Supplemental Information

for

Hole-transporting side-chain polystyrenes based on TCTA with tuned glass transition and optimized electronic properties

Felix R. P. Limberg,[a] Arunas Miasojedovas,[b] Patrick Pingel,[a] Felix Reisbeck,[a] Silvia Janietz,[a] Andrew P. Monkman,[b] Hartmut Krüger*[a]

Email: hartmut.krueger@iap.fraunhofer.de

[a]Fraunhofer Institute for Applied Polymer Research, Wissenschaftspark Golm,
Geiselbergstr. 69, D-14476 Potsdam, Germany

[b]Physics Department, University of Durham South Road, Durham DH1 3LE, UK

Additional graphs

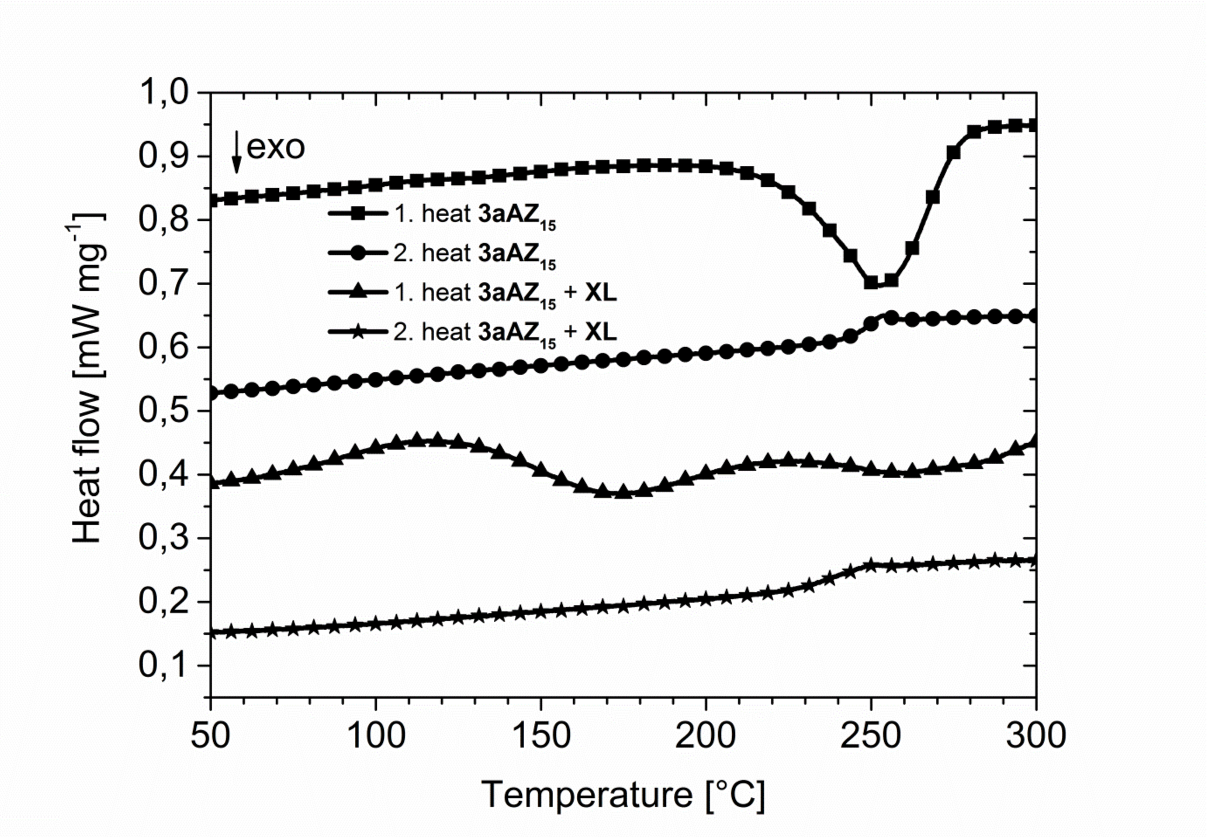

Fig. S1 Differential-scanning calorimetry scans of polymer **3aAZ$_{15}$** with and without **XL**. The first and second heating cycles are displayed

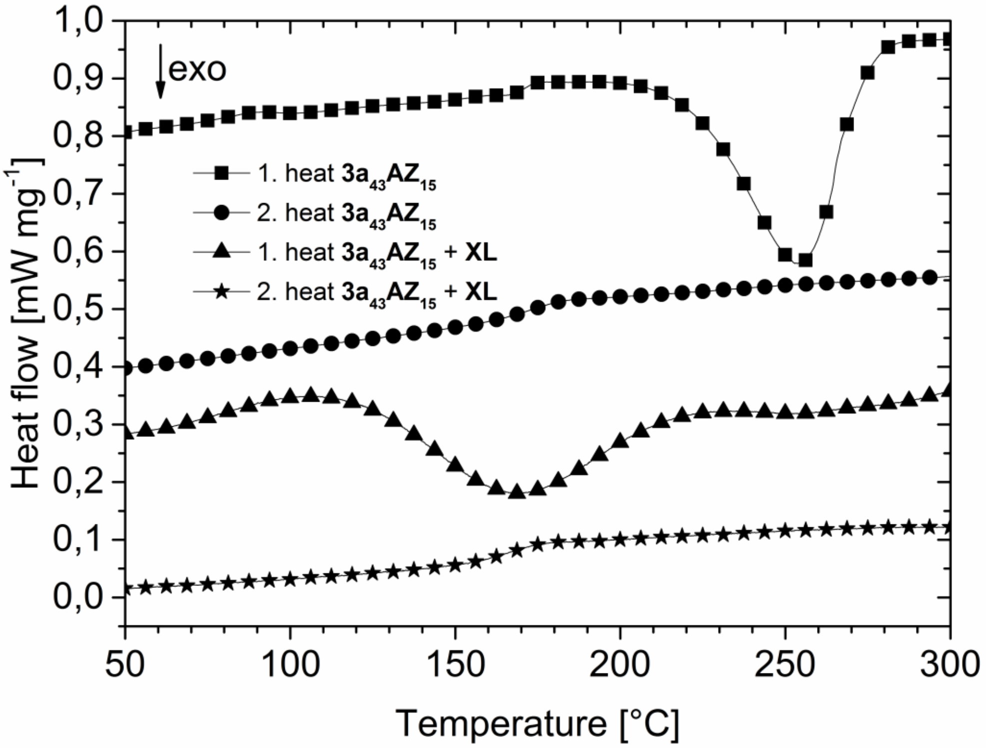

Fig. S2 Differential-scanning calorimetry scans of polymer **$3a_{43}AZ_{15}$** with and without **XL**. The first and second heating cycles are displayed

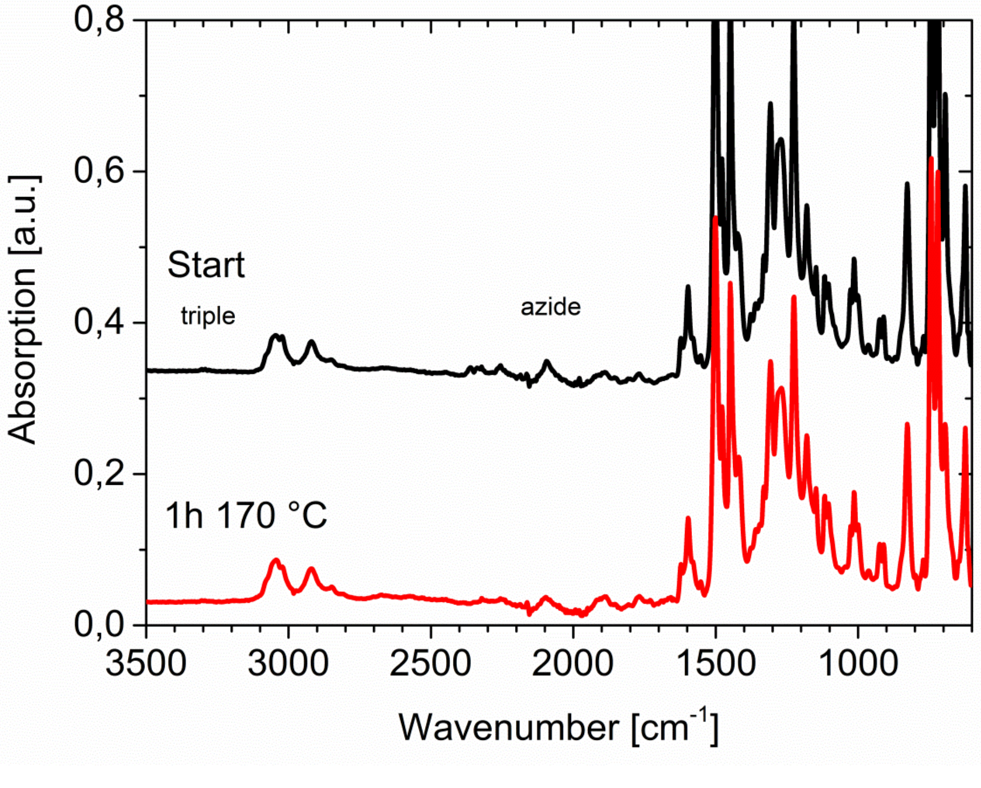

Fig. S3 ATR-FTIR scans of polymer **3aAZ$_{15}$** with **XL** at 170 °C. The first spectrum is recorded at t = 0 min and the second at t = 1 hour (25 % azide consumption).

