Figure S17: $^1\text{H-NMR}$ spectrum of **P1** in CDCl_3 (600 MHz).

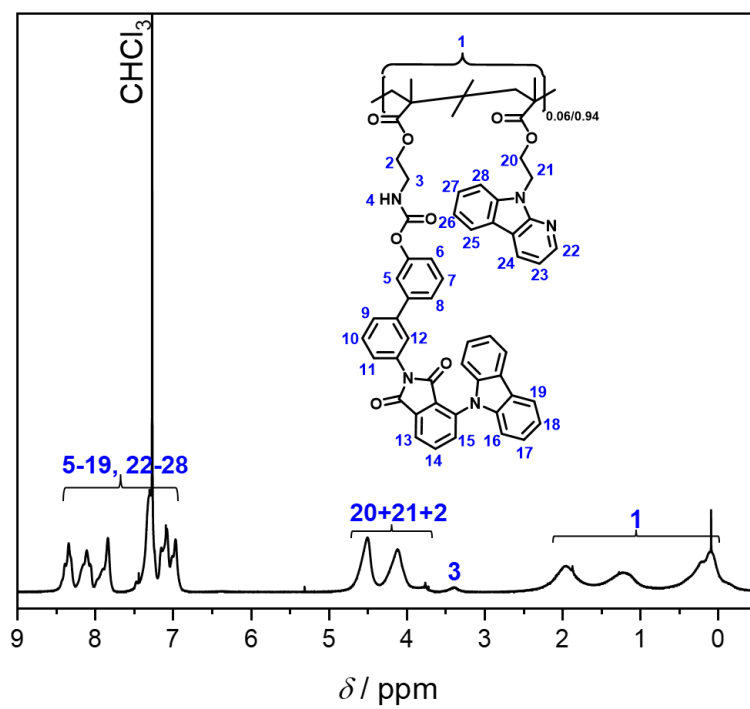


Figure S18: $^1\text{H-NMR}$ spectrum of **P2** in CDCl_3 (600 MHz).

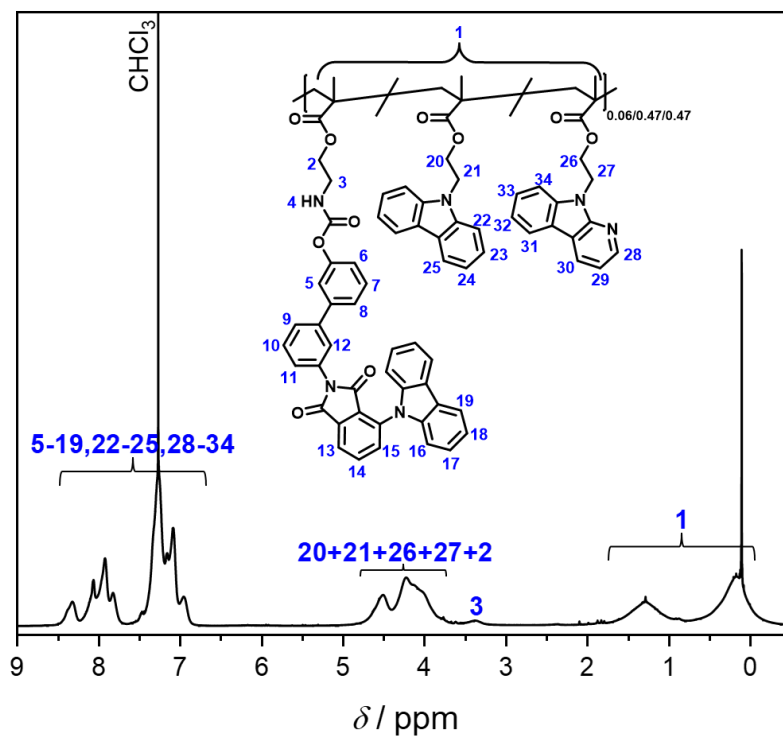
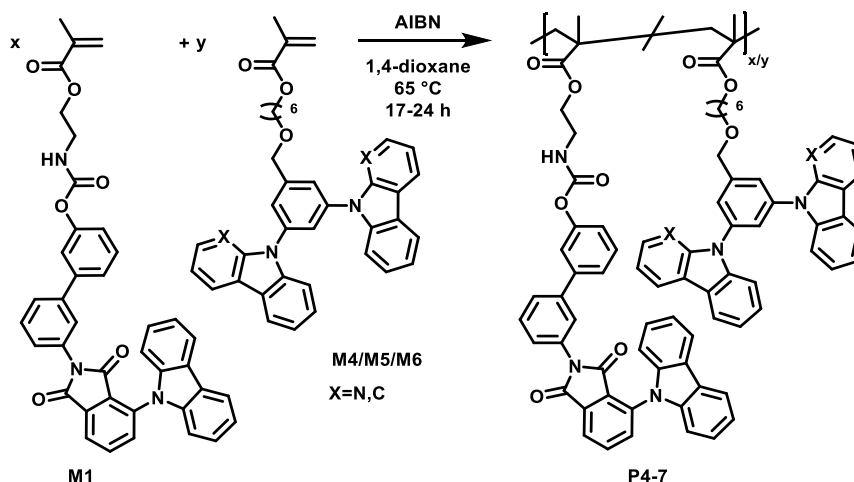


Figure S19: $^1\text{H-NMR}$ spectrum of **P3** in CDCl_3 (600 MHz).

