

Supplementary Information

Alkyl fluorene-based cross-linkable hole transport materials with high triplet energy for high-efficiency solution-processed green PHOLEDs

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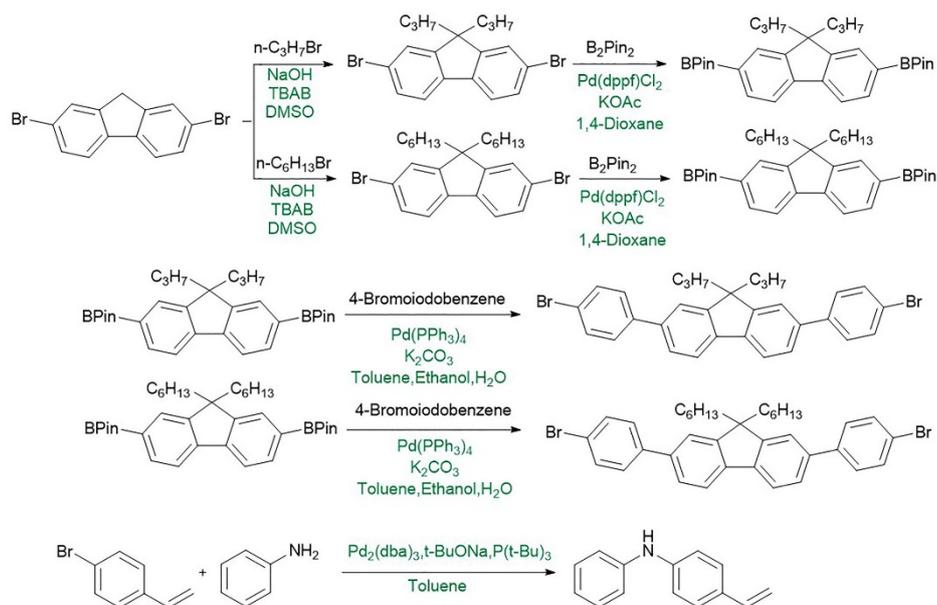


Fig. S1 Synthetic routes and structures of intermediates.

Synthesis of 2,7-dibromo-9,9-dipropyl-9H-fluorene (1)

2,7-dibromofluorene (3.31 g, 10 mmol), 1-bromopropane (2.04 mL, 22 mmol) and TABA (0.16 g, 0.5 mmol) were dissolved in DMSO (40 mL). The reaction was stirred at room temperature under an inert atmosphere, and 50% NaOH solution was added. After 5 hours of reaction, added appropriate amount of water and extracted with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether to obtain compound 1 as a white yellowish solid (3.39 g, 75.2%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 6.7 Hz, 4H), 1.97 – 1.85 (m, 4H), 0.73 – 0.60 (m, 10H).

Synthesis of 2,2'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborane) (2)

Compound 1 (2.25 g, 5 mmol), binary borate (5.18 g, 20 mmol), potassium acetate (3.97 g, 40 mmol), PdCl₂(dppf) (0.392 g, 0.525 mmol) were dissolved in 1, 4-dioxane (40 mL). The mixture was reacted at 80 °C for 10 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with dichloromethane. The solvent was evaporated under

reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether/dichloromethane (20:1) to obtain compound 2 as a white crystal (2.64 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.69 (m, 4H), 1.99 (s, 4H), 1.39 (s, 24H), 0.63 (s, 10H).

Synthesis of 2,7-bis(4-bromophenyl)-9,9-dipropyl-9H-fluorene (3)

Compound 2 (1.63 g, 3 mmol), 4-bromiodobenzene (1.91 g, 6.6 mmol), anhydrous potassium carbonate (1.26 g, 9 mmol), Pd(PPh₃)₄ (0.3 mmol, 0.35 g) and toluene-ethanol-water (30 mL, 15 mL, 15 mL) were added to a two-necked round bottom flask respectively. The mixture was stirred and reacted at 115 °C for 48 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether to obtain compound 3 as a white crystal (1.02 g, 56.5%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.3 Hz, 4H), 8.07 (d, *J* = 7.3 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 4H), 7.55 (s, 6H), 7.39 (dd, *J* = 19.3, 7.6 Hz, 10H), 7.20 (d, *J* = 4.3 Hz, 8H), 7.11 (s, 4H), 6.93 (d, *J* = 6.7 Hz, 2H), 6.74 – 6.52 (m, 2H), 5.59 (d, *J* = 14.7 Hz, 2H), 5.10 (d, *J* = 10.8 Hz, 2H), 2.07 (s, 4H), 1.14 (s, 12H), 0.96 (s, 4H), 0.79 (s, 6H).

Synthesis of *N*-phenyl-4-vinyl aniline (4)

Sodium tert-butoxide (2.94 g, 30 mmol), Pd₂(dba)₃ (0.28 g, 0.3 mmol), aniline (1.1 mL, 12 mmol), *p*-bromostyrene (1.31 mL, 10 mmol), tert-butyl phosphorus (toluene solution) (1.49 mL, 0.73 mmol) and toluene (60 mL) were added to a two-necked round bottom flask respectively. The mixture was stirred and reacted at 90 °C for 10 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with ethyl acetate. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on Al₂O₃ eluted with petroleum ether/ethyl acetate (70:1) to obtain compound 4 as a white solid (1.38g, 70.9%). ¹H NMR (400 MHz, DMSO) δ 8.27 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.24 (t, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.03 (d,

$J = 8.5$ Hz, 2H), 6.84 (t, $J = 7.3$ Hz, 1H), 6.63 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.61 (d, $J = 18.4$ Hz, 1H), 5.06 (d, $J = 10.9$ Hz, 1H).

Synthesis of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl) aniline) (5)

Compound 3 (0.90 g, 1.5 mmol), compound 4 (0.64 g, 3.3 mmol), Sodium tert-butoxide (0.44 g, 4.5 mmol), Pd₂(dba)₃ (0.05 g, 0.045 mmol), tri-tert-butyl phosphine (toluene solution) (0.24 mL, 0.12 mmol) and toluene (40 mL) were added to a two-necked round bottom flask respectively. The mixture was stirred and reacted at 90 °C for 16 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with ethyl acetate. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on Al₂O₃ eluted with petroleum ether/EtOAc (100:1) to obtain compound 5 as a white solid (0.78 g, 65.5%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, $J = 8.4$ Hz, 1H), 7.62 – 7.53 (m, 4H), 7.35 – 7.26 (m, 4H), 7.18 (t, $J = 8.0$ Hz, 4H), 7.13 – 6.99 (m, 3H), 6.69 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.67 (d, $J = 17.6$ Hz, 1H), 5.18 (d, $J = 11.0$ Hz, 1H), 2.02 (dd, $J = 9.6, 5.7$ Hz, 2H), 0.75 (dt, $J = 12.7, 6.1$ Hz, 2H), 0.68 (t, $J = 6.5$ Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 151.71, 147.63, 147.47, 146.95, 139.90, 139.51, 136.38, 136.03, 132.25, 129.48, 127.97, 127.27, 125.70, 124.71, 124.39, 123.92, 123.25, 121.11, 120.06, 112.36, 55.58, 42.99, 17.32, 14.58.

Synthesis of 2,7-dibromo-9,9-dihexyl-9H-fluorene (6)

2,7-dibromofluorene (2.32 g, 7 mmol), 1-bromohexane (2.18 mL, 15.4 mmol) and TBAB (0.12 g, 0.35 mmol) were dissolved in DMSO (40 mL). The reaction was stirred at room temperature under an inert atmosphere, and 50% NaOH solution was added. After 5 hours of reaction, added appropriate amount of water and extracted with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether to obtain compound 6 as a white yellowish solid (2.68g, 77.8%). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, $J = 8.4$ Hz, 1H), 7.62 – 7.53 (m, 4H), 7.35 – 7.26 (m, 4H), 7.18 (t, $J = 8.0$ Hz, 4H), 7.13 – 6.99 (m, 3H), 6.69 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.67 (d, $J = 17.6$

Hz, 1H), 5.18 (d, $J = 11.0$ Hz, 1H), 2.02 (dd, $J = 9.6, 5.7$ Hz, 2H), 0.75 (dt, $J = 12.7, 6.1$ Hz, 2H), 0.68 (t, $J = 6.5$ Hz, 3H).

Synthesis of 2,2'-(9,9-dihexyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborane) (7)

Compound 6 (2.46 g, 5 mmol), binaryl borate (5.18 g, 20 mmol), potassium acetate (3.97 g, 40 mmol), PdCl₂(dppf) (0.392 g, 0.525 mmol) were dissolved in 1, 4-dioxane (40 mL). The mixture was reacted at 80 °C for 10 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether/CH₂Cl₂ (20:1) to obtain compound 7 as a white crystal (2.87 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, $J = 7.5$ Hz, 2H), 7.76 – 7.70 (m, 4H), 2.04 – 1.95 (m, 4H), 1.39 (s, 24H), 1.11 – 0.97 (m, 12H), 0.74 (t, $J = 7.1$ Hz, 6H), 0.60 – 0.49 (m, 4H).

Synthesis of 2,7-bis(4-bromophenyl)-9,9-dihexyl-9*H*-fluorene (8)

Compound 7 (1.76 g, 3 mmol), 4-bromoiodobenzene (1.91 g, 6.6 mmol), anhydrous potassium carbonate (1.26 g, 9 mmol), Pd(PPh₃)₄ (0.3 mmol, 0.35 g) and toluene-ethanol-water (30 mL, 15 mL, 15 mL) were added to a two-necked round bottom flask respectively. The mixture was stirred and reacted at 115 °C for 48 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with dichloromethane. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel eluted with petroleum ether to obtain compound 8 as a white crystal (1.08 g, 56.1%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, $J = 8.3$ Hz, 4H), 8.07 (d, $J = 7.3$ Hz, 2H), 7.86 (d, $J = 8.5$ Hz, 4H), 7.55 (s, 6H), 7.47 – 7.31 (m, 10H), 7.20 (d, $J = 4.3$ Hz, 8H), 7.11 (s, 4H), 6.93 (d, $J = 5.9$ Hz, 2H), 6.76 – 6.56 (m, 2H), 5.59 (d, $J = 18.0$ Hz, 2H), 5.10 (d, $J = 12.3$ Hz, 2H), 2.05 (s, 4H), 1.14 (s, 12H), 0.95 (s, 4H), 0.78 (d, $J = 6.3$ Hz, 6H).

