

Supporting Information

Linker engineering to regulate solid-state emission of spirodifluorene-based conjugated porous polymers for white light-emitting devices

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1. General information:

All other solvents are used directly without any treatment unless otherwise specified. Toluene and tetrahydrofuran are first dried over molecular sieves, then heated and refluxed with sodium and benzophenone before use. Nuclear magnetic resonance (NMR) spectrometry was performed on a Bruker DRx600 (600 MHz) NMR spectrometer with deuterated chloroform (CDCl_3) or deuterated dimethylsulfoxide (DMSO-d_6) as the solvent. The chemical shifts of the hydrogen NMR spectra were recorded in units of part per million (ppm) with tetramethylsilane (TMS) ($\delta=0$ ppm) as the standard. The cleavage of the H signals is indicated by the following notation: s (singlet) single peak, d (doublet) doublet peak, t (triplet) triplet peak, and m (multiplet) multiplet peak. FT-IR spectra were performed on a Bruker Tensor27 IR spectrometer using KBr pellets in the frequency range of $500\text{-}4000\text{ cm}^{-1}$. SEM images were obtained on LYRA3 XMH microscope. Transmission electron microscopies (TEM) was performed on a FEI model Tecani 20 microscope. Powder X-ray diffraction (PXRD) measurement was carried out on X-ray diffractometer Rigaku model DX-2700 diffractometer.

The glass transitions temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) on Q100 V9.4 under nitrogen flow at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Thermogravimetric analyses (TGA) were performed on a TG 209 F3 under nitrogen flow at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a BK122W analyser and the samples were degassed at $120\text{ }^\circ\text{C}$ for 12 h under vacuum

(1.3 kPa) before analysis. The pore size was calculated with the density functional theory (DFT)/BLYP method. UV-Vis absorption spectra were recorded on a HITACHI U-3900 UV spectrophotometer. PL spectra were recorded on a Horiba FluoroMax-4 fluorescence spectrophotometer. The transient fluorescence spectra of the materials were tested by an Edinburgh FLS 980 transient fluorescence spectrometer, and the quantum yields were tested by an integrating sphere HORIBA FluoroMax-4 spectrometer fitted on the FLS 980 instrument.

2. Materials synthesis

2.1 Synthesis of spiro [3,3] heptane-2,6-bis (2',2'',7',7''-tetrabromo) spirofluorene

(TBrSDF): 2,7-Dibromofluorene (6.48 g, 20 mmol) was added to ultra dry tetrahydrofuran (100 mL), sodium hydride (1.2 g, 50 mmol) was added in four portions under nitrogen atmosphere and stirred at 70 °C for 1 h. Then pentaerythritol tetrabromide (1.71 g, 4.42 mmol) solution of tetrahydrofuran was added slowly dropwise over a period of two hours. After the dropwise addition, the reaction was stirred at 70 °C for 12 h. After cooling the reaction solution to room temperature, the solvent was evaporated under reduced pressure, the reaction mixture was dissolved in dichloromethane and the organic phase was washed with deionised water, dried over anhydrous MgSO₄, filtered and the solvent was evaporated under reduced pressure. The product was purified by recrystallisation with methylene chloride to give white crystals (4.247 g, 0.006 mol) in 60% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.70 (d, *J* = 1.7 Hz, 4H), 7.53 (d, *J* = 8 Hz, 4H), 7.48 (dd, *J* = 8.2, 1.9 Hz, 4H), 3.06 (s, 8H); ¹³C NMR (600 MHz, CDCl₃) δ (ppm): 156.55, 140.45, 133.45, 129.26, 124.72, 124.02, 49.65, 49.42,

33.76; MS (MALDI-TOF): m/z 752.6 [$M+K^+$]. Elemental Anal. Calcd. for $C_{31}H_{20}Br_4$: C 52.29, H 2.83; found: C 52.64, H 2.98.

2.2 Synthesis of 2,7-diethynyl-9,9-dioctylfluorene (M_2)

(1) Synthesis of 2,7-bis(trimethylsilyl)ethynyl-9,9-dioctylfluorene (M_2 -TMS):

9,9-dioctyl-2,7-dibromofluorene (548.45 mg, 1 mmol) was added to a 100 mL two-necked flask, followed by triethylamine (15 mL) as solvent and stirring in an ice bath, then ketone iodide (10 mg, 0.05 mmol) and tetrakis(triphenylphosphine)palladium (115 mg, 0.1 mmol) were added to the reaction flask as catalyst. After stirring under an ice bath for 30 min, trimethylethylsilyl (1.27 mL, 9 mmol) was added and stirring was continued for 30 min, and the reaction system was heated to 80 °C for 24 h. After the reaction was completed, the reaction flask was cooled to room temperature, the solvent was removed by rotary evaporation, and the crude product was purified by column chromatography using hexane as the eluent (silica column, 200~300 mesh), and the product M_2 -TMS (225 mg, 0.38 mmol) was obtained in 33% yield. 1H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, $J = 7.8, 0.5$ Hz, 2H), 7.47–7.39 (m, 4H), 1.95–1.89 (m, 4H), 1.54 (s, 3H), 1.25–0.98 (m, 21H), 0.82 (t, $J = 7.3$ Hz, 6H), 0.38–0.21 (m, 18H).

