Electronic Supplementary Information

Creating a Thermally Activated Delayed Fluorescence Channel in a Single Polymer System to Enhance Exciton Utilization Efficiency for Bluish-Green Electroluminescence

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Synthesis

General Information:

The solvents were dried using standard procedures. All other reagents were used as received from commercial sources unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were measured on a MERCURYVX300 or Bruker Advanced II (400 MHz) spectrometers. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. GC-Mass spectra were measured on a Thermo Trace DSQ II GC/MS. UV-Vis absorption spectra were recorded on a Shimadzu UV-2501 recording spectrophotometer. PL spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The PL lifetimes was measured by a single photon counting spectrometer from Edinburgh Instruments (FLS920) with a Picosecond Pulsed UV-LASTER (LASTER377) as the excitation source. Gel permeation chromatography (GPC) was carried out on a Waters 2690 D system using arefractive detector and THF as the eluent. Absolute PLQYs were obtained using a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics) and all the samples were excited at 330 nm.

Synthetic Procedures:

9-(6-(9H-carbazol-9-yl)hexyl)-3,6-dibromo-9H-carbazole (**M1**), 10-(4-(5-(4-methoxyphenyl)-1,3,4-oxadiazol-2-yl)phenyl)-10*H*-phenoxazine (**1**) and (4-(diphenylamino)phenyl)methanol (**3**) were synthesized according to the literature methods.[1]

4-(5-(4-(10H-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenol (2): Boron tribromide (2.5 mL, 25 mmol) was added dropwise to a stirring mixture of compound **1** (2.17 g, 5 mmol) in dry CH_2Cl_2 (50 mL) at -78 °C for 0.5 h. After stirring for 2 h at -78 °C, the reaction mixture was slowly warmed to room temperature and stirred for 24 h. Then the reaction mixture was poured into cold methanol to provide green precipitation. After filtration and evaporation of the solvent, the residue was dried under vacuum at 60 °C to provide a green powder (4.11 g, 98%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.36 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.1 Hz, 2H), 6.72-6.63 (m, 6H), 5.99 (d, J = 7.2 Hz, 2H), 5.49 (br, 1H). MS (EI): *m/z* 418.6 $[M-1]^+$. Anal. Calcd for $C_{26}H_{17}N_3O_3$: C, 74.45; H, 4.09; N, 11.44. Found: C, 74.21; H, 3.98; N, 11.11.

4-(((6-(3,6-Dibromo-9H-carbazol-9-yl)hexyl)oxy)methyl)-N,N-diphenylaniline (4): 3,6-Dibromo-9-(6-bromohexyl)-9*H*-carbazole (9.74 g, 20 mmol) in 50 mL dry DMF was added to a stirring mixture of (4-(diphenylamino)phenyl)methanol (5.51 g, 20 mmol) and sodium hydride (0.576 g, 24 mmol) in 100 mL dry DMF at room temperature under argon. After stirring at 80 °C for 24 h, the reaction mixture was cooled to room temperature, poured into water (600 mL), and extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/CH_2Cl_2 5:1) to give a transparent oily matter (7.75 g, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.13 (s, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.51-7.20 (m, 8H), 7.08-6.97 (m, 8H)，4.42 (s, 2H), 4.22 (t, J = 6.9 Hz, 2H), 3.47 (t, J = 6.3 Hz, 2H), 1.88-1.74 (m, 2H), 1.62-1.60 (m, 2H), 1.28-1.24 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 147.7, 139.2, 132.8, 129.1, 128.9, 128.8, 124.1, 124.0, 123.3, 123.2, 122.6, 111.9, 110.3, 72.6, 70.5, 43.2, 29.7, 29.3, 28.8, 27.1, 26.1. MS (EI): *m/z* 680.4 $[M]^+$. Anal. Calcd for $C_{37}H_{34}Br_2N_2O$: C, 65.11; H, 5.02; N, 4.10. Found: C, 65.06; H, 5.10; N, 4.26.