Synthesis of 4,4'-(9,9-dihexyl-9*H*-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl) aniline) (9)

Compound 8 (0.97 g, 1.5 mmol), compound 4 (0.64 g, 3.3 mmol), sodium tert-butoxide (0.44 g, 4.5 mmol), Pd₂(dba)₃ (0.05 g, 0.045 mmol), tri-tert-butyl phosphine (toluene solution) (0.24 mL, 0.12 mmol) and toluene (40 mL) were added to a two-necked round bottom flask respectively. The mixture was stirred and reacted at 90 °C for 16 hours under an inert atmosphere. After cooling to room temperature, water was added to quench the reaction and the mixture was extracted with ethyl acetate. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on Al₂O₃ eluted with petroleum ether/EtOAc (100:1) to obtain compound 9 as a white solid (0.8 g, 61.2%). ¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, J = 8.3 Hz, 4H), 8.07 (d, J = 7.3 Hz, 2H), 7.86 (d, J = 8.5 Hz, 4H), 7.55 (s, 6H), 7.47 – 7.31 (m, 10H), 7.20 (d, J = 4.3 Hz, 8H), 7.11 (d, J = 3.9 Hz, 4H), 6.93 (d, J = 6.7 Hz, 2H), 6.76 – 6.56 (m, 2H), 5.59 (d, J = 17.0 Hz, 2H), 5.10 (d, J = 8.8 Hz, 2H), 2.07 (s, 4H), 1.14 (s, 12H), 0.96 (s, 4H), 0.78 (d, J = 6.3 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 151.88, 147.64, 147.48, 146.93, 139.81, 139.47, 136.38, 136.11, 132.28, 129.45, 127.92, 127.27, 125.65, 124.71, 124.45, 123.97, 123.29, 121.07, 120.05, 112.42, 55.34, 40.66, 31.63, 29.83, 23.94, 22.67, 14.22.

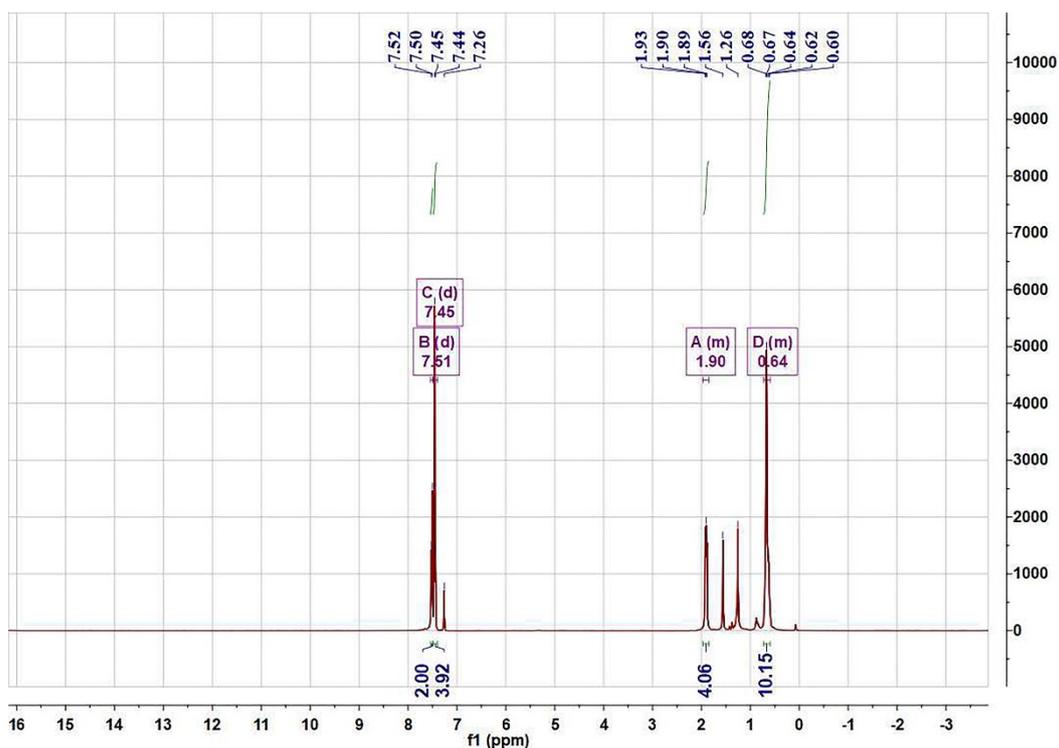


Fig. S2 ^1H NMR spectra of 2,7-dibromo-9,9-dipropyl-9H-fluorene.

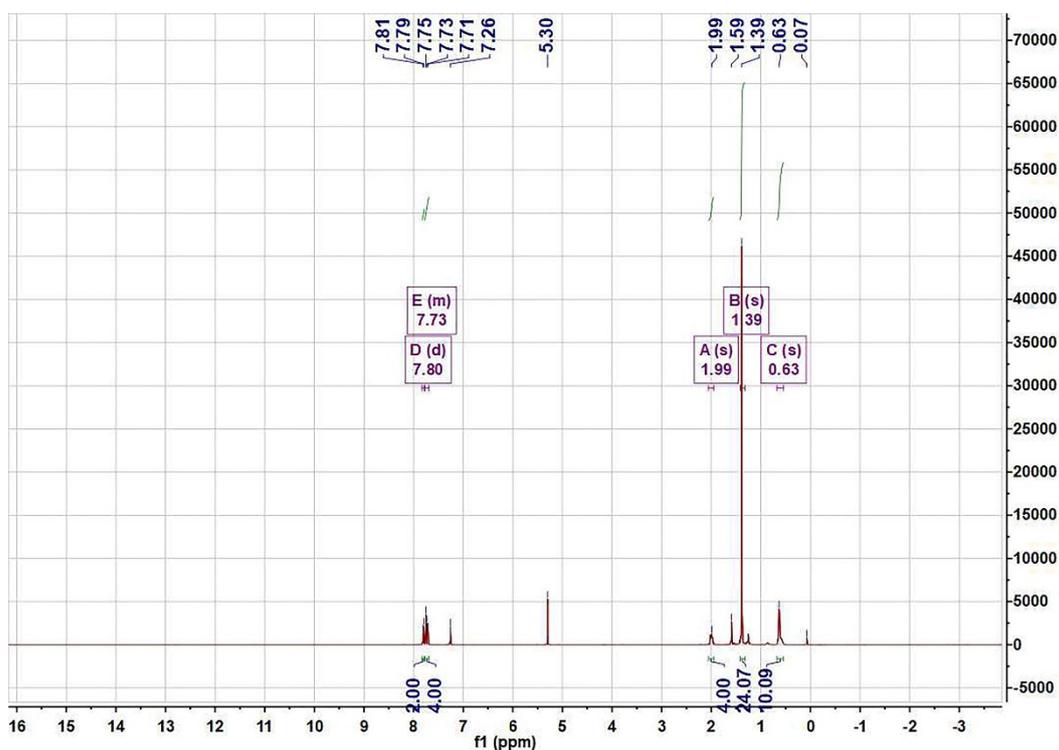


Fig. S3 ^1H NMR spectra of 2,2'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborane).

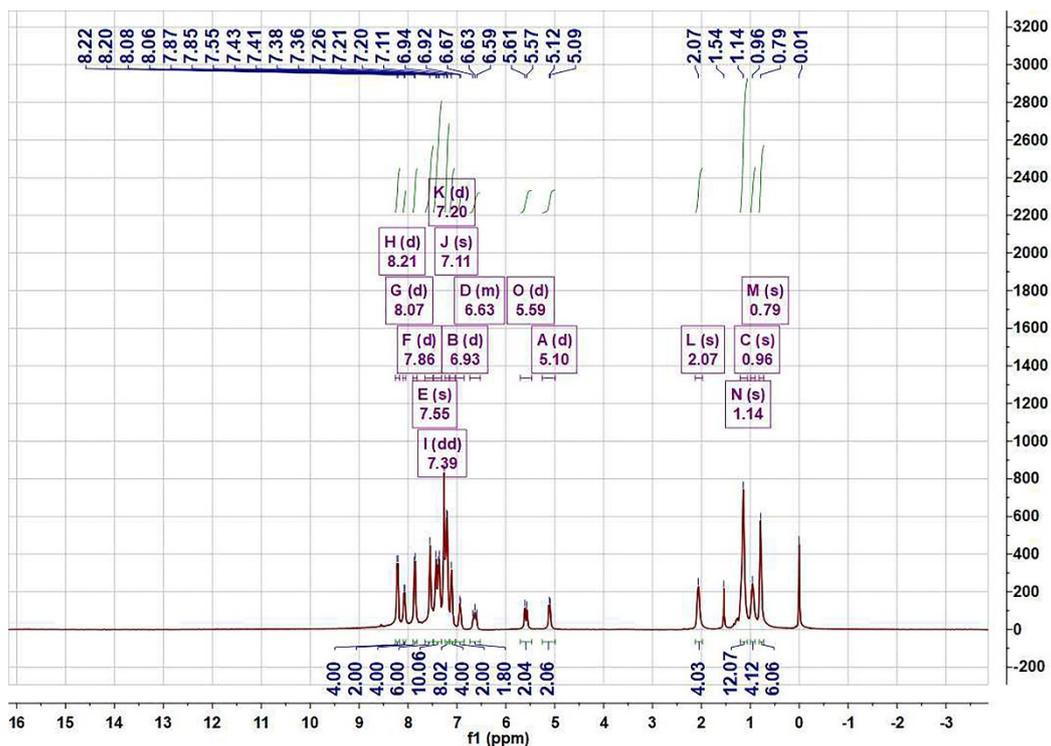


Fig. S4 ^1H NMR spectra of 2,7-bis(4-bromophenyl)-9,9-dipropyl-9H-fluorene.

