Supplementary Information

Trap-Controlled Operational Stability in Dibenzofuran-Based Hosts for Blue TADF OLEDs

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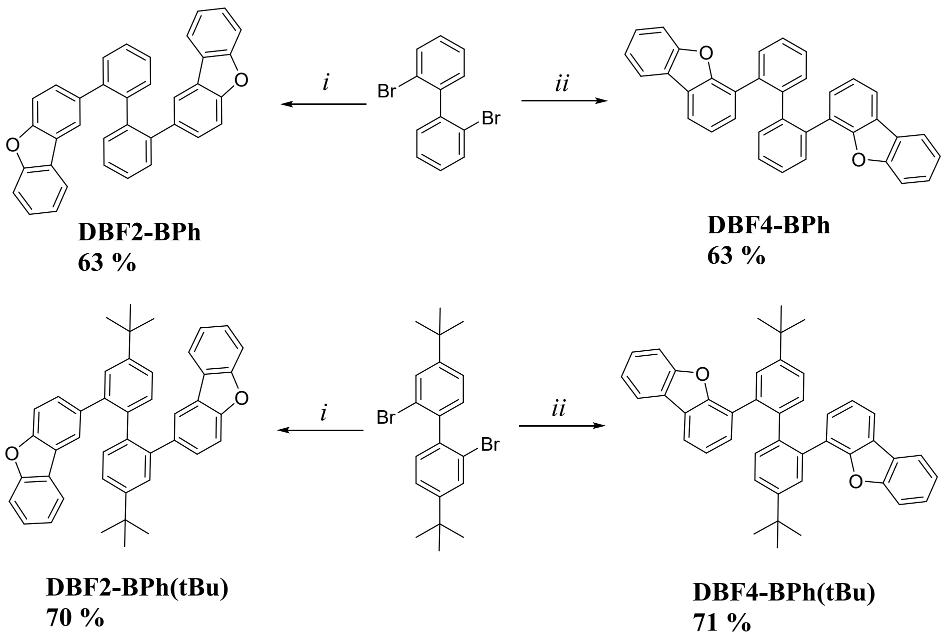
Synthesis and characterization

The target compounds were synthesized via a one-step Suzuki cross-coupling reaction from commercially available starting materials, affording the products in 63–71% yield. All the target compounds were obtained as white crystalline substances.



Scheme S1. Synthesis of the DBF–biphenyl hosts. *i:* dibenzo[b,d]furan-2-ylboronic acid, K_2CO_3, $PdCl_2(PPh_3)_2$, dioxane:water (v/v 10:1), Ar, b. p. 24 h; *ii*: dibenzo[b,d]furan-4-ylboronic acid, K_2CO_3, $PdCl_2(PPh_3)_2$, dioxane:water (v/v 10:1), Ar, b. p. 24 h.

General procedure (GP) of synthesis for compounds **DBF2-BPh**, **DBF4-BPh**, **DBF2-BPh(tBu)** and **DBF4-BPh(tBu)**:

Solution of corresponding dibromobiphenyl (1 eq.), corresponding dibenzofuranylboronic acid (2.6 eq.), K_2CO_3 (4 eq.) in freshly distilled dioxane and water mixture (v/v 10:1) was thoroughly degassed using a vacuum pump and argon gas. Then a catalytic amount (1 mol%) of PdCl2(PPh3)2 was added, and the reaction mixture was stirred overnight at the boiling point under an argon atmosphere. After the completion of the reaction, an aqueous solution of NaCl was added, and the product was extracted with ethyl acetate (3 × 100 ml). Organic layers were combined, dried over sodium sulphate, and volatiles were removed under reduced pressure. The crude target compounds were purified by the methods described below.

2,2'-Bis(dibenzo[b,d]furan-2-yl)-1,1'-biphenyl (**DBF2-BPh**) was synthesized according to GP. The dibenzo[b,d]furan-2-ylboronic acid (1.76 g, 8.32 mmol), 2,2’-dibromo-1,1’-biphenyl (1 g, 3.2 mmol), K_2CO_3 (1.76 g, 12.75 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), 33 ml of dioxane:water (v/v 10:1) were used. The product was purified by recrystallization from a mixture of THF and methanol, yielding the target compound as white crystals (0.98 g, 63%). ^{1}H NMR (400 MHz, THF-*d₈*) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.39 (m, 4H), 7.38 – 7.26 (m, 6H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.11 – 7.00 (m, 4H), 6.95 (d, *J* = 1.8 Hz, 2H), 6.65 (dd, *J* = 8.5, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, THF-d_8) δ: 157.3, 155.8, 141.9, 141.4, 137.0, 132.5, 131.0, 129.5, 128.4, 128.0, 127.6, 125.0, 124.7, 123.5, 122.0, 120.9, 112.0, 110.8. Elemental analysis. Calcd for $C_{36}H_{22}O_2$ (%): C 88.87, H 4.56, O 6.58; found (%): C 88.85, H 4.58, O 6.57.

2,2'-Bis(dibenzo[b,d]furan-4-yl)-1,1'-biphenyl (**DBF4-BPh**) was synthesized according to GP. The dibenzo[b,d]furan-4-ylboronic acid (1.76 g, 8.32 mmol), 2,2’-dibromo-1,1’-biphenyl (1 g, 3.2 mmol), K_2CO_3 (1.76 g, 12.75 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), 33 ml of dioxane:water (v/v 10:1) were used. The product was purified by recrystallization from a mixture of THF and methanol, yielding the target compound as white crystals (0.99 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.30 (m, 2H), 7.29 – 7.17 (m, 10H), 7.17 – 7.10 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 2H), 6.55 (d, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 161.0, 158.6, 146.2, 140.9, 137.3, 136.2, 134.4, 133.1, 132.7, 131.8, 130.3, 129.3, 129.1, 127.5, 127.1, 125.5, 124.1, 116.5. Elemental analysis. Calcd for $C_{36}H_{22}O_2$ (%): C 88.87, H 4.56, O 6.58; found (%): C 88.89, H 4.57, O 6.59.

2,2'-(4,4'-Di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF2-BPh(tBu)**) was synthesized according to GP. The dibenzo[b,d]furan-2-ylboronic acid (1.30 g, 6.1 mmol), 2,2’-dibromo-4,4’-di-*tert*-butyl-1,1’-biphenyl (1 g, 2.4 mmol), K_2CO_3 (1.3 g, 9.42 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), 22 ml of dioxane:water (v/v 10:1) were used. The crude product was purified by flash chromatography on silica gel using hexane as the eluent and recrystallized from methanol, yielding the target compound as white crystals (0.98 g, 70%). ^{1}H NMR (400 MHz, THF-d_8) δ: 7.51 – 7.43 (m, 6H), 7.38 – 7.27 (m, 4H), 7.19 (s, 2H), 7.10 – 7.00 (m, 4H), 6.93 (s, 2H), 6.66 (d, *J* = 8.5 Hz, 2H), 1.34 (s, 18H). ^{13}C NMR (101 MHz, THF-d_8) δ: 157.4, 155.9, 151.3, 141.6, 138.8, 137.8, 132.4, 129.8, 128.0, 127.7, 125.2, 125.2, 124.7, 123.5, 122.1, 121.1, 112.1, 110.8, 35.4, 31.9. Elemental analysis. Calcd for $C_{44}H_{38}O_2$ (%): C 88.26, H 6.40, O 5.36; found (%): C 88.23, H 6.38, O 5.38.