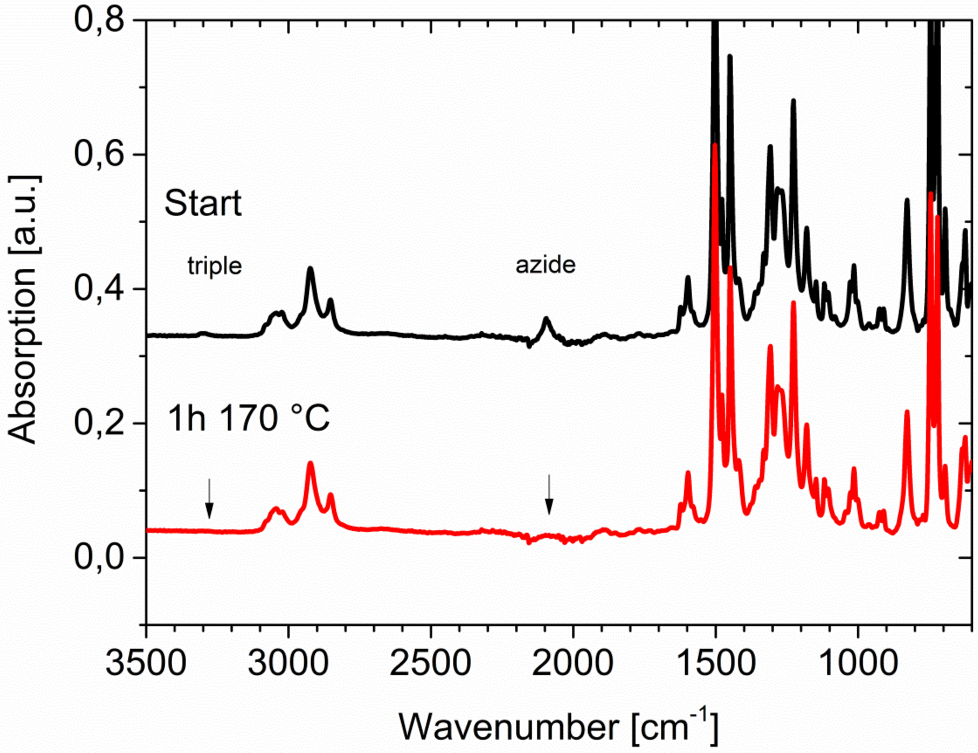

Fig. S4 ATR-FTIR scans of polymer **3a$_{43}$AZ$_{15}$** with **XL** at 170 °C. The first spectrum is recorded at t = 0 min and the second at t = 1 hour (100 % azide consumption).

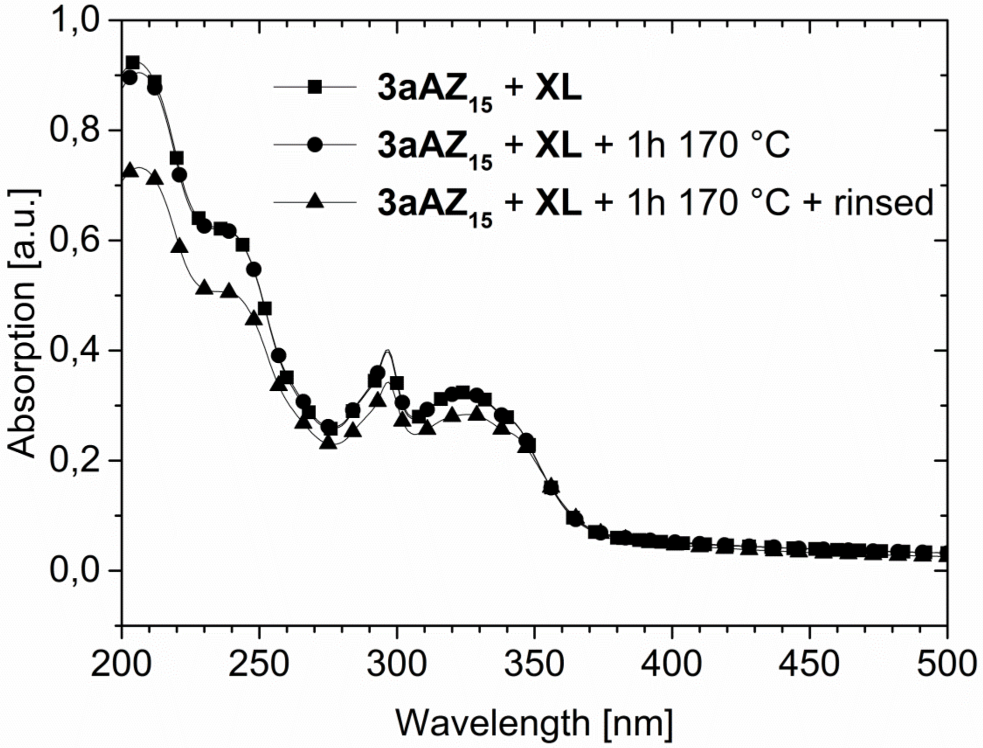

Fig. S5 UV/Vis scans of **3aAZ$_{15}$** (with **XL)** polymer films on quartz-substrates**.** Spectra were recorded before and after crosslinking at 170 °C for 40 Minutes and after a rinsing-step with toluene.

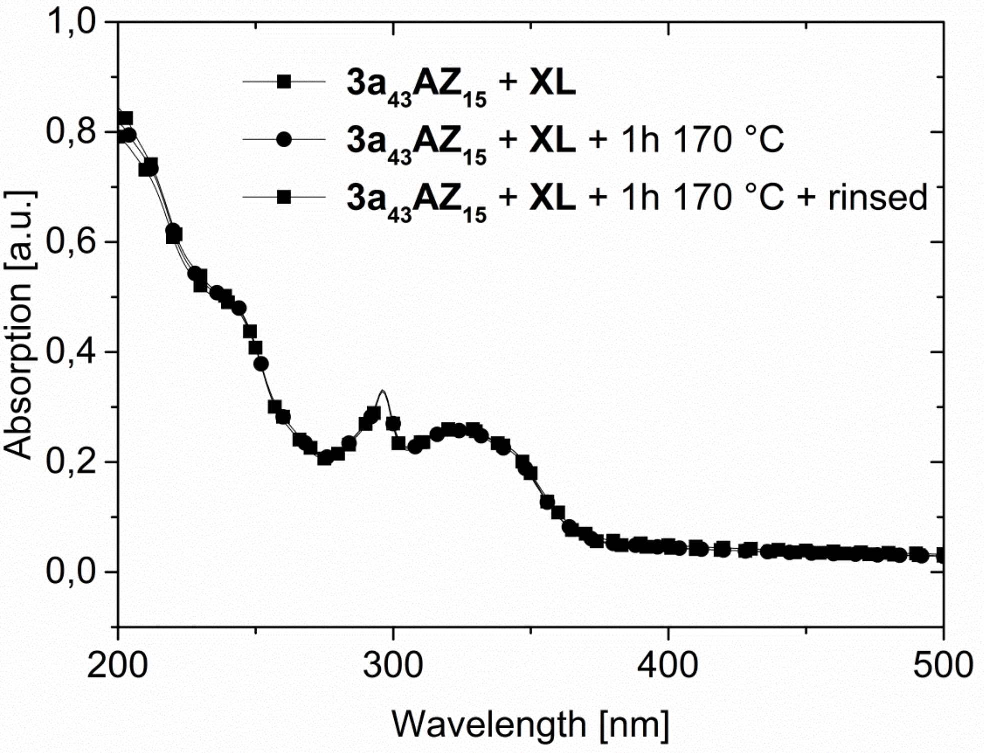

Fig. S6 UV/Vis scans of **$3a_{43}AZ_{15}$** (with **XL)** polymer films on quartz-substrates**.** Spectra were recorded before and after crosslinking at 170 °C for 40 Minutes and after a rinsing-step with toluene.