Example Polymerization Procedure for P4-7.



P5: Anhydrous 1,4-dioxane was passed over basic alumina and degassed by argon purge for 30 min prior to utilization. The TADF emitter methacrylate **M1** (14.7 mg, 0.02 mmol, 12.7 eq.) and **M6** (97.1 mg, 0.16 mmol, 87.3 eq.) were carefully weighed in a dry headspace vial, sealed airtight, evacuated and backfilled with argon three times. Degassed dioxane (0.18 mL) was added and the mixture was stirred at room temperature to dissolve. A stock solution of AIBN in dioxane (5 μ L, $6 \cdot 10^{-5}$ mg ml⁻¹) was added and the vial was placed in a preheated oil bath at 65 °C. After stirring at 65 °C for 17 h, the vial was opened to air and the polymer was precipitated from ice-cold methanol. After filtration, the pale yellow polymer was dried *in vacuo* (75 mg, 67%).

¹H-NMR (600 MHz, CDCl₃): δ (ppm) = 8.36 (s, 2H, Ar-**H**), 8.1.7 (s, 2H, Ar-**H**), 7.96 (s, 0.35H Ar-**H**), 7.86 (s, 2H, Ar-**H**), 7.76 (s, 1H, Ar-**H**), 7.68-7.50 (m, 4H, Ar-**H**), 7.31 (s, 2H, Ar-**H**), 7.23-6.96 (m, 5H, Ar-**H**), 6.79 (s, 0.14H, Ar-**H**), 4.51 (s, 2H, Ar-CH₂-O), 3.73 (s, 2H, CH₂-O, NH-CH₂), 3.37 (s, 2H, CH₂-O), 2.32-1.64 (m, 10H, CH₂-CH₂), 1.44 (s, 5H, CH₂/CH₃), 1.18 (s, 5H, CH₂/CH₃), 1.00-0.60 (m, 4H, CH₂-CH₂).

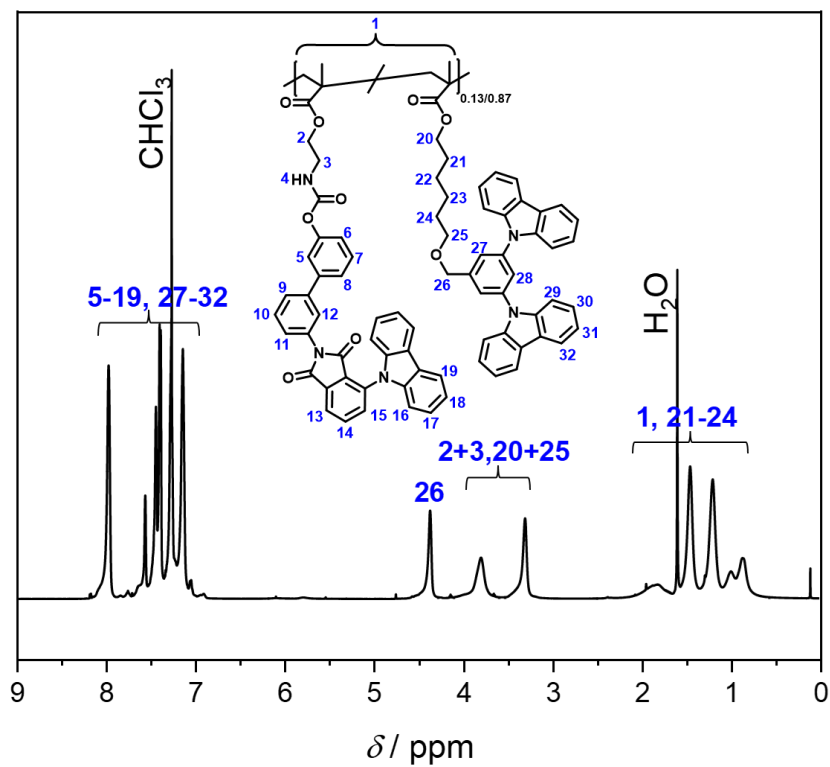


Figure S20: $^1\text{H-NMR}$ spectrum of **P4** in CDCl_3 (600 MHz).

