

## Electronic Supplementary Information

### Sky-Blue Thermally Activated Delayed Fluorescence Polymers by Using a Conjugation-Confined Poly(aryl ethers) Main Chain

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#### General Information

All reagents were used as received from commercial sources unless otherwise stated. Tetrahydrofuran and toluene were dried by sodium-potassium alloy. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured on a Bruker Advanced II (400 MHz) spectrometers. High resolution mass spectra were measured on a LCQ-Orbitrap Elite (Thermo-Fisher Scientific, Waltham, MA, USA) mass spectrometer. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C min<sup>-1</sup> from room temperature to 600 °C. 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 a refractive detector and THF as the eluent. Absolute PLQYs were obtained using a Quantaury-QY measurement system (C11347-11, Hamamatsu Photonics) and all the samples were excited at 330 nm.

### **Synthetic process**

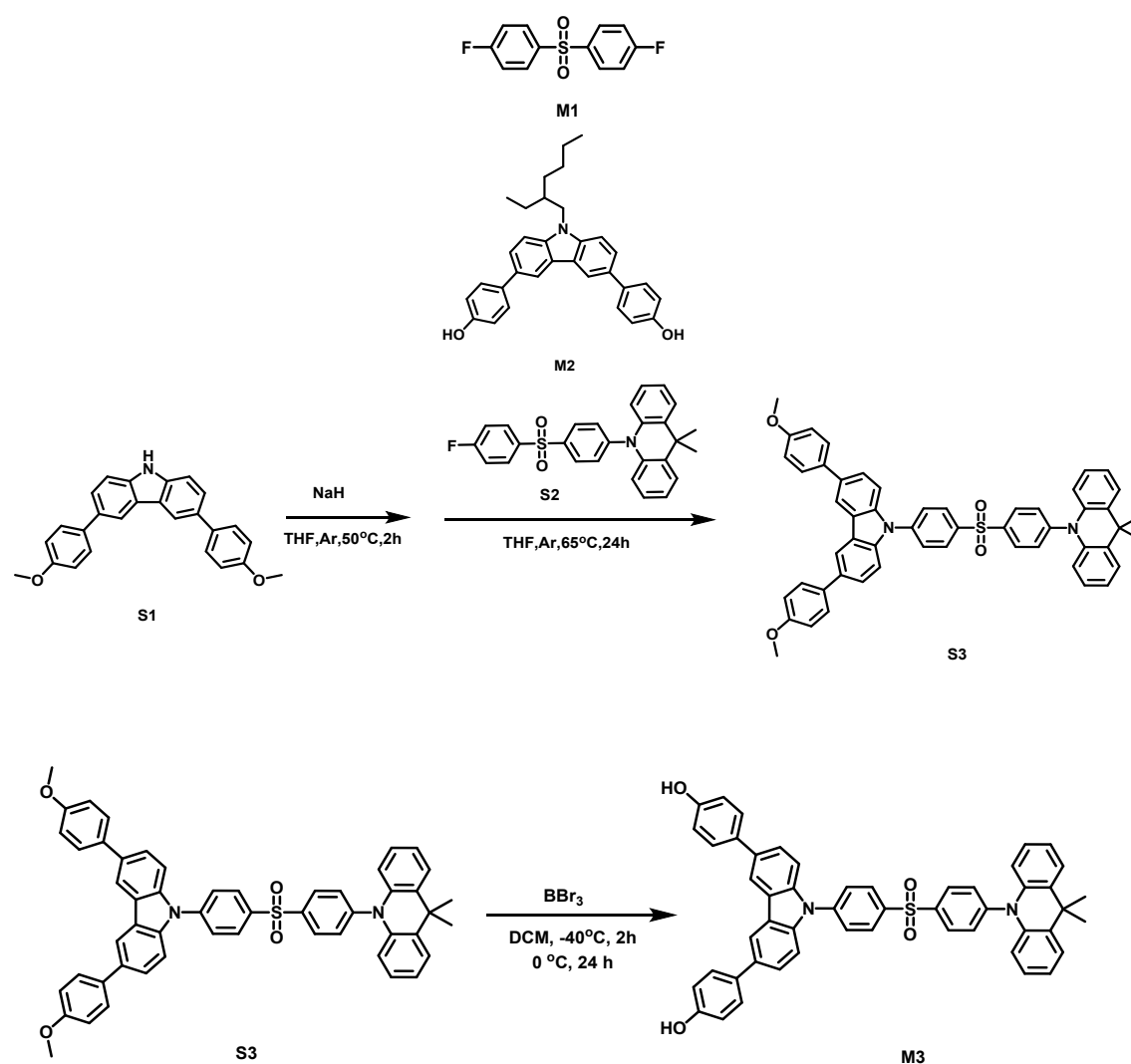
4,4'-sulfonylbis(fluorobenzene) (**M1**) was purchased from commercial sources and purified by column chromatography (silica, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> v/v 1:1). 4,4'-(9-(2-ethylhexyl)-9*H*-carbazole-3,6-diyl)diphenol (**M2**), 3,6-bis(4-methoxyphenyl)-9*H*-carbazole (S1), and 10-(4-((4-fluorophenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (S2) were synthesized according to the literature methods.<sup>1</sup>

