Electronic Supplementary Information

Dual-core star-shape single white polymers: Effect of host structure

on the luminescence

Yan Zhao,^{ab} Huimei Yao,^a Kexi Wei,^a Hongyu Zhen,^a E Yang,^a Zhenghuan Lin^{a*} and Qidan Ling^{a*}

^a Fujian Key Laboratory of Polymer Materials, College of Materials Science and Engineering, Fujian Normal University, Fuzhou 350007, China ^b College of Resources and Chemical Engineering, San Ming University, San Ming 365007, China E-mail: zhlin@fjnu.edu.cn, qdling@fjnu.edu.cn



Scheme S1 Synthetic routes of DC-PFMs and SC-PFMs.



Fig. S1 Absorption (a) and emission (b) spectra of S-PF and DC-PFMs in toluene.



Fig. S2 (a) Absorption spectra of S-PF and DC-PFMs in film. (b) Emission spectra of DC-PFM02 excited at 470nm.



Fig. S3 Decay curves of SC-PFMs (a) and DC-PFMs (b) $% \left(b\right) =0$



Fig. S4 (a) TGA curves of DC-PFM01 and DC-PFM02 polymers. (b) DSC curves of SC-PFM01and DC-PFM01.



Fig. S5 CV curves of DC-PFMs.

Devices	Turn on (V) ^a	Maximum brightness (cd/m ²)	Maximum LE (cd/A)	Maximum PE (lm/W)	Maximum EQE (%)	CIE (x, y) ^b
DC-PFM003	5.5	4380	3.66	1.44	3.42	0.19, 0.14
DC-PFM005	6.0	6130	7.68	2.68	4.19	0.24, 0.25
DC-PFM01	5.4	9704	13.16	5.9	5.6	0.29, 0.33
DC-PFM02	5.8	12610	15.76	6.29	7.29	0.33, 0.36
SC-PFM01	5.2	6940	4.58	2.88	2.47	0.26, 0.31
SC-PFM02	5.8	9244	10.3	5.68	5.1	0.28, 0.30

Table S1 Device performances of DC-PFMs.

 $^{a)}$ at the brightness of 1cd/m²; $^{b)}$ at the voltage of 10V.



Fig. S6 EL spectra of the device based on DC-PFM01 (a) and DC-PFM02 (b).



Fig. S7 Brightness-voltage-current density (a) and efficiency-density (b) characteristics of the device based on DC-PFM01.



Fig. S8 Brightness-voltage-current density (a) and efficiency-density (b) characteristics of the device based on SC-PFM01.



Fig. S9 Amplitude images of SC-PFM02 (a), DC-PFM02 (b) film.



Fig. S10 Current density-voltage characteristic of the hole only devices of ITO/PEDOT:PSS/SC-PFM-02 or DC-PFM-02/MoO₃ /Al.

Experimental Details

General methods: NMR spectra were measured in CDCl₃ on a Bruker Ascend 400 FT-NMR spectrometer, ¹H and ¹³C chemical shifts were quoted relative to the internal standard tetramethylsilane. UV-vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer. The PL spectra were probed on a Shimadzu RF-5301 PC spectrophotometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration with a Waters 1515 instrument. Thermal analyses were performed with a Mettler 851e analysis system. Differential scanning calorimetry was done on a Mettler DSC822e instrument. The nanoscale morphology of the films was observed with tapping mode-AFM by Agilent 5500. Time-resolved fluorescence decay time measurements were conducted on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 405 nm pulsed diode laser having the pulse duration of Ca. 59.7 picosecond as the exciting light source. The quantum efficiency measurements were conduct with the same device with gaseous flash nanosecond lamp as the exciting light source and with 380 nm or 470 nm wavelength excitation. All of the films for test were spin coated on the pre-cleaning quartz plate with toluene as solvent in a concentration of 10 mg/mL. The films thickness was measured on the Profilometer (Dektak XT, Bruker).