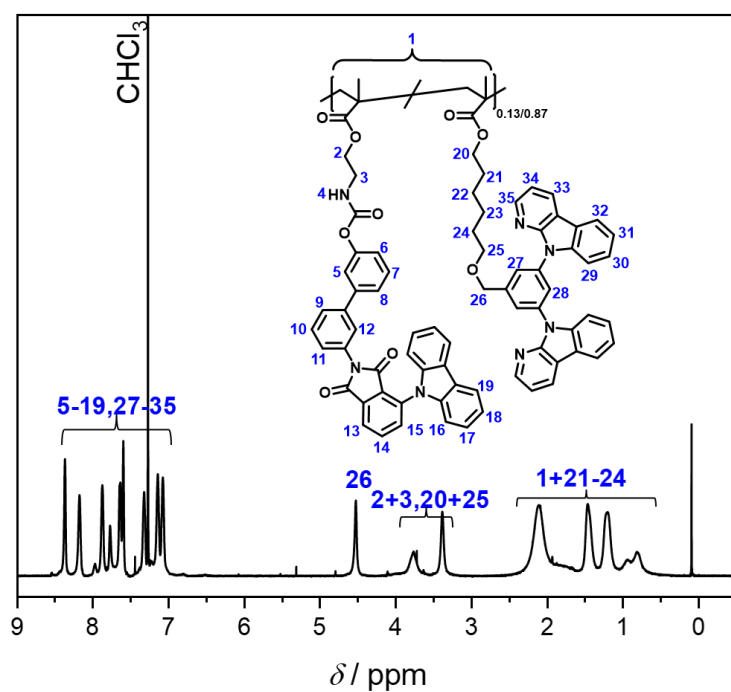


Figure S21: $^1\text{H-NMR}$ spectrum of **P5** in CDCl_3 (600 MHz).

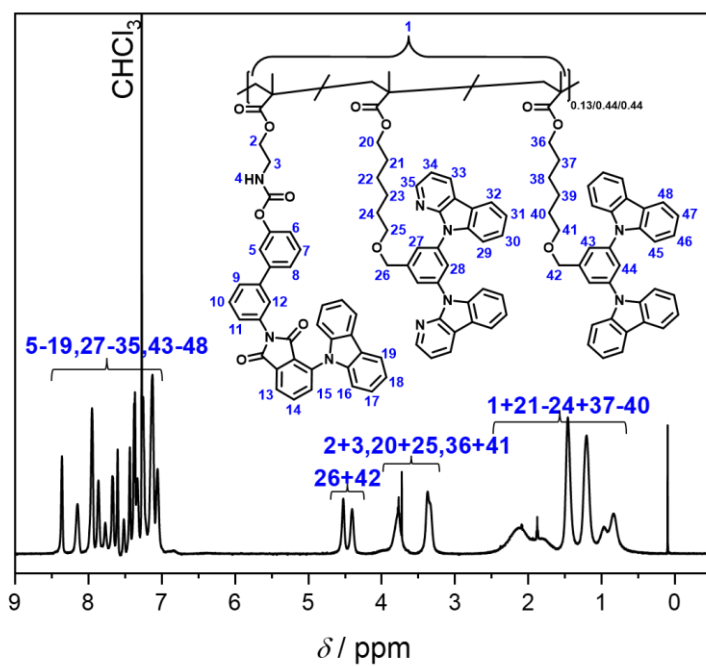


Figure S22: $^1\text{H-NMR}$ spectrum of **P6** in CDCl_3 (600 MHz).

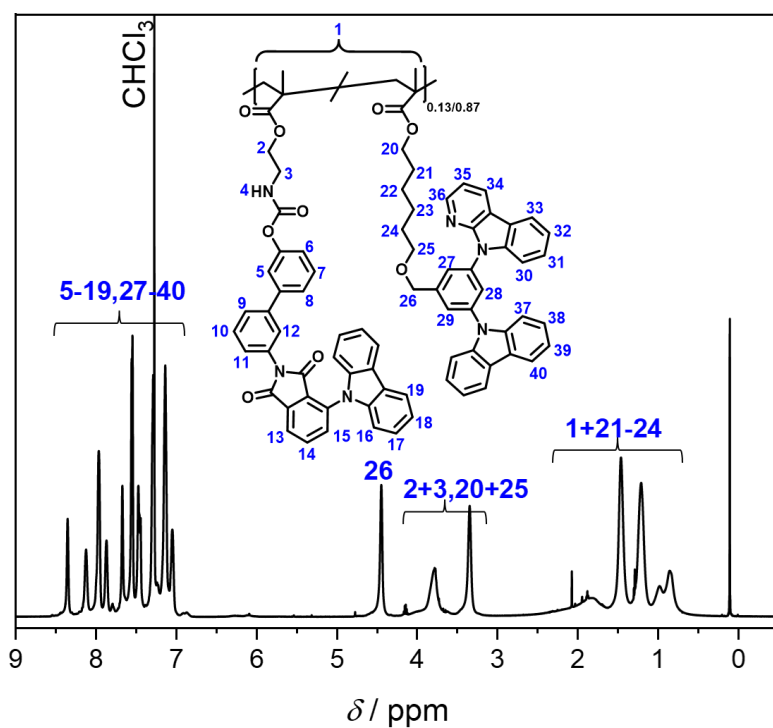


Figure S23: $^1\text{H-NMR}$ spectrum of **P7** in CDCl_3 (600 MHz).