**10-(4-((4-(3,6-bis(4-methoxyphenyl)-9*H*-carbazol-9-yl)phenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (S3):** 3,6-bis(4-methoxyphenyl)-9*H*-carbazole (S1) (1.89 g, 5 mmol) and sodium hydride (60%, 240 mg, 6 mmol) were dissolved in dry THF (40 mL) under argon atmosphere. After stirring at 50 °C for 2 h, 10-(4-((4-fluorophenyl)sulfonyl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (S2) (1.77 g, 4 mmol) was added into the solution, and then the mixture was stirred at 65 °C for 24 h.

After cooling, the reaction mixture was poured into water and extracted with dichloromethane. After evaporation of the solvent, the residue was purified by column chromatography (silica, n-hexane/CH<sub>2</sub>Cl<sub>2</sub> v/v 1:4) to give a white powder (2.56 g, 3.2 mmol). Yield: 80%. <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 8.42-8.19 (m, 6H), 7.97-7.82 (m, 2H), 7.69-7.63 (m, 6H), 7.61-7.54 (m, 4H), 7.50-7.43 (m, 2H), 7.09-6.94 (m, 8H), 6.44-6.29 (m, 2H), 3.89 (s, 6H), 1.67 (s, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ(ppm): 158.92, 146.85, 142.81, 140.24, 140.00, 139.44, 139.23, 134.41, 134.12, 131.92, 130.69, 130.50, 129.88, 128.31, 126.93, 126.45, 125.71, 125.41, 124.75, 121.82, 118.59, 115.18, 114.34, 110.02, 55.43, 36.27, 30.71. HRMS (ESI) *m/z* calcd for C<sub>53</sub>H<sub>43</sub>N<sub>2</sub>O<sub>4</sub>S<sup>+</sup> (M+H)<sup>+</sup> 803.2938, found 803.2935.

**4,4'-(9-(4-((4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)sulfonyl)phenyl)-9*H*-carbazole-3,6-diyl)diphenol (M3):** Boron tribromide (2.5 mL, 25mmol) was added dropwise to a stirring mixture of compound **3** (1.61g, 3mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at -40 °C in 0.5 h. After stirring for 2 h at -40 °C, the reaction 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 to provide a green powder (2.23 g, 2.9 mmol). Yield: 96%. <sup>1</sup>H NMR (400MHz, DMSO) δ(ppm): 9.54 (s, 2H), 8.61 (d, *J* = 2.2 Hz, 2H), 8.43-8.20 (m, 4H), 8.14-7.92 (m, 2H), 7.75-7.42 (m, 12H), 7.06-6.93 (m, 4H), 6.92-6.83 (m, 4H), 6.35-6.18 (m, 2H), 1.60 (s, 6H). <sup>13</sup>C NMR (100MHz, DMSO) δ(ppm): 157.15, 146.57, 142.43, 140.17, 139.02, 138.91, 134.05, 131.83, 131.24, 131.01, 130.34, 128.24, 127.35, 127.08, 125.97, 125.43, 124.80, 122.06, 118.61,

116.21, 115.39, 110.79, 36.27, 31.22. HRMS (ESI)  $m/z$  calcd for  $C_{51}H_{39}N_2O_4S^+$  (M+H)<sup>+</sup> 775.26250, found 775.26172.



