

Supplementary information

Instrumentation

NMR spectra were obtained using a Varian Mercury 300 MHz instrument. Gel permeation chromatography (GPC) was performed using a Waters Associates GPCV2000 liquid chromatography system with it's a red laser light scattering detector at 40 °C using two Waters Styragel HR-5E columns (10 microns PD, 7.8 mm ID, 300 mm length) with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/minute. UV/vis/NIR absorbance spectra were recorded with a Cary 5E spectrophotometer. Fluorescence measurements were carried out on a Jobin Yvon fluorescence spectrometer. Film thickness was measured using a Dektak 3030 (Veeco Instruments Inc.) profilometer. DSC and TGA were done under nitrogen at a heating rate of 10 °C /minute using a TA Model 1000 Instrument.

Materials

Triethylamine, palladium (II) acetate and tri(o-tolyl) phosphine were purchased from Aldrich. Potassium t-butoxide, DMF, methyl triphenyl phosphonium bromide, and phosphorus oxychloride were purchased from Acros. Xylene, triethylamine and THF were dried following standard procedures.

1) Synthesis and polymerization of AB₂-type monomer (A=Bromo; B=Vinyl)

The synthesis of the hyperbranched polymer is outlined in Scheme 1 in the main text of the paper. 4-bromo-N,N-diphenylaniline was prepared according to a literature procedure.¹

a) 4,4,'-(4-Bromophenylazanediyl)dibenzaldehyde 2 : 6 g of triphenylamine (18.5 mmol) was dissolved in 23 mL of DMF (21.6 g, 296 mmol) in a 250 mL, 3-necked

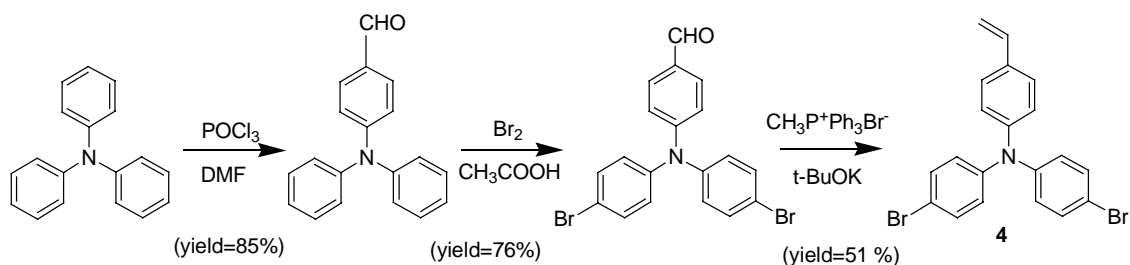
round-bottomed flask. Under cooling with ice was added 30.36 g (18.5 mL, 198 mmol) of phosphorus oxychloride dropwise. After that the solution was heated for 20 h at 100 °C. After cooling the reaction was quenched by pouring it into ice-cold water. The reaction solution was neutralized with 2N NaOH solution, whereby a brown solid precipitated out. The solid was filtered, washed with water and ethanol. Thin layer chromatography on silica gel showed the presence of dialdehyde and monoaldehyde. The mixture was separated by column chromatography over silica gel column using methylene chloride and hexane (3:1 ratio). Yield=6 g (85.3%). M.p.: 202 °C. ¹H NMR (CDCl₃) δ [ppm]: 9.9 (s, 2H, CHO); 7.77-7.81 (d, 4H, Ar, o-to CHO); 7.49-7.52 (2H, Ar, o-to Br); 7.17-7.19 (d, 4H, m-to CHO); 7.04-7.07 (d, 2H, m-to Br). ¹³C NMR (CDCl₃) δ [ppm]: 190.7, 151.8, 144.9, 133.5, 131.9, 131.6, 128.5, 123.2. ESI-MS (m/z): calcd: 382.02; Found: 382.02. Anal.Calcd for C₂₀H₁₄BrNO₂: C, 63.18; H, 3.71; Br, 21.01; N, 3.68; O, 8.42. Found: C, 63.16; H, 3.70; N, 3.69.