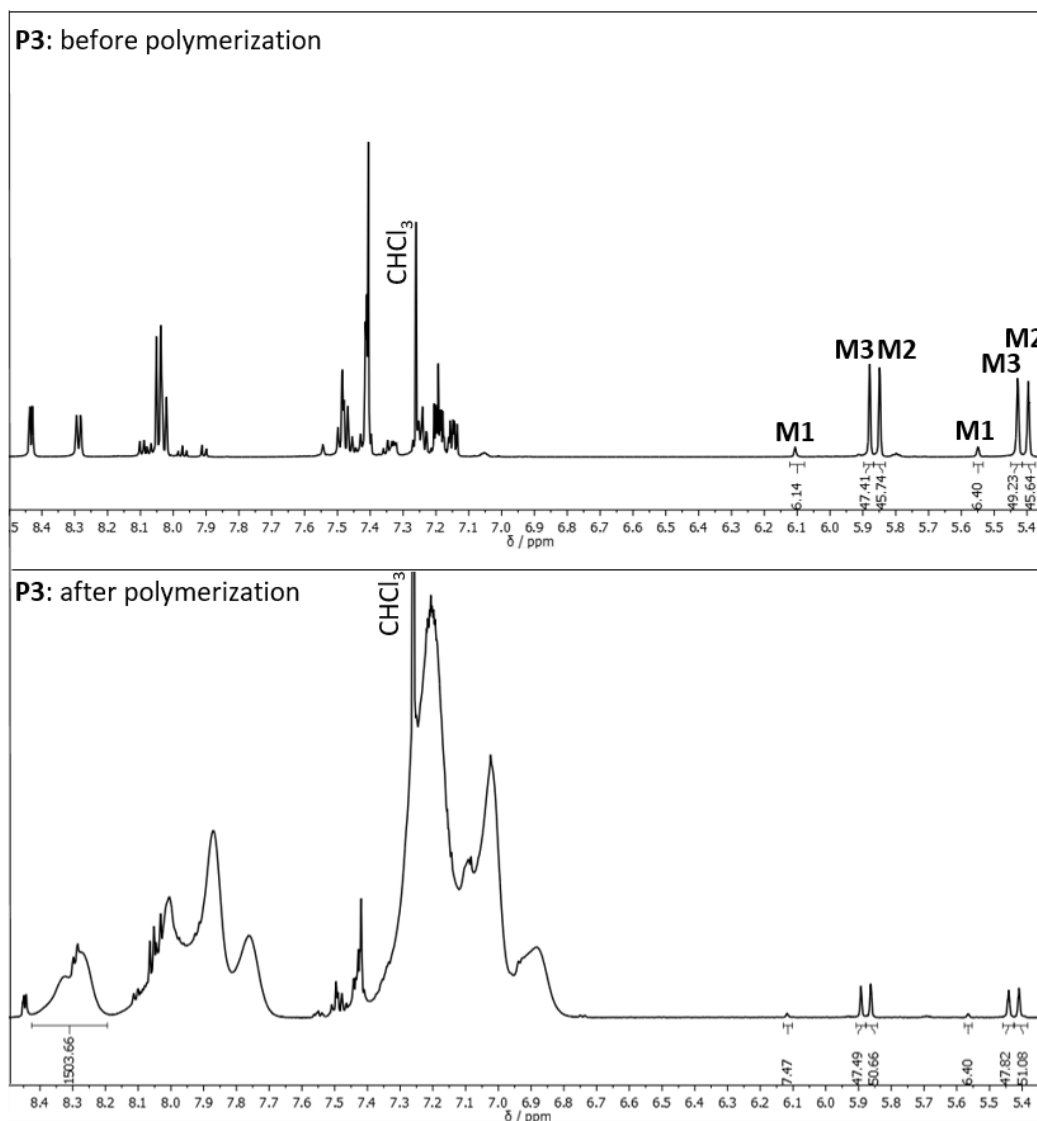


Figure S24: ¹H-NMR spectra (zoom) of the reaction mixture of **P3** before (top) and after (bottom) free radical polymerization (CDCl₃, 600 MHz).