**Scheme S1.** Synthetic routes of the monomers.

**General synthetic procedure for the polymers:** The polymerization was performed according to general procedures of aromatic nucleophilic substitution reaction. Under argon, different ratios of **M1**, **M2**, and **M3**, K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), N,N-dimethylacetamide (2.0 mL) and toluene (3.0 mL) were added to a 10 mL flask equipped with a magnetic stir bar, an oil-water separator, and a gas adapter. The

reaction was stirred at 140 °C for 3h and then at 165 °C for 24h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated and then precipitated in a mixture solvent (250 mL methanol and 30 mL acetone). After that, the precipitated polymer was dried under vacuum to provide white powder.

**P0:** **M1** (0.127 g, 0.50 mmol) and **M2** (0.232 g, 0.50 mmol) were used in polymerization (yield: 75%) <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 8.32 (d, *J* = 1.8 Hz, 2H), 7.95-7.83 (m, 4H), 7.76-7.64 (m, 6H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.16-7.01 (m, 8H), 4.33-4.11 (m, 2H), 2.16-1.98 (m, 1H), 1.47-1.17 (m, 8H), 0.90 (dt, *J* = 25.4, 7.2 Hz, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ(ppm):162.12, 153.75, 140.92, 139.07, 135.46, 131.33, 129.79, 128.85, 125.22, 123.40, 120.72, 118.72, 117.70, 109.55, 39.50, 31.01, 28.82, 24.40, 23.07, 14.06, 10.93. GPC: *M<sub>n</sub>* = 73029, *M<sub>w</sub>* = 126545, PDI = 1.73

**P5:** **M1** (0.127 g, 0.50 mmol), **M2** (0.209 g, 0.45 mmol), **M3** (0.039 g, 0.05 mmol) were used in polymerization (yield: 78%) <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm):8.32 (m, 2.3H), 7.88 (d, *J* = 8.6 Hz, 4.1H), 7.77-7.61 (m, 5.7H), 7.61-7.52(m, 0.4H), 7.45 (d, *J* = 8.6 Hz, 1.9H), 7.20- 6.92 (m, 8H), 6.42-6.31 (m,0.2H), 4.36-3.95 (m, 1.7H), 2.10 (p, *J* = 6.1 Hz, 0.9H), 1.56 (s, 0.5H), 1.49-1.16 (m, 7.3H), 0.89 (dt, *J* = 25.2, 7.2 Hz, 5.4H).<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ(ppm):162.12, 153.75, 140.92, 139.07, 135.47, 131.33, 129.79, 128.95, 128.85, 125.22, 123.41, 120.72, 118.73, 117.70, 109.55, 47.68, 39.50, 31.02, 28.82, 24.41, 23.07, 14.07, 10.94. GPC: *M<sub>n</sub>* = 74751, *M<sub>w</sub>* = 134416, PDI