4-(((6-(3,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)hexyl)oxy)methyl)-N,N-diphenylaniline (M2): Compound **4** (6.8 g, 10 mmol), bis(pinacolato)diboron (6.01 g, 24 mmol), Pd(dppf)Cl_2 (326 mg, 0.4 mmol) and potassium acetate (6.87 g, 70 mmol) were added into 80 mL dry DMF under argon. After stirring for 12 h at 80 °C, the reaction mixture was cooled to room temperature, poured into water (200 mL), and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica, petroleum ether/CH_2Cl_2 5:1) to give a white powder (6.2 g, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.66 (s, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.22-7.17 (m, 6H), 7.08-6.96 (m, 8H), 4.39 (s, 2H), 4.30 (t, J = 6.9 Hz, 2H), 3.43 (t, J = 6.3 Hz, 2H), 1.98-1.90 (m, 2H), 1.38 (s, 24H), 1.20-1.09 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 171.9, 168.4, 147.7, 147.2, 142.6, 132.8, 131.9, 129.1, 128.8, 128.0, 124.1, 123.9, 122.6, 108.0, 83.4, 72.5, 70.2, 43.0, 29.5, 28.8, 27.0, 25.9, 24.9. MS (EI): *m/z* 776.4 $[M]^+$. Anal. Calcd for $C_{49}H_{58}B_2N_2O_5$: C, 75.78; H, 7.53; N, 3.61. Found: C, 75.53; H, 7.68; N, 3.64.

10-(4-(5-(4-((6-(3,6-Dibromo-9H-carbazol-9-yl)hexyl)oxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)-10H-phenoxazine (M3): A mixture of compound **2** (1.89 g, 4.5 mmol), potassium carbonate (1.24 g, 9 mmol) and 3,6-dibromo-9-(6-bromohexyl)-9H-carbazole (2.44 g, 5 mmol) in 50 mL dry DMF was stirred at 80 ^{o}C under argon for 24 h. After slowly cooling to room temperature, the reaction mixture was poured into water (200 mL) to give precipitation of green solid. After filtration and evaporation of the solvent, the residue was subjected to column chromatography (silica, petroleum ether/CH_2Cl_2 1:1) to provide a green powder (2.48 g, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm] 8.35 (d, J = 8.1 Hz, 2H), 8.14 (s, 2H), 8.07 (d, J = 9.0 Hz, 2H), 7.54 (d, J = 7.2 Hz, 4H), 7.27 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.74-6.60 (m, 6H), 5.98 (d, J = 7.5 Hz, 2H), 4.28 (t, J = 6.9 Hz, 2H), 3.98 (t, J = 6.0 Hz, 2H), 1.92-1.74 (m, 4H), 1.52-1.41 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ [ppm] 165.1, 163.6, 162.2, 144.2, 142.4, 139.5, 134.0, 132.0, 129.8, 129.3, 129.0, 124.3, 123.7, 123.5, 122.1, 116.3, 116.0, 115.2, 113.5, 112.2, 110.6, 68.1, 43.4, 29.2, 29.1, 27.2, 26.1. MS (EI): *m/z* 824.0 $[M]^+$. Anal. Calcd for $C_{44}H_{34}Br_2N_4O_3$: C, 63.94; H, 4.15; N, 6.78. Found: C, 63.83; H, 4.21; N, 6.82.

General synthetic procedure for the polymers: The polymerization was performed according to general procedures of palladium(0) catalyzed Suzuki polycondensation. Under argon, different ratios of **M1**, **M2** and **M3**, potassium carbonate (0.22 g, 1.6 mmol), 1 mL $Pd(PPh_3)_4$ solution (0.01 mmol in 10 mL toluene), 0.8 mL methyl trioctyl ammonium chloride solution (aliquant 336, 280 mg in 16 mL water) and 4 mL toluene were added into a 50 mL flask and stirred at 110 ^{o}C for 72 h. Then the polymers were capped by adding phenylboronic acid (0.2 g in 1 mL toluene) by continuous stirring for 12 h, and then iodobenzene (0.20 mL) followed by reacting for another 12 h. After cooling to room temperature, the whole mixture was poured in a mixture solvent (250 mL MeOH and 30 mL acetone) for sedimentation. 10 mL H_2O_2 (5%) was added into the precipitated polymer in CH_2Cl_2, and stirred for 5 h at room temperature. After that, the combined organic phases were dried over Na_2SO_4, and purified by a short column chromatography (silica, CH_2Cl_2). After sedimentation in a mixture solvent (250 mL methyl alcohol and 30 mL acetone) twice, the precipitated polymer was washed with acetone in a Soxhlet apparatus for 3 days and continuously washed with *n*-hexane for another 3 days. After that, the residue was dried under vacuum at room temperature to provide a green powder.