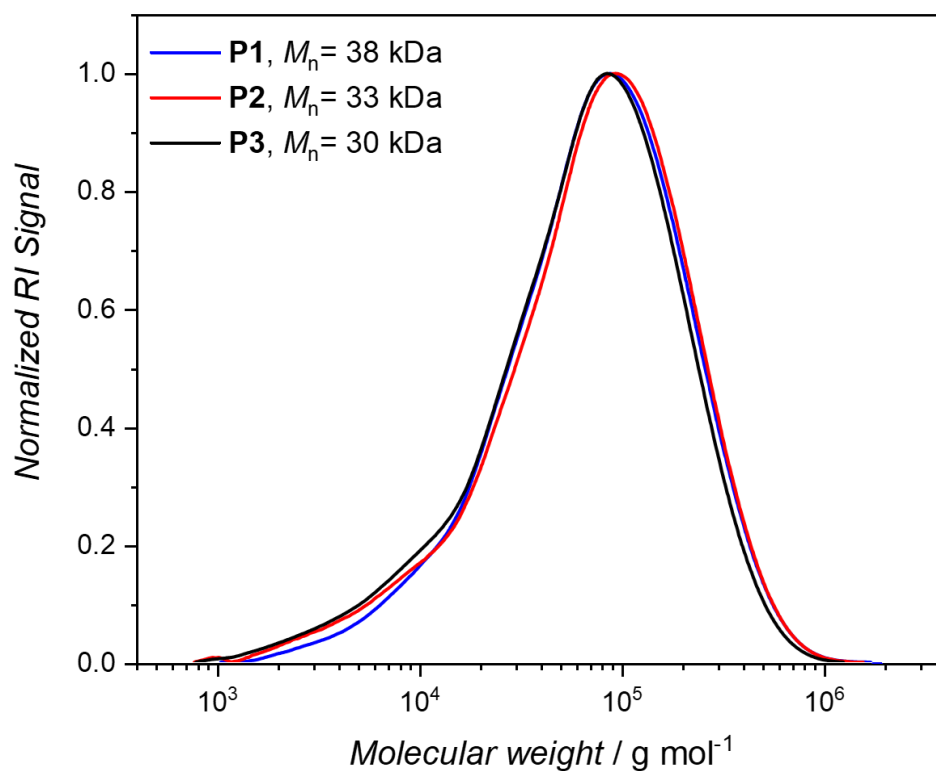


Figure S25: Size exclusion chromatograms of **P1-3** in THF (PMMA calibration).

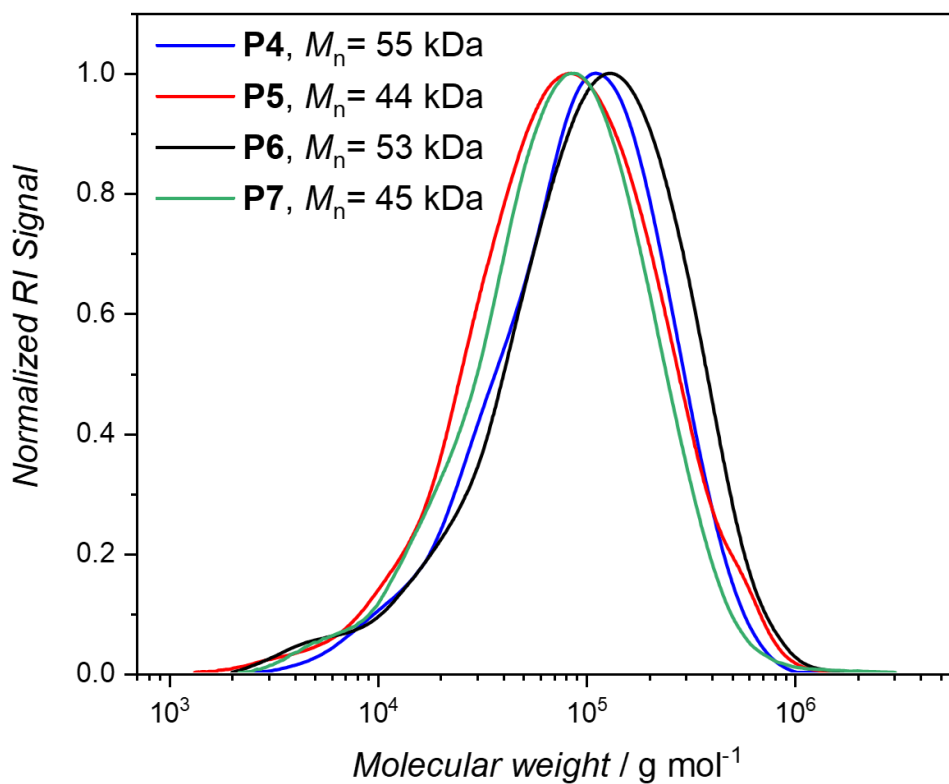


Figure S26: Size exclusion chromatograms of **P4-7** in THF (PMMA calibration).