= 1.80

**P10:** **M1** (0.127 g, 0.50 mmol), **M2** (0.186 g, 0.40 mmol), **M3** (0.078 g, 0.10 mmol) were used in polymerization (yield: 73%)  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 8.39-8.20 (m, 2.5H), 7.88 (d,  $J = 8.4$  Hz, 4.2H), 7.77-7.62 (m, 5.6H), 7.56 (m, 1H), 7.45 (dd,  $J = 9.1, 3.1$  Hz, 1.9H), 7.20-6.89 (m, 8.4H), 6.43-6.34 (m, 0.3H), 4.19 (t,  $J = 5.4$  Hz, 1.39H), 2.09 (q,  $J = 6.3$  Hz, 0.8H), 1.57 (s, 1.1H), 1.50-1.14 (m, 6.6H), 0.89 (dt,  $J = 25.3, 7.2$  Hz, 4.8H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 162.12, 153.75, 140.92, 139.07, 135.46, 131.33, 130.56, 129.79, 128.95, 128.85, 126.42, 125.23, 123.40, 120.72, 118.73, 117.79, 117.70, 109.56, 39.50, 31.02, 30.68, 28.82, 24.41, 23.07, 14.07, 10.94. GPC:  $M_n = 65706$ ,  $M_w = 119208$ , PDI = 1.84

**P15:** **M1** (0.127 g, 0.50 mmol), **M2** (0.162 g, 0.35 mmol), **M3** (0.116 g, 0.15 mmol) were used in polymerization (yield: 72%)  $^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 8.42-8.14 (m, 3.2H), 7.98-7.80 (m, 4.9H), 7.79-7.62 (m, 6.2H), 7.55 (dd,  $J = 8.7, 3.5$  Hz, 1.2H), 7.45 (dd,  $J = 9.2, 2.8$  Hz, 2H), 7.21-6.89 (m, 9.7H), 6.33 (dd,  $J = 6.8, 2.4$  Hz, 0.6H), 4.19 (d,  $J = 7.1$  Hz, 1.4H), 2.09 (q,  $J = 6.4, 5.7$  Hz, 0.9H), 1.56 (s, 1.9H), 1.49-1.17 (m, 6.6H), 0.89 (dt,  $J = 25.2, 7.1$  Hz, 4.7H).  $^{13}\text{C}$  NMR (100MHz,  $\text{CDCl}_3$ )  $\delta(\text{ppm})$ : 162.12, 153.75, 140.93, 140.21, 139.88, 139.07, 135.47, 132.02, 131.33, 130.54, 129.95, 129.80, 128.95, 128.85, 127.03, 126.42, 125.42, 125.23, 124.66, 123.41, 121.87, 120.77, 120.72, 118.73, 117.79, 117.70, 115.24, 109.56, 39.50, 36.27, 31.02, 30.68, 28.82, 24.41, 23.07, 14.07, 10.94. GPC:  $M_n = 574844$ ,  $M_w = 99973$ ,

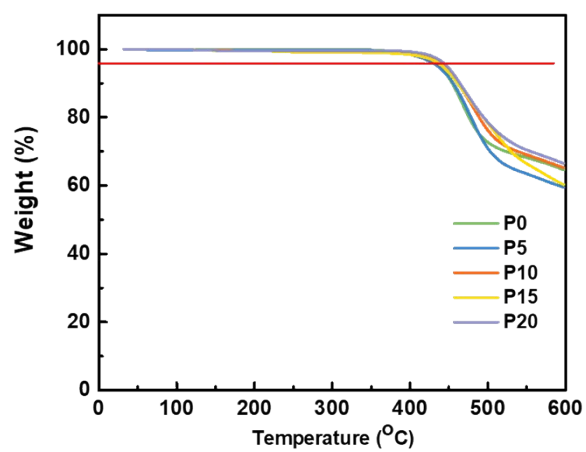
PDI = 1.73

**P20:** **M1** (0.127 g, 0.50 mmol), **M2** (0.139 g, 0.30 mmol), **M3** (0.155 g, 0.20 mmol) were used in polymerization (yield: 71%) <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm):8.40-8.19 (m, 3.4H), 7.93-7.80 (m, 4.9H), 7.68 (dd, *J* = 20.9, 8.7 Hz, 5.9H), 7.61-7.51 (m, 1.6H), 7.50-7.40 (m, 2H), 7.17-7.01 (m, 8H), 7.02-6.88 (m, 1.7H), 6.43-6.10 (m, 0.8H), 4.19 (s, 1.2H), 2.13-2.04 (m, 0.6H), 1.65-1.60(s, 2.3H), 1.47-1.21 (m, 5.3H), 0.89 (dt, *J* = 25.4, 7.1 Hz, 3.8H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ(ppm): 162.56, 151.99, 140.92, 140.20, 137.70, 135.28, 130.51, 129.78, 128.94, 128.84, 127.17, 124.75, 123.67, 123.39, 122.14, 120.71, 119.16, 118.72, 117.78, 117.69, 114.23, 111.38, 110.47, 110.01, 109.78, 105.89, 39.62, 36.69, 30.68, 24.41, 23.07, 14.07, 10.94. GPC: *M<sub>n</sub>* = 70582, *M<sub>w</sub>* = 138176, PDI = 1.96

