Supporting Information

Two-armed skeleton extension strategy for the design of novel spirobifluorene-based small molecule donors

Yanli Guo[a†], Yueting Liang[a†], Lunxiang Yin[a*], Chang Liu[a] and Yanqin Li[a*]

[a]*School of Chemistry, Dalian University of Technology, Dalian, 116024, China.*

**Corresponding authors:*

Email: lxyin@dlut.edu.cn; liyanqin@dlut.edu.cn. Tel:+86-155-24572530

[†]*These authors contributed equally to this work and should be regarded as co-first authors.*

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1. Synthesis

Scheme S1 Synthetic routes of the intermediates

In order to synthesize the series of target products, **SF(DPP)$_2$**, **SF(aDPP)$_2$**, **SF(DPPCz)$_2$** and **SF(aDPPCz)$_2$**, the synthetic routes of the intermediates are shown in **Scheme S1**, and the details of the synthesis are described below as the reference reported.[1-6]

1.1 The synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (SF1)

A mixture of 2,7-dibromo-9,9'-spirobi[fluorene] (119 mg, 0.25mmol), bis(pinacolato)diboron (190 mg, 0.75 mmol), KOAc (98 mg, 1.0 mmol), Pd(PPh$_3$)$_4$ (29 mg, 0.03 mmol) and 15 mL 1,4-dioxane was heated at 95℃ for 5 h under nitrogen atmosphere. After the reaction mixture was cooled down, 10 mL of water was added, the precipitate was collected as a crude product by suction filtration. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (1:1, v/v) as eluent to afford a white solid (54 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 -7.83 (m, 6H), 7.38-7.34 (t, *J* = 7.5 Hz, 2H), 7.13 (s, 2H), 7.09 (t, *J* = 7.6 Hz,

2H), 6.69 (d, *J* = 7.5 Hz, 2H), 1.24 (s, 24H).

1.2 The synthesis of 2,7-bis((trimethylsilyl)ethynyl)-9,9'-spirobi[fluorene] (S1)

Under nitrogen atmosphere, 2,7-dibromo-9,9'-spirobi[fluorene] (284 mg, 0.60 mmol), trimethylsilyl acetylene (0.20 mL, 1.44 mmol), $Pd(PPh_3)_2Cl_2$ (21 mg, 0.03 mmol), PPh_3 (32 mg, 0.12 mmol) and CuI (23 mg, 0.12 mmol) were added in a 50 ml three-neck flask, and then diisopropylamine (3 ml) and anhydrous tetrahydrofuran (12 mL) were injected into the reaction mixture. The mixture was heated at 60℃ for 24 h. The reaction solution was cooled down and poured into 10 mL water. After being extracted with dichloromethane (3 × 15 mL), The organic layer was dried over anhydrous sodium sulfate, then the solvent was removed under reduced pressure. The residue was purified by silica column chromatography using CH_2Cl_2/petroleum ether (1:4, v/v) as eluent to give a white solid (277 mg, 91%). M.p.: 281-282 ℃.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.48 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.82 (s, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 0.15 (s, 18H).

1.3 The synthesis of 2,7-diethynyl-9,9'-spirobi[fluorene] (SF2)

Compound S1 (1.02 g, 2 mmol) was dissolved in 30 mL ethanol and 30 mL tetrahydrofuran, and anhydrous potassium carbonate (2.764 g, 20 mmol) was added. The reaction mixture was stirred at room temperature overnight. Then the precipitate was filtered off and filtrate was collected. After removed the solvent under reduced pressure, the residue was purified by silica column chromatography eluting with CH_2Cl_2/petroleum ether (1:2, v/v) to obtain a white solid (0.71 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.51 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.86 (s, 2H), 6.71 (d, *J* = 7.5 Hz, 2H), 2.98 (s, 2H).

1.4 The synthesis of 3-bromo-9*H*-carbazole (S2)

9*H*-carbazole (1.67 g, 10 mmol) was dissolved in a solution of 30 mL DMF. A solution of N-bromosuccinimide (NBS, 1.78 g, 10 mmol) in 15 mL DMF was added dropwise at 0 ℃. The reaction mixture was stirred at room temperature for 5 h in the dark. Then, the mixture was poured into water (200 mL). The white precipitate was collected by suction filtration, and the filter cake was recrystallized with ethanol to obtain a white solid (1.50 g, 61%). M.p.: 197-197 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.41-7.45 (m, 2H), 7.21-7.26 (m, 2H).

1.5 The synthesis of 3-bromo-9-octyl-9*H*-carbazole (S3)

Compound S2 (676 mg, 2.8 mmol), Bu_4NBr (9 mg,0.28 mmol) and KOH (308 mg, 5.50 mmol) were dissolved in acetone (15 mL). The reaction mixture was added $C_8H_{17}Br$ (0.72 mL, 4.13 mmol) and heated at 57℃ for 5h. After the reaction solution was cooled down, the precipitate was filtered out and collected. The filtrate was purified by silica column chromatography eluting with petroleum ether to afford a colorless oily substance (905 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.49 (td, *J* = 7.6, 7.0, 1.3 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 4.26 (t, *J* = 7.3 Hz, 2H), 1.87-1.83 (m, 2H), 1.34-1.23 (m, 10H), 0.87 (t, *J* = 6.8 Hz, 3H).