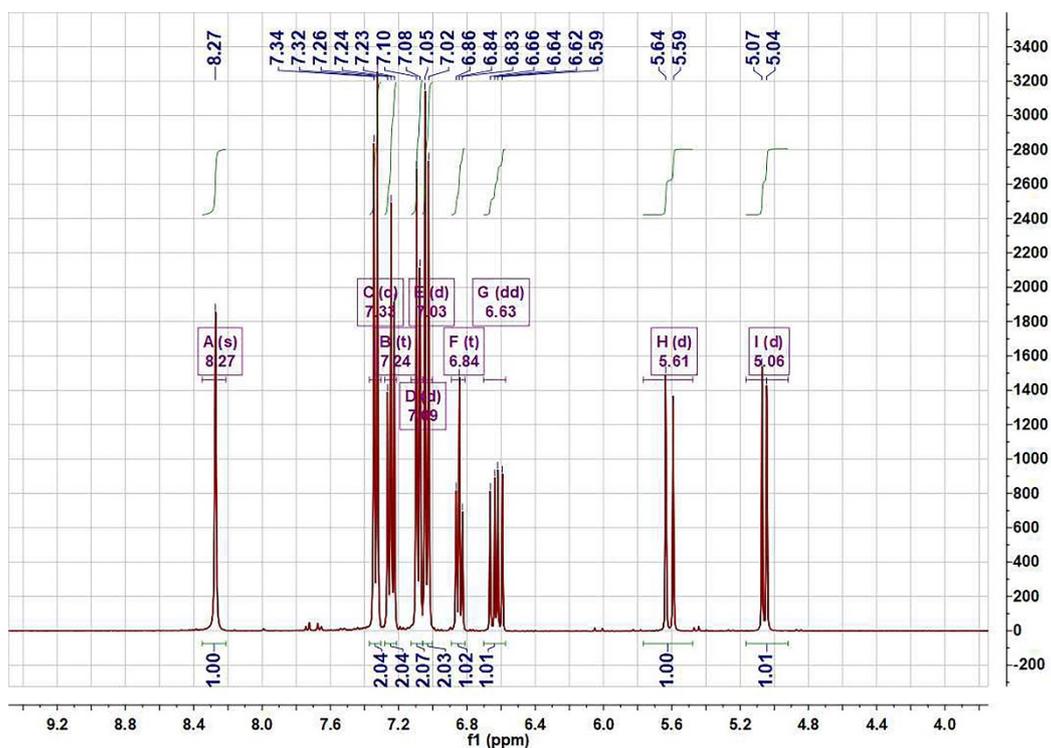


Fig. S5 ^1H NMR spectra of *N*-phenyl-4-vinyl aniline.

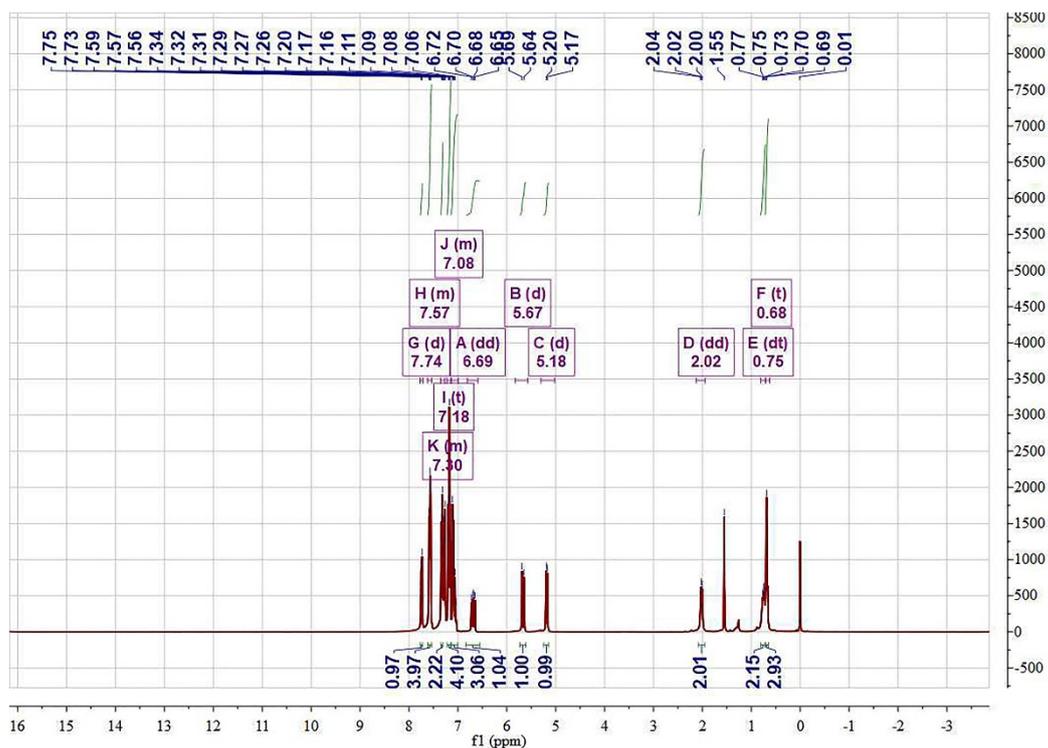


Fig. S6 ^1H NMR spectra of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

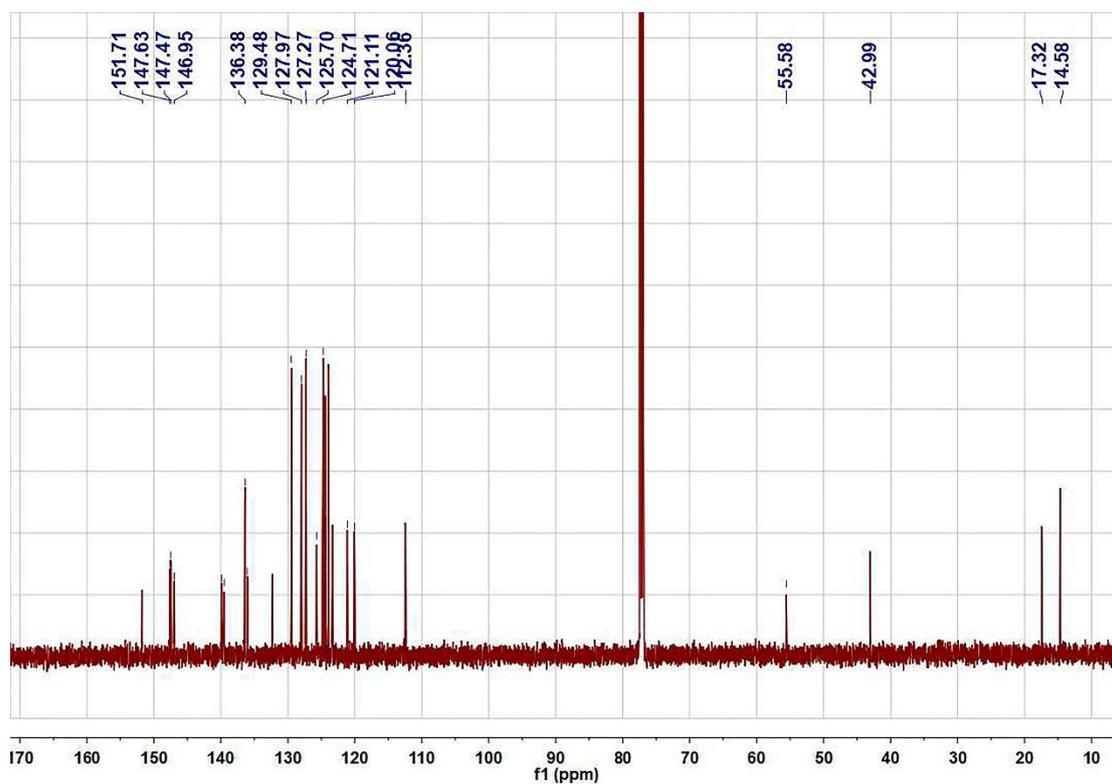


Fig. S7 ^{13}C NMR spectra of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

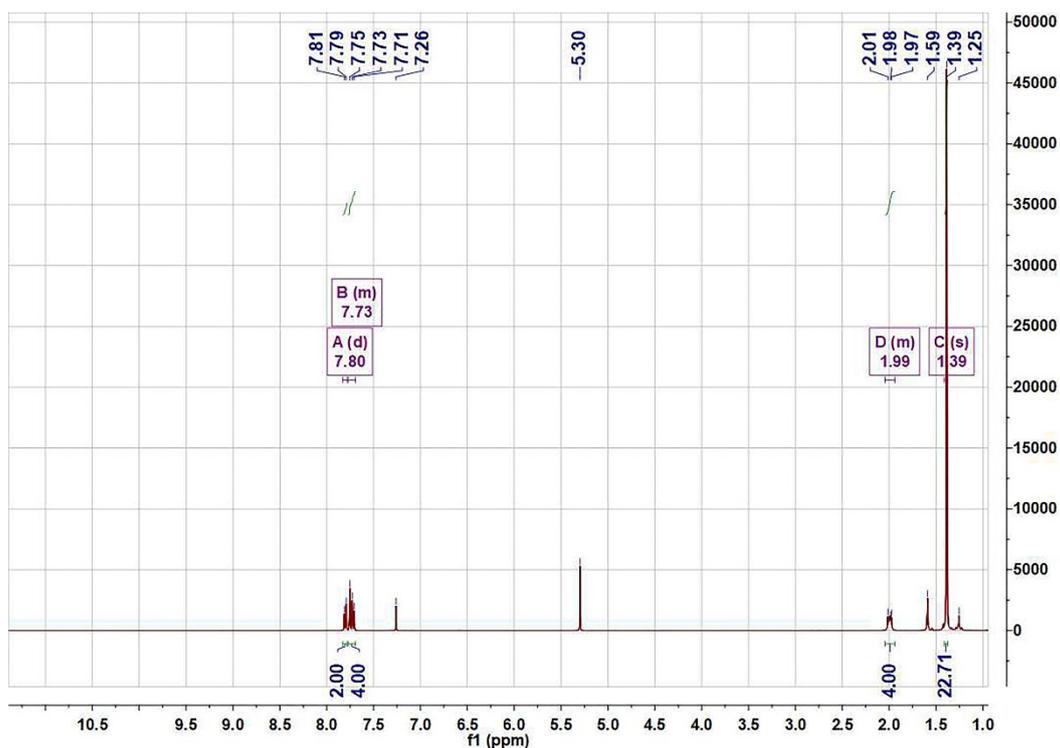


Fig. S8 ^1H NMR spectra of 2,7-dibromo-9,9-dihexyl-9H-fluorene.