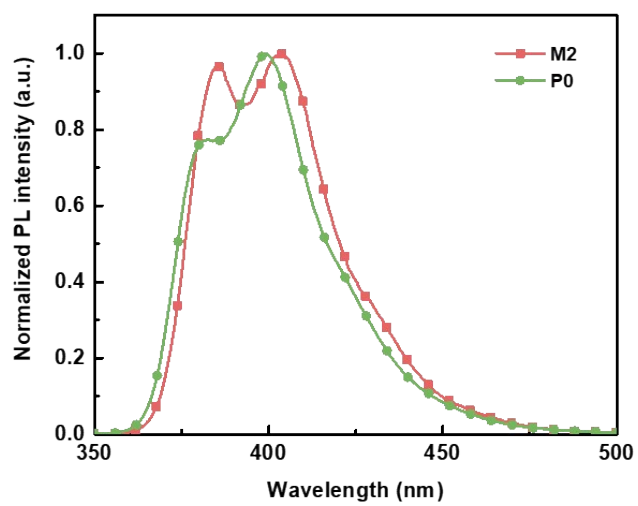
**Table S1.** The calculated data of DMAC-DP-CZPhSO and DMAC-DP-CZ

Compound	S <sub>1</sub> /T <sub>1</sub> [eV]	HOMO/LUMO [eV]
DMAC-DP-CZPhSO	3.02/2.83	-5.50/-2.05
DMAC-DP-CZ	3.20/2.84	-5.42/-2.02