4,4'-(4,4'-Di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF4-BPh(tBu)**) was synthesized according to GP. The dibenzo[b,d]furan-4-ylboronic acid (1.30 g, 6.1 mmol), 2,2'-dibromo-4,4'-di-*tert*-butyl-1,1'-biphenyl (1 g, 2.4 mmol), K_2CO_3 (1.3 g, 9.42 mmol), $PdCl_2(PPh_3)_2$ (1 mol%), 22 ml of dioxane:water (v/v 10:1) were used. The crude product was purified by flash chromatography on silica gel using hexane as the eluent and recrystallized from methanol, yielding the target compound as white crystals (1 g, 71%). ^{1}H NMR (400 MHz, THF-d_8) δ: 7.63 (d, J = 7.6 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.44 – 7.29 (m, 8H), 7.24 (d, J = 8.1 Hz, 2H), 7.17 (t, J = 7.4 Hz, 2H), 6.76 (t, J = 7.6 Hz, 2H), 6.71 – 6.65 (m, 2H), 1.25 (s, 18H). ^{13}C NMR (101 MHz, THF-d_8) δ: 156.8, 154.2, 150.2, 139.2, 136.0, 132.4, 129.6, 128.6, 127.3, 126.9, 125.14, 125.10, 124.8, 122.9, 122.6, 121.0, 119.3, 112.0, 67.5, 35.1, 31.7, 25.4. Elemental analysis. Calcd for $C_{44}H_{38}O_2$ (%): C 88.26, H 6.40, O 5.36; found (%): C 88.24, H 6.41, O 5.35.

BDE calculations

Table S1. Calculated bond dissociation energies (BDE) of DBF–biphenyl hosts (refer to Figure S1).

Bond	B1 BDE (eV)			B2 BDE (eV)			B3 BDE (eV)		
Compound	Neutral	Cationic	Anionic	Neutral	Cationic	Anionic	Neutral	Cationic	Anionic
DBF2-BPh	4.61	3.57	5.44	4.82	3.89	2.42	-	-	-
DBF4-BPh	4.56	3.61	5.43	4.87	3.14	2.38	-	-	-
DBF2-BPh(tBu)	4.66	3.57	5.48	4.81	3.87	2.44	3.93	2.86	4.01
DBF4-BPh(tBu)	4.61	3.63	5.47	4.86	3.16	2.40	3.93	3.02	4.02

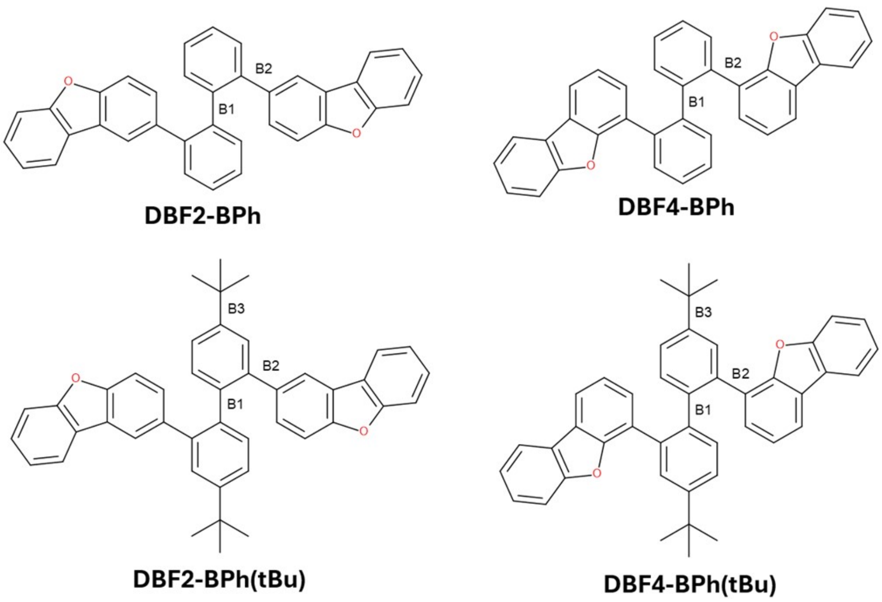


Figure S1. DBF–biphenyl host molecule structures with marked bonds for BDE calculation.

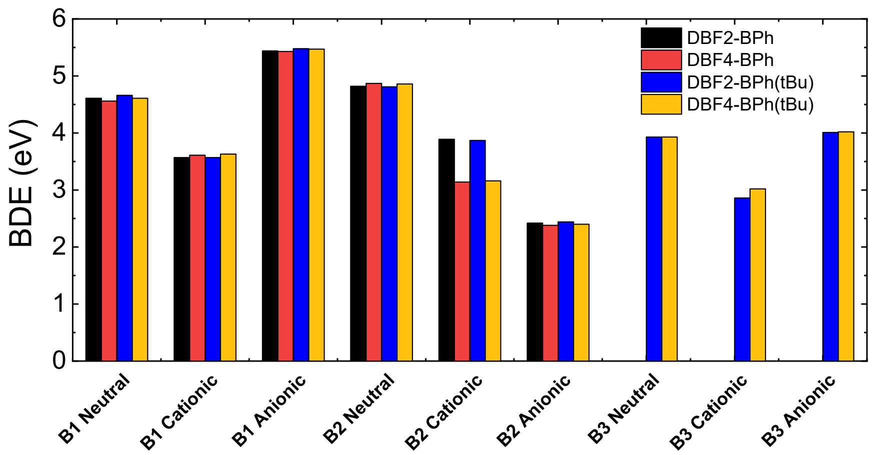


Figure S2. Bar chart of BDEs for DBF–biphenyl hosts in the neutral, cationic, and anionic states (values taken from Table S1).

Thermal characterization

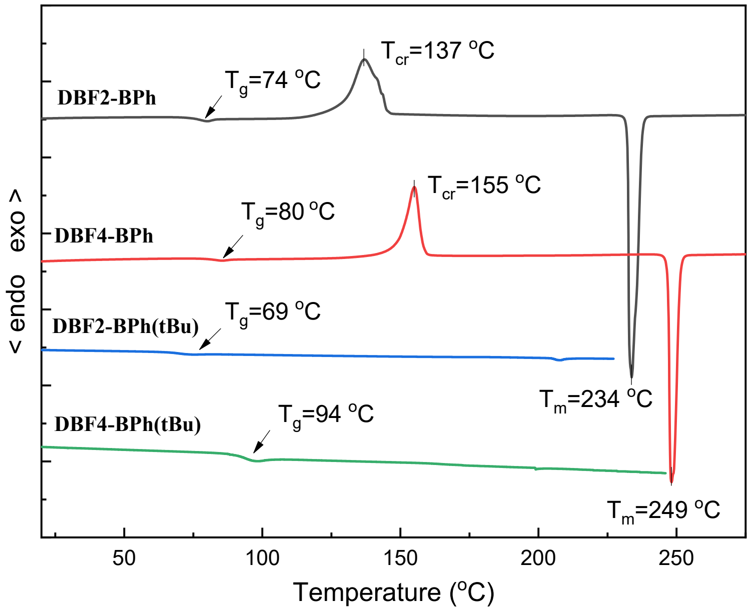


Figure S3. DSC 2nd heating scans of the DBF–biphenyl hosts recorded under nitrogen atmosphere at a heating rate of 10 °C/min. Glass-transition (T_g), crystallization (T_{cr}), and melting (T_m) temperatures, indicated.