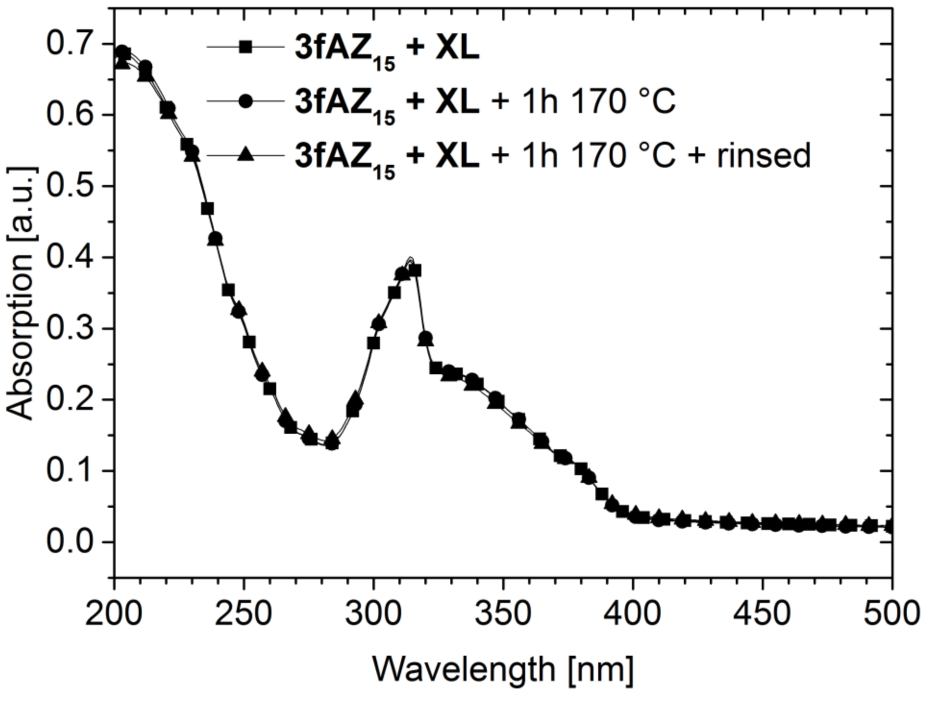

Fig. S7 UV/Vis scans of **$3a_{43}AZ_{15}$** (with **XL)** polymer films on quartz-substrates**.** Spectra were recorded before and after crosslinking at 170 °C for 40 Minutes and after a rinsing-step with toluene.

Materials and Methods

All materials were obtained from *Sigma-Aldrich Chemical Company* (Munich, Germany), *Acros Organics* (Geel, Belgium), Lumtec (Taiwan) or *Synthon Acmari Chemie* (Wolfen, Germany) and used without any further purification unless otherwise stated. Silica gel 60 (Merck) (Darmstadt, Germany) was used in the separation and purification of compounds by column chromatography. Separations with gradient column chromatography were obtained using a *TELEDYNE ISCO CombiFlash Rf* system. Solvents for column chromatography, recrystallization, and purification were received from *Th. Geyer GmbH* (Berlin, Germany) and *J. T. Baker* (Deventer, Netherlands). Dry solvents were received from *Sigma-Aldrich Chemical Company*, stored over molecular sieve and sealed under an inert atmosphere. All reactions were done in inert atmosphere in argon or nitrogen by using common Schlenk techniques.

Thin layer chromatography was done with POLYGRAM SIL G/UV_{254} TLC-plates.

High-resolution (500 MHz) ^{1}H-NMR and ^{13}C-NMR (125 MHz) spectra were recorded on a *UNITY INOVA 500* spectrometer from Varian at room temperature.

Size exclusion chromathography (SEC) has been performed at 25 °C in THF to determine the molecular weights using a combination of Separation module 2695e (Waters), Dual λ Absorbance Detector 2487, and Refractive Index Detector 2414. A SEC-column set with 5 µm high crosslinked porous polystyrene-divinylbenzene matrix from Waters (7.8 mm x 300 mm; Styragel Guard column, HR3, HR4, HR5) for separation and narrowly distributed, linear polystyrene standards from Agilent Polymer Laboratories (Varian) for weight determination were used. Polymer solutions (2 mg l^{-1} in THF) were stirred for 24 h at 22 °C and filtered (1 µm PTFE) before 2 x 100 µl of the solution was injected. Molecular weights were calculated with the Empower software from Waters.

Isothermal ATR-FTIR Spectroscopy was done with a Digilab Scimitar FTS2000 FTIR Spectrometer, connected to a Golden Gate Mk II ATR-system (Specac) coupled with a heating stage (max. 200 °C). Dissolved samples were drop-casted onto the pre-heated sample stage, the first measurement was started after complete solvent evaporation (around 3 seconds) and additional spectra were recorded in certain time-intervals until completed reaction.

Thermal analysis of 3-5 mg per polymer sample was performed with differential scanning calorimetry (DSC) using a Netzsch DSC 204 Phoenix with a scanning rate of 10 K min^{-1}. The glass transition was obtained from the second heating cycle.

UV/Vis and photoluminescence spectra: About 30 nm thick films were spun from toluene solutions (concentrations 5 g l^{-1}, 1000 rpm) onto silica glass substrates. Absorption was measured using a Cary 5000 UV/Vis spectrometer.

Photoelectron spectroscopy was performed using a Riken Keiki AC-2 at a power of 50 nW. Investigated polymer layers were prepared by drop-casting onto glass substrates. All measurements were carried out at least three times.

CV measurements: Voltammograms were obtained with an EG&G Parc model 273 potentiostat. A three electrode configuration was used in an undivided cell, which consisted of a glassy carbon electrode (area 0.5 cm^2) onto which the polymer film was deposited, a platinum mesh as the counter electrode, and an Ag/AgCl (3 M NaCl and sat. AgCl) reference electrode. 0.1 M Bu_4NBF_4 in acetonitrile was used as electrolyte and prior to each measurement the electrochemical cell has been deoxygenated with nitrogen. The electrochemical cell was calibrated by the use of a ferrocene standard (-4.8 eV against standard hydrogen electrode)[1–3] and the ferrocene half-wave potential has been determined to be 512 mV for this assembly. 1 wt% polymer solutions in $CHCl_3$ were prepared and 5 µl were deposited on the glassy carbon electrodes. The prepared electrodes were kept under vacuum and dried at 60 °C for 2 h. The oxidation potential was determined by the peak potential of measured polymer films as marked in **Fig. S7**. The corresponding HOMO levels were calculated using **equation S1** and **S2**.

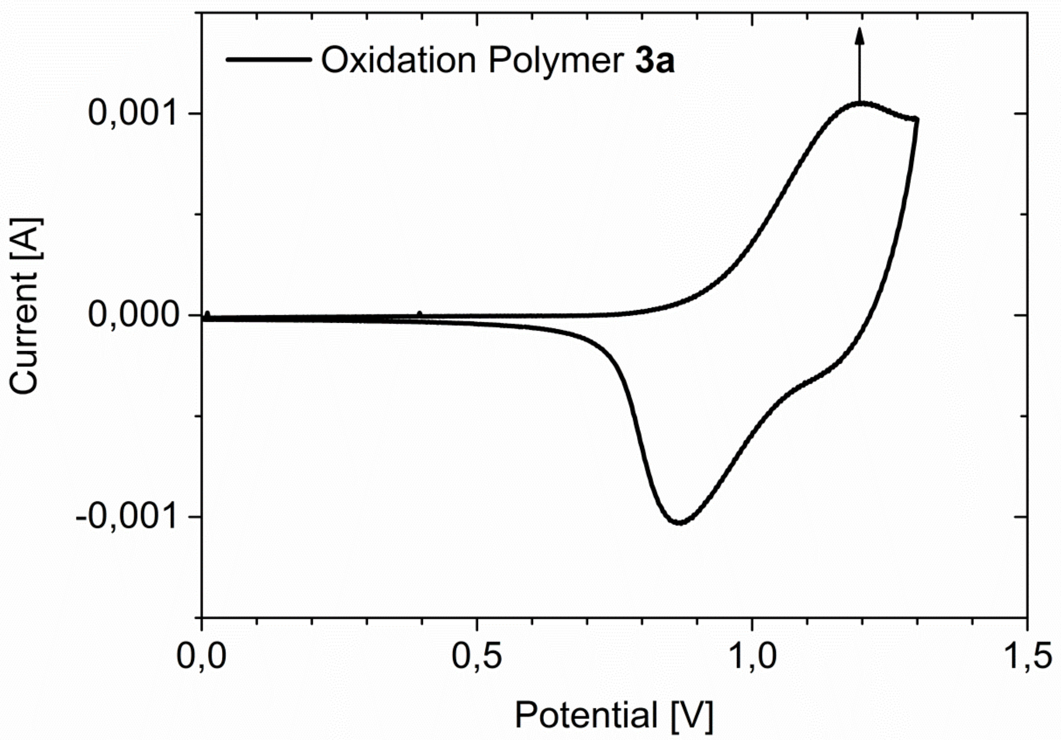

Fig. S7 Exemplary cyclic voltammogram of polymer **3a.** The arrow marks the read out oxidation potential.

$$E^{OX}_{Fc/Fc^{+}}(\boldsymbol{Polymer}) = -\left(E^{OX}_{Ag/AgCl}(\boldsymbol{Polymer}) - E_{1/2}(Ferrocene)\right)V \qquad \textbf{(S1)}$$

$$E^{HOMO}(\boldsymbol{Polymer}) = -\left(4.8 + E^{OX}_{Fc/Fc^{+}}(\boldsymbol{Polymer})\right)eV \qquad \textbf{(S2)}$$

Hole-only current diode fabrication: Hole-only devices were prepared on patterned ITO glass substrates. After thorough cleaning of the substrates in an ultrasonic bath with Mucasol^{TM} detergent, deionized water, acetone, and isopropanol, a ca. 50-nm-thick layer of PEDOT:PSS (Clevios^{TM} P VP AI4083) was spin-coated under ambient conditions. All further preparation and measurements were done in inert nitrogen atmosphere. The PEDOT:PSS layer underwent annealing at 200°C for 5 minutes. 80-100 nm-thick polymer layers were then prepared by spin-coating from 15 g/l solutions in toluene, followed by annealing at 185°C for 5 minutes. Dissolution of polymer **3b** was assisted by slight heating prior to spin-coating. A 75 nm-thick Al cathode was evaporated to define 9 mm^2-sized pixels. Electrical characterization has been performed repeatedly on at least three different pixels to ensure the repeatability and representativeness of the results.