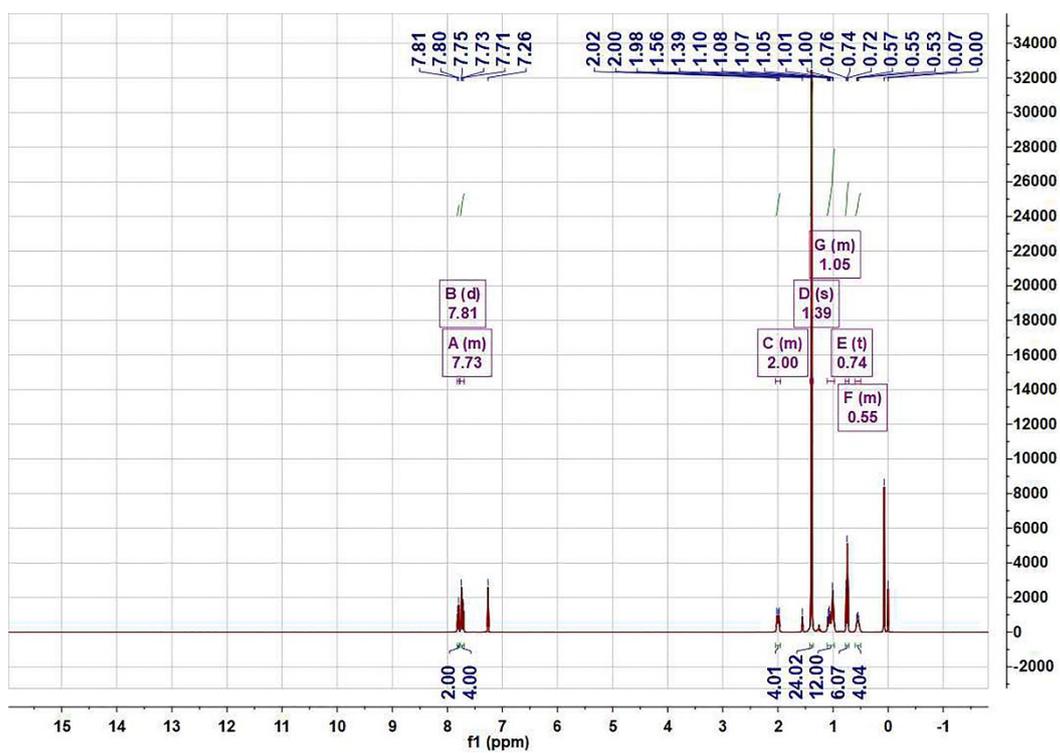


Fig. S9 ^1H NMR spectra of 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborane).

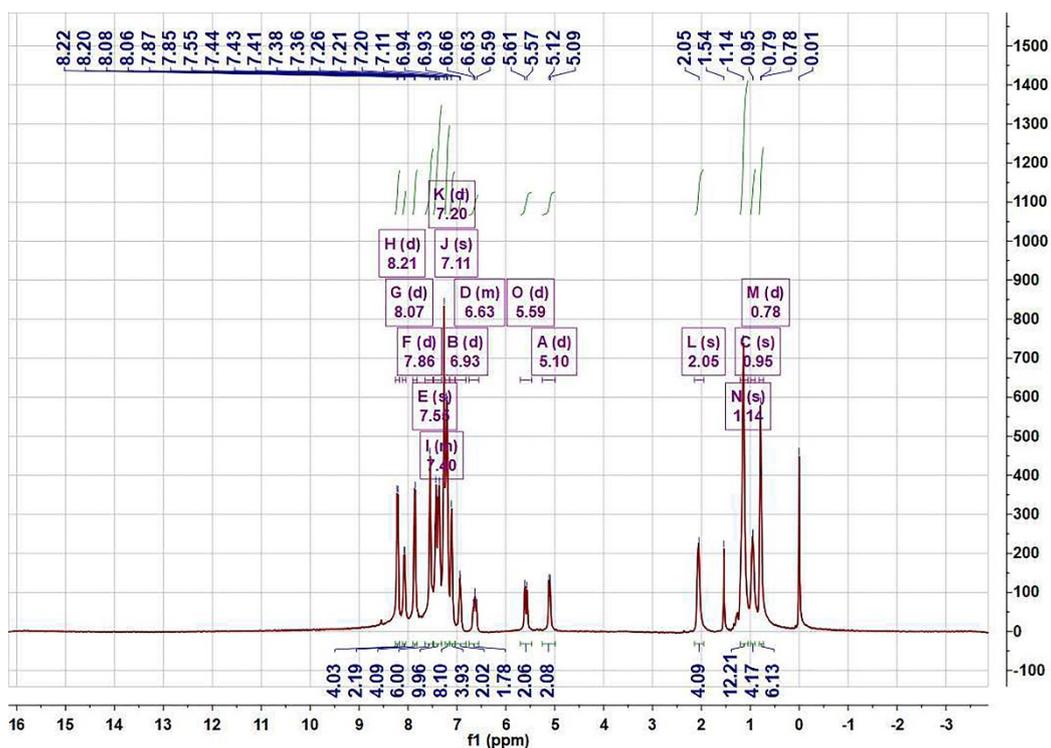


Fig. S10 ^1H NMR spectra of 2,7-bis(4-bromophenyl)-9,9-dihexyl-9H-fluorene.