Theoretical data by DFT theory calculations B3LYP-D3(BJ)/def2-svp level

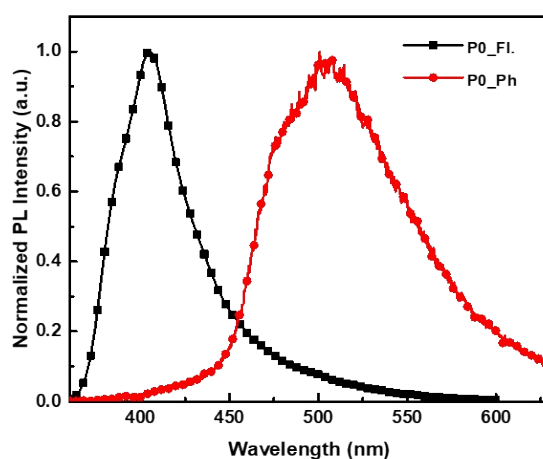


**Fig. S1** TGA traces of P0-P20 recorded at heating rate of 10 °C min<sup>-1</sup>

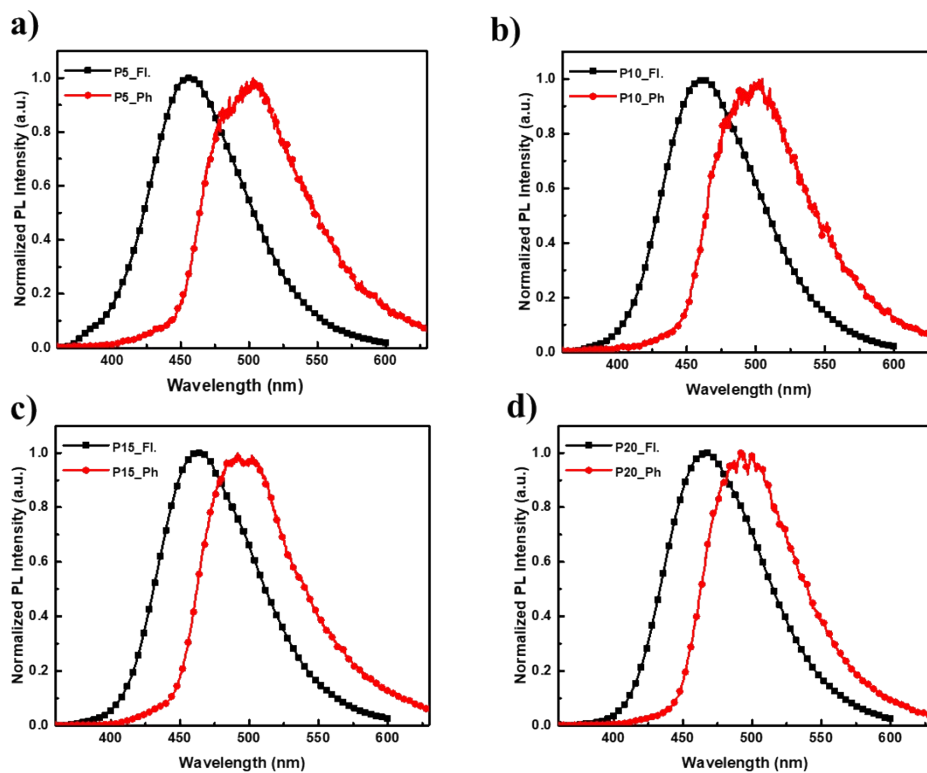


**Fig. S2** Fluorescence spectra of M2 and P0 in dilute toluene solution.

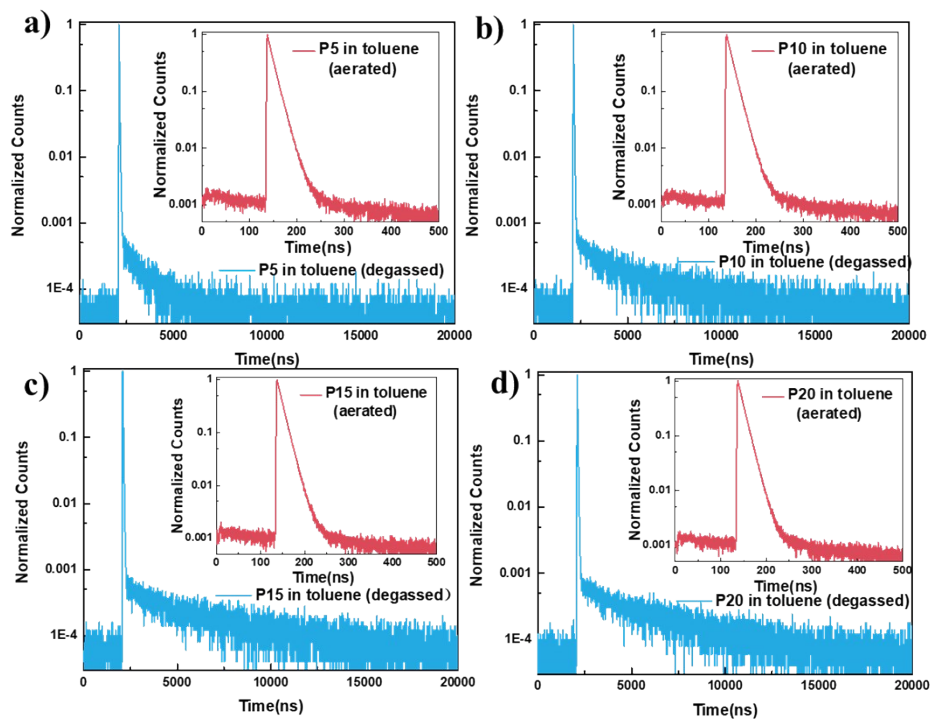




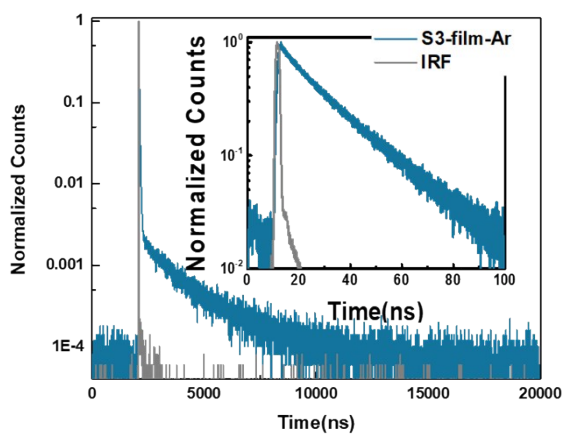