Multilayer OLED fabrication: Patterned ITO glass substrates were cleaned and coated with a PEDOT:PSS layer as described in the above section. Further preparation and measurements were conducted in inert N_2 atmosphere. For the devices with additional hole-transport layer (HTL), the HTL material was spin-coated from a 4 g/l toluene solution at 2000 rpm. The resulting layer thickness was ca. 15-20 nm. Crosslinking of the HTL was performed by heating at 170°C for 40 min. Then, the ternary emission layer blend (Ir-based emitter:co-Host-001:polymer **9a** 0.5:2:1 per wt.[4] was spin-coated from a 20 g/l solution in toluene at 2000 rpm, followed by heating at 180°C for 30 min. The cathode materials were evaporated under high vacuum conditions: 5 nm Ba at ca. 0.5 Å/sec, followed by 100 nm Ag at ca. 5 Å/sec.

PL transients where recorded exciting films at 355 nm with 150 ps length YAG laser (EKSPLA) pulses and collecting light using Jobin Yvon spectrograph and gated iCCD camera (Stanford Computer Optics) by exponentially increasing delayed and integration times as described in ref.[5] This allows to record up to 10 orders of magnitude in time and intensity of the PL decay.[6]

Synthesis

Synthesis of 4,4'-(propane-2,2-diyl)bis((prop-2-yn-1-yloxy)benzene) XL

This reaction was performed according to a literature procedure.[7] A suspension of 4,4'-(propane-2,2-diyl)diphenol (6.90 g, 30.0 mmol, 1.00 equiv), potassium carbonate (10.4 g, 75.0 mmol, 2.50 equiv) and 3-Bromo-1-propyne (5.70 g, 75.0 mmol, 2.50 equiv) in *anhydrous* acetone (90 mL), was refluxed for 24 hours. After completion (judged by TLC) the solvent is removed *in vacuo* and the reaction mixture suspended in EtOAc, washed with brine (3 × 50 mL), dried over Na_2SO_4 and filtered. The filtrate was adsorbed on silica and purification by flash chromatography on silica with a gradient of *n*-heptane and EtOAc afforded the product (8.60 g, 29.0 mmol, 98 % yield) as a colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.14 (m, 4H), 6.94 – 6.86 (m, 4H), 4.67 (d, *J* = 2.9 Hz, 4H), 2.53 (t, *J* = 2.4 Hz, 2H), 1.66 (s, 6H).

Synthesis of 1-(azidomethyl)-4-vinylbenzene

This reaction was performed according to a literature procedure.[8] A suspension of 1-(chloromethyl)-4-vinylbenzene (5.00 g, 32.8 mmol, 1.00 equiv) and sodium azide (6.40 g, 98.7 mmol, 3.00 equiv) in *anhydrous* DMF (40 mL), was stirred for 24 hours at RT. After completion (judged by TLC) the solvent is removed *in vacuo* and the reaction mixture suspended in Et_2O, washed with brine (3 × 50 mL), dried over Na_2SO_4 and filtered. The filtrate was adsorbed on silica and purification by flash chromatography on silica with a gradient of *n*-heptane and EtOAc afforded the product (4.80 g, 30.2 mmol, 92 % yield) as pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.2, 1.9 Hz, 2H), 7.26 (dd, J = 8.2, 1.6 Hz, 2H), 6.71 (ddd, J = 17.7, 10.9, 2.1 Hz, 1H), 5.76 (ddd, J = 17.6, 2.5, 0.9 Hz, 1H), 5.27 (ddd, J = 10.9, 2.4, 0.9 Hz, 1H), 4.30 (s, 2H).

Synthesis of 2-methoxy-9H-carbazole

This reaction was performed according to modified literature procedures.[9,10] To a suspension of copper(I)iodide (7.7 g, 40.6 mmol, 2.0 equiv) and 2-bromo-9H-carbazole (5.0 g, 20.3 mmol, 1.0 equiv) in *anhydrous* DMF (22 mL), sodium methanolate (61 mL, 267 mmol, 13 equiv) was added. The reaction mixture was stirred for 4 hours at 120 °C. After completion (judged by TLC) the reaction mixture was filtrated through celites and directly adsorbed on silica. Purification by chromatography on silica ($CHCl_3$ 100 %) afforded the product (3.9 g, 19.5 mmol, 96 % yield) as a white solid.

^{1}H NMR (500 MHz, DMF-d_7) δ 11.11 (s, 1H), 8.03 – 7.97 (m, 3H), 7.54 – 7.42 (m, 1H), 7.36 – 7.24 (m, 1H), 7.12 (td, J = 7.4, 0.9 Hz, 1H), 7.06 (d, J = 2.3 Hz, 1H), 6.80 (dd, J = 8.5, 2.3 Hz, 1H), 3.87 (s, 3H).

^{13}C NMR (126 MHz, DMF-d_7) δ 159.19, 141.75, 140.40, 124.25, 123.31, 120.91, 119.29, 118.75, 116.82, 110.73, 107.88, 94.65, 55.19.

Synthesis of 3,6-diethoxy-9*H*-carbazole

This reaction was performed according to modified literature procedures.[9,10] To a suspension of copper(I)iodide (11.7 g, 61.6 mmol, 4.0 equiv) and 3,6-dibromo-9H-carbazole (5.0 g, 15.4 mmol, 1.0 equiv) in *anhydrous* DMF (16 mL), sodium ethanolate (57 mL, 154 mmol, 10 equiv) was added. The reaction mixture was stirred for 3 hours at 120 °C. After completion (judged by TLC) the reaction mixture was filtrated through celites and directly adsorbed on silica. Purification by flash chromatography on silica with a gradient of *n*-hexane and ethyl acetate afforded the product (3.0 g, 11.7 mmol, 76 % yield) as a yellow solid.

^{1}H NMR (500 MHz, THF-d_8) δ 9.81 (s, 1H), 7.50 (d, *J* = 2.4 Hz, 2H), 7.24 (dd, *J* = 8.7, 0.6 Hz, 2H), 6.94 (dd, *J* = 8.7, 2.5 Hz, 2H), 4.09 (q, *J* = 6.9 Hz, 4H), 1.40 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, THF-d_8) δ 153.62 , 136.84 , 124.54 , 116.20 , 111.97 , 104.27 , 64.65 , 15.53 .

Synthesis of 3,6-dibutoxy-9*H*-carbazole

This reaction was performed according to modified literature procedures.[9,10] To a suspension of sodium hydride (11.1 g (98 %), 460 mmol, 10 equiv) in *anhydrous* DMF (50 mL), *anhydrous* butanol (57 mL, 154 mmol, 10 equiv) was added at RT until the gas evolution stopped. After an additional hour of stirring the solution was poured to a suspension of copper(I)iodide (35 g, 18,0 mmol, 4.0 equiv) and 3,6-dibromo-9H-carbazole (15.0 g, 46,2 mmol, 1.0 equiv) in *anhydrous* DMF (50 mL). The reaction mixture was stirred for 1 hour at 120 °C. After completion (judged by TLC) the reaction mixture was poured over ice water (100 mL). The precipitate was filtrated and hereafter dissolved in THF and filtered again, to remove any residual inorganics. The resulting filtrate was adsorbed on silica and purification by flash chromatography on silica with a gradient of *n*-hexane and ethyl acetate afforded the product (12.3 g, 39.5 mmol, 86 % yield) as a white solid.

^{1}H NMR (500 MHz, THF-d_8) δ 9.81 (s, 1H), 7.51 (d, *J* = 2.4 Hz, 2H), 7.23 (dd, *J* = 8.8, 0.5 Hz, 2H), 6.94 (dd, *J* = 8.7, 2.4 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 4H), 1.88 – 1.75 (m, 4H), 1.65 – 1.47 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.17, 135.35, 123.89, 115.89, 111.54, 104.12, 68.89, 31.74, 19.50, 14.09.

Synthesis of 2,7-dibutoxy-9*H*-carbazole

This reaction was performed according to modified literature procedures.[9,10] To a suspension of sodium hydride (11.1 g (98 wt%), 460 mmol, 10 equiv) in *anhydrous* DMF (50 mL), *anhydrous* butanol (57 mL, 154 mmol, 10 equiv) was added at RT until the gas evolution stopped. After an additional hour of stirring the solution was poured to a suspension of copper(I)iodide (35 g, 18.0 mmol, 4.0 equiv) and 3,6-dibromo-*9H*-carbazole (15.0 g, 46.2 mmol, 1.0 equiv) in *anhydrous* DMF (50 mL). The reaction mixture was stirred for 1 hour at 120 °C. After completion (judged by TLC) the reaction mixture was poured over ice water (100 mL). The precipitate was filtrated and hereafter dissolved in THF and filtered again, to remove any residual inorganics. The resulting filtrate was adsorbed on silica and purified by flash chromatography on silica using DCM as eluent afforded the product (11.0 g, 35.2 mmol, 77 % yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 2H), 6.87 (d, *J* = 2.2 Hz, 2H), 6.81 (dd, *J* = 8.5, 2.2 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 4H), 1.88 – 1.76 (m, 4H), 1.58 – 1.48 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, THF) δ 158.65, 142.51, 120.30, 118.31, 108.38, 96.23, 68.49, 32.63, 20.30, 14.31.