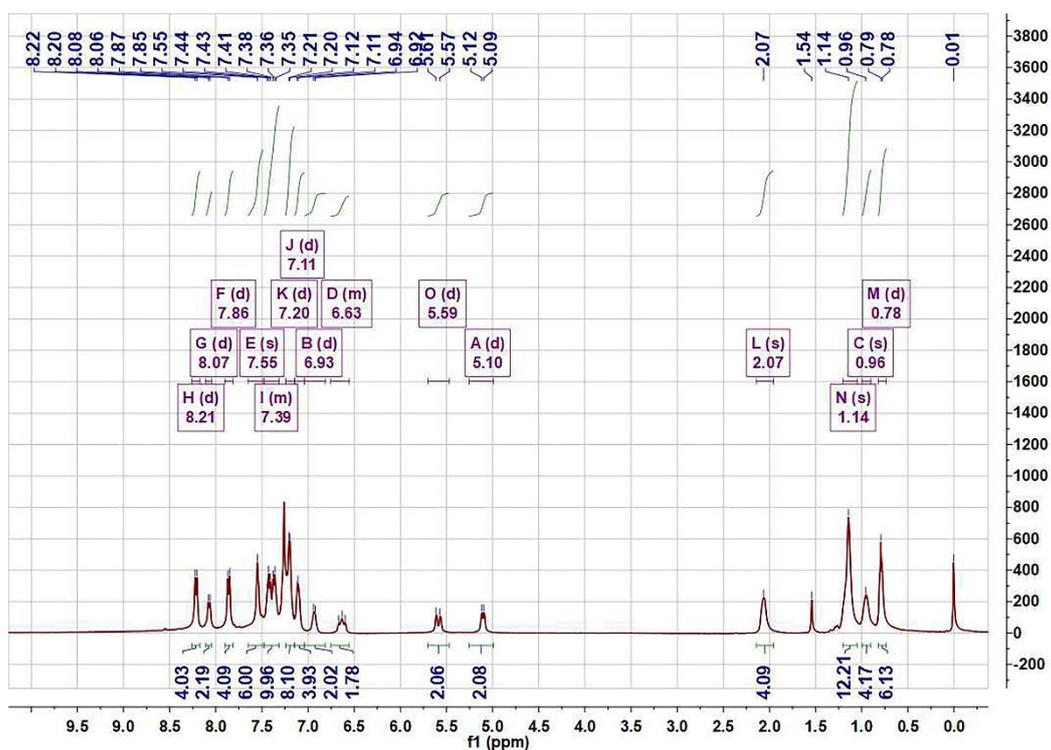


Fig. S11 ^1H NMR spectra of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

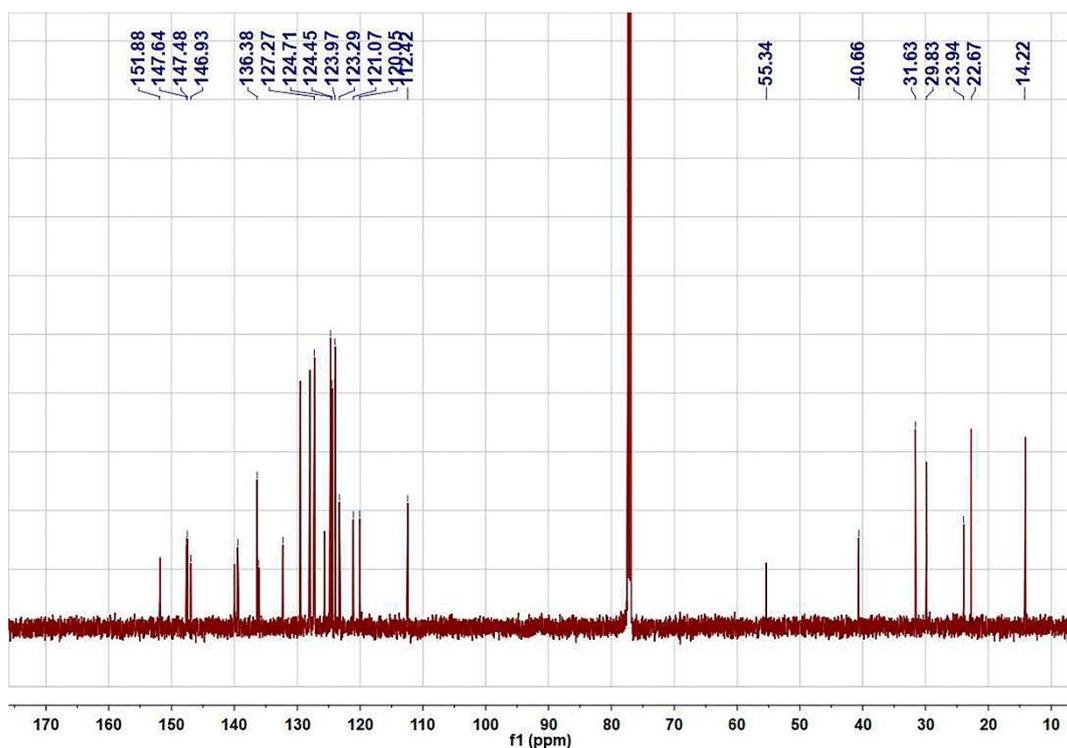


Fig. S12 ^1H NMR spectra of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

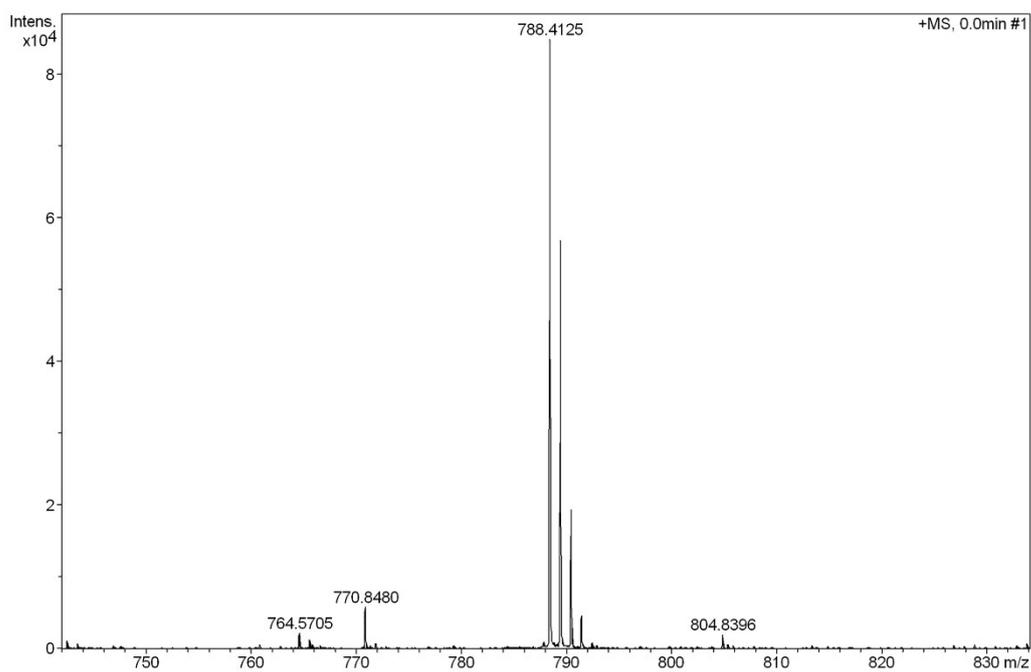


Fig. S13 Mass spectra of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

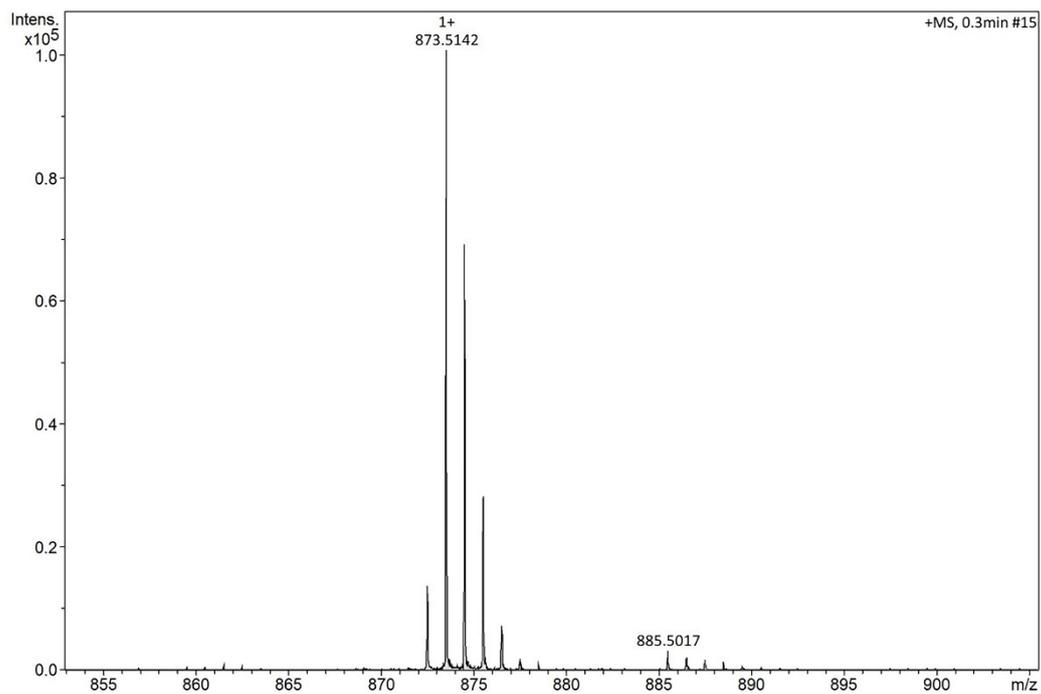


Fig. S14 Mass spectrum of 4,4'-(9,9-dipropyl-9H-fluorene-2,7-diyl)bis(*N*-phenyl-*N*-(4-vinylphenyl)aniline).

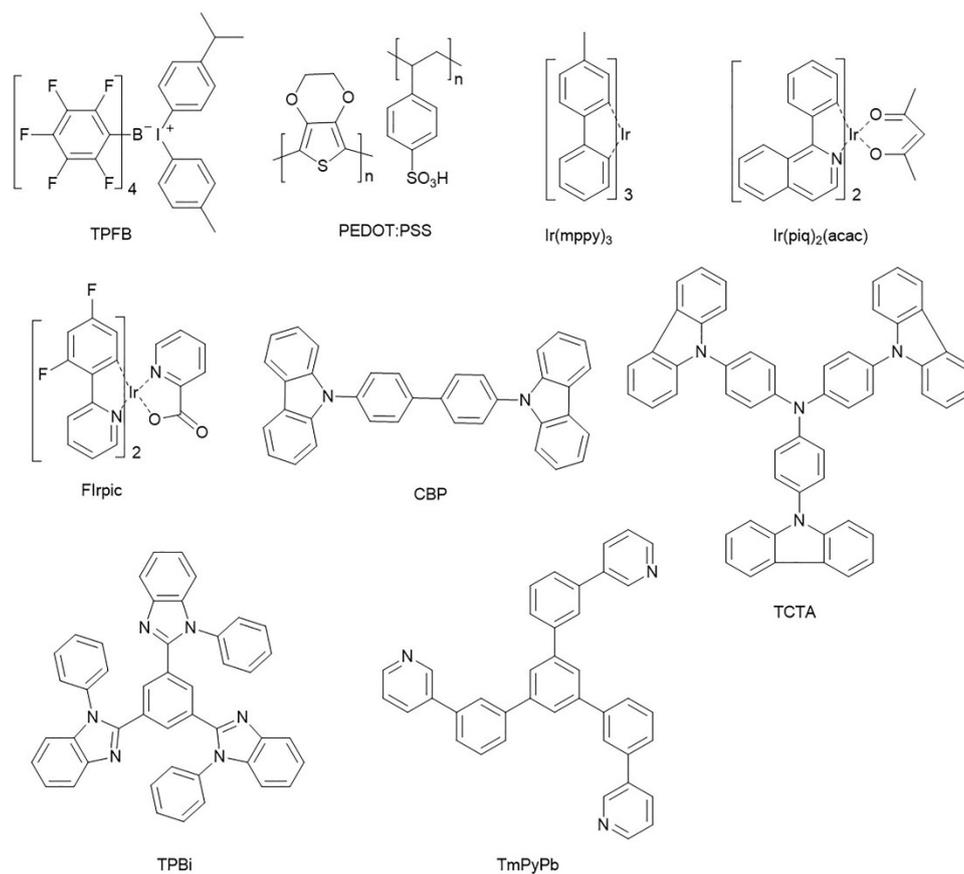


Fig. S15 The structures of 4-isopropyl-4'-methyl-diphenyliodonium tetrakis(pentafluorophenyl)borate (TPFB), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), tris[2-(*p*-tolyl)pyridine]iridium(III) (Ir(mppy)₃), bis(1-phenyl-isoquinoline)(acetylacetonato)iridium(III) (Ir(piq)₂(acac)), bis(4,6-difluorophenylpyridine)(picolinate)iridium(III) (Flrpic), 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl (CBP), tris(4-carbazolyl-9-ylphenyl)amine (TCTA), 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBi) and 1,3,5-tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPb).