b) 4-Bromo-N,N-bis(4-vinylphenyl)aniline 3: To a solution of methyltriphenylphosphoniumbromide (10.33 g, 28.9 mmol) in 30 mL of THF, potassium-t-butoxide (3.25 g, 28.9 mmol) was added under cooling, during which the solution changes to yellow color. The reaction solution was stirred for another 30 min and then 4,4'-(4-Bromophenylazanediyl)dibenzaldehyde (5 g, 13.15 mmol) was added. The reaction was stirred for 5 h at RT, whereby the color changed to orange. Monomer **3** was purified by column chromatography with petroleum ether as eluent. Yield: 77 %. M.p.: 48-50 °C. ¹H NMR (CDCl₃) δ [ppm]: 7.36-7.27 (m, 6H, Ar, m-to-N); 7.04-7.02 (m, 6H, Ar, o-to-N); 6.99-6.63 (q, 1H, vinyl, CH); 5.70-5.64 (d, J=17.4 Hz, 1H, vinyl, *cis*-CH); 5.21-5.18 (d, J=10.8 Hz, 1H, vinyl, *trans*-CH). ¹³C NMR (CDCl₃) δ [ppm]: 146.9,

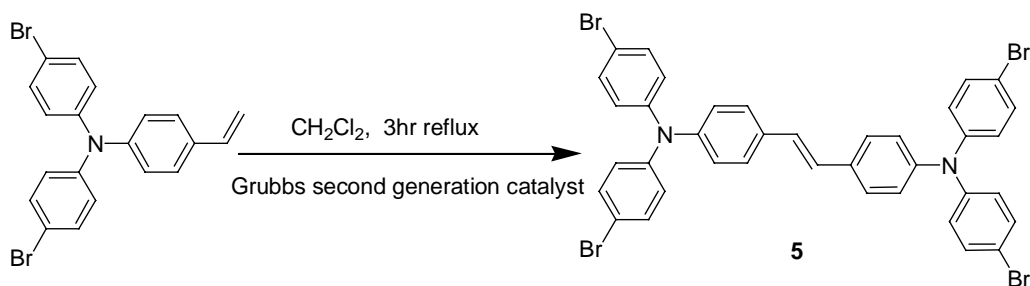
146.8, 136.3, 132.9, 132.5, 127.5, 125.8, 124.3, 115.5, 112.9. ESI-MS (*m/z*): calcd: 382.02; Found: 382.02. Anal. Calcd for C₂₂H₁₈BrN: C, 70.22; H, 4.82; Br, 21.23; N, 3.72; Found: C, 70.23; H, 4.79; N, 3.71.

c) Hyperbranched triphenylamine-vinylene polymer HB-BVPA: 0.6 mL of triethylamine (4.1 mmol) was added to a solution of 600 mg of monomer **1** (1.59 mmol), 18 mg Pd(OAc)₂ (7.9 μmol), and 97 mg tri(o-tolyl phosphine) (0.3 mmol) in 2.5 mL DMF and 2.5 mL xylene. The reaction mixture was heated to 110 °C under Argon for 48 hours and poured into methanol. The precipitated solid was purified by dissolving in THF, filtering and reprecipitating into methanol to obtain as dark yellow polymer, which was dried at reduced pressure. Yield: 62%. ¹H NMR (CDCl₃) δ [ppm]: 7.40-7.37 (broad, 6H, m-to-N); 7.33-7.29 (broad, 8H, o-to-N and stilbenoid); 6.72-6.62 (q, vinyl CH); 5.69-5.63 (d, *J*=17.4 Hz, vinyl, *cis*-CH); 5.21-5.18 (d, *J*=11.4 Hz, 1H, vinyl, *trans*-CH). Anal. Calcd for C₂₂H₁₇N: C, 89.46; H, 5.80; N, 4.74. Found: C, 84.12; H, 5.63; N, 4.37.