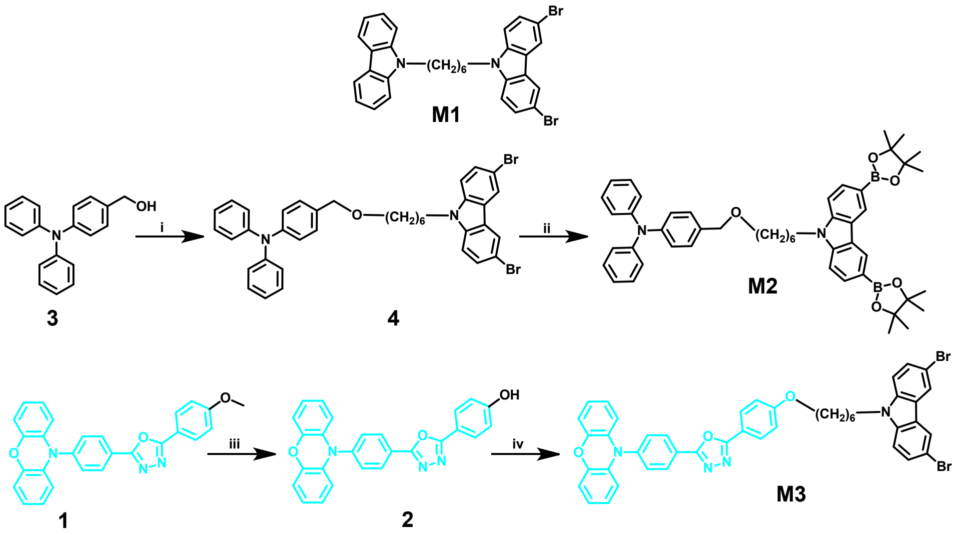
P0: **M1** (286 mg, 0.50 mmol) and **M2** (404 mg, 0.52 mmol) were used in the polymerization (yield: 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.51 (s, 4H), 8.16-7.92 (m, 2H), 7.92-7.60 (m, 6H), 7.60-7.30 (m, 8H), 7.24-7.09 (m, 8H), 7.09-6.88 (m, 6H), 4.57 (s, 2H), 4.44-3.80 (m, 6H), 3.64-3.24 (m, 2H), 2.08-1.70 (m, 4H), 1.50-1.03 (m, 10H), 1.00-0.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 141.9, 132.9, 129.2, 126.5, 124.1, 121.9, 120.4, 118.5, 108.6, 70.8, 67.7, 50.9, 44.3, 31.5, 26.8, 21.3, 14.3. Anal. Calcd: C, 85.86; H, 6.45; N, 5.98. Found: C, 85.72; H, 6.31; N, 5.93. GPC, M_n = 3191, PDI = 1.67.

P3: **M1** (268.9 mg, 0.47 mmol), **M2** (404 mg, 0.52 mmol) and **M3** (24.7 mg, 0.03 mmol) were used in the polymerization (yield: 48%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.51 (s, 4H), 8.16-7.92 (m, 2H), 7.92-7.60 (m, 6H), 7.60-7.30 (m, 8H), 7.24-7.09 (m, 8H), 7.09-6.88 (m, 6H), 6.88-6.50 (m, 0.19H), 6.02-5.8 (m, 0.06H) 4.57 (s, 2H), 4.44-3.80 (m, 6H), 3.64-3.24 (m, 2H), 2.08-1.70 (m, 4H), 1.50-1.03 (m, 10H), 1.00-0.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 147.8, 140.3, 132.9, 129.2, 128.8, 125.6, 124.1, 124.0, 122.7, 118.8, 108.6, 72.6, 70.7, 31.6, 29.6, 25.2, 22.7, 19.0, 14.2. Anal. Calcd: C, 85.56; H, 6.40; N, 6.06. Found: C, 85.57; H, 6.44; N, 5.96. GPC, M_n = 4406, PDI = 1.67.

P6: **M1** (251.7 mg, 0.44 mmol), **M2** (404 mg, 0.52 mmol) and **M3** (49.4 mg, 0.06 mmol) were used in the polymerization (yield: 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.51 (s, 4H), 8.16-7.92 (m, 2H), 7.92-7.60 (m, 6H), 7.60-7.30 (m, 8H), 7.24-7.09 (m, 8H), 7.09-6.88 (m, 6H), 6.88-6.50 (m, 0.39H), 6.02-5.80 (m, 0.13H), 4.57 (s, 2H), 4.44-3.80 (m, 6H), 3.64-3.24 (m, 2H), 2.08-1.70 (m, 4H), 1.50-1.03 (m, 10H), 1.00-0.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 147.8, 140.3, 133.2, 132.0, 129.2, 128.8, 125.6, 124.1, 123.8, 122.7, 118.7, 108.8, 72.7, 70.5, 42.7, 31.6, 29.9, 27.7, 22.7, 14.2. Anal. Calcd: C, 85.26; H, 6.35; N, 6.14. Found: C, 85.24; H, 6.27; N, 6.03. GPC, M_n = 3414, PDI = 1.62.