Table S2. Thermal properties of the DBF–biphenyl hosts.

Host	$T_{-5\%}{}^{a}$, °C	$T_g{}^{b*}$, °C	$T_{cr}{}^{b*}$, °C	$T_m{}^{b}$, °C
DBF2-BPh	312	74	137	234
DBF4-BPh	318	80	155	249
DBF2-BPh(tBu)	293	69	-	190
DBF4-BPh(tBu)	309	94	-	175

[a] Measured by TGA under nitrogen atmosphere at a heating rate of 20 °C/min.

[b] Measured by DSC under nitrogen atmosphere at a heating rate of 10 °C/min.

*Determined from DSC 2nd heating curves.

Electrochemistry and additional device data

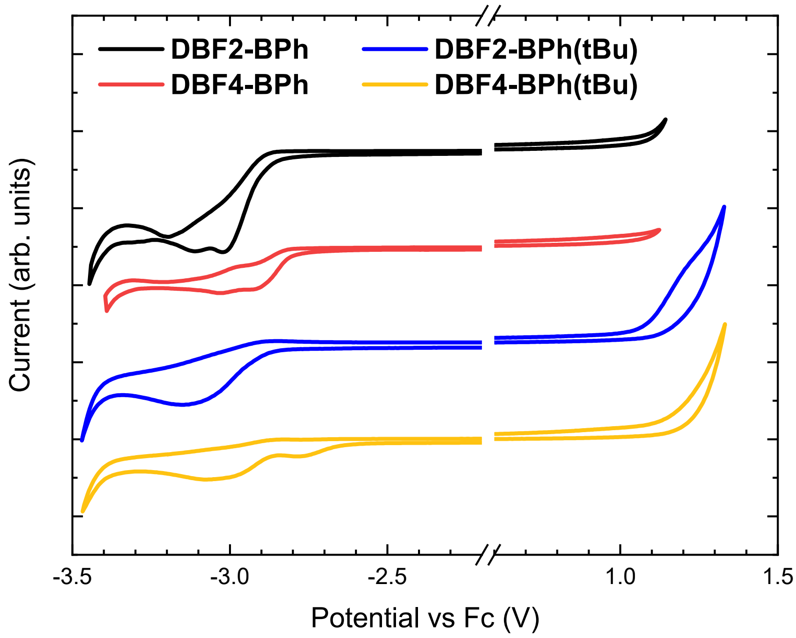


Figure S4. Cyclic voltammograms of the DBF–biphenyl hosts.

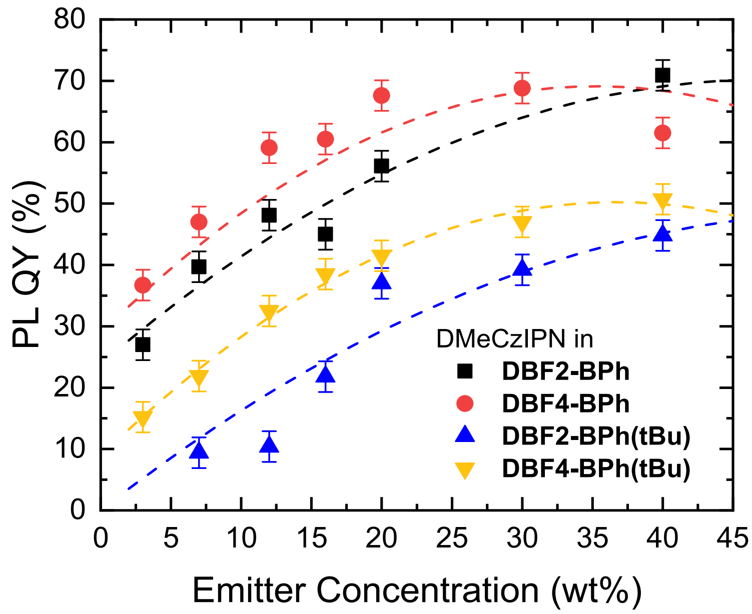


Figure S5. PL QY of DMeCzIPN-doped host films as a function of emitter concentration.

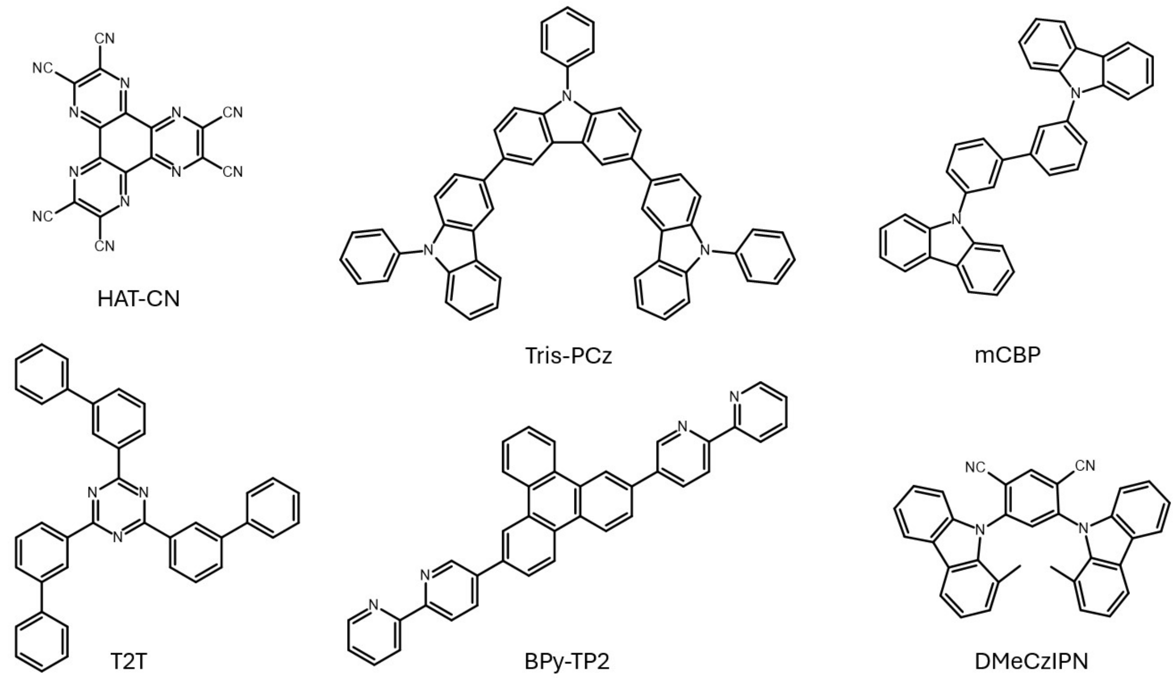


Figure S6. Chemical structures of HAT-CN, Tris-PCz, mCBP, T2T, BPy-TP2 and DMeCzIPN used in OLED fabrication.