Fabrication of devices: Indium-tin oxide (ITO) with a sheet resistance $< 50 \Omega$ was used as the substrate, and washed with detergent, deionized water, acetone and isopropyl alcohol in sequence. The ITO glass substrates were dried with nitrogen flow, and followed by oxygen plasma cleaning for 4 min. A 30 nm thickness of poly-(ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated onto the ITO substrate, followed by baking at 150°C for 15 minutes. The polymer layer with 80 nm thickness was then spin-coated on top of the PEDOT: PSS layer from a chlorobenzene solution (15 mg/mL) through a Teflon filter (0.45 µm). An electron-transporting layer 2,2',2''-(1,3,5-benzeneriyl)tris(1-phenyl-1H-benzimidazole) (TPBI) was grown through thermal evaporation using at a chamber under pressure of 3×10^{-5} Pa. And then a thin layer of LiF (1 nm) was deposited onto the TPBI layer, followed by aluminum layer (120 nm). Lastly, the device was encapsulated with UV-curing glue in glove box. The current-voltage and light-intensity measurements were done on Keithly 2400 source meter and a PR-655 Spectra Scan Spectrophotometers in air atmosphere.

Materials and syntheses: All of the used reagents and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. Thin layer chromatography (TLC) was performed on MERKY silica Gel 60 thick layer plates. Column chromatography was performed on Sorbent Technologies brand silica gel (230-400 mesh).

General polymerization procedure of DC-PFMs: To a mixture monomer M2, M3 and M1,Tetrakis(triphenylphosphine)palladium(0) (20 mg,0.018 mmol),toluene (5 mL), potassium carbonate (2 M, 2 mL) solution was added. The mixture was refluxed for 48 h under nitrogen atmosphere. Then the polymer was end-capped by adding benzeneboronic acid (0.11 g, 1.0 mmol) followed by stirring for 8h, and by adding bromobenzene (0.30 mL, 3.0 mmol) followed by stirring for another 8h. The reaction was cooled to room temperature and poured into methanol/water. The precipitates were collected by filtration, and further purified by extracting with acetone for 24h by using Soxhlet apparatus. The reprecipitation procedure in dichloromethane-methanol was then repeated several times. The final product was obtained after drying in vacuum.

DC-PFM003: M2 (400 mg, 0.672 mmol), M1 (7.05 mg, 0.0224 mmol) and M3 (0.116 mg, 2.016×10^{-4} mmol) were used in the polymerization. Yield 88%. GPC: M_n=15743, PDI=2.52. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (t, 2H), 7.71 (s, 4H), 2.20 (d, 4H), 1.17 (s, 20H), 0.84 (dd, 4.2 Hz, 10H).

DC-PFM005: M2 (400 mg, 0.672 mmol), M1 (7.05 mg, 0.0224 mmol) and M3 (0.194 mg, 3.36×10^{-4} mmol) were used in the polymerization. Yield 91%. GPC: M_n=17161, PDI=2.49. ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.78 (m, 2H), 7.78 – 7.62 (m, 4H), 2.31 – 1.93 (m, 4H), 1.18 (d, 20H), 0.94 – 0.76 (m, 10H).

DC-PFM01: M2 (400 mg, 0.672 mmol), M1 (7.05 mg, 0.0224 mmol) and M3 (0.387 mg, 6.72×10^{-4} mmol) were used in the polymerization. Yield 90%. GPC: M_n=16859, PDI=2.56. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, 2H), 7.67 (d, 4H), 2.15 (s, 4H), 1.17 (s, 20H), 0.85 (s, 10H).

DC-PFM02: M2 (400 mg, 0.672 mmol), M1 (7.05 mg, 0.0224 mmol) and M3 (0.774 mg, 1.344×10^{-3} mmol) were used in the polymerization. Yield 85%. GPC: M_n=10444, PDI=1.76. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, 2H), 7.67 (d, 4H), 2.14 (s, 4H), 1.23 (d, 20H), 0.84 (s, 10H).

All of the polymers showed similar NMR spectrum, a typical spectrum of DC-PFM01: ¹³C NMR (100 MHz, CDCl₃) δ 151.83, 140.50, 140.02, 127.20, 126.16, 121.51, 119.97, 55.35, 40.39, 31.79, 30.04, 29.22, 23.94, 22.60, 14.05.