1.6 The synthesis of 9-octyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole (S4)

A mixture of compound S3 (1.22 g, 3.39 mmol), bis(pinacolato)diboron (1.03 g, 4.07 mmol), KOAc (997 mg, 10.17 mmol), $Pd(PPh_3)_2Cl_2$ (48 mg, 0.07 mmol), PPh_3 (36 mg, 0.14 mmol) and 50 mL anhydrous toluene was heated at 110 ℃ for 24 h under nitrogen atmosphere. After the reaction mixture was cooled down, 20 mL water was poured into the solution, and the mixture was extracted with $CHCl_3$ (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1, v/v) as eluent to afford a colorless oily substance (1.06 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 7.93-7.90 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 4.28 (t, *J* = 7.2 Hz, 2H), 1.88-1.82 (m, 2H), 1.39 (s, 12H), 1.35-1.20 (m, 10H), 0.85 (t, *J* = 6.9 Hz, 3H).

1.7 The synthesis of 3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (S5)

A mixture of sodium (2.20 g, 96 mmol), $FeCl_3$ (0.05 g, 0.30 mmol) and 48 mL dry tert-amyl alcohol was stirring at 120 ℃ under nitrogen atmosphere until the sodium disappeared completely. Then 2-carbonitrile thiophene (4.46 ml, 48 mmol) was added to the mixture solution. A solution of succinic acid dimethyl ester (2.80 g, 19.20 mmol) in 20 mL dry tert-amyl alcohol was added dropwise. After stirring at 120 ℃ for 24 h, 20 mL AcOH was added and kept stirring for another 1 hour. After being cooled to room temperature, the precipitate was filtered, then washed with water and methanol to afford a red solid compound (5.46 g, 95 %). The crude product was used directly in the next step.

1.8 The synthesis of 2-(2-ethylhexyl)-5-(3-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione(S6)

A mixture of compound S5 (900mg, 3mmol), K_2CO_3 (1.24 g, 9 mmol) and 50 mL anhydrous DMF was stirring at 120℃ for 1 h under nitrogen atmosphere. Then 2-ethylhexyl bromide (1.33 mL, 7.50 mmol) was added dropwise to the flask and the reaction mixture was stirred for 12 h. After being cooled to room temperature, the mixture was poured into 80 mL water and stirred for 1 h. The reaction solution was washed with 20 mL water, extracted with $CHCl_3$ (3 × 30 mL), and the collected organic phase was dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatograph eluting with CH_2Cl_2/petroleum ether(3:1, v/v) as the eluent to afford a purple-brown solid (637mg, 40%).^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 3.8 Hz, 2H), 7.63 (d, *J* = 5.0 Hz, 2H), 7.28 (t, *J* = 4.1 Hz, 2H), 4.09-3.97 (m, 4H), 1.90-1.82 (m, 2H), 1.39-1.26 (m, 16H), 0.89-0.84 (t, *J* = 10.3 Hz, 12H).

1.9 The synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (DPP-Br)

Compound S6 (840 mg, 1.60 mmol) was dissolved in 42 mL $CHCl_3$ and a solution of NBS (302 mg, 1.70 mmol) in 20 mL $CHCl_3$ was added dropwise to the solution. Then the reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatograph eluting with CH_2Cl_2/petroleum

ether (3:2, v/v) to afford a purple solid (585 mg, 61%). M.p.: 125-127℃. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.93-8.87 (m, 1H), 8.63 (d, *J* = 4.2 Hz, 1H), 7.69-7.58 (m, 1H), 7.28 (d, *J* = 4.3 Hz, 1H), 7.22 (d, *J* = 4.2 Hz, 1H), 4.04-3.87 (m, 4H), 1.85 (d, *J* = 5.1 Hz, 2H), 1.37-1.20 (m, 16H), 0.92-0.82 (m, 12H).

1.10 The synthesis of 2,5-bis(2-ethylhexyl)-3-(5-(9-octyl-9H-carbazol-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (S7)

A mixture of DPP-Br (407 mg, 0.67 mmol), compound S4 (249 mg, 0.61 mmol), $Pd(PPh_3)_4$ (36 mg, 0.03 mmol) and anhydrous potassium carbonate (3.38 g, 24.52 mmol) in toluene (24 mL), ethanol (6 mL) and deionized water (12 mL) was stirred at 110 ℃ for 24 h under a nitrogen atmosphere. After being cooled to room temperature, the reaction solution was poured into 20 mL of water and extracted with dichloromethane (3 ×20 mL). The combined organic phase was dried over anhydrous sodium sulfate. The solvent was evaporated, and the residue was purified by silica column chromatography with ethyl acetate/petroleum ether (16 :1, v/v) as the eluant to give a purple solid (421 mg, 86%). M.p.:138-139℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 (d, *J* = 4.0 Hz, 1H), 8.86 (d, *J* = 3.4 Hz, 1H), 8.38 (d, *J* = 1.4 Hz, 1H), 8.15 (d, *J* = 7.7 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.60 (d, *J* = 4.7 Hz, 1H), 7.53-7.50 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 8.5, 6.1 Hz, 2H), 4.31 (t, *J* = 7.2 Hz, 2H), 4.13-4.03 (m, 4H), 2.02-1.96 (m, 1H), 1.91-1.86 (m, 3H), 1.40-1.24 (m, 26H), 0.94-0.86 (m, 15H).