2-((2-ethylhexyl)oxy)-9*H*-carbazole

This reaction was performed according to a modified literature procedure.[11] To a suspension of K_2CO_3 (15.0 g, 109 mmol, 4.0 equiv) and 9*H*-carbazol-2-ol (5.0 g, 27.3 mmol, 1.0 equiv) in *anhydrous* DMF (100 mL), 3-(bromomethyl)heptane (48 mL, 53 g, 270 mmol, 10 equiv) was added. The reaction mixture was stirred for 20 hours at 100 °C. After completion (judged by TLC) the reaction mixture was washed, filtered and the solvent of the filtrate removed *in vacuo.* Purification by flash chromatography on silica (toluene 100 %) afforded the product (6.22 g, 21 mmol, 77 % yield) as a pale yellow solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 24.1, 8.1 Hz, 2H), 7.88 (s, 1H), 7.41 – 7.29 (m, 2H), 7.20 (ddt, *J* = 7.7, 6.6, 1.2 Hz, 1H), 6.93 – 6.82 (m, 2H), 3.92 (dd, *J* = 5.8, 2.0 Hz, 2H), 1.78 (p, *J* = 6.2 Hz, 1H), 1.64 – 1.28 (m, 8H), 0.94 (dt, *J* = 18.4, 7.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.02, 140.95, 139.59, 124.54, 123.71, 121.05, 119.60, 119.55, 117.12, 110.41, 108.96, 95.50, 71.09, 39.62, 30.74, 29.28, 24.07, 23.23, 14.27, 11.31.

1-(4-vinylphenyl)decan

This reaction was performed according to a literature procedure.[12] The yield was 55 % over three steps.

Activation of copper bronze

This reaction was performed according to a modified literature procedure. The copper bronze needs to be freshly activated prior Ullmann coupling. Long storage-periods led to reduction of product yields. A suspension of dendritic copper (2.00 g, 31.5 mmol, 1.0 equiv) and iodine (0.40 g, 3.15 mmol, 0.1 equiv) were stirred for ten min. at RT. The solvent was filtered off and the residual solid was washed with acetone and subsequently stirred for 20 min. in *conc.* HCl (20 mL) and acetone (20 mL). After filtration the solid was dried *in vacuo* with additional heating. The resulting copper bronze was kept under inert conditions until it was used as a catalyst.

Synthesis of 4-(bis(4-(9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1a

This reaction was performed according to a literature procedure.[13] A suspension of 9*H*-carbazole (17.65 g, 106 mmol, 3.0 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (18.0 g, 34.3 mmol, 1.0 equiv), copper bronze (15.2 g, 240 mmol, 6.0 equiv),18-Crown-6 (3.27 g, 12.0 mmol, 0.3 equiv) and K_2CO_3 (61.14 g, 443 mmol, 13 equiv) in *anhydrous o*-DCB (120 mL), was stirred for 60 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with toluene and filtered through celites. The solvent of the filtrate was removed *in vacuo* and column chromatography with toluene as eluent afforded the product (16.51 g, 80 %) as pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.18 (d, *J* = 7.7 Hz, 4H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 4H), 7.55 – 7.44 (m, 12H), 7.36 – 7.30 (m, 6H).

Synthesis of 4-(bis(4-(2-methoxy-9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1b

This reaction was performed according to a modified literature procedure.[13] A suspension of 2-methoxy-9H-carbazole (3.80 g, 19.3 mmol, 2.2 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (4.60 g, 8.76 mmol, 1.0 equiv), copper bronze (1.20 g, 18.4 mmol, 2.1 equiv),18-Crown-6 (0.46 g, 1.8 mmol, 0.2 equiv) and K_2CO_3 (3.6 g, 26.3 mmol, 3.0 equiv) in *anhydrous o*-DCB (c=0.5 mol·L^{-1}), was stirred for 48 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with toluene and filtered. The solvent of the filtrate was removed *in vacuo* and subsequent recrystallization out of toluene gives the product (2.74 g, 47%) as pale yellow solid.

^{1}H NMR (500 MHz, THF-d_8) δ 9.88 (s, 1H), 8.05 – 8.00 (m, 4H), 7.87 – 7.81 (m, 2H), 7.69 – 7.64 (m, 4H), 7.60 – 7.55 (m, 4H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.23 – 7.16 (m, 2H), 6.96 (d, *J* = 2.2 Hz, 2H), 6.89 (dd, *J* = 8.5, 2.2 Hz, 2H), 3.83 (s, 6H).

^{13}C NMR (126 MHz, THF-d_8) δ 190.12 , 160.56 , 153.69 , 146.42 , 143.09 , 142.01 , 135.33 , 132.02 , 131.92 , 129.71 , 129.22 , 128.95 , 128.04 , 126.08 , 125.35 , 124.76 , 122.00 , 121.72 , 120.92 , 120.16 , 118.26 , 110.26 , 109.07 , 95.13 , 55.79 .

Synthesis of 4-(bis(4-(2-((2-ethylhexyl)oxy)-9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1c

This reaction was performed according to a modified literature procedure.[13] A suspension of 2-((2-ethylhexyl)oxy)-9*H*-carbazole (9.30 g, 31.4 mmol, 2.4 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (6.90 g, 13.1 mmol, 1.0 equiv), copper bronze (1.70 g, 27.5 mmol, 2.1 equiv), 18-crown-6 (0.70 g, 2.60 mmol, 0.2 equiv) and K_2CO_3 (5.40 g, 39.3 mmol, 3.0 equiv) in *anhydrous o*-dichlorobenzene (40 mL), was stirred for 24 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with toluene and filtered through celites. The solvent of the filtrate was removed *in vacuo* and column chromatography with toluene as eluent afforded the product (10.21 g, 90 %) as pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.06 (ddd, *J* = 7.7, 1.2, 0.7 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.89 – 7.83 (m, 2H), 7.64 – 7.58 (m, 4H), 7.54 – 7.48 (m, 4H), 7.44 (dt, *J* = 8.2, 0.9 Hz, 2H), 7.37 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 6.97 (d, *J* = 2.2 Hz, 2H), 6.94 (dd, *J* = 8.5, 2.2 Hz, 2H), 4.01 – 3.88 (m, 4H), 1.77 (p, *J* = 6.1 Hz, 2H), 1.64 – 1.22 (m, 14H), 0.95 (t, *J* = 7.5 Hz, 6H), 0.93 – 0.85 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.62 , 159.16 , 152.98 , 145.14 , 142.23 , 141.08 , 138.01 , 134.53 , 131.67 , 130.46 , 129.17 , 128.41 (d, *J* = 11.0 Hz), 127.15 , 125.43 , 124.79 , 123.82 , 121.14 (d, *J* = 6.3 Hz), 120.32 , 119.64 , 117.37 , 109.60 , 108.60 , 95.41 , 71.14 , 39.65 , 30.73 , 29.29 , 24.01 , 23.21 , 21.61 , 14.27 , 11.34 , 0.15 .

Synthesis of 4-(bis(4-(2,7-dibutoxy-9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1d

This reaction was performed according to a modified literature procedure.[13] A suspension of 2,7-dibutoxy-9*H*-carbazole (10.0 g, 32.0 mmol, 2.4 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (7.00 g, 13.0 mmol, 1.0 equiv), copper bronze (2.00 g, 32.0 mmol, 2.4 equiv), 18-crown-6 (0.85 g, 3.20 mmol, 0.24 equiv) and K_2CO_3 (5.40 g, 39.0 mmol, 3.0 equiv) in *anhydrous* *o*-dichlorobenzene (60 mL), was stirred for 24 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with toluene and filtered through celites. The filtrate was washed with brine, dried over Na_2SO_4, filtered and the solvent removed *in vacuo*. Column chromatography with a gradient of *n*-hexane and toluene as eluent afforded the product (10.40 g, 90 %) as a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 4H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.59 – 7.55 (m, 4H), 7.51 – 7.46 (m, 4H), 7.34 – 7.30 (m, 2H), 6.92 (d, *J* = 2.2 Hz, 4H), 6.89 (dd, *J* = 8.5, 2.2 Hz, 4H), 4.04 (t, *J* = 6.5 Hz, 8H), 1.87 – 1.73 (m, 8H), 1.59 – 1.46 (m, 8H), 0.98 (t, *J* = 7.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.52 , 157.85 , 152.85 , 145.03 , 142.32 , 134.32 , 131.54 , 130.38 , 129.04 , 128.28 (d, *J* = 11.2 Hz), 126.98 , 125.30 , 121.10 , 120.09 , 117.54 , 107.96 , 95.66 , 68.27 , 31.51 , 19.34 , 13.93 .