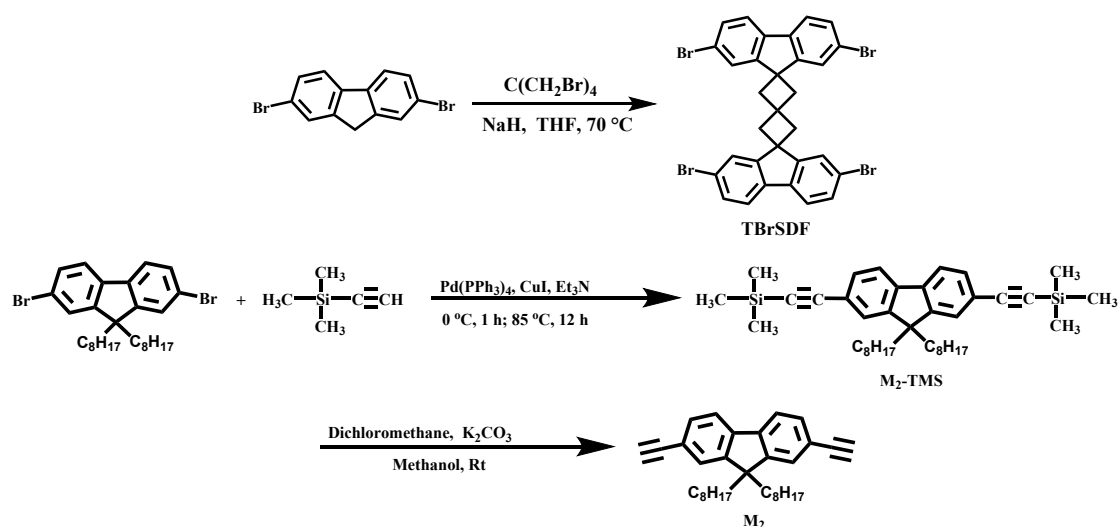
(2) Synthesis of 2,7-diethynyl-9,9-dioctylfluorene (M_2): The prepared M_2 -TMS (598.44 mg, 1 mmol) and potassium carbonate (316 mg, 2.27 mmol) were added to methanol (10 mL) and methylene chloride (10 mL) with stirring and the reaction was carried out overnight at room temperature. After the reaction was complete, the solvent was removed by rotary evaporator, and the remaining solid was redissolved in 430 mL of dichloromethane and washed three times with deionized water, dried with anhydrous

magnesium sulfate, and then filtered to remove the anhydrous magnesium sulfate solid, and the crude product was purified by column chromatography using n-hexane as the eluent (silica gel column, 200-300 mesh) to afford **M₂** (200 mg, 0.21 mmol) in 35% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.48 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.46 (s, 2H), 3.15 (s, 2H), 1.95–1.91 (m, 4H), 1.26–1.00 (m, 24H), 0.82 (t, *J* = 7.3 Hz, 6H).

2.3 Synthesis of CPP-1: TBrSDF (356.06 mg, 0.5 mmol), 9,9-dioctylfluorene-2,7-diboronic acid (**M₁**) (502.194 mg, 1.05 mmol), 2M aqueous potassium carbonate (10 mL) and 30 mL toluene solution were added to a two-necked flask. Tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (0.05 mmol, 0.057 g) and Aliquant 336 phase transfer catalyst (1 mL) were added and the reaction was continued for 96 h at 110 °C under reflux by slowly increasing the temperature to 110 °C. At the end of the reaction, the mixture was cooled to room temperature. The mixture was washed with deionized water and the organic phase was concentrated under reduced pressure and dialyzed with anhydrous methanol (300 mL), stirred for 2 h and then filtered to give a brown powder, and the green powder was Soxhleted with acetone for 72 h to give the product (0.63 g) in 76% yield. IR (KBr): $\nu = 2910, 2850, 1605, 1352, 1150, 808 \text{ cm}^{-1}$.