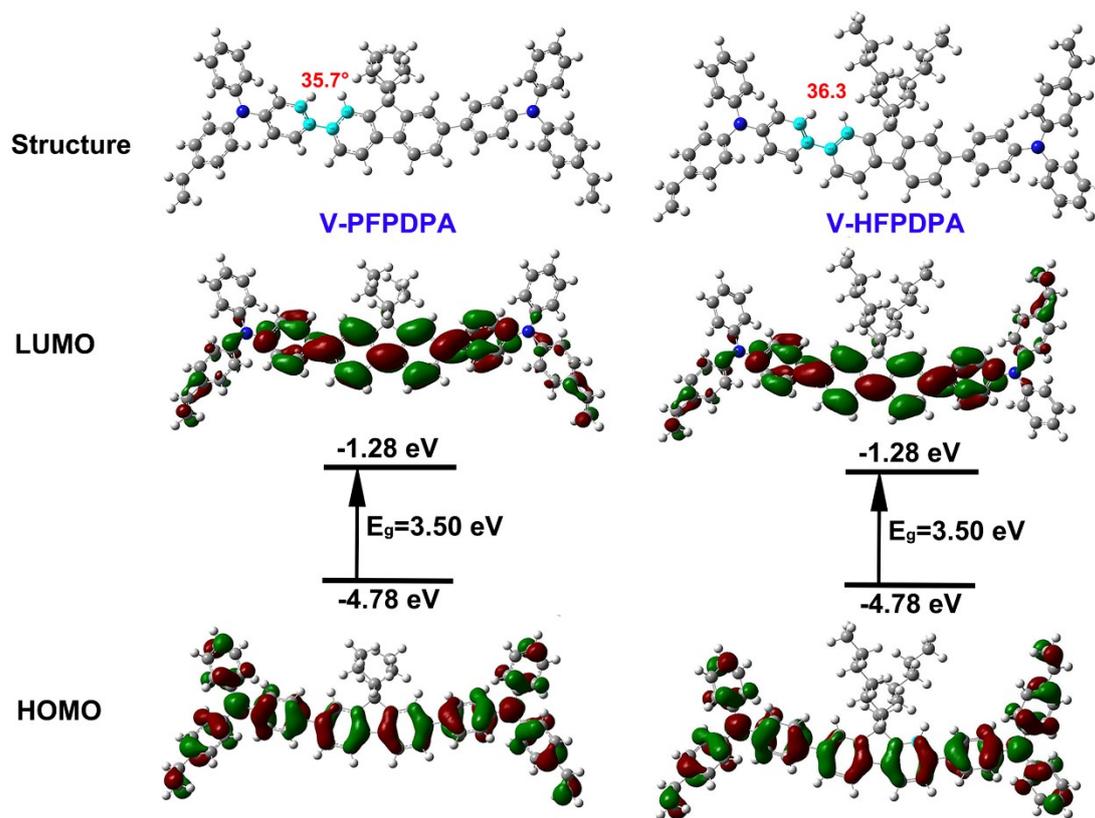


Fig. S16 HOMO and LUMO energy levels and distribution of V-PFPDPA and V-HFPDPA.

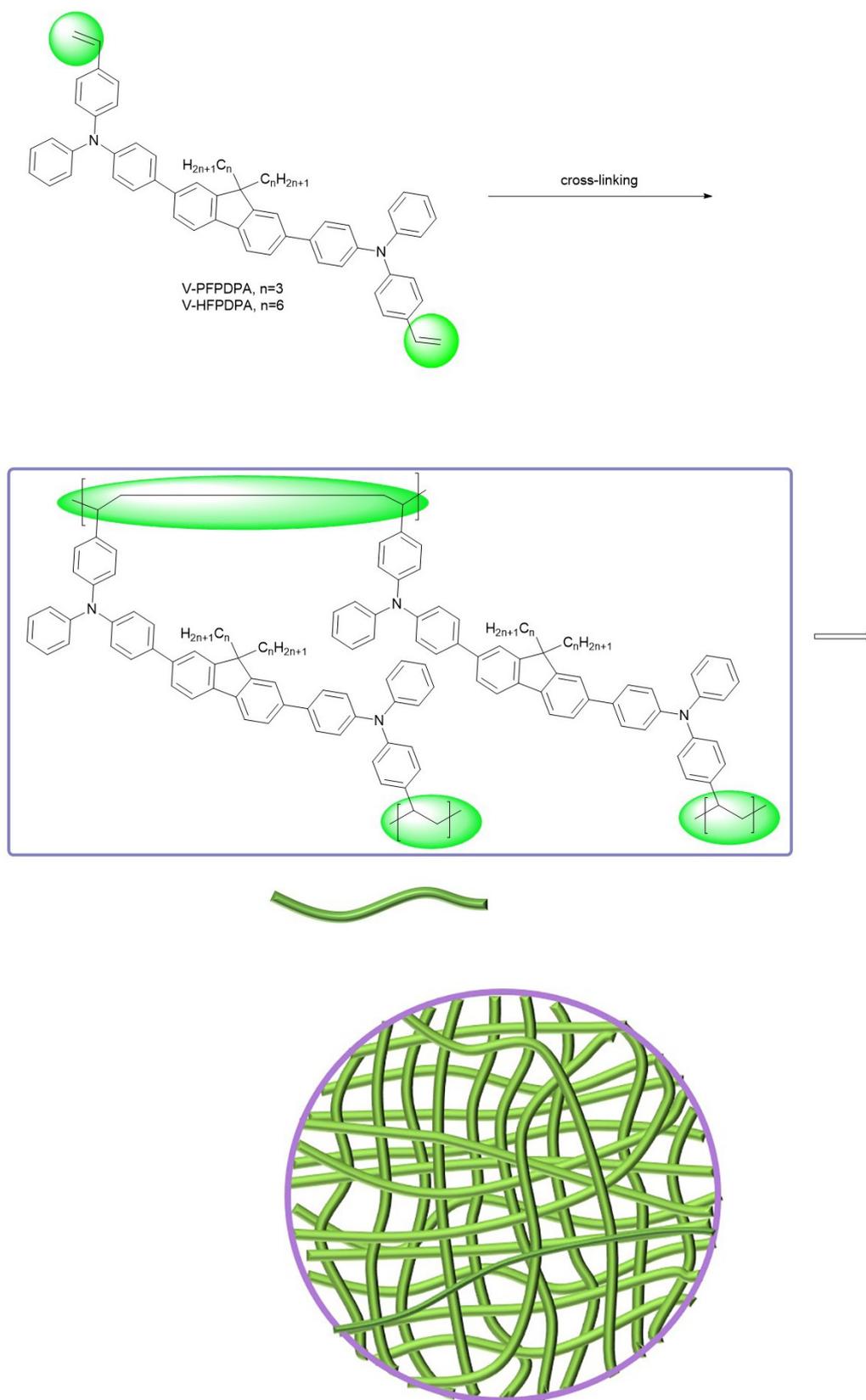


Fig. S17 Schematic diagram of the formation of cross-linked films.

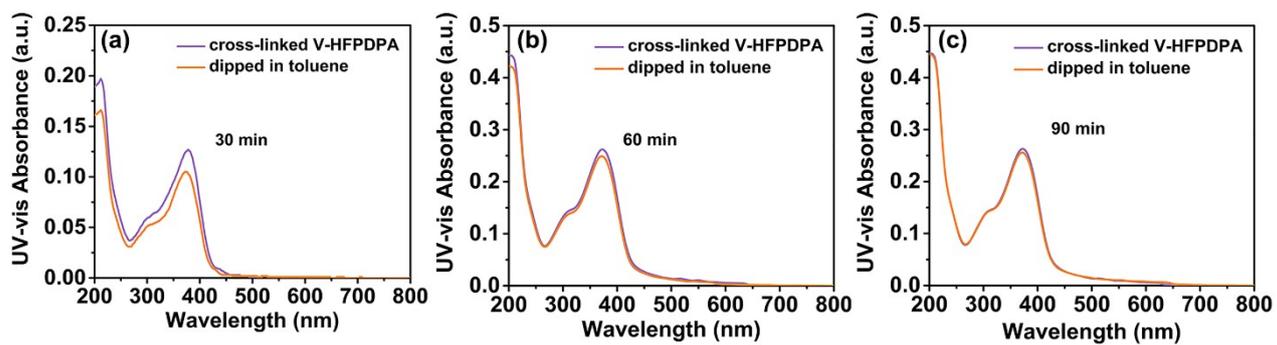


Fig. S18 The UV-vis absorption spectra of V-HFPDPA films heated at 160 °C for (a) 30 min, 60 min and (c) 90 min before and after immersion in toluene.

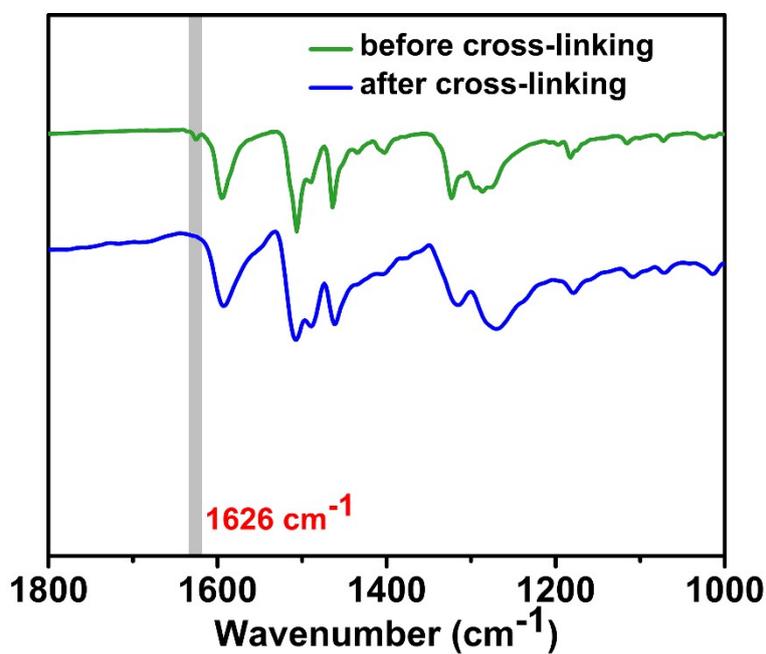


Fig. S19 FT-IR spectra of V-PFPDPA film and cross-linked V-PFPDPA film.