1.11 The synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(5-(9-octyl-9H-carbazol-2-yl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (CzDPP-Br)

Compound S7 (514 mg, 0.64 mmol) was dissolved in 45 mL $CHCl_3$ and a solution of NBS (126 mg, 0.71 mmol) in 10 mL $CHCl_3$ was added dropwise. The mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatograph eluting with CH_2Cl_2/petroleum ether (2:1, v/v) to afford a purple solid (484 mg, 61%). M.p.: 157-158℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.07 (d, *J* = 4.1 Hz, 1H), 8.59 (d, *J* = 4.1 Hz, 1H), 8.38 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 4.3 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 4.1 Hz, 1H), 4.31 (t, *J* = 7.3 Hz, 2H), 4.15-4.05 (m, 2H), 4.02-3.91 (m, 2H), 2.02-1.97 (m, 1H), 1.92-1.82 (m, 3H), 1.40 -1.25 (m, 26H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.90-0.86 (m, 12H).

2. ^{1}H-NMR and ^{13}C-NMR spectra

Fig. S1 ^{1}H-NMR spectrum of **SF(DPP)$_2$**

Fig. S2 ^{13}C-NMR spectrum of **SF(DPP)$_2$**

Fig. S3 ^{1}H-NMR spectrum of **SF(aDPP)$_2$**

Fig. S4 ^{13}C-NMR spectrum of **SF(aDPP)$_2$**

Fig. S5 ^{1}H-NMR spectrum of **SF(DPPCz)$_2$**

Fig. S6 ^{13}C-NMR spectrum of **SF(DPPCz)$_2$**

Fig. S7 ^{1}H-NMR spectrum of **SF(aDPPCz)$_2$**

Fig. S8 ^{13}C-NMR spectrum of **SF(aDPPCz)$_2$**

Fig. S9 ^{1}H-NMR spectrum of **S7**

Fig. S10 ^{1}H-NMR spectrum of **CzDPP-Br**

3. TD-DFT calculated electronic transitions

Table S1 The data of electronic transitions of the four SMDs calculated by TD-DFT.

Compound	State	$E_g^{TD\text{-}DFT}$ (eV)	λ_{max} (nm)	f	Composition
SF(DPP)$_2$	S1	1.97	629	1.75	HOMO→LUMO (71%)
	S4	2.30	539	0.63	HOMO-1→LUMO+1(70%)
	S21	3.71	334	0.24	HOMO→LUMO+5(41%)
SF(aDPP)$_2$	S1	1.92	647	2.38	HOMO→LUMO (70%)
	S4	2.21	561	0.77	HOMO-1→LUMO+1(70%)
	S16	3.42	363	0.41	HOMO-4→LUMO+1(51%)
SF(DPPCz)$_2$	S1	1.83	676	2.72	HOMO→LUMO (70%)
	S4	2.15	576	0.85	HOMO-1→LUMO+1(70%)
	S35	3.66	339	0.78	HOMO-2→LUMO+2(40%)
SF(aDPPCz)$_2$	S1	1.79	693	3.46	HOMO→LUMO (70%)
	S4	2.07	598	0.94	HOMO-1→LUMO+1(70%)
	S26	3.37	369	0.44	HOMO-8→LUMO+1(57%)

4. Photovoltaic properties of the devices based on $PC_{61}BM$

Fig. S11 *J-V* curves of devices based on **SF(DPP)$_2$**, **SF(aDPP)$_2$**, **SF(DPPCz)$_2$** and **SF(aDPPCz)$_2$** with $PC_{61}BM$ as acceptor under an illumination of 100 mW cm^{-2}.

Table S2 Photovoltaic data of the devices based on **SF(DPP)$_2$**, **SF(aDPP)$_2$**, **SF(DPPCz)$_2$** and **SF(aDPPCz)$_2$** with $PC_{61}BM$ as acceptor.

SMD	J_{sc} (mAcm^{-2})	V_{oc} (V)	FF (%)	PCE [PCE^{ave}][c] (%)
SF(DPP)$_2$ [a]	9.90	0.90	28.8	2.57(2.41)
SF(aDPP)$_2$ [a]	7.13	0.93	26.7	1.77(1.61)
SF(DPPCz)$_2$ [a]	12.87	0.78	42.0	4.22(4.06)
SF(DPPCz)$_2$ [b]	17.66	0.76	52.2	7.00(6.70)
SF(aDPPCz)$_2$ [a]	12.42	0.80	35.0	3.48(3.40)
SF(aDPPCz)$_2$ [b]	18.24	0.74	51.3	6.93(6.62)

a As-cast.

b With CH_2Cl_2-SVA treatment for 30 s.

c The data in parentheses are the average values of PCE obtained from at least 8 devices.

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