2.4 Synthesis of CPP-2: The polymer **CPP-2** was prepared by Sonogashira-Hagihara coupling polymerization by dissolving TBrSDF (360 mg, 0.5 mmol) and 2,7-diethynyl-9,9-dioctylfluorene (460 mg, 1.0 mmol) in DMF (70 mL in a 250 mL round bottom flask) and triphenylamine (30 mL). It was degassed by a freeze-extract-thaw

cycle. Tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) and cuprous iodide (10 mg, 0.05 mmol) were rapidly added to the system. The system was degassed again and finally heated to 90 °C under a nitrogen atmosphere for 96 h. After completion of the reaction, the system was cooled to room temperature, the mixture was washed with deionized water, the organic phase was concentrated under reduced pressure and dialyzed with anhydrous methanol (300 mL), stirred for 2 h and then filtered, and the filter cake was washed with water, methanol and CH₂Cl₂, respectively, to remove unreacted monomers and residual catalysts. The product was further purified by Soxhlet extraction with acetone for 72 h. A yellow solid (0.79 g) was obtained in 72% yield. IR (KBr): $\nu = 3280, 2910, 2845, 1455, 814, 653 \text{ cm}^{-1}$.



Scheme. S1 Synthesis routes of the monomer **TBrSDF** and **M₂**.

3. Thermal stabilities and Porous Properties of the CPPs

Table S1 Thermal stabilities and porosity properties of the conjugated porous polymers **CPP-1** and **CPP-2**.

CPPs	T_d (°C)	T_g (°C)	$S_{\text{Langmuir}}^{\text{a)}$ (m^2/g)	$V_{\text{total}}^{\text{b)}$ (cm^3/g)	Pore size distribution ^{c)}
CPP-1	407	182	35	0.086	1.28
CPP-2	400	170	35	0.026	1.72

a) Langmuir specific surface area: calculated from the adsorption line portion of the nitrogen adsorption and desorption isotherm using Langmuir's equation.

b) Total pore volume: calculated at $P/P_0 = 0.993$ and 0.996 for polymer **CPP-1** and **CPP-2**, respectively.

c) obtained from the pore size distribution curve.

4. Electroluminescent properties of LEDs

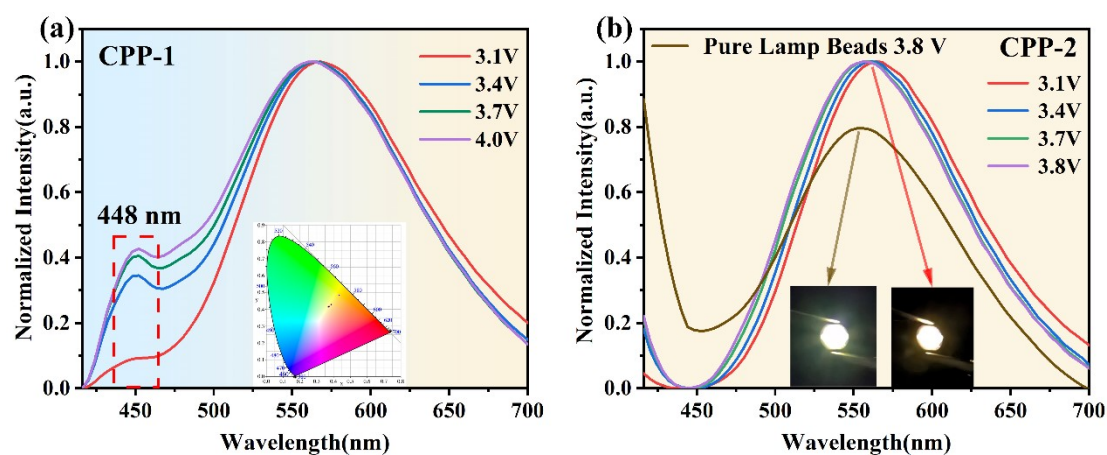


Fig. S1 (a) Emission spectra of the LEDs coated with 3 layers of **CPP-1** at different excitation voltages with corresponding CIE coordinate plots (inset). (b) Emission spectra of the LEDs coated with 5 layers of **CPP-2** at different excitation voltages as well as the emission spectra of UV LED chips at 3.8 V, and their photographs when activated (inset).

Table S2 Electroluminescent properties of LEDs coated with 3 layers of polymer **CPP-1**

<i>V</i> (V)	<i>CD</i> (mA/cm ²)	<i>L_m</i> (cd/m ²)	<i>CE</i> (cd/A)	<i>PE</i> (lm/W)	CIE 1931 X	CIE 1931 Y	CCT(K)	CRI
3.10	27.14	30.96	0.11	0.12	0.433	0.485	3612	67
3.40	367.77	270.40	0.07	0.07	0.385	0.428	4212	74
3.70	917.33	624.40	0.07	0.06	0.374	0.418	4418	76
4.00	1552.36	1018.00	0.07	0.05	0.369	0.415	4521	77

Table S3 Electroluminescent properties of LEDs coated with 5 layers of polymer **CPP-1**

<i>V</i> (V)	<i>CD</i> (mA/cm ²)	<i>L_m</i> (cd/m ²)	<i>CE</i> (cd/A)	<i>PE</i> (lm/W)	CIE 1931 X	CIE 1931 Y	CCT(K)	CRI
3.10	27.52	82.01	0.30	0.30	0.398	0.473	4157	66
3.40	335.26	614.50	0.18	0.17	0.347	0.391	5041	77
3.70	808.53	1334.00	0.16	0.14	0.334	0.371	5461	80
3.80	1005.70	1646.00	0.16	0.14	0.331	0.368	5571	81

Table S4 Electroluminescent properties of LEDs coated with 5 layers of polymer **CPP-2** and UV

LED chips.