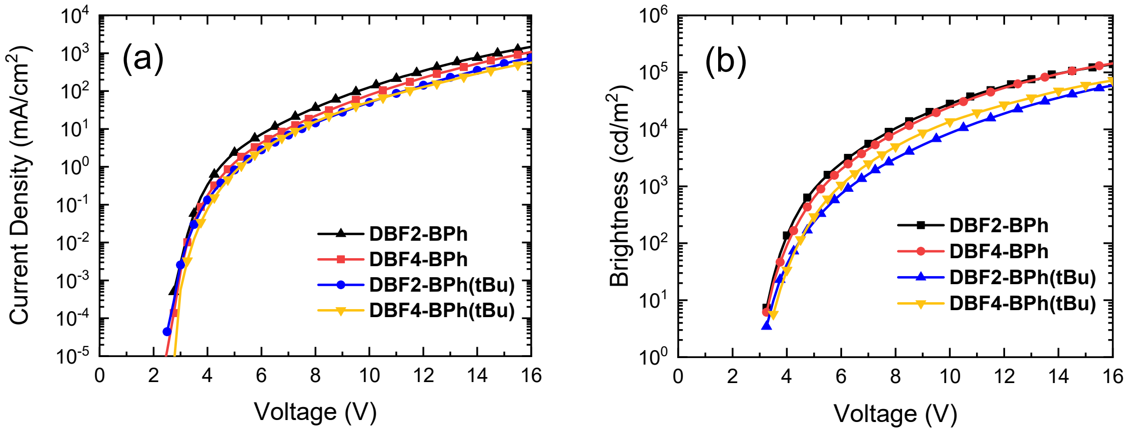


Figure S7. Device performance of blue TADF-OLEDs based on the DBF-biphenyl hosts: (a) current density vs voltage, (b) brightness vs voltage.

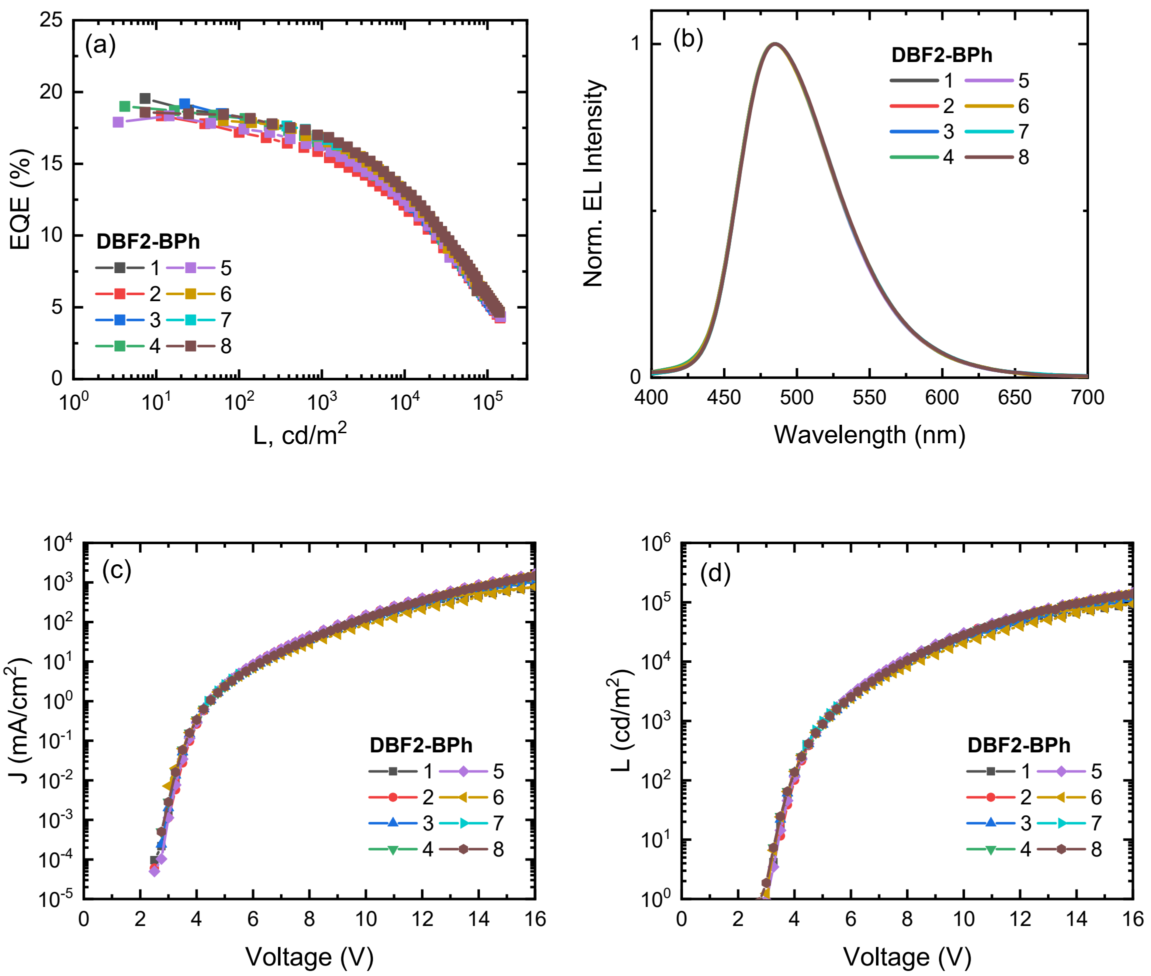


Figure S8. Device-to-device reproducibility for blue TADF OLEDs based on **DBF2-BPh** host, measured for several independently fabricated pixels (1–8): (a) EQE vs luminance, (b) EL spectra at 10 mA cm^{-2}, (c) current density vs voltage, (d) brightness vs voltage curves.