Synthesis of 4-(bis(4-(3,6-diethoxy-9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1e

This reaction was performed according to a modified literature procedure.[13] A suspension of 3,6-diethoxy-9*H*-carbazole (2.30 g, 8.94 mmol, 2.2 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (2.13 g, 4.06 mmol, 1.0 equiv), copper bronze (0.54 g, 8.53 mmol, 2.1 equiv), 18-crown-6 (0.21 g, 0.81 mmol, 0.2 equiv) and K_2CO_3 (1.68 g, 12.2 mmol, 3.0 equiv) in *anhydrous o*-dichlorobenzene (13 mL), was stirred for 24 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with THF and filtered through celites, washed with brine (3×100 mL), dried over Na_2SO_4 and filtrated again. The solvent was removed *in vacuo* and subsequent recrystallization out of toluene gives the product (2.33 g, 74%) as yellow solid.

^{1}H NMR (500 MHz, THF-d_8) δ 9.87 (s, 1H), 7.87 – 7.75 (m, 2H), 7.65 – 7.61 (m, 8H), 7.56 – 7.48 (m, 4H), 7.38 (d, *J* = 8.9 Hz, 4H), 7.33 – 7.26 (m, 2H), 7.23 – 7.15 (m, 2H), 7.01 (dd, *J* = 8.9, 2.5 Hz, 4H), 4.13 (q, *J* = 7.0 Hz, 8H), 1.43 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (126 MHz, THF-d_8) δ 190.3, 154.83 , 153.94 , 145.84 , 138.59 , 137.07 , 136.20 , 132.00 , 131.76 , 129.83 , 129.07 , 128.77 , 128.32 , 126.20 , 125.08 , 121.44 , 116.56 , 111.37 , 104.64 , 64.84 , 21.65 , 15.58 .

Synthesis of 4-(bis(4-(3,6-dibutoxy-9*H*-carbazol-9-yl)phenyl)amino)benzaldehyde 1f

This reaction was performed according to a modified literature procedure.[13] A suspension of 3,6-dibutoxy-9*H*-carbazole (9.00 g, 29.0 mmol, 2.4 equiv), 4-(bis(4-iodophenyl)amino)benzaldehyde (6.30 g, 29.0 mmol, 1.0 equiv), copper bronze (1.60 g, 25.0 mmol, 2.1 equiv), 18-crown-6 (0.63 g, 2.40 mmol, 0.20 equiv) and K_2CO_3 (5.00 g, 36.0 mmol, 3.0 equiv) in *anhydrous o*-dichlorobenzene (30 mL), was stirred for 24 hours at 200 °C. After completion (judged by TLC) the reaction mixture was diluted with toluene and filtered through celites. The solvent was removed *in vacuo* and subsequent recrystallization out of toluene afforded the product (9.00 g, 84%) as bright yellow solid.

^{1}H NMR (500 MHz, THF-d_8) δ 9.86 (s, 1H), 7.85 – 7.77 (m, 2H), 7.66 – 7.60 (m, 8H), 7.57 – 7.49 (m, 4H), 7.38 (d, *J* = 8.9 Hz, 4H), 7.32 – 7.26 (m, 2H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 4H), 4.09 (t, *J* = 6.5 Hz, 8H), 1.85 – 1.79 (m, 8H), 1.64 – 1.49 (m, 8H), 1.02 (t, *J* = 7.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.60, 153.74, 153.09, 144.53, 136.16, 135.20, 131.66, 130.11, 127.93, 127.28, 123.92, 120.48, 115.93, 110.69, 104.11, 68.90, 31.72, 19.51, 14.10.

Synthesis of *N,N*-bis(4-(9*H*-carbazol-9-yl)phenyl)-4-vinylaniline 2a

This reaction was performed according to a literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (15.0 g, 42.0 mmol, 1.6 equiv) and potassium *tert*-butoxide (4.90, 44.0 mmol, 1.6 equiv) in *anhydrous* THF (500 mL) was stirred for two hours at 0 °C. 4-(bis(4-(9H-carbazol-9-yl)phenyl)amino)benzaldehyde **1a** (2.2 g, 3.33 mmol, 1.0 equiv) dissolved in *anhydrous* THF (300 mL) was added at this temperature. The reaction mixture was stirred for 4 hours at this temperature. After completion (judged by TLC) the reaction mixture was washed with brine (3×500 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. Purification by flash chromatography on silica using toluene as eluent afforded the product (12.6 g, 20.9 mmol, 78 % yield) as a white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.25 (d, *J* = 7.7 Hz, 4H), 7.60 (d, *J* = 8.7 Hz, 4H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.48–7.43 (m, 8H), 7.40(d, *J* = 8.7 Hz, 4H), 7.32–7.23 (m, 6H), 6.75 (dd, *J* = 17.6,11.0 Hz, 1H,), 5.79 (d, *J* = 17.6 Hz, 1H,), 5.24 (d, *J* = 11.0 Hz, 1H)

Synthesis of 4-(2-methoxy-9*H*-carbazol-9-yl)-*N*-(4-(2-methoxy-9*H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline 2b

This reaction was performed according to a modified literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (1.37 g, 3.84 mmol, 1.2 equiv) and *n*-BuLi (1.6M, 2.29 mL, 3.66 mmol, 1.1 equiv) in *anhydrous* THF (80 mL) was stirred for 30 minutes at 0 °C. 4-(bis(4-(2-methoxy-9H-carbazol-9-yl)phenyl)amino)benzaldehyde **1b** (2.2 g, 3.33 mmol, 1.0 equiv) dissolved in *anhydrous* THF (55 mL) was added at this temperature. The reaction mixture was stirred for 4 hours at this temperature. After completion (judged by TLC) the reaction mixture was diluted with THF (150 mL) and washed with brine (3×150 mL). The organic phase was separated, dried over anhydrous Na2SO4, filtrated and concentrated *in vacuo.* Purification by flash chromatography on silica using toluene as eluent afforded the product (1.20 g, 1.80 mmol, 55 % yield) as a white solid.

^{1}H NMR (500 MHz, THF-d_8) δ 8.06 – 7.96 (m, 4H), 7.60 – 7.51 (m, 4H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.46 – 7.43 (m, 4H), 7.36 (dt, *J* = 8.2, 0.9 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.21 – 7.16 (m, 3H), 6.92 (d, *J* = 2.2 Hz, 2H), 6.87 (dd, *J* = 8.5, 2.2 Hz, 2H), 6.74 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.18 (dd, *J* = 11.0, 1.0 Hz, 1H), 3.81 (s, 6H).

^{13}C NMR (126 MHz, THF-d_8) δ 161.00, 148.43, 148.10, 143.74, 142.66, 138.95, 137.72, 135.01, 133.92, 130.18, 129.42, 129.40, 128.92, 126.56, 126.44, 126.29, 125.73, 125.11, 122.13, 121.20, 120.56, 118.60, 113.52, 110.73, 109.51, 95.45, 56.23, 22.01.

Synthesis of 4-(2-((2-ethylhexyl)oxy)-9*H*-carbazol-9-yl)-*N*-(4-(2-((2-ethylhexyl)oxy)-9*H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline 2c

This reaction was performed according to a modified literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (12.3 g, 34.4 mmol, 3.0 equiv) and potassium *tert*-butoxide (3.70 g, 33.3 mmol, 2.9 equiv) in *anhydrous* THF (100 mL) was stirred for 2 hours at 0 °C. 4-(bis(4-(2-((2-ethylhexyl)oxy)-9H-carbazol-9-yl)phenyl)amino)benzaldehyde **1c** (10.0 g, 11.6 mmol, 1.0 equiv) dissolved in *anhydrous* THF (40 mL) was added at this temperature. The reaction mixture was stirred for 3 hours at this temperature. After completion (judged by TLC) the reaction mixture was washed with brine (3×150 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. Purification by flash chromatography on silica (*n*-hexane/CH_2Cl_2 2:1) afforded the product (9.33 g, 10.9 mmol, 93 % yield) as a white solid.

^{1}H NMR (500 MHz CDCl$_3$) δ 8.04 (dt, *J* = 7.7, 1.0 Hz, 2H), 8.00 (dd, *J* = 8.4, 0.6 Hz, 2H), 7.53 – 7.39 (m, 12H), 7.35 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.28 – 7.23 (m, 2H), 6.98 – 6.84 (m, 4H), 6.74 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.74 (dd, *J*

= 17.6, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.93 (dd, *J* = 5.7, 1.2 Hz, 4H), 1.76 (hept, *J* = 6.1 Hz, 2H), 1.63 – 1.12 (m, 16H), 1.12 – 0.58 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.99, 146.78, 146.44, 142.34, 141.19, 136.06, 133.36, 132.33, 128.04, 127.53, 125.05, 124.83, 124.54, 123.55, 120.96, 119.93, 119.42, 117.06, 113.12, 109.55, 108.49, 95.13, 70.96, 39.54, 30.62, 29.17, 23.91, 23.09, 14.15, 11.23, 0.03.