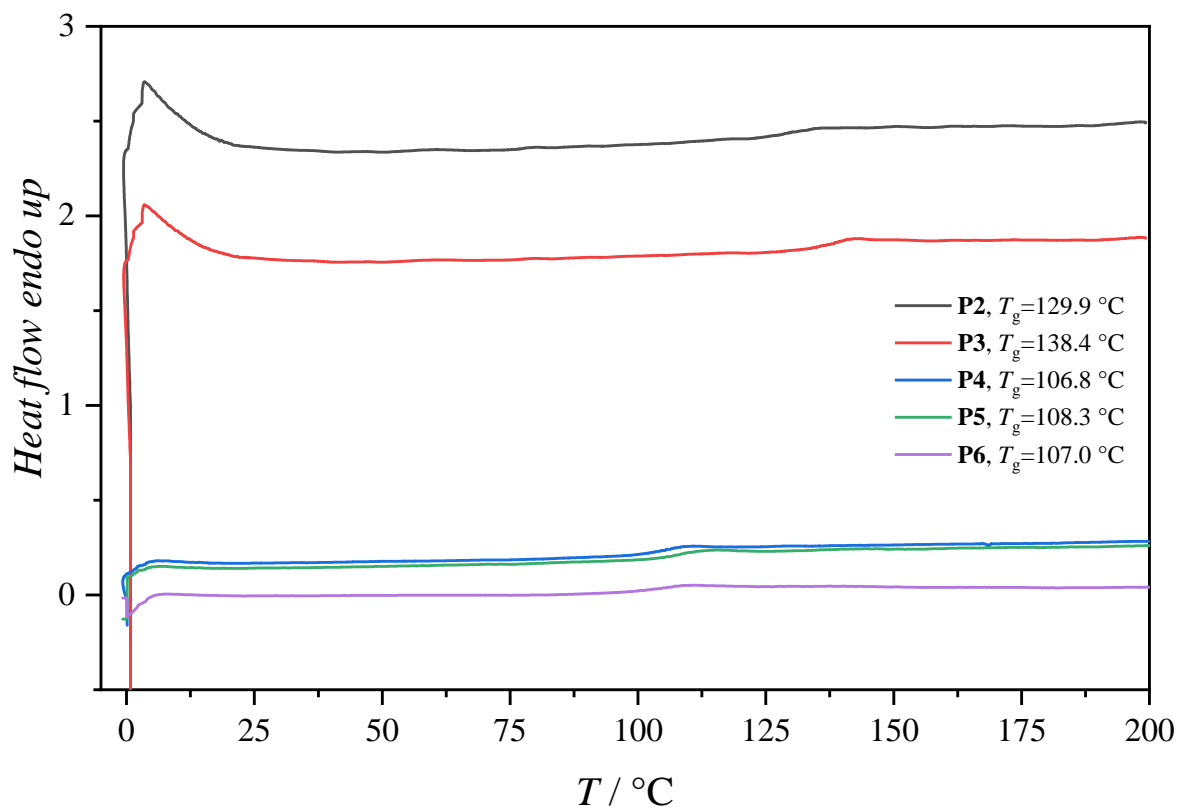


Figure S27: Differential Scanning Calorimetry curves of polymers **P2-6** with glass transition temperatures measured under nitrogen atmosphere (heating rate 10 K/min).