P9: **M1** (223.5 mg, 0.41 mmol), **M2** (404 mg, 0.52 mmol) and **M3** (74.2 mg, 0.09 mmol) were used in the polymerization (yield: 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.51 (s, 4H), 8.16-7.92 (m, 2H), 7.92-7.60 (m, 6H), 7.60-7.30 (m, 8H), 7.24-7.09 (m, 8H), 7.09-6.88 (m,6H), 6.88-6.50 (m, 0.57H), 6.02-5.80 (m, 0.19H), 4.57 (s, 2H), 4.44-3.80 (m, 6H), 3.64-3.24 (m, 2H), 2.08-1.70 (m, 4H), 1.50-1.03 (m, 10H), 1.00-0.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 147.8, 140.3, 132.8, 129.2, 128.9, 125.6, 124.1, 124.0, 122.7, 120.3, 118.8, 118.2, 108.6, 72.7, 70.3, 43.1, 31.6, 29.6, 28.9, 27.2, 22.7, 14.2. Anal. Calcd: C, 84.96; H, 6.30; N, 6.22. Found: C, 84.95; H, 6.43; N, 6.16. GPC, M_n = 3825, PDI = 1.64.

P12: **M1** (217.4 mg, 0.38 mmol), **M2** (404 mg, 0.52 mmol) and **M3** (98.9 mg, 0.12 mmol) were used in the polymerization (yield: 47%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.51 (s, 4H), 8.16-7.92 (m, 2H), 7.92-7.60 (m, 6H), 7.60-7.30 (m, 8H), 7.24-7.09 (m, 8H), 7.09-6.88 (m, 6H), 6.88-6.50 (m, 0.79H), 6.02-5.80 (m, 0.25H) 4.57 (s, 2H), 4.44-3.80 (m, 6H), 3.64-3.24 (m, 2H), 2.08-1.70 (m, 4H), 1.50-1.03 (m, 10H), 1.00-0.88 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] 147.8, 140.3, 132.8, 129.2, 128.9, 127.2, 125.6, 124.1, 124.0, 123.7, 122.7, 120.4, 118.8, 116.6, 108.6, 72.2, 70.3, 31.6, 28.8, 27.1, 22.7, 14.2. Anal. Calcd: C, 84.66; H, 6.25; N, 6.30. Found: C, 84.80; H, 6.20; N, 6.29. GPC, M_n = 3280, PDI = 1.77.



Scheme S1. Synthetic routes of the monomers.

Reagents and conditions: (i) 3,6-dibromo-9-(6-bromohexyl)-9*H*-carbazole, NaH, THF, Ar, 65 ^{o}C, 18 h; (ii) bis(pinacolato)diboron, Pd(dppf)Cl$_2$, KOAc, DMF, Ar, 80 ^{o}C, 12 h; (iii) BBr$_3$, CH$_2$Cl$_2$, Ar, -78 ^{o}C, 2 h; (iv) 3,6-dibromo-9-(6-bromohexyl)-9*H*-carbazole, K$_2$CO$_3$, DMF, Ar, 80 ^{o}C, 24 h.