Synthesis of 4-(2,7-dibutoxy-9*H*-carbazol-9-yl)-*N*-(4-(2,7-dibutoxy-9*H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline 2d

This reaction was performed according to a modified literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (11.0 g, 33.6 mmol, 2.7 equiv) and potassium *tert*-butoxide (3.40 g, 30.2 mmol, 2.7 equiv) in *anhydrous* THF (100 mL) was stirred for 2 hours at 0 °C. 4-(bis(4-(2,7-dibutoxy-*9H*-carbazol-9-yl)phenyl)amino)benzaldehyde **1d** (10.0 g, 11.2 mmol, 1.0 equiv) dissolved in *anhydrous* THF (200 mL) was added at this temperature. The reaction mixture was stirred for 0.5 hours at this temperature. After completion (judged by TLC) the reaction mixture was washed with brine (3×150 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. Purification by flash chromatography on silica using toluene as eluent afforded the product (9.40 g, 10.6 mmol, 94 % yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (dt, *J* = 8.3, 0.8 Hz, 4H), 7.60 – 7.32 (m, 10H), 7.33 – 7.26 (m, 2H), 6.99 – 6.80 (m, 8H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.74 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.25 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.03 (t, *J* = 6.5 Hz, 8H), 1.87 – 1.73 (m, 8H), 1.56 – 1.47 (m, 8H), 0.98 (td, *J* = 7.4, 0.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 207.13, 157.93, 146.88, 146.57, 142.67, 136.20, 133.53, 132.37, 129.18, 128.16, 127.67, 125.27, 124.93, 120.14, 117.51, 108.10, 95.65, 68.37, 31.65, 31.09, 19.48, 14.07.

Synthesis of 4-(3,6-diethoxy-9*H*-carbazol-9-yl)-*N*-(4-(3,6-diethoxy-9*H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline 2e

This reaction was performed according to a modified literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (4.13 g, 11.6 mmol, 4.1 equiv) and potassium *tert*-butoxide (1.27 g, 11.4 mmol, 4.0 equiv) in *anhydrous* THF (80 mL) was stirred for 2 hours at 0 °C. 4-(bis(4-(3,6-diethoxy-*9H*-carbazol-9-yl)phenyl)amino)benzaldehyde **1e** (2.2 g, 2.82 mmol, 1.0 equiv) dissolved in *anhydrous* THF (40 mL) was added at this temperature. The reaction mixture was stirred for 1 hour at this temperature. After completion (judged by TLC) the reaction mixture was diluted with THF (150 mL) and washed with brine (3×150 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. Purification by flash chromatography on silica (toluene 100 %) afforded the product (1.81 g, 2.33 mmol, 83 % yield) as a white solid.

^{1}H NMR (500 MHz, THF-d_8) δ 7.61 (d, J = 2.4 Hz, 4H), 7.54 – 7.49 (m, 4H), 7.48 – 7.43 (m, 2H), 7.43 – 7.38 (m, 4H), 7.34 (d, J = 8.8 Hz, 4H), 7.30 – 7.21 (m, 2H), 6.99 (dd, J = 8.8, 2.5 Hz, 4H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.72 (dd, J = 17.6, 1.0 Hz, 1H), 5.17 (dd, J = 10.9, 1.0 Hz, 1H), 4.13 (q, J = 6.9 Hz, 8H), 1.43 (t, J = 7.0 Hz, 12H).

^{13}C NMR (126 MHz, THF-d_8) δ 154.69 , 148.27 , 147.22 , 137.31 , 134.27 (d, J = 6.0 Hz), 128.55 , 126.10 , 125.56 , 124.90 , 116.52 , 112.91 , 111.35 , 104.61 , 64.84 , 15.59 .

Synthesis of 4-(3,6-dibutoxy-9*H*-carbazol-9-yl)-*N*-(4-(3,6-dibutoxy-9*H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline 2f

This reaction was performed according to a modified literature procedure.[13] A suspension of methyltriphenylphosphonium bromide (9.60 g, 26.9 mmol,3.0 equiv) and potassium *tert*-butoxide (2.90 g, 26.1 mmol, 2.9 equiv) in a mixture of *anhydrous* 1,4-dioxane (200 mL) and toluene (100 mL) was stirred for 2 hours at 0 °C. 4-(bis(4-(3,6-dibutoxy-*9H*-carbazol-9-yl)phenyl)amino)benzaldehyde **1f** (8.00 g, 8.97 mmol, 1.0 equiv) dissolved in *anhydrous* toluene (200 mL) was added at this temperature. The reaction mixture was stirred for 30 minutes at this temperature. After completion (judged by TLC) the reaction mixture was washed with brine (3×300 mL). The organic phase was separated, dried over anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. Purification by flash chromatography on silica (*n*-heptane/toluene 1:2) afforded the product (7.23 g, 8.12 mmol, 91 % yield) as a white solid.

^{1}H NMR (500 MHz, THF-d_8) δ 7.64 (d, *J* = 2.5 Hz, 4H), 7.56 – 7.46 (m, 10H), 7.46 – 7.41 (m, 4H), 7.36 (d, *J* = 8.9 Hz, 4H), 7.31 – 7.27 (m, 4H), 7.02 (dd, *J* = 8.9, 2.4 Hz, 4H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H), 4.10 (t, *J* = 6.5 Hz, 8H), 1.87 – 1.82 (m, 8H), 1.62 – 1.54 (m, 8H), 1.04 (t, *J* = 7.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.39, 146.90, 145.97, 136.30, 132.96, 132.91, 129.01, 128.20, 127.55, 127.41, 124.94, 124.52, 123.52, 115.71, 110.59, 103.90, 68.77, 31.58, 19.36, 13.94.

Polymer Synthesis 3a-f

All polymerizations were performed according to a literature procedure[13] in a glove-box under argon atmosphere. *Anhydrous* THF was distilled prior use to remove stabilizers. *N,N*-azobisisobutyronitrile was recrystallized in MeOH by dissolution at RT and crystallization at -20 °C.

General technique I

The monomer(s) (1 equiv) and AIBN (0.02 equiv) were stirred in THF (toluene for **3f**) with a concentration of 0.1 g·L^{-1} for 72 hours at 50 °C. The resulting solution was allowed to cool down to RT and was demonomerized by precipitation in *n*-heptane/EAc 4:1 (for **3c**, **3f** in MeOH/Et$_2$O 2:1). The precipitate was filtered using Teflon-filters (20 µm). The solid was dissolved in THF (toluene for **3f**) and the precipitation process was repeated until all residual monomer was removed (as judged by TLC with precipitation solvent as eluent).

Synthesis of poly(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline) 3a

Using general technique I, monomer **2a** (1.00 equiv), yield 92 %, T_g = 247 °C, Λ_{max}= 3.79 eV, M_w = 112 kg mol^{-1}, M_n = 27.6 kg mol^{-1}, ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.40-7.60 (aromatic) 7.60-6.78 (aromatic), 2.60-0.40 (backbone), Elemental analysis, found: C, 86.52; H, 5.68; N, 6.33; calculated: C, 87.82; H, 5.19; N, 6.98

Synthesis of poly[(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline)$_{75}$-ran-(1-(4-vinylphenyl)decan-1-one)$_{25}$] 3a$_{25}$

Using general technique I, monomer **2a** (0.75 equiv) and 1-(4-vinylphenyl)decan-1-one) (0.25 equiv), white solid, yield 76 %, resulting co-monomer ratio determined by ^{1}H-NMR: 0.75:0.25 (**2a**: 1-(4-vinylphenyl)decan-1-one), The co-monomer ratio was determined by the comparison of the integral of aromatic signals and the integral of the terminal CH$_3$ group: ^{1}H NMR (500 MHz, THF-*d*$_8$) δ 7.8 – 8.1 (s, 11.75 H), 6.0 –

7.2 (s, 77.64 H), 0.8-0.9 (s, 3H). T_g = 203 °C, Λ_{max}= 3.79 eV, M_w = 111 kg mol^{-1}, M_n = 33.3 kg mol^{-1}, Elemental analysis, found: C, 87.24; H, 6.07; N, 6.18; calculated: C, 87.90; H, 5.95; N, 6.15

Synthesis of poly[(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline)$_{50}$-ran-(1-(4-vinylphenyl)decan-1-one)$_{50}$] 3a$_{50}$

Using General technique I, monomer **2a** (0.50 equiv) and 1-(4-vinylphenyl)decan-1-one) (0.50 equiv), white solid, yield 67 %, resulting co-monomer ratio determined by ^{1}H-NMR: 0.52:0.48 (**2a**: 1-(4-vinylphenyl)decan-1-one), The co-monomer ratio was determined by the comparison of the integral of aromatic signals and the integral of the terminal -CH_3 group: ^{1}H NMR (500 MHz, THF-d_8) δ 7.8 – 8.1 (s, 4.43 H), 6.0 – 7.2 (s, 29.66 H), 0.8-0.9 (s, 3H). T_g = 162 °C, Λ_{max}= 3.79 eV, M_w = 70.9 kg mol^{-1}, M_n = 29.4 kg mol^{-1}, Elemental analysis, found: C, 88.01; H, 6.71; N, 5.53; calculated: C, 88.00; H, 7.03; N, 4.96

Synthesis of poly[(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline)$_{25}$-ran(1-(4-vinylphenyl)decan-1-one)$_{72}$] 3a$_{75}$