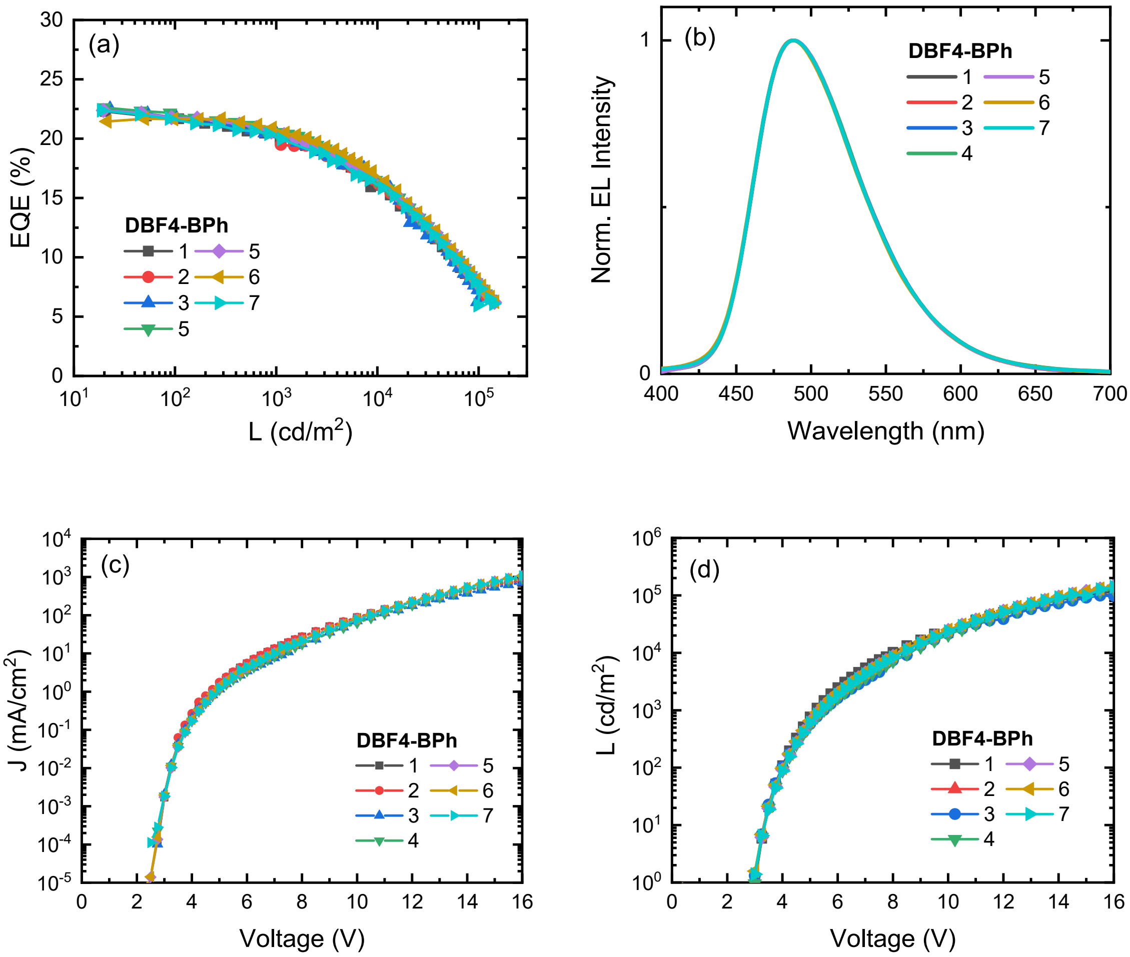


Figure S9. Device-to-device reproducibility for blue TADF OLEDs based on **DBF4-BPh** host, measured for several independently fabricated pixels (1–7): (a) EQE vs luminance, (b) EL spectra at 10 mA cm^{-2}, (c) current density vs voltage, (d) brightness vs voltage curves.

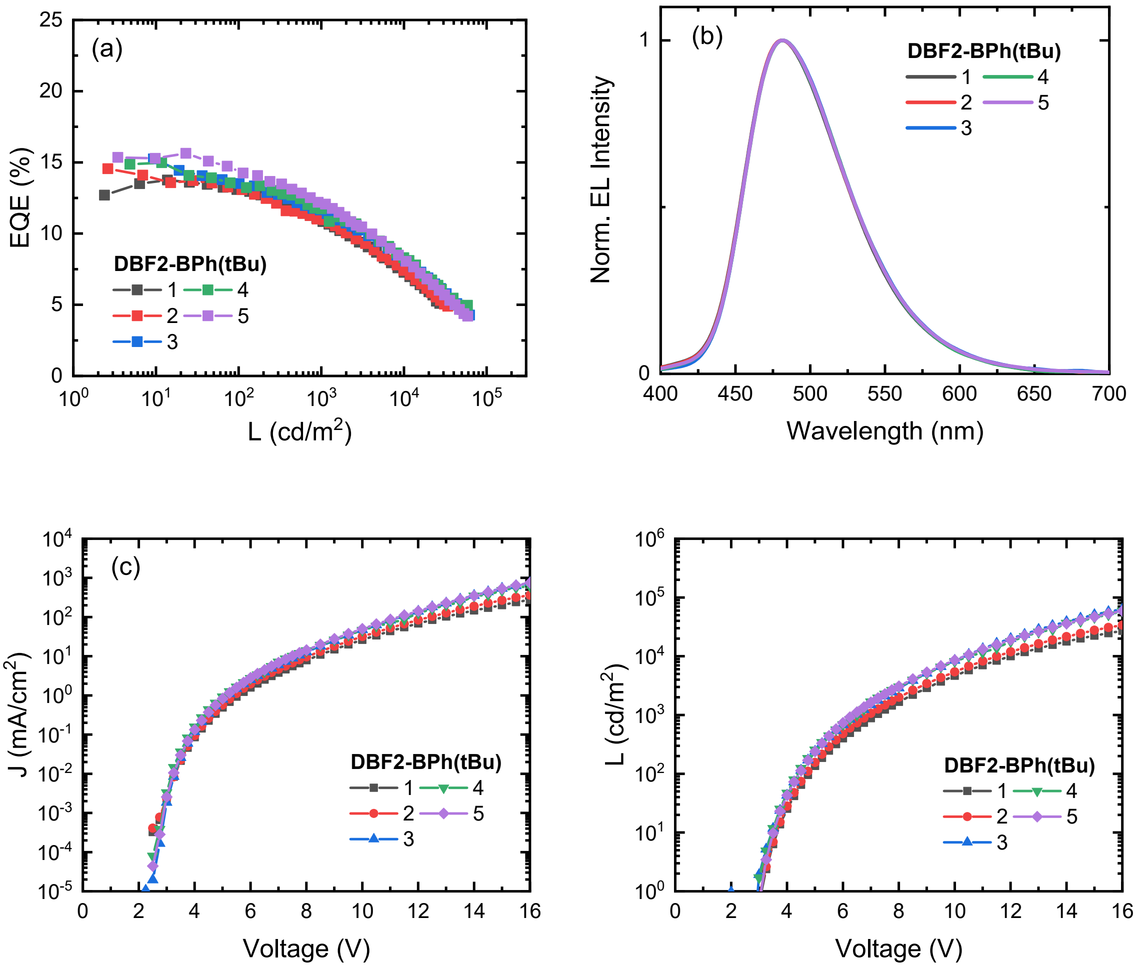


Figure S10. Device-to-device reproducibility for blue TADF OLEDs based on **DBF2-BPh(tBu)** host, measured for several independently fabricated pixels (1–5): (a) EQE vs luminance, (b) EL spectra at 10 mA cm^{-2}, (c) current density vs voltage, (d) brightness vs voltage curves.