2) Synthesis of A₂B-type monomer (A=Bromo; B=Vinyl) for the dimer:



Scheme S-1 Synthesis of the A₂B-type monomer



Scheme S-2 Synthesis of model compound **5** via olefin metathesis reaction on the A₂B-type monomer.

a) 4-bromo-N-(4-bromophenyl)-N-(4-vinylphenyl)aniline, **4.**

4-(bis(4-bromophenyl) amino)benzaldehyde was prepared according to literature procedures.² To a solution of methyltriphenylphosphoniumbromide (6.2 g, 17.3 mmol) in 20 mL of anhydrous THF, potassium-*t*-butoxide (1.95 g, 17.3 mmol) was added under cooling, during which the solution changes to yellow color. The ice bath was removed and the reaction solution was stirred for another 1h. Once again the solution was cooled to 5°C and 4-(bis(4-bromophenyl)amino)benzaldehyde (5 g, 11.5 mmol) was added directly under argon. The ice bath was removed and the reaction was allowed to stir for 24 h at RT, whereby the color changed to orange. The solvent was evaporated and resulting mixture was diluted with CH₂Cl₂ and poured into water. The mixture was extracted three times with 20ml CH₂Cl₂. The extracted solution was washed with brine and dried over sodium sulfate. Monomer **4** was purified by column chromatography using methylene chloride and hexane (1:1 ratio). Yield= 4.5 g (91%). M.p.: 84-85 °C. ¹H NMR (CDCl₃) δ [ppm]: 7.36-7.29 (m, 6H, Ar, *m*-to-N); 7.01-6.96 (m, 6H, Ar, *o*-to-N); 6.71-6.62 (q, 1H, vinyl, CH); 5.69-5.63 (d, *J*=17.7 Hz, 1H, vinyl, *cis*-CH); 5.22-5.18 (d, *J*=17.7 Hz, 1H, vinyl, *trans*-CH). ¹³C NMR (CDCl₃) δ [ppm]: 146.6, 146.5, 136.2, 133.2,

132.6, 127.5, 125.8, 124.4, 115.9, 113.2. Anal. Calcd. for $C_{20}H_{15}Br_2N$: C, 55.97; H, 3.52; N 3.26; Found: C, 56.78; H, 3.44, N 3.25.

b) Synthesis of model compound 5 via olefin metathesis of the A_2B -type monomer:

Triple freeze-thawed methylene chloride (20 mL) was added, under Ar atmosphere, to 1 g of 4 (2.33 mMoles), followed by the addition of 98 mg of Grubbs' second generation catalyst (0.1 mMole). It was allowed to reflux under Ar for 12 h. After cooling the crude product, 6-7 drops of ethyl-vinyl ether was added to quench the catalyst and stirred for 15 min. The product was purified by passing the solution directly over a silica gel column, using flash column chromatography and (5:1) methylene chloride: hexane as an eluent mixture. Removal of the solvent afforded the pure dimer in 83% yield. 1H NMR ($CDCl_3$) δ [ppm]: 7.39-7.32 (m, 6H, Ar, m-to-N); 7.03-6.92 (m, 8H, Ar, o-to-N and stilbenoid). ^{13}C NMR ($CDCl_3$) δ [ppm]: 146.5, 132.6, 127.7, 127.1, 125.9, 124.4, 115.9.