Using General technique I, monomer **2a** (0.25 equiv) and 1-(4-vinylphenyl)decan-1-one) (0.75 equiv), white solid, yield 58 %, resulting co-monomer ratio determined by ^{1}H-NMR: 0.29:0.71 (**2a**: 1-(4-vinylphenyl)decan-1-one), The co-monomer ratio was determined by the comparison of the integral of the aromatic signals and the integral of the terminal -CH_3 group:^{1}H NMR (500 MHz, THF-d_8) δ 7.8 – 8.1 (s, 1.65 H), 6.0 – 7.2 (s, 13.85 H), 0.8-0.9 (s, 3H), T_g = 87.2 °C, Λ_{max}= 3.78 eV, M_w = 47.3 kg mol^{-1}, M_n = 20.8 kg mol^{-1}, Elemental analysis, found: C, 88.25; H, 8.26; N, 3.84; calculated: C, 88.17; H, 8.68; N, 3.15

Synthesis of poly(4-(2-methoxy-*9H*-carbazol-9-yl)-N-(4-(2-methoxy-*9H*-carbazol-9-yl)phenyl)-N-(4-vinylphenyl)aniline) 3b

Using General technique I, monomer **2b** with a concentration of 0.02 g/mL in THF, white solid, Yield 56 %, T_g = 220 °C, Λ_{max}= 4.01 eV, M_w = 22.7 kg mol^{-1}, M_n = 9.05 kg mol^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 8.20-5.60 (aromatic), 4.20-2.90 (CH_3-O-), 1.80-1.75 (backbone), Elemental analysis, found: C, 82.74; H, 5.42; N, 6.55; O, 4.93; calculated: C, 83.48; H, 5.33; N, 6.35; O, 4.83

Synthesis of poly(4-(2-((2-ethylhexyl)oxy)-*9H*-carbazol-9-yl)-*N*-(4-(2-((2-ethylhexyl)oxy)-*9H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline) 3c

Using General technique I and monomer **2c**, white solid, yield 81 %, T_g = 144 °C, Λ_{max}= 4.01 eV, M_w = 73.7 kg mol^{-1}, M_n = 18.5 kg mol^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 8.20-7.60 (aromatic) 7.60-5.60 (aromatic), 5.20-2.90 (-CH_2-O-), 2.60-0.40 (backbone+aliphatic), Elemental analysis, found: C, 83.56; H, 7.54; N, 5.03; O, 3.70; calculated: C, 83.98; H, 7.40; N, 4.90; O, 3.73

Synthesis of poly(4-(2,7-dibutoxy-*9H*-carbazol-9-yl)-*N*-(4-(2,7-dibutoxy-*9H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline) 3d

Using General technique I and monomer **2d** white solid, yield 60 %, T_g = 146 °C, Λ_{max}= 3.83 eV, M_w = 51.1 kg mol^{-1}, M_n = 20.9 kg mol^{-1}, ^1H NMR (500 MHz, $CDCl_3$) δ 8.20-5.60 (aromatic), 4.20-2.90 (-CH_2-O-), 1.80-1.75 (backbone) 1.60-0.40 (-CH_3), Elemental analysis, found: C, 80.60; H, 7.28; N, 4.87; O, 7.03; calculated: C, 80.96; H, 7.13; N, 4.72; O, 7.19

Synthesis of poly(4-(3,6-diethoxy-*9H*-carbazol-9-yl)-*N*-(4-(3,6-diethoxy-*9H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline) 3e

Using General technique I and monomer **2e** with a concentration of 0.08 g/mL in THF. white solid, yield 72 %, T_g = 184 °C, Λ_{max}= 3.94 eV, M_w = 60.9 kg mol^{-1}, M_n = 29.2 kg mol^{-1}, ^{1}H NMR (500 MHz, THF-d_8) δ 8.20-5.60 (aromatic), 5.20-2.90 (-CH_2-O-), 2.60-0.40 (backbone+aliphatic), Elemental analysis, found: C, 79.53; H, 6.24; N, 4.97; O, 8.20; calculated: C, 80.28; H, 6.09; N, 5.40; O, 8.23

Synthesis of poly(4-(3,6-dibutoxy-*9H*-carbazol-9-yl)-*N*-(4-(3,6-dibutoxy-*9H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline) 3f

Using General technique I and monomer **2f** with toluene as solvent and the polymer was precipitated in MeOH/EAc 2:1, white solid, yield 64 %, T_g = 150 °C, Λ_{max}= 3.94 eV, M_w = 57.8 kg mol^{-1}, M_n = 24.3 kg mol^{-1}, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85–6.15 (aromatic), 4.29–3.40 (alkoxy), 2.48–0.55 (aliphatic + backbone), Elemental analysis, found: C, 80.85; H, 7.15; N, 4.68; O, 7.02; calculated: C, 80.96; H, 7.13; N, 4.72; O, 7.19

Synthesis of poly[(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline)$_{43}$-ran(1-(4-vinylphenyl)decan-1-one)$_{42}$-ran-(1-(azidomethyl)-4-vinylbenzene)$_{15}$] 3a$_{43}$AZ$_{15}$

Using General technique I, monomer **2a** (0.43 equiv) and 1-(4-vinylphenyl)decan-1-one) (0.42 equiv), and 1-(azidomethyl)-4-vinylbenzene (0.15 equiv.) white solid, yield 61 %, resulting co-monomer ratio determined by ^{1}H-NMR: 0.46:0.42:0.12 (**2a**: 1-(4-vinylphenyl)decan-1-one: 1-(azidomethyl)-4-vinylbenzene), The co-monomer ratio was determined by the comparison of the aromatic integrals, the benzylic integral and the –CH_3 integral:^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40-7.60 (4 H, aromatic) 7.60-6.80 (27.4 H, aromatic), 4.40-3.17 (0.51 H, benzylic), 2.60-1.60 (3.50 H, CH_3), 1.45-0.50 (15 H, backbone+aliphatic). The azide content was additionally investigated by crosslinker consumption (**XL**) during thermal crosslinking monitored by FT-IR measurements. In here the azide content matches exactly the monomer feed. T_g = 172 °C (before-crosslinking), T_g = 159 °C (crosslinked with **XL**), T_g = 173 °C (self-crosslinked), Λ_{max}= 3.78 eV, M_w = 46.6 kg mol^{-1}, M_n = 21.8 kg mol^{-1}, Elemental analysis, found: C, 86.40; H, 6.59; N, 6.79; calculated: C, 86.75; H, 6.92; N, 6.32

Synthesis of poly[(*N,N*-bis(4-(*9H*-carbazol-9-yl)phenyl)-4-vinylaniline)$_{85}$-ran-(1-(azidomethyl)-4-vinylbenzene)$_{15}$] 3aAZ$_{15}$

Using General technique I, monomer **2a** (0.85 equiv) and 1-(azidomethyl)-4-vinylbenzene (0.15 equiv.) white solid, yield 81 %, resulting co-monomer ratio determined by ^{1}H-NMR: 0.89:0.11 (**2a**: 1-(azidomethyl)-4-vinylbenzene), The co-monomer ratio was determined by the comparison of the aromatic integrals and the benzylic integral:^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40-7.60 (4 H, aromatic) 7.60-6.78 (23 H, aromatic), 4.40-3.17 (0.23 H, benzylic), 2.60-0.40 (5.13 H, backbone). The azide content was additionally investigated by crosslinker consumption (**XL**) during thermal crosslinking monitored by FT-IR measurements. In here the azide content matches exactly the monomer feed. T_g = - (before-crosslinking), T_g = 241 °C (crosslinked with **XL**), T_g = 251 °C (self-crosslinked), Λ_{max}= 3.78 eV, M_w = 60.8 kg mol^{-1}, M_n = 20.6 kg mol^{-1}, Elemental analysis, found: C, 86.80; H, 5.27; N, 7.90; calculated: C, 86.93; H, 5.21; N, 7.85

Synthesis of poly(4-(3,6-dibutoxy-*9H*-carbazol-9-yl)-*N*-(4-(3,6-dibutoxy-*9H*-carbazol-9-yl)phenyl)-*N*-(4-vinylphenyl)aniline)$_{85}$-ran-(1-(azidomethyl)-4-vinylbenzene)$_{15}$] 3fAZ$_{15}$

Using General technique I and monomer **2f** and 1-(azidomethyl)-4-vinylbenzene (0.15 equiv.) with toluene as solvent and the polymer was precipitated in MeOH/EAc 2:1, white solid, yield 71 %, resulting co-monomer ratio determined by ATR-FTIR through triple-bond consumption during cross-linking reaction: ATR-FTIR: 0.85:0.15 (**2f**: 1-(azidomethyl)-4-vinylbenzene), ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85–6.15 (aromatic), 4.29–3.40 (alkoxy, benzylic), 2.48–0.55 (aliphatic + backbone), T_g = - (before-crosslinking), T_g = 144 °C (crosslinked with **XL**), T_g = 150 °C (self-crosslinked), Λ_{max}= 3.94 eV, M_w = 30.3 kg mol^{-1}, M_n = 16.9 kg mol^{-1}, Elemental analysis, found: C, 80.34; H, 7.22; N, 5.40; O, 6.94; calculated: C, 80,56 ; H, 7,09; N, 5,38; O, 6,97

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