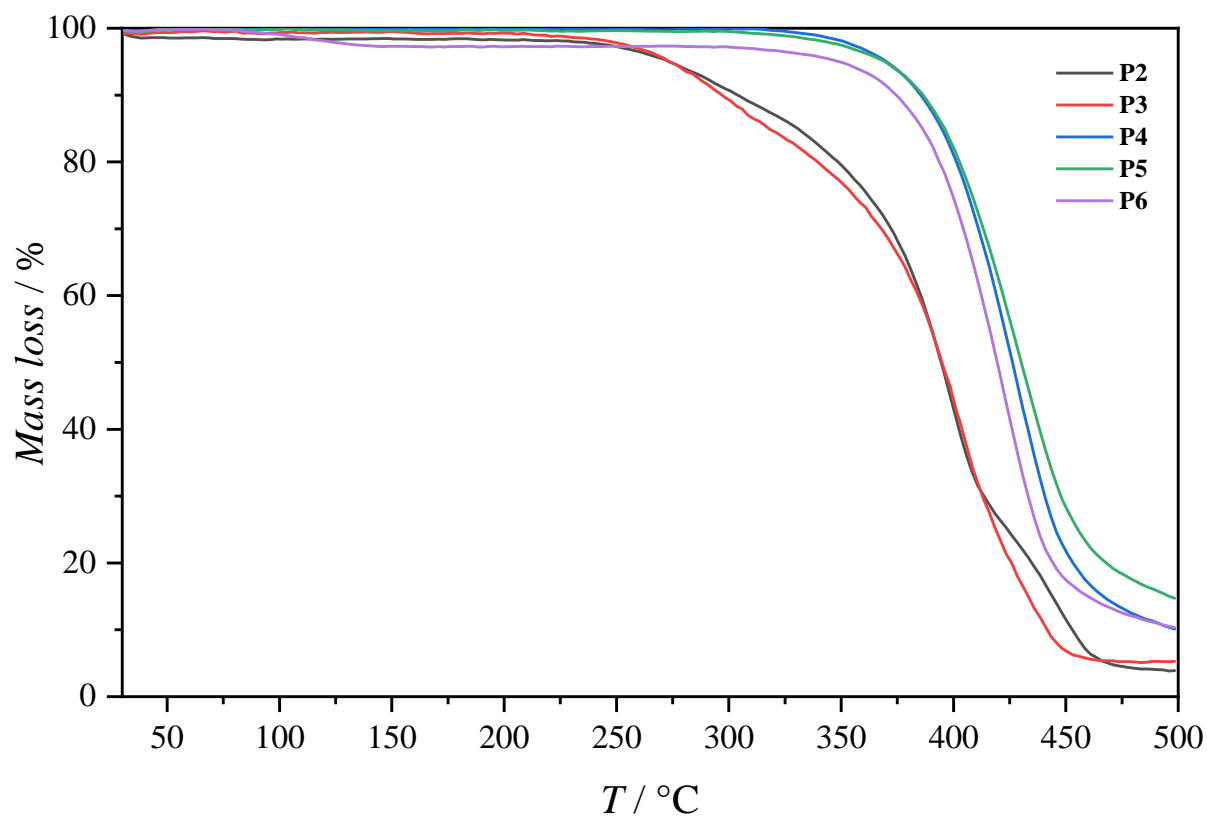
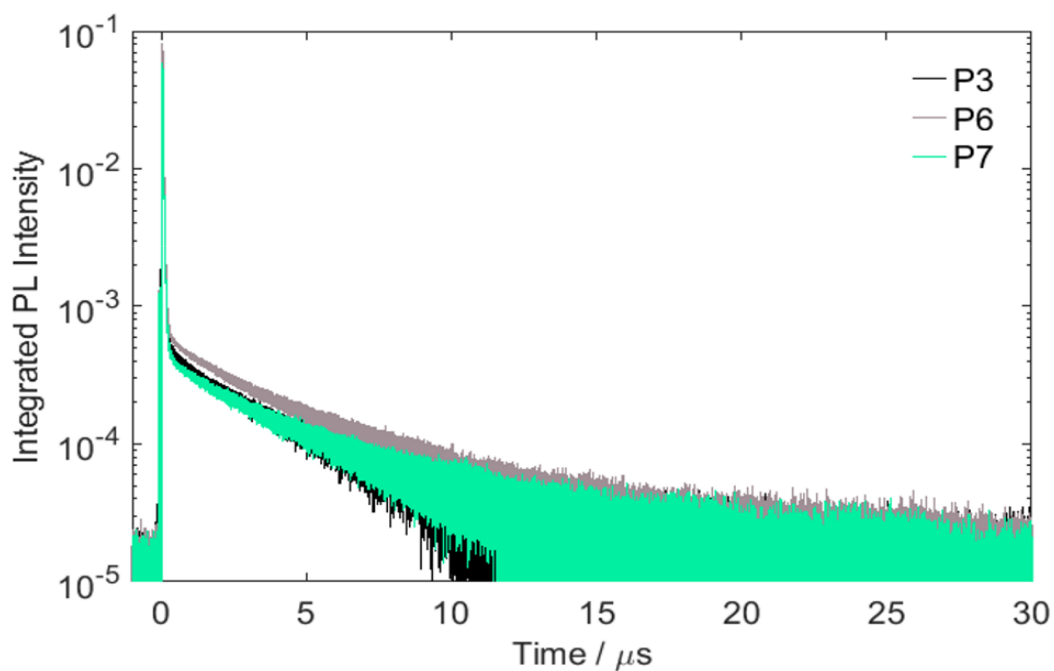


Figure S28: Thermal Gravimetric Analysis curves of polymers **P2-6** under nitrogen atmosphere (heating rate 10 K/min).

Table S1: S1, T1 and ΔE_{ST} for **P3**, **P6** and **P7**.

Material	S1 (eV)	T1 (eV)	ΔE_{ST} (eV)
P3	2.792	2.749	0.043
P6	2.805	2.780	0.025
P7	2.811	2.786	0.025

**Figure S29:** TRPL of P3, P6 and P7 at 300 K, excited at 325 nm.**Table S2:** Energy levels of the frontier orbitals of the unfunctionalized monomers reported in literature.

Monomer	Reference	HOMO / eV	LUMO / eV
M2	PEMA (from ref. ⁶)	-5.61	-2.1
M4	mCP (from ref. ⁷)	-5.9	-2.4
M5	CzCb1 (from ref. ⁸)	-6.06	-2.55
M6	NmCP1 (from ref. ⁹)	-5.61	-2.35