**Fig. S3** Fluorescence spectra (back line) and phosphorescence spectra (red line) of P0 in neat film.



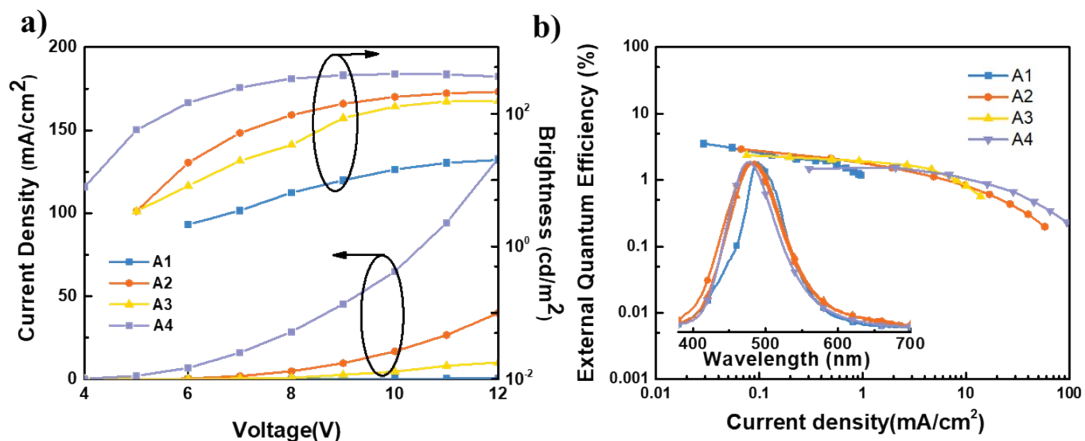
**Fig. S4** Fluorescence spectra (back line) and phosphorescence spectra (red line) of (a) P5, (b) P10, (c) P15, (d) P20 in neat film.



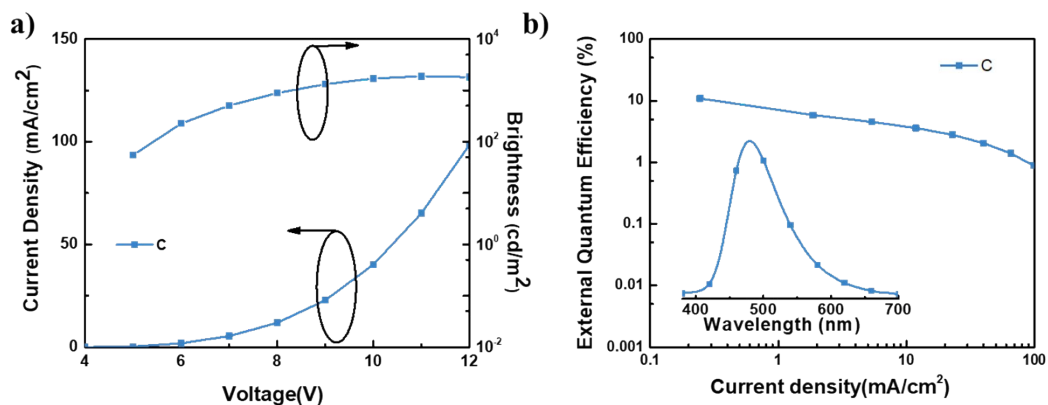
**Fig. S5** Transient PL decay curves of the polymers (a) P5, (b) P10, (c) P15, and (d) P20 in toluene under the aerated and degassed conditions.