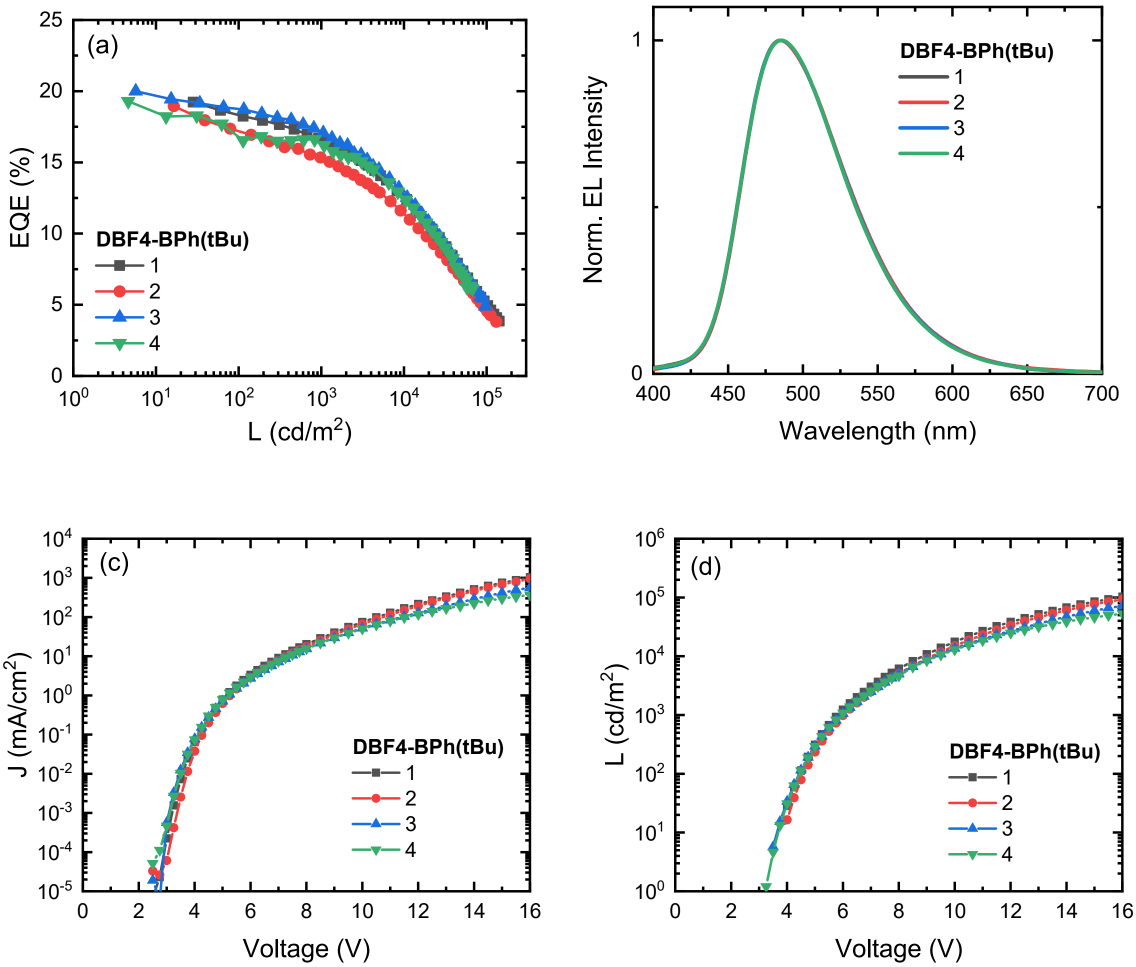


Figure S11. Device-to-device reproducibility for blue TADF OLEDs based on **DBF4-BPh(tBu)** host, measured for several independently fabricated pixels (1–4): (a) EQE vs luminance, (b) EL spectra at 10 mA cm^{-2}, (c) current density vs voltage, (d) brightness vs voltage curves.

Impedance fitting results

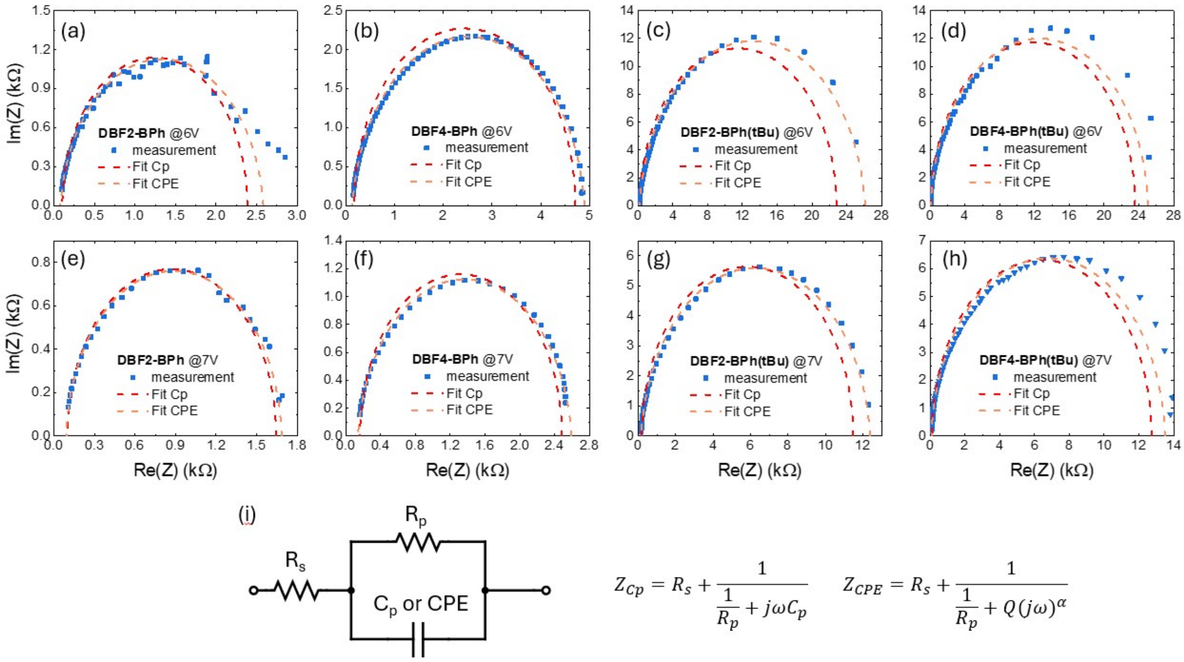


Figure S12. Nyquist plots of DMeCzIPN-based OLEDs using **DBF2-BPh** (a, e), **DBF4-BPh** (b, f), **DBF2-BPh(tBu)** (c, g), and **DBF4-BPh(tBu)** (d, h) as hosts measured at DC biases of 6 V (a-d) and 7 V (e-h), with equivalent-circuit fits using Z(ω)=R_s+(R_p‖C_p) and Z(ω)=R_s+(R_p‖CPE). The equivalent circuit schematics and corresponding impedance expressions are shown in (i).

Table S3. Equivalent-circuit fitting parameters obtained using the Rs+(Rp‖CPE) model for impedance spectra of DMeCzIPN-based OLEDs with the DBF-biphenyl hosts at typical operating biases.