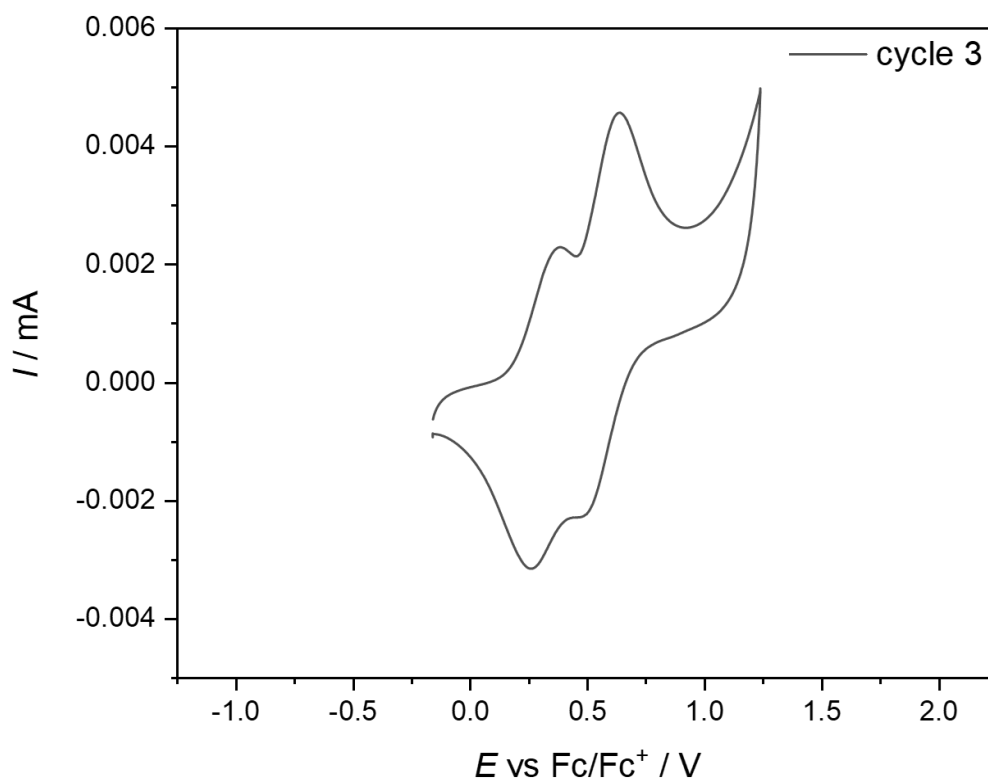


Figure S30: Cyclic voltammogram of **P2** referenced to the internal standard ferrocene (0.1 mM in DCM, $n\text{Bu}_4\text{NPF}_6$ (0.1 M) as electrolyte, working electrode: platinum, scan rate 100 mVs^{-1}).

Table S3: HOD average current densities at a range of voltages for **P3**, **P6** and **P7**.

Voltage (V)	P3 (mA cm^{-2})	P6 (mA cm^{-2})	P7 (mA cm^{-2})
-5	3.5 ± 1.2	2.0 ± 0.9	5.4 ± 6.7
-2	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1
0	$1.6 \pm 0.4 \times 10^{-5}$	$1.3 \pm 1.4 \times 10^{-5}$	$1.0 \pm 0.7 \times 10^{-5}$
2	0.4 ± 0.2	0.2 ± 0.1	0.3 ± 0.1
5	2.1 ± 0.9	1.1 ± 0.5	1.2 ± 0.5

References:

- 1 N. Greenham, I. Samuel, G. Hayes, R. Phillips, Y. Kessener, S. Moratti, A. Holmes, R. Friend *Chem. Phys. Lett.*, **1995**, *241*, 89-96.
- 2 Puttock, E. V.; Ranasinghe, C. S. K.; Babazadeh, M.; Jang, J.; Huang, D. M.; Tsuchiya, Y.; Adachi, C.; Burn, P. L.; Shaw, P. E. *Macromolecules* **2020**, *53*, 10375–10385.
- 3 Kunz, S. V.; Cole, C. M.; Welle, A.; Shaw, P. E.; Sonar, P.; Thobes, N.-P.; Baumann, T.; Yambem, S. D.; Blasco, E.; Blinco, J. P., Barner-Kowollik, C., *Macromolecules* **2019**, *52*, 9105–9113.
- 4 Huang, Q.; Mei, X.; Xie, Z.; Wu, D.; Yang, S.; Gong, W.; Chi, Z.; Lin, Z.; Ling, Q, *J. Mater. Chem. C* **2019**, *7* (9), 2530–2534.
- 5 Rungta, P.; Tsyalkovsky, V.; Huebner, C. F.; Bandera, Y. P.; Foulger, S. H., *Synth. Met.* **2010**, *160* (23–24), 2486–2493.
- 6 Laha, J. K.; Petrou, P.; Cuny, G. D., *J. Org. Chem.* **2009**, *74* (8), 3152–3155.
- 7 McFarlane, T. M.; Zdyrko, B.; Bandera, Y.; Worley, D.; Klep, O.; Jurča, M.; Tonkin, C.; Foulger, S. H.; Vilčáková, J.; Saha, P. Pflieger, J., *J. Mater. Chem. C* **2018**, *6* (10), 2533–2545.
- 8 Ossila. mCP <https://www.ossila.com/products/mcp> (accessed: May, 2021).
- 9 Im, Y.; Lee, J. Y., *Chem. Commun.* **2013**, *49* (53), 5948–5950.
- 10 Im, Y.; Lee, H. L.; Lee, J. Y, *Org. Electron.* **2019**, *70*, 48–54.