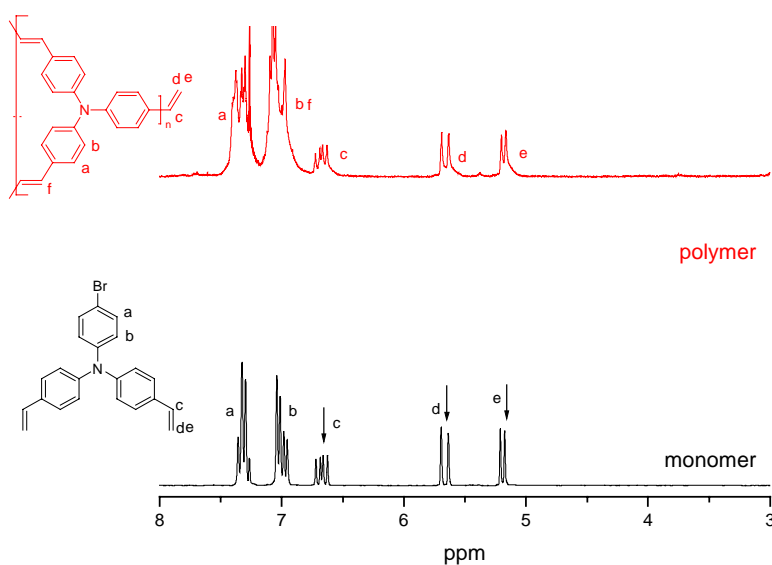


Figure S-1. 1H NMR spectra of the BVPA monomer and BVPA-HB polymer

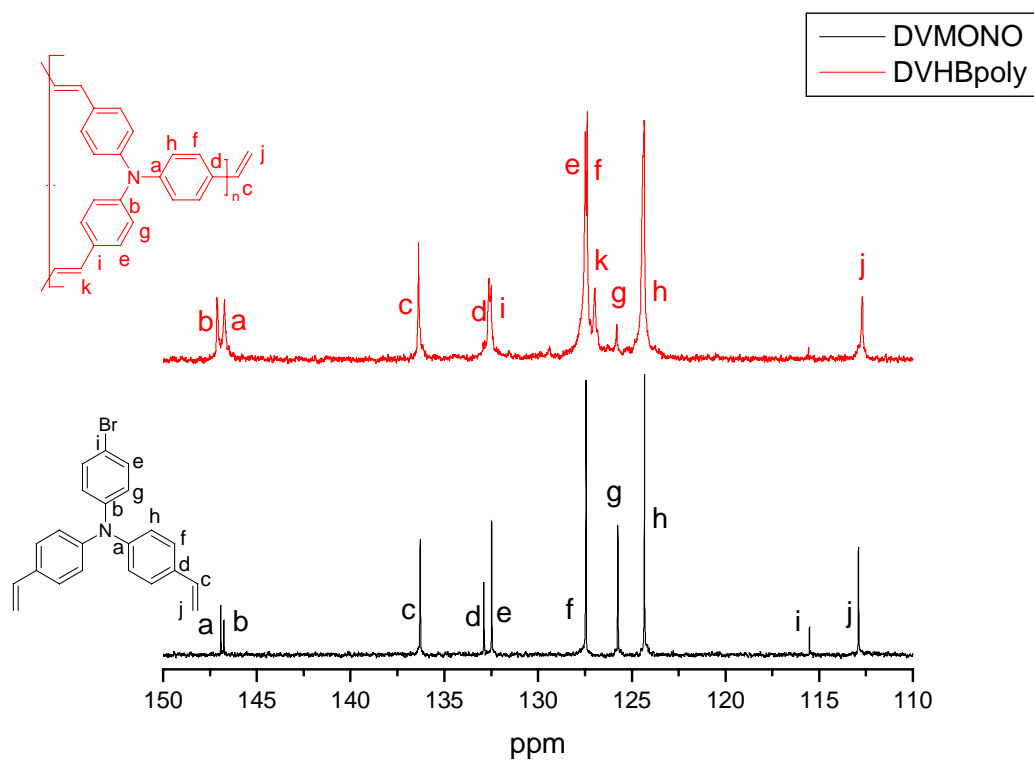


Figure S-2. ^{13}C NMR spectra of the BVPA monomer and HB-BVPA polymer

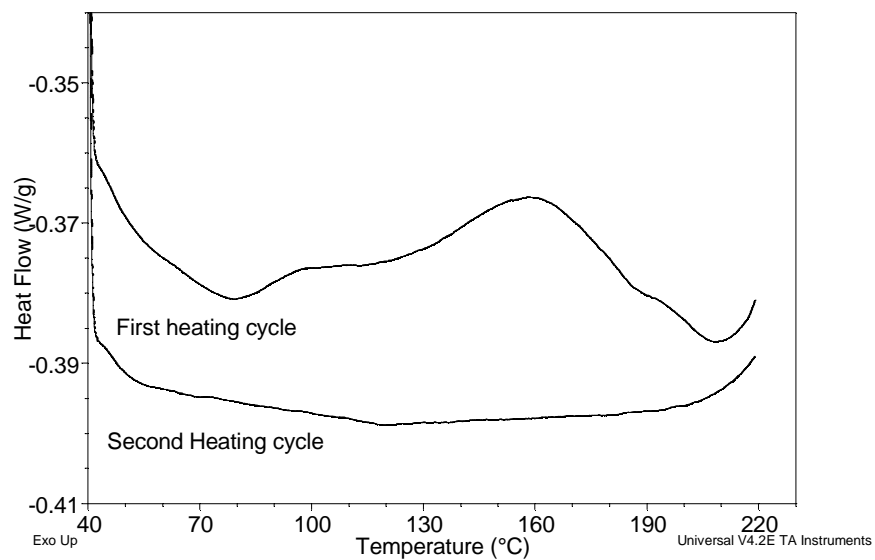


Figure S-3. DSC thermogram of the BVPA-HB polymer

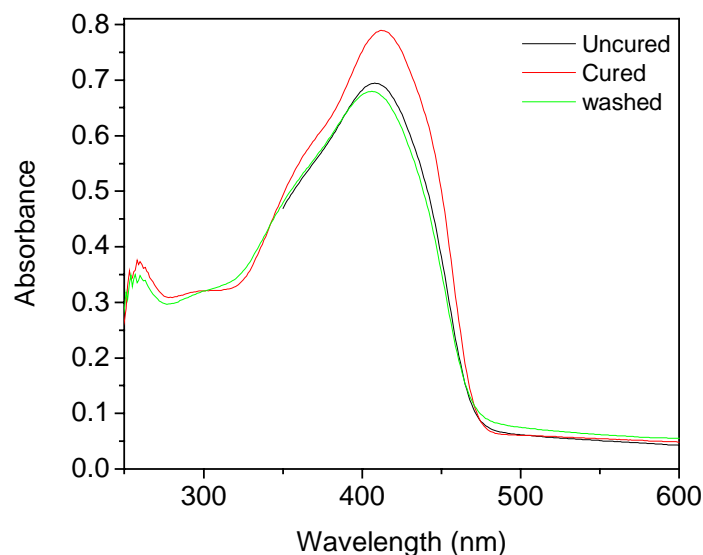


Figure S-3. UV-visible absorption spectra of the polymer HB-BVPA before and after crosslinking and after washing with warm THF.

3) EL Device Fabrication and Characterization

Electroluminescent devices were prepared by first masking, then etching ITO glass (Delta Technologies, $R_s = 8\text{-}12\ \Omega$). After etching, the ITO glass was sequentially cleaned by sonication in sodium dodecyl sulfate, SDS (Fisher), Milli-Q water, acetone, and isopropyl alcohol, then plasma (oxygen) treated for 15 minutes. Films of the two different hole injection/transport layers on ITO were prepared as follows. Solution of the HB polymer (10 mg/ml in chloroform) was spin-cast on ITO substrates to make a ~ 80 nm thick film and then heated in vacuum for 2 hrs @ 150°C for crosslinking. A 40 nm thick hole transport layer of PEDOT-PSS (Bayer Bytron P VP Al 4083) was spin-coated onto the ITO surface and dried in vacuum at 150°C for 2 hrs. Solutions of the MEH-PPV (5 mg/mL in 1,2-dichloroethane) were spin-coated onto the substrate (300 μL for each substrate) to make ~ 50 nm thick films. The resulting films were dried under vacuum (10^{-6} torr) for 12 hrs at room temperature and then Ca (50 Å) and Al (2000 Å) layers were