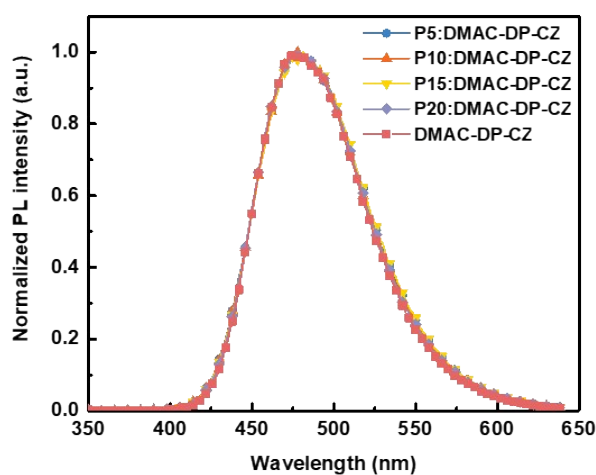
**Fig. S6** Transient PL decay curves of the S3 in neat film at room temperature (inset: prompt components).



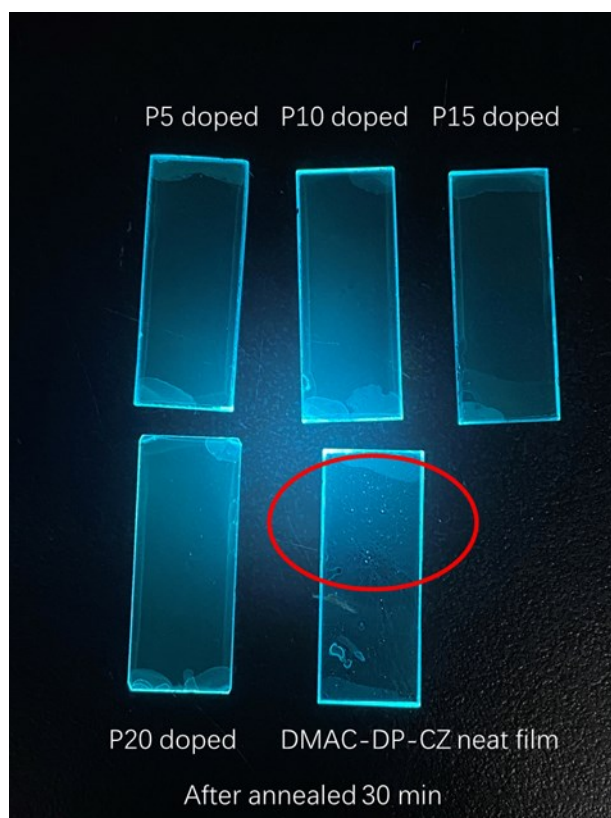
**Fig. S7** (a) Current density-voltage-luminance curves of the devices A1-A4. (b) External quantum efficiency versus current density for the devices A1-A4 (inset: the normalized EL spectra of the devices A1-A4)



**Fig. S8** (a) Current density-voltage-luminance curves of the device C. (b) External quantum efficiency versus current density for the device C (inset: the normalized EL spectra of the device C)



**Fig. S9** Fluorescence spectra of the polymers doped in DMAC-DP-CZ with the weight ratios of 80:20 (DMAC-DP-CZ: polymers) and DMAC-DP-CZ in neat film.



**Fig. S10** Photograph of DMAC-DP-CZ/Polymer doped film and DMAC-DP-CZ neat film after annealed at 150 °C for 30 min under UV illumination (Red cycle: the crystallization of DMAC-DP-CZ).

**Reference:**

- 1 L. Lin, X. Wu, Y. Han, H. Zhang, Z. Jiang and Z. Chen, *J. Appl. Polym. Sci.*, 2018, **135**, 1–11.