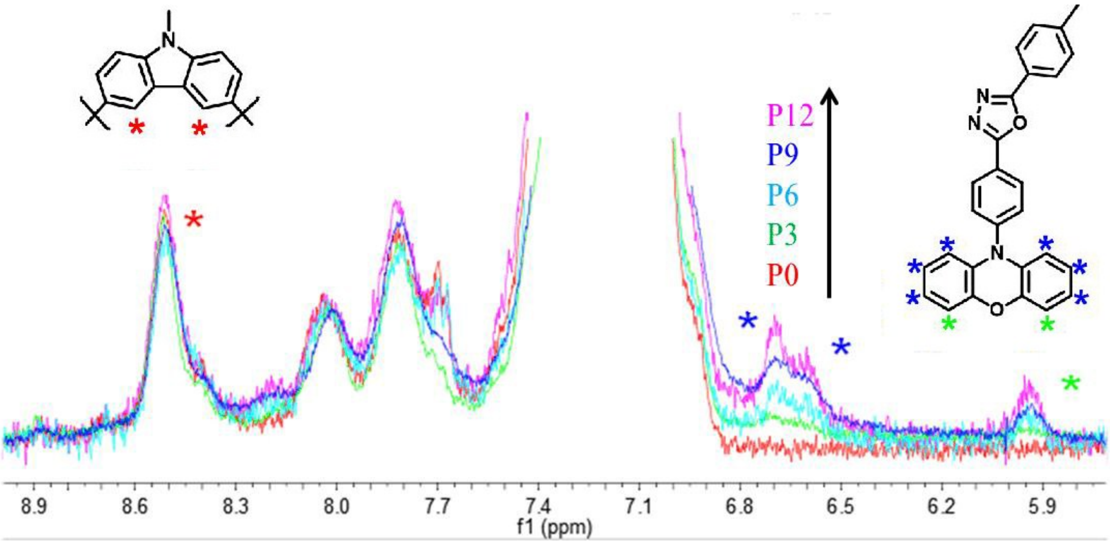


Figure S1. ^{1}H NMR spectra of P0-P12.

Spectra characteristic

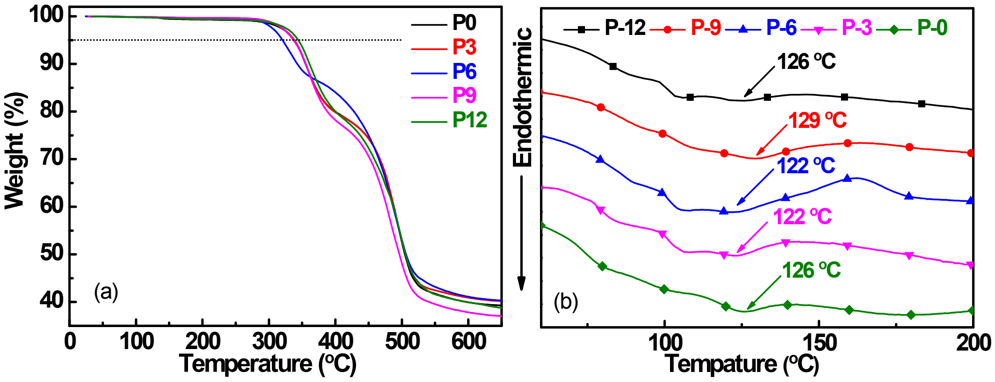


Figure S2. (a) TGA traces of P0-P12 recorded at a heating rate of 10 °C min^{-1}. (b) DSC traces of P0-P12 recorded at a heating rate of 10 °C min^{-1}.

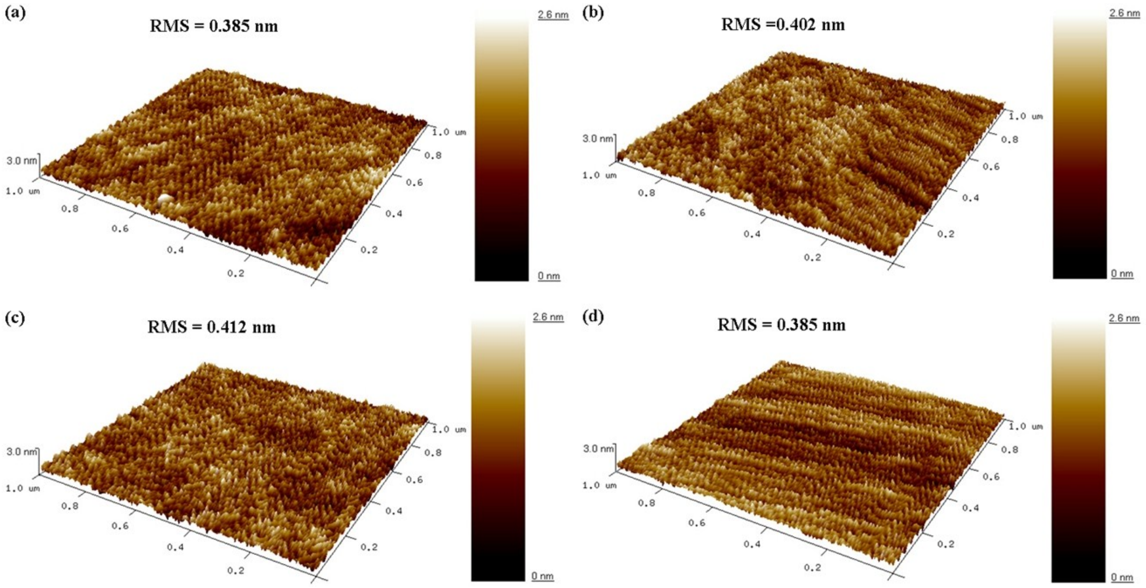


Figure S3. AFM topographic images of the solution-processed (a) P3, (b) P6, (c) P9 and (d) P12 films after drying at 80 °C.