deposited by thermal evaporation at 4×10^{-7} torr without breaking the vacuum between metal depositions. The resulting devices were encapsulated with epoxy (Loctite quick-set) to minimize exposure to oxygen and moisture. All device measurements were made at room temperature.

Power for electroluminescence (EL) measurements was supplied using a Keithley 228 voltage-current source. EL spectra were corrected on an ISA-SPEX Triax 180 spectrometer fitted with a liquid N₂ cooled CCD detector (Hamamatsu back-illuminated CCD, 1024×64 pixel, 400-1100 nm). Measurements were made normal to the surface of the devices, and in the computation of the EL quantum efficiencies it was assumed that the spatial distribution of the emission was Lambertian. External device quantum efficiencies were calculated as described in literature.^{3,4}

4) Hole-mobility measurements:

Hole dominated devices were fabricated the same way as polymer LEDs except the top contact was Au (80nm) to prevent electron injection from the cathode. Current-Voltage characteristics of the devices were measured at room temperature using a Keithley 2400 sourcemeter unit. Zero-field hole mobility ($\mu(0)$), field dependence factor (γ), and built-in voltage (V') were all determined from the best fits of the J-V curve. A device without the semiconductor polymer layer (ITO/PEDOT-PSS/Au) was fabricated and tested to determine the series resistance (~60 Ohms).

The hole transport of devices show SCLC and follows the equation

$$J = \frac{9}{8} \epsilon_r \epsilon \mu_h \frac{V^2}{L^3} \quad (1)$$

where J is the current density, V is the applied voltage, μ_h is the hole mobility, L is the thickness of the polymer layer, and ϵ_r and ϵ are the permittivity of the polymer and air, respectively. The voltage is corrected by subtracting the voltage drop due to the contact resistance, which was obtained from the linear J-V curve of an ITO/PEDOT-PSS/Au device. If the mobility is field dependent, which is often the case for polymers,⁵⁻⁷. μ_h is then given by $\mu_h = \mu(0)e^{\gamma\sqrt{V}/L}$ where $\mu(0)$ is the zero-field mobility and γ is the field dependence factor. Incorporating this into Equation (1), the J-V data are fitted using

$$J = \frac{9}{8} \epsilon_r \epsilon \mu(0) e^{\gamma\sqrt{(V-V')}/L} \frac{(V-V')^2}{L^3} \quad (2)$$

and $\mu(0)$, γ , and V' (built-in voltage) values are determined from the fitting parameters

Table S-1. Fitting parameters obtained iterating the field-dependent mobility equation

$J = \frac{9}{8} \epsilon_r \epsilon \mu(0) e^{\gamma\sqrt{(V-V')}/L} \frac{(V-V')^2}{L^3}$. R^2 values show the coefficient of determination for the fits ($R^2 = 1$ is a perfect fit).

Polymer film thickness (nm)	$\mu(0)$ (cm ² /V.s)	γ ((m/V) ^{1/2})	V'	R^2
Non-crosslinked polymers				
68	7.12×10^{-8}	1.37×10^{-4}	0.20	0.9998
136	2.87×10^{-8}	3.99×10^{-3}	0.30	0.9998
Crosslinked polymers				
25.5	7.93×10^{-8}	1.88×10^{-3}	0.30	0.9998
46.5	9.60×10^{-8}	4.59×10^{-3}	0.15	0.9990
90	8.48×10^{-8}	3.02×10^{-3}	0.28	0.9998

References

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