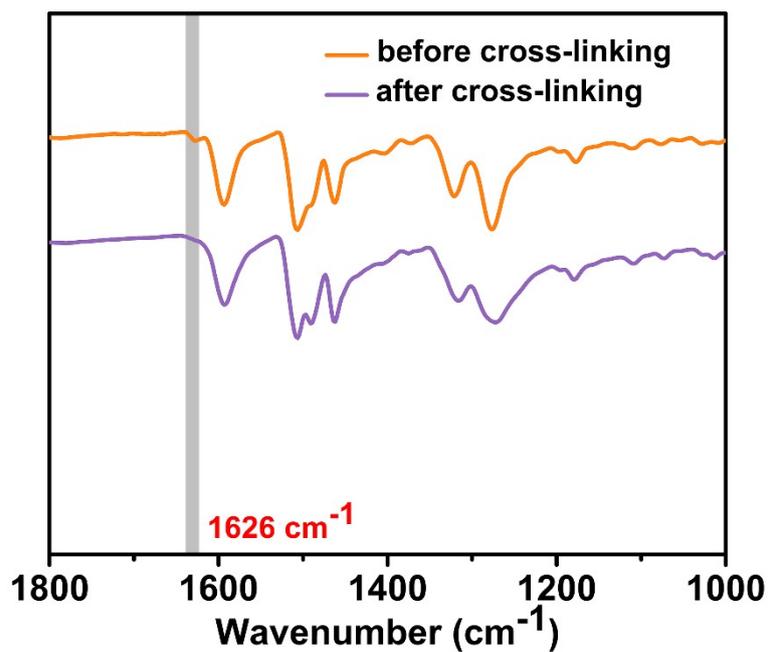


Fig. S20 FT-IR spectra of V-HFPDPA film and cross-linked V-HFPDPA film.

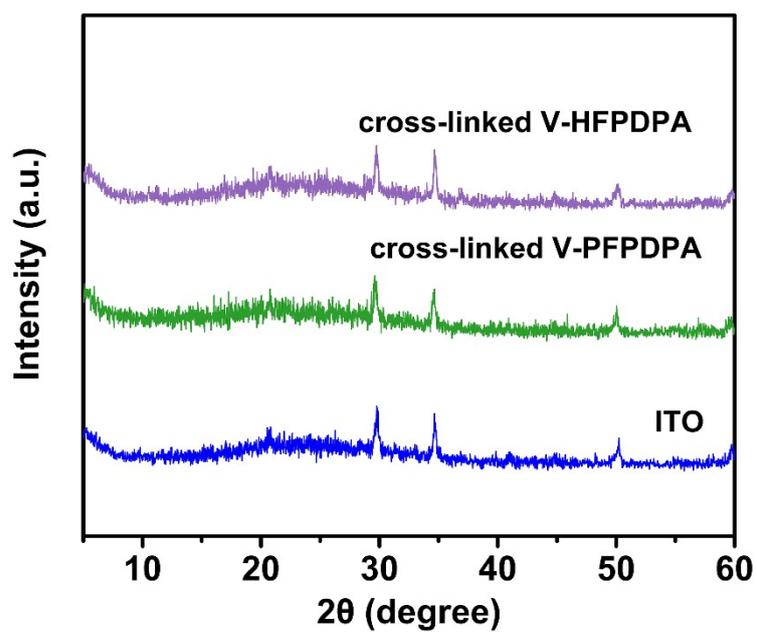
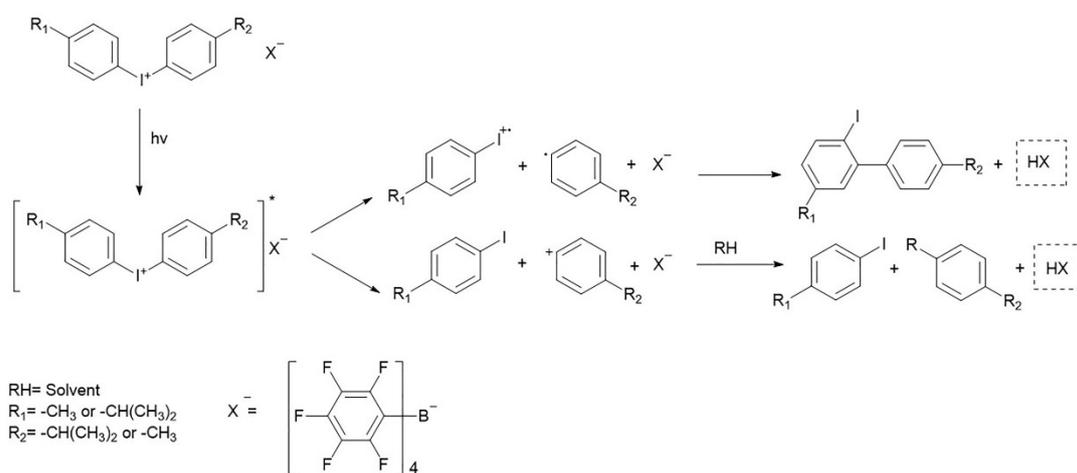


Fig. S21 X-ray diffraction spectra of ITO substrate, cross-linked V-PFPDPA film, and cross-linked V-HFPDPA film on ITO substrate after annealing at 200°C for 30 min.

Table S1 Zero-field hole mobility of doped and undoped HTLs

HTLs	Zero-field hole mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
V-PFPDPA / V-HFPDPA	$1.48 \times 10^{-5} / 2.82 \times 10^{-5}$
V-PFPDPA / V-HFPDPA:1 wt%TPFB	$1.74 \times 10^{-4} / 4.63 \times 10^{-4}$
V-PFPDPA / V-HFPDPA:2.5 wt%TPFB	$2.49 \times 10^{-3} / 3.48 \times 10^{-3}$
V-PFPDPA / V-HFPDPA:5 wt%TPFB	$6.74 \times 10^{-2} / 2.47 \times 10^{-1}$

**Fig. S22** Mechanism for the generation of hydrogen tetrakis(pentafluorophenyl)borate.

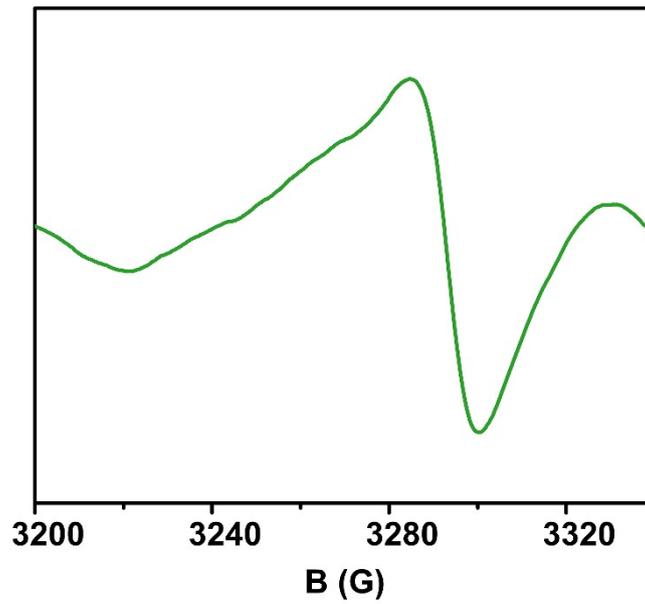


Fig. S23 EPR spectrum of V-HFPDPA: 30 wt% TPFB.

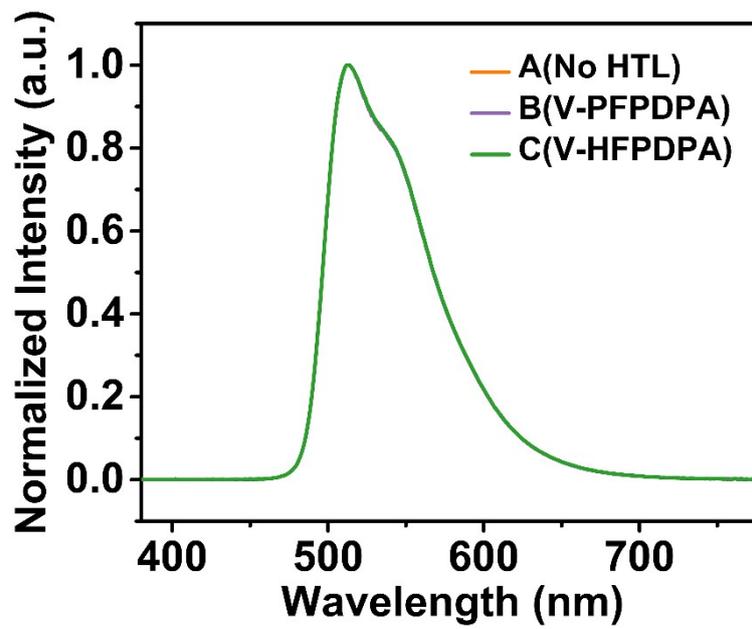


Fig. S24 Normalized EL spectra of green PHOLEDs.