Table S1. Comparison of the physical properties of the polymers and the monomer M3.

Polymer/ monomer	λ_{abs} [a] [nm]	λ_{em}[b] [nm]	λ_{em}[c] [nm]	T_d [°C]	T_g [°C]
M3	282, 303, 365	491	505	-	-
P0	239, 263, 298	427	428	337	126
P3	239, 263, 298	427, 491	470	338	122
P6	239, 263, 298	427, 491	479	320	122
P9	239, 263, 298	427, 491	491	336	129
P12	239, 263, 298	427, 491	494	342	126

[a] Absorption in film. [b] Peak wavelength in toluene. [c] Peak wavelength in film.

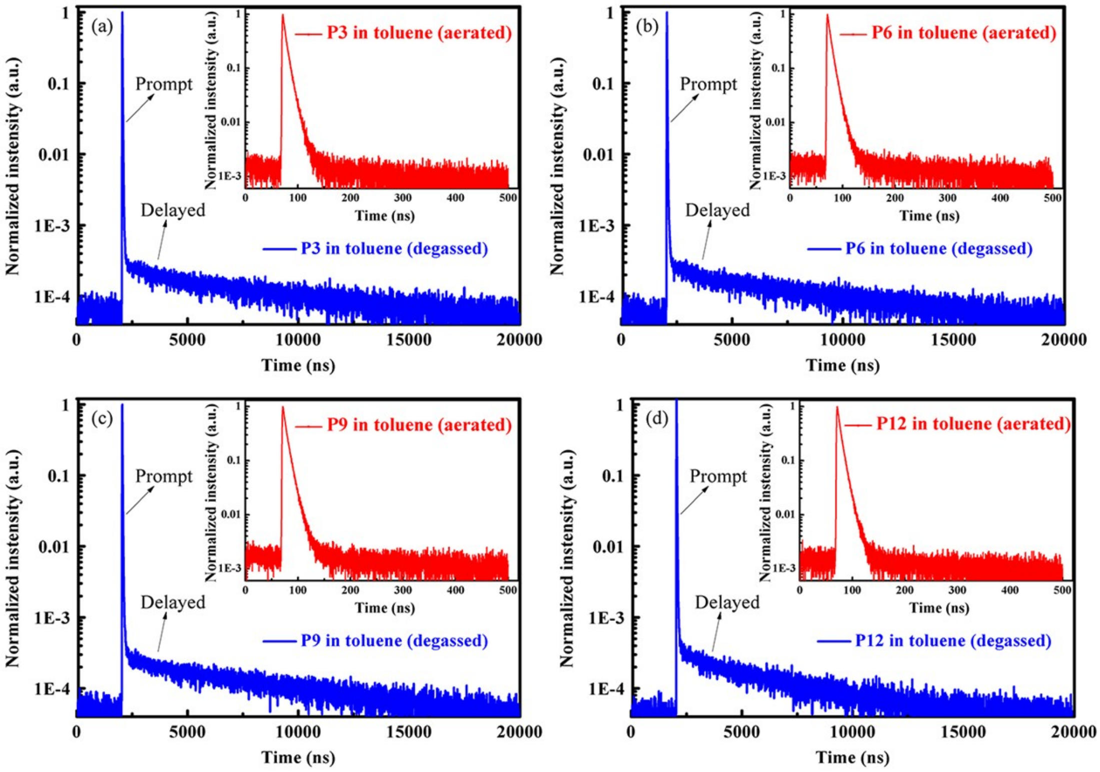


Figure S4. The transient photoluminescence decay spectra of the polymers (a) P3, (b) P6, (c) P9, and (d) P12 in toluene under the aerated and degassed conditions.

Table S2. Comparison of the lifetimes and rate constants of the materials in toluene under aerated and degassed conditions.