Bias voltage, V	Host	R_s, Ω	R_p, Ω	Q, F·$s^{\alpha-1}$	α
6	**DBF2-BPh**	66.46	2733	$5.47\cdot10^{-9}$	0.89
	DBF4-BPh	133.8	4764	$2.42\cdot10^{-9}$	0.94
	DBF2-BPh(tBu)	153.9	25950	$2.17\cdot10^{-9}$	0.94
	DBF4-BPh(tBu)	67.44	24950	$1.36\cdot10^{-9}$	0.98
7	**DBF2-BPh**	91.22	1594	$1.82\cdot10^{-9}$	0.97
	DBF4-BPh	137.8	2455	$2.28\cdot10^{-9}$	0.94
	DBF2-BPh(tBu)	156.5	12210	$2.03\cdot10^{-9}$	0.95
	DBF4-BPh(tBu)	64.89	13750	$1.58\cdot10^{-9}$	0.97

Copies of ^{1}H NMR and ^{13}C NMR spectra

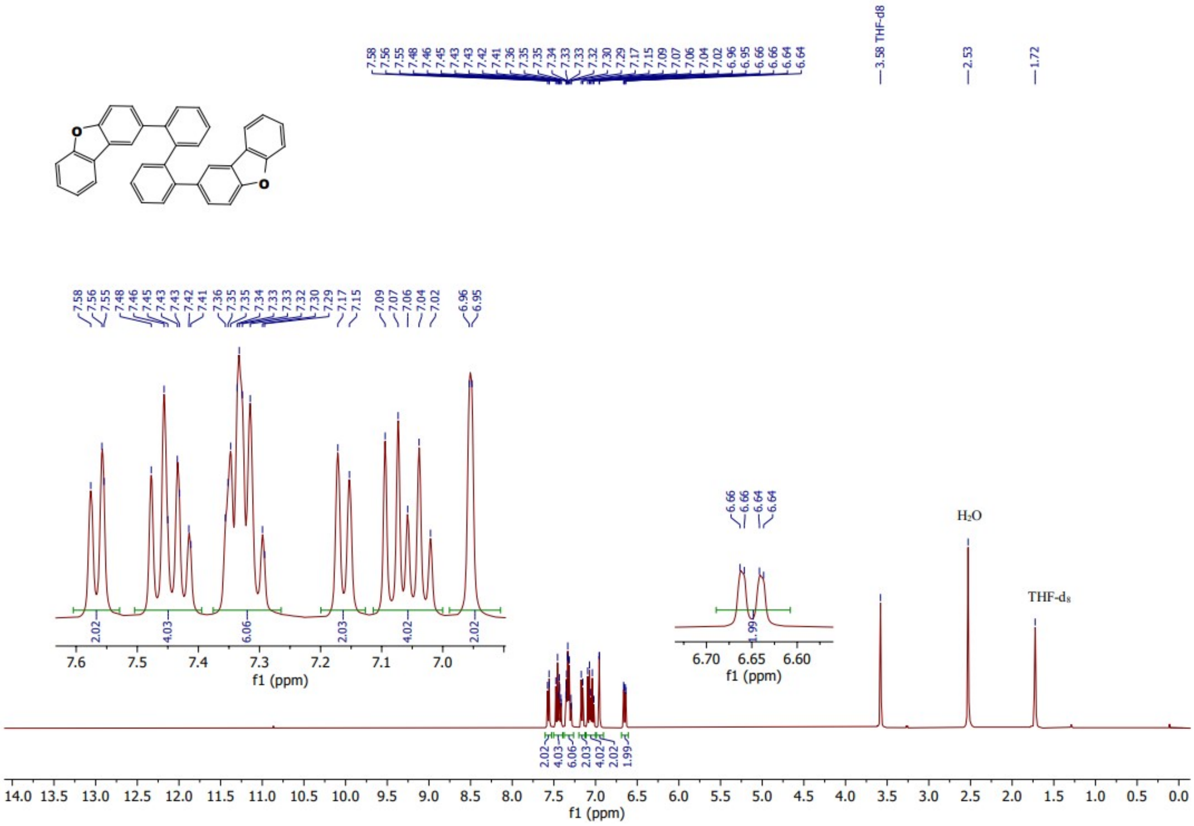


Fig. S13. ^{1}H NMR spectra of 2,2'-bis(dibenzo[b,d]furan-2-yl)-1,1'-biphenyl (**DBF2-BPh)**

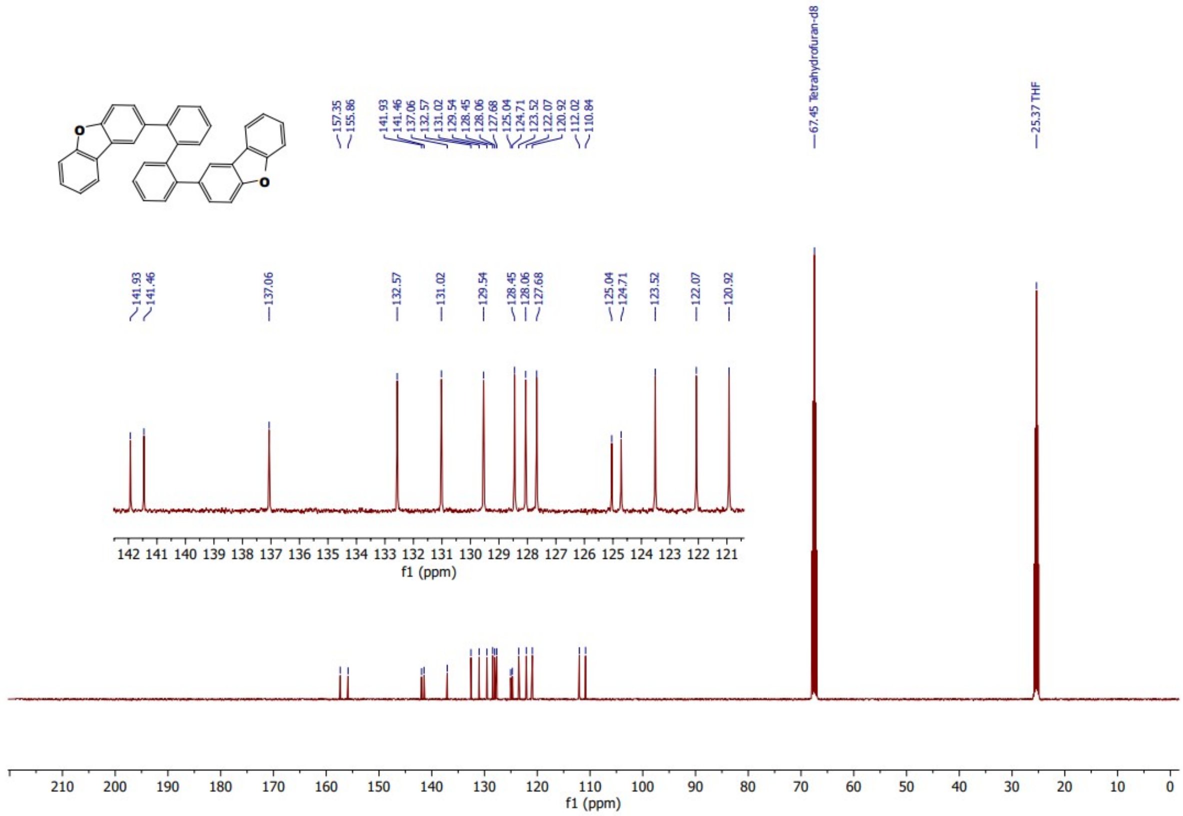


Fig. S14. ^{13}C NMR spectra of 2,2'-bis(dibenzo[b,d]furan-2-yl)-1,1'-biphenyl (**DBF2-BPh)**