	<i>V</i> (V)	<i>CD</i> (mA/cm ²)	<i>L_m</i> (cd/m ²)	<i>CE</i> (cd/A)	<i>PE</i> (lm/W)	CIE 1931 X	CIE 1931 Y	CCT(K)	CRI
CPP-2	3.10	26.05	77.98	0.30	0.30	0.434	0.502	3696	62
	3.40	332.03	743.10	0.22	0.21	0.408	0.480	4001	67
LEDS	3.70	807.99	1795.00	0.22	0.19	0.397	0.477	4200	67
	3.80	1007.07	2191.00	0.22	0.18	0.392	0.474	4271	68
chips	3.80	1040.48	3907.00	0.38	0.31	0.345	0.385	5096	79

5. Emission spectra of CPP-1 and CPP-2 in different polar solvents

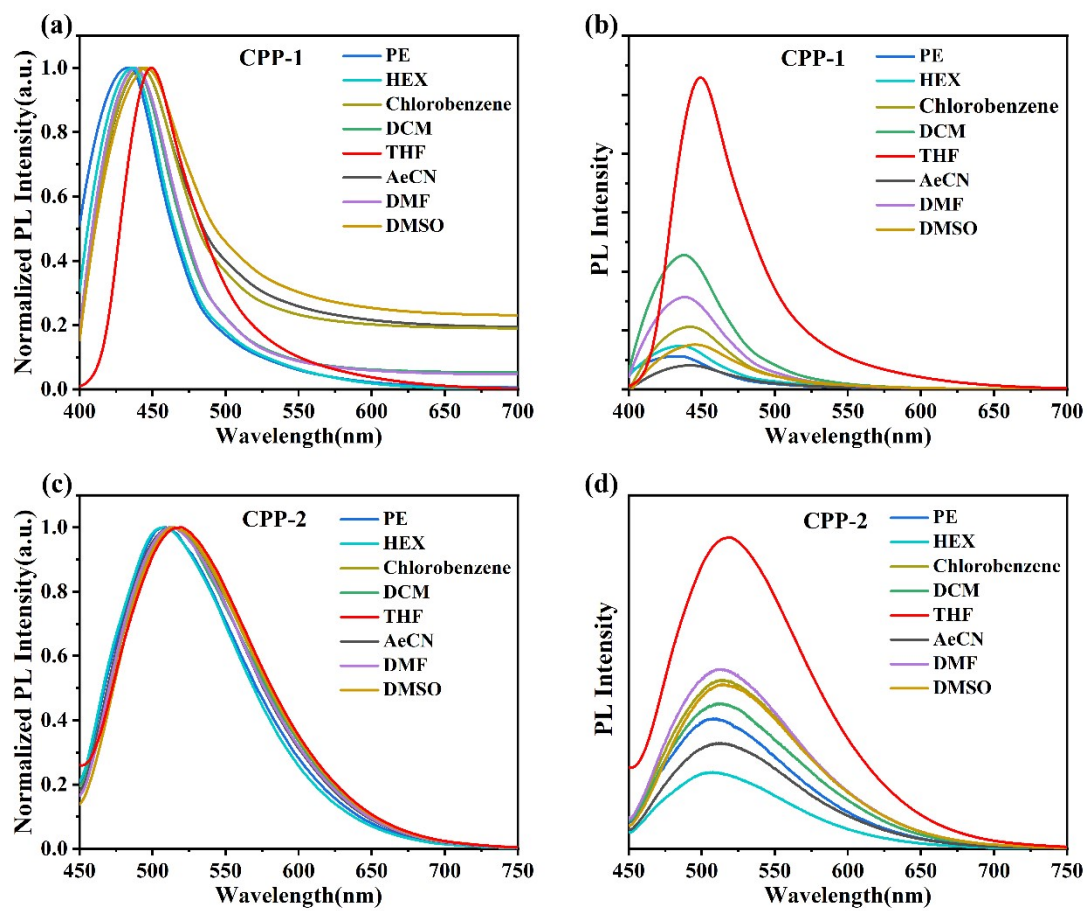


Fig. S2 Emission spectra of (a) (b) CPP-1 and (c) (d) CPP-2 in different polar solvents.