	Polymer/monomer	M3	P3	P6	P9	P12
aerated	□ τ_f[a] (ns)	6.83	7.24	7.23	7.61	7.32
	k_f[b] ($\times 10^7$ s^{-1})	1.96	1.57	1.60	1.66	1.75
degassed	□ τ_f (ns)	9.86	10.2	9.97	10.26	9.59
	□ τ_d[c] (μs)	2.84	5.35	5.06	6.08	4.06
	Ratio[d] of τ_d (%)	5.61	9.70	9.90	13.9	7.30
	Φ_f [e] (%)	18.1	16.6	16.7	17.2	18.9
	k_f ($\times 10^7$ s^{-1})	1.84	1.63	1.68	1.68	1.97
	Φ_d[f] (%)	1.08	1.80	1.80	2.80	1.50
	k_d[g] ($\times 10^5$ s^{-1})	3.80	3.36	3.56	4.61	3.69

[a]The lifetime of the prompt component. [b]The rate constant for prompt fluorescence. □[c]The lifetime of the delayed component. [d]R_f: calculated as the integrated intensity of the delayed component devided by the totally integrated intensity of the decay curve. [e]The prompt fluorescence quantum yield. [f]Φ_d: the delayed fluorescence quantum yield. [g]The rate constant for delayed fluorescence.

Table S3. Summary of the temperature dependent lifetimes of the PF and the DF components measured in film.

Compound	T (K)	τ_p (ns)	τ_d (μs)	Ratio of τ_d (%)
M3	200	11.70	1.02	2.93
	250	12.44	1.43	7.48
	300	11.44	2.01	11.46
P3	200	7.34	0.44	1.95
	250	7.68	2.11	4.03
	300	8.47	2.36	8.40
P6	200	9.91	0.47	6.65
	250	9.93	1.27	9.46
	300	9.80	2.53	13.81
P9	200	11.19	0.76	6.67
	250	11.42	1.32	10.24
	300	12.76	2.23	20.74
P12	200	8.44	1.02	3.87
	250	8.84	1.86	5.86
	300	8.82	2.36	13.27

Table S4. Comparison of the lifetimes and rate constants of the materials in film under aerated and degassed conditions.

	Polymer/monomer	M3	P3	P6	P9	P12
aerated	τ_p[a] (ns)	8.06	5.96	7.00	9.06	6.20
	Φ_p[b] (%)	32.8	17.9	17.0	19.8	21.9
	k_p[c] ($\times 10^7$ s^{-1})	4.07	3.00	2.43	2.19	3.64
degassed	□ τ_p (ns)	11.44	8.47	9.80	12.76	8.82
	□ τ_d[d] (μs)	2.01	2.36	2.53	2.23	2.36
	Ratio of τ_d (%)	11.46	8.40	13.81	20.74	13.27
	Φ_p[e] (%)	47.3	25.2	23.4	26.7	29.2
	k_p ($\times 10^7$ s^{-1})	4.13	2.98	2.39	2.09	3.31
	Φ_d[f] (%)	6.5	2.3	3.8	7.0	4.5
	k_d[g] ($\times 10^6$ s^{-1})	3.23	0.97	1.50	3.14	1.91

[a]The lifetime of the prompt component. [b]The fluorescence quantum yield. [c]The rate constant for prompt fluorescence. [d]The lifetime of the delayed component. [e]Φ_p: The prompt fluorescence quantum yield. [f]Φ_d: the delayed fluorescence quantum yield. [g]k_d: The rate constant for delayed fluorescence.

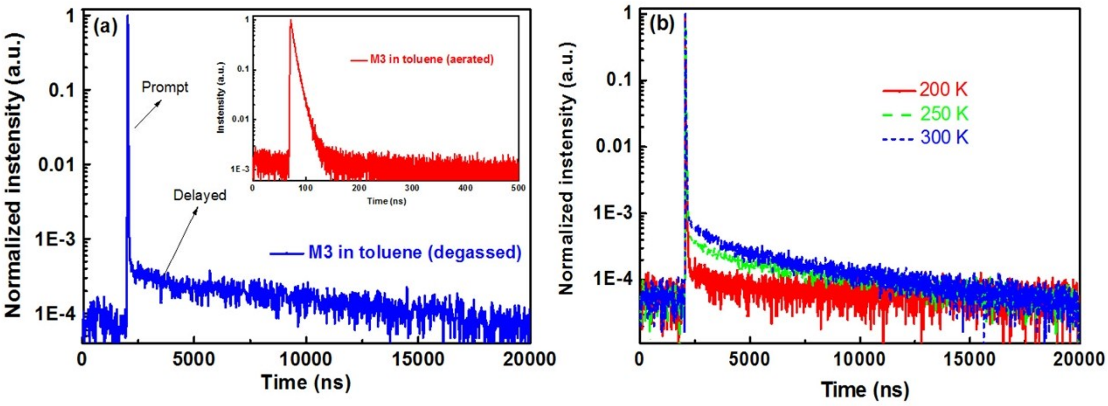


Figure S5. (a) Transient PL decay of M3 in the aerated and the degassed toluene. (b) Temperature dependence of transient PL decay of M3 in film.