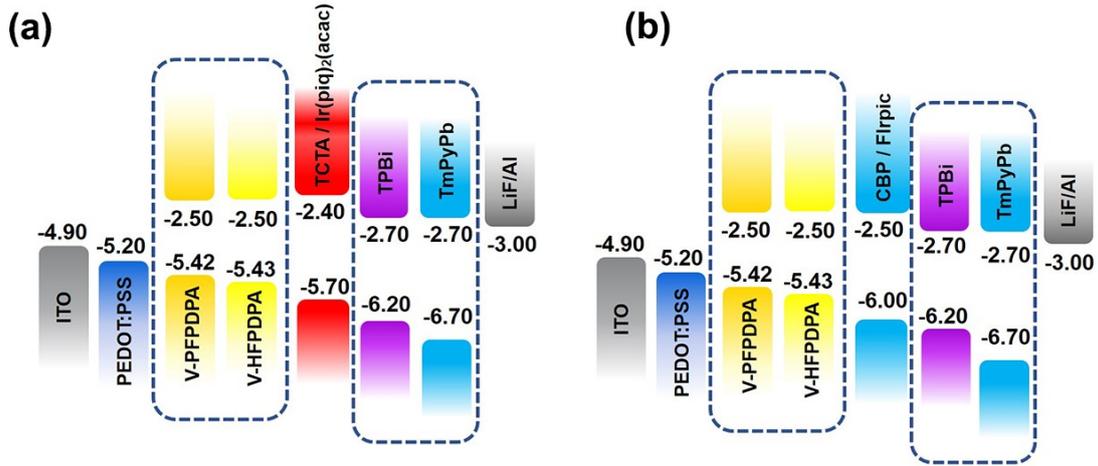


Fig. S25 Energy level diagram of red and blue PHOLEDs.

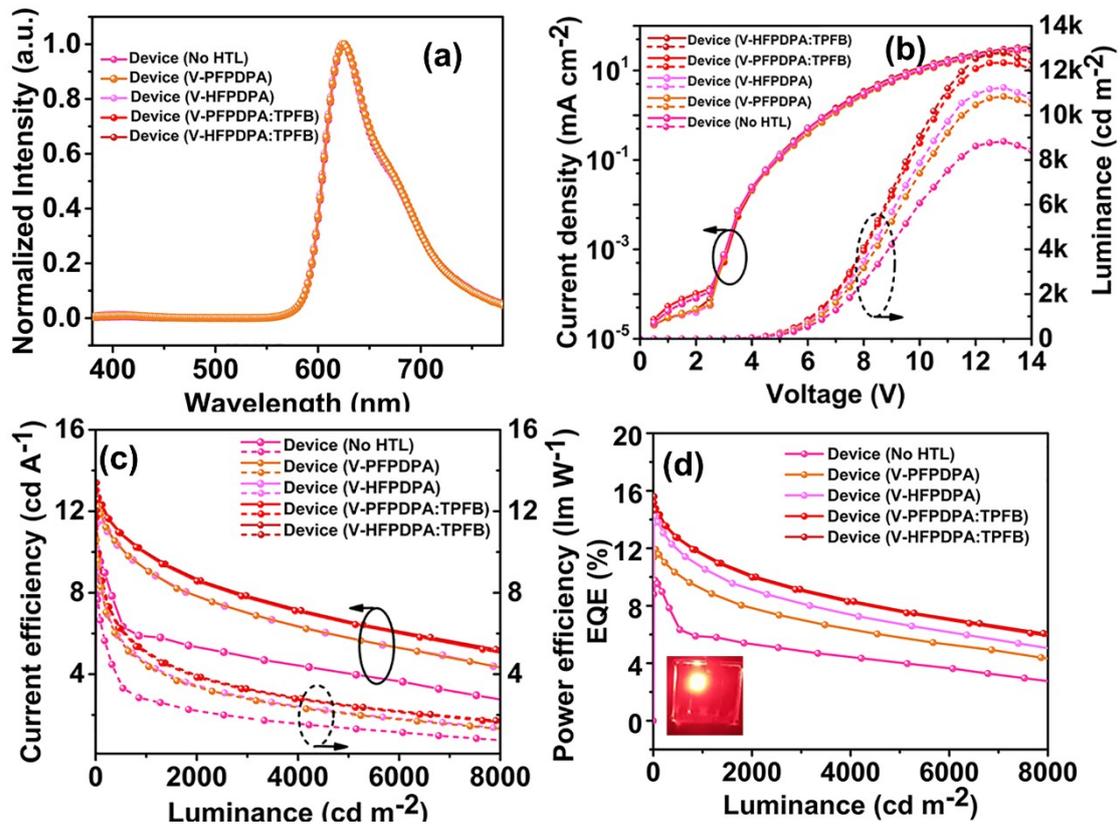


Fig. S26 (a) Normalized EL spectra of red PHOLEDs; (b) Current density (J)–voltage (V)–luminance (L) curves; (c) current efficiency (CE)– L –power efficiency (PE) curves; and (d) EQE– L curves of red PHOLEDs (insert: device photo at 10 V).

Table S2 Performance of solution-processed red PHOLEDs

Device	HTL	V_{on}^a (V)	CE / PE / EQE		CIE ^b (x, y)
			(cd A ⁻¹ / lm W ⁻¹ / %)		
			maximum	at 1000 cd m ⁻²	
R1	-	3.3	9.76 / 7.90 / 11.41	5.85 / 2.91 / 5.86	(0.67, 0.32)
R2	V-PFPDPA	3.2	11.39 / 10.23 / 11.92	9.13 / 4.58 / 9.16	(0.67, 0.32)
R3	V-HFPDPA	3.2	11.81 / 10.60 / 13.75	9.14 / 4.47 / 10.64	(0.67, 0.32)
R4	V-PFPDPA:TPFB	3.1	13.03 / 11.70 / 15.18	9.92 / 5.05 / 11.55	(0.67, 0.32)
R5	V-HFPDPA:TPFB	3.1	13.40 / 12.02 / 15.60	9.98 / 5.12 / 10.30	(0.67, 0.32)

a: measured at 1 cd m⁻².

b: measured at 6 V.

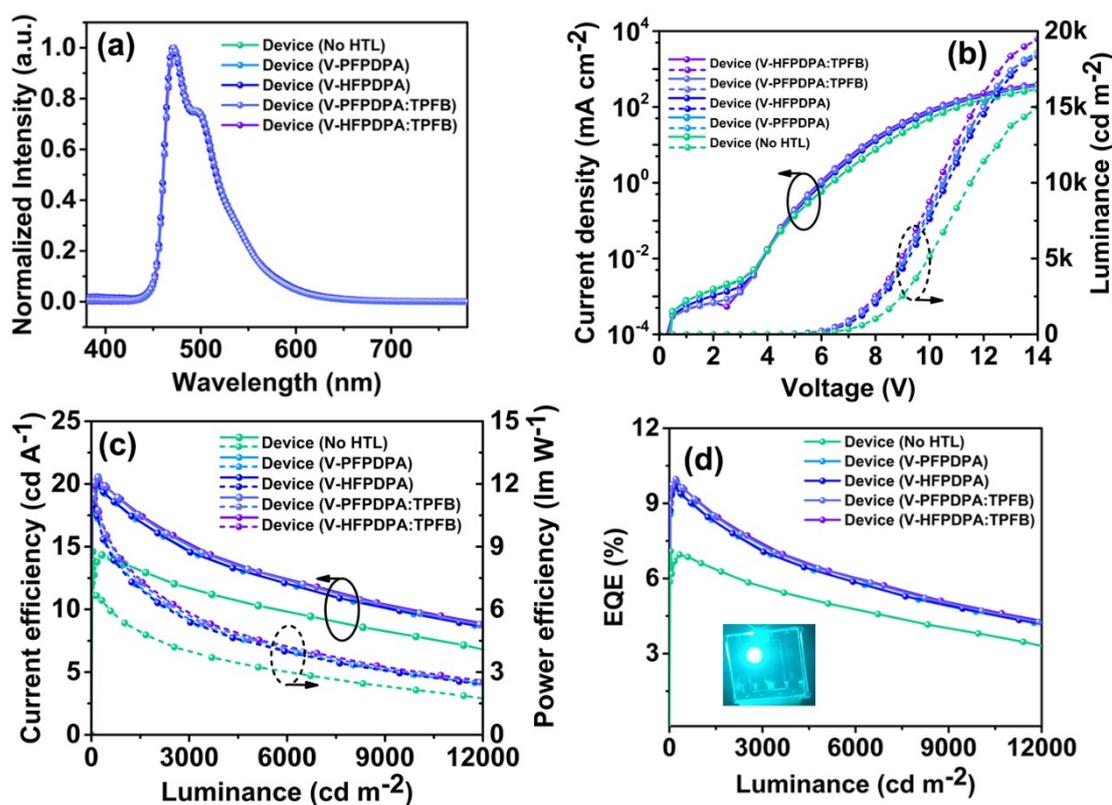


Fig. S27 (a) Normalized EL spectra of blue PHOLEDs; (b) Current density (J)–voltage (V)–luminance (L) curves; (c) current efficiency (CE)– L –power efficiency (PE) curves; and (d) EQE– L curves of blue PHOLEDs (insert: device photo at 10 V).

Table S3 Performance of solution-processed blue PHOLEDs

Device	HTL	V_{on}^{a} (V)	CE / PE / EQE ($\text{cd A}^{-1} / \text{lm W}^{-1} / \%$)		CIE ^b (x, y)

			maximum	at 1000 cd m^{-2}	
B1	-	4.6	14.60 / 8.34 / 7.08	13.64 / 5.38 / 6.87	(0.16, 0.35)
B2	V-PFPDPA	4.5	19.74 / 11.09 / 9.40	17.97 / 7.86 / 8.72	(0.16, 0.35)
B3	V-HFPDPA	4.5	19.98 / 11.00 / 9.34	17.94 / 7.83 / 8.70	(0.16, 0.35)
B4	V-PFPDPA:TPFB	4.5	20.39 / 11.73 / 9.59	18.56 / 8.14 / 9.00	(0.16, 0.35)
B5	V-HFPDPA:TPFB	4.5	20.54 / 11.61 / 9.74	18.51 / 8.15 / 8.98	(0.16, 0.35)

a: measured at 1 cd m^{-2} .

b: measured at 6 V.