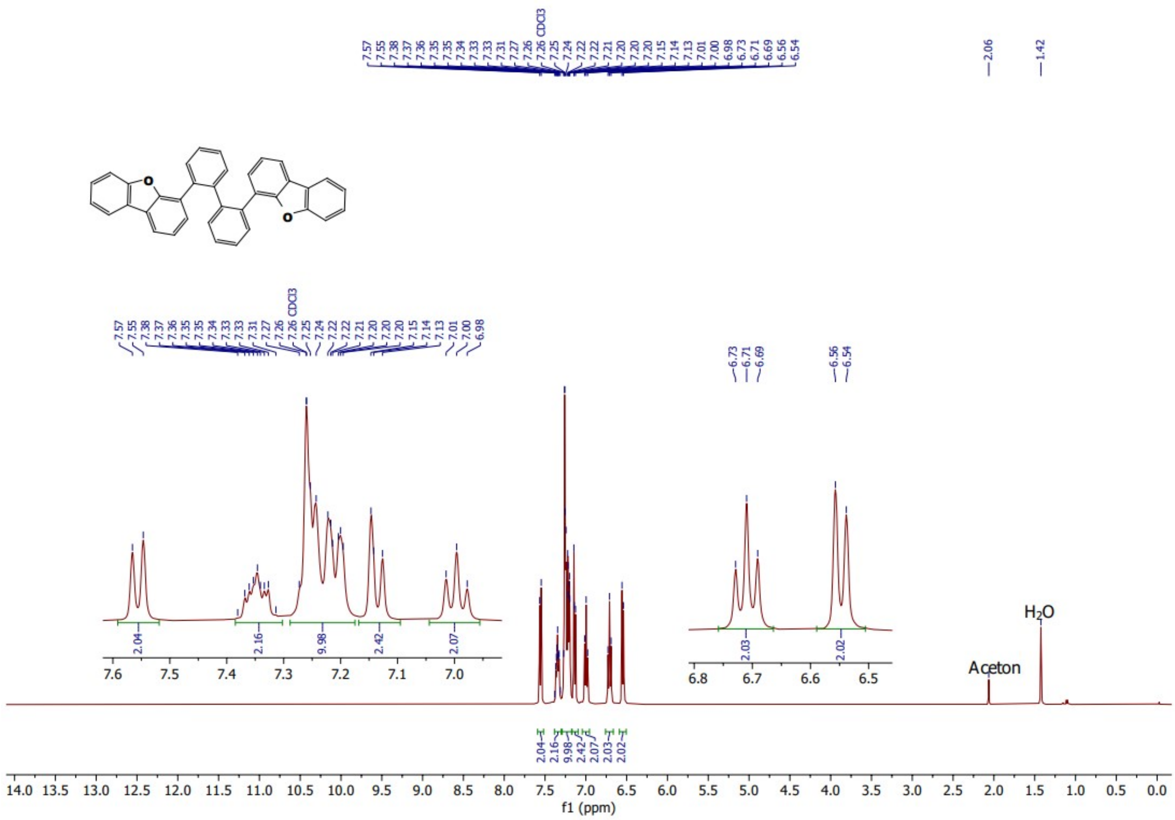


Fig. S15. [1]H NMR spectra of 2,2'-bis(dibenzo[b,d]furan-4-yl)-1,1'-biphenyl (**DBF4-BPh**)

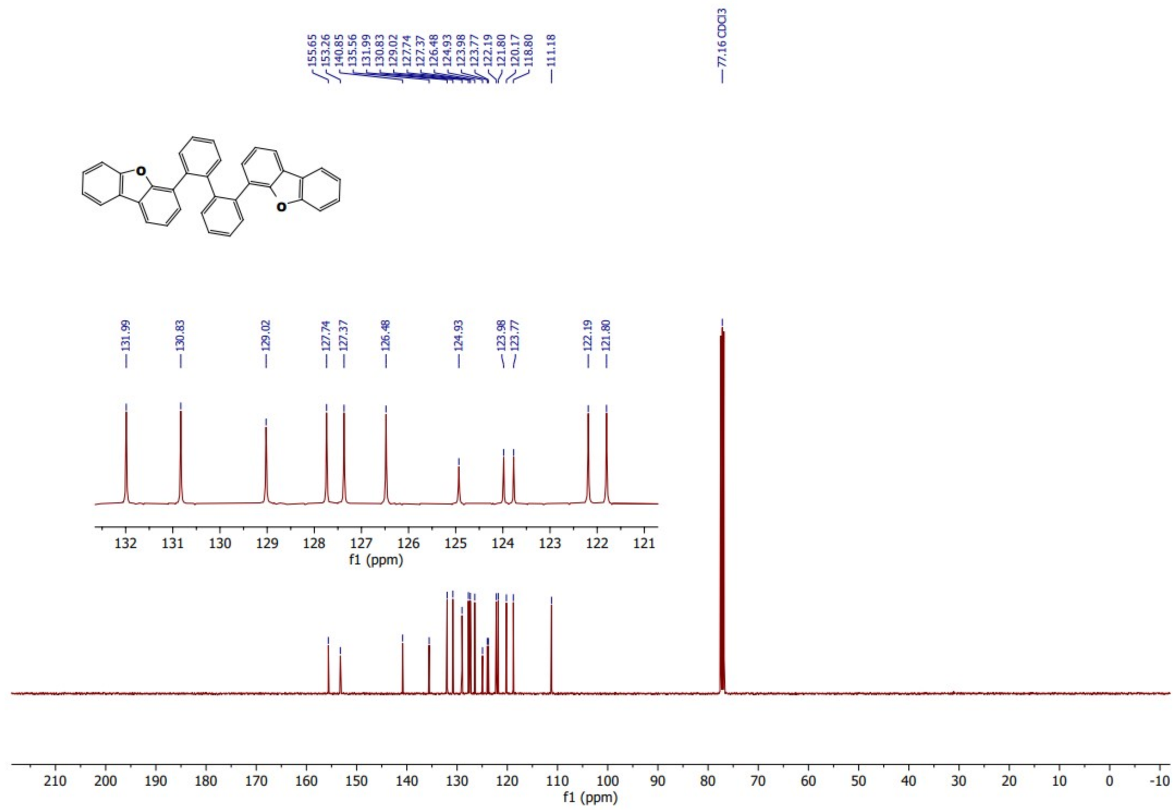


Fig. S16. [13]C NMR spectra of 2,2'-bis(dibenzo[b,d]furan-4-yl)-1,1'-biphenyl (**DBF4-BPh**)