Devices measurements and characterization

The ITO substrates were degreased in acetone and ethanol consecutively in an ultrasonic bath before UV-ozone treatment for 10 minutes. A layer of 30 nm thick PEDOT:PSS was spin-coated onto the ITO substrate and then baked at 120 °C for 10 minutes. Poly-TPD was spin-coated onto the PEDOT:PSS layer from a chlorobenzene solution. Another baking at 100 °C for 10 minutes was conducted before spin-coating the light emitting polymers. To enhance the electron injection into the emitting layer, a layer of TmPyPB was thermally deposited onto the polymers. After the evaporation of the composite Ba/Al cathode, all the devices were encapsulated with UV-curable resin. The current-voltage-luminance characteristics and the EL spectra were measured simultaneously by a customized software controlling a PR735 spectrascan spectrometer and a Keithley 2400 source measurement unit. The power efficiency and the external quantum efficiency were calculated by assuming a Lambertion emission profile.

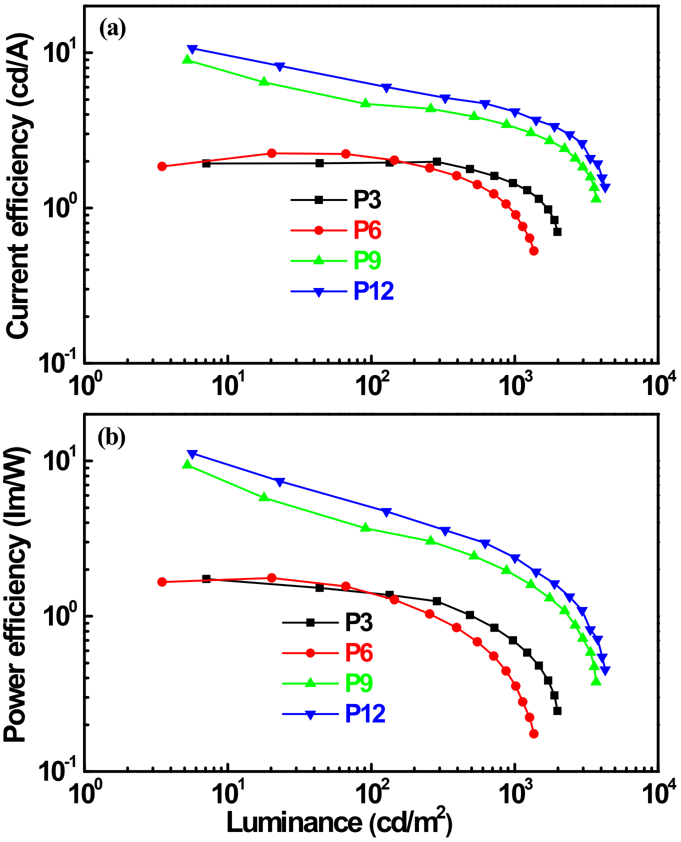


Figure S6. (a) Current efficiency versus luminance for the devices. (b) Power efficiency versus luminance for the devices.

Reference

(1) (a) J. Lee, K. Shizu, H. Tanaka, H. Nomura, T. Yasuda, C. Adachi, *J. of Mater. Chem. C* 2013, **1**, 4599; (b) P. A. More, B. L. Gadilohar, G. S. Shankarling, *Catal. Lett.* 2014, **144**, 1393; (c) O. I. Negru, M. Grigoras, *Iran. Polym. J.* 2013, **22**, 641; (d) G. I. Nosova, D. A. Lypenko, R. Y. Smyslov, I. A. Berezin, E. V. Zhukova, E. I. Mal'tsev, A. V. Dmitriev, L. S. Litvinova, N. A. Solovskaya, O. V. Dobrokhotov, I. G. Abramov, A. V. Yakimanskii, *Polym. Sci. Ser. B* 2014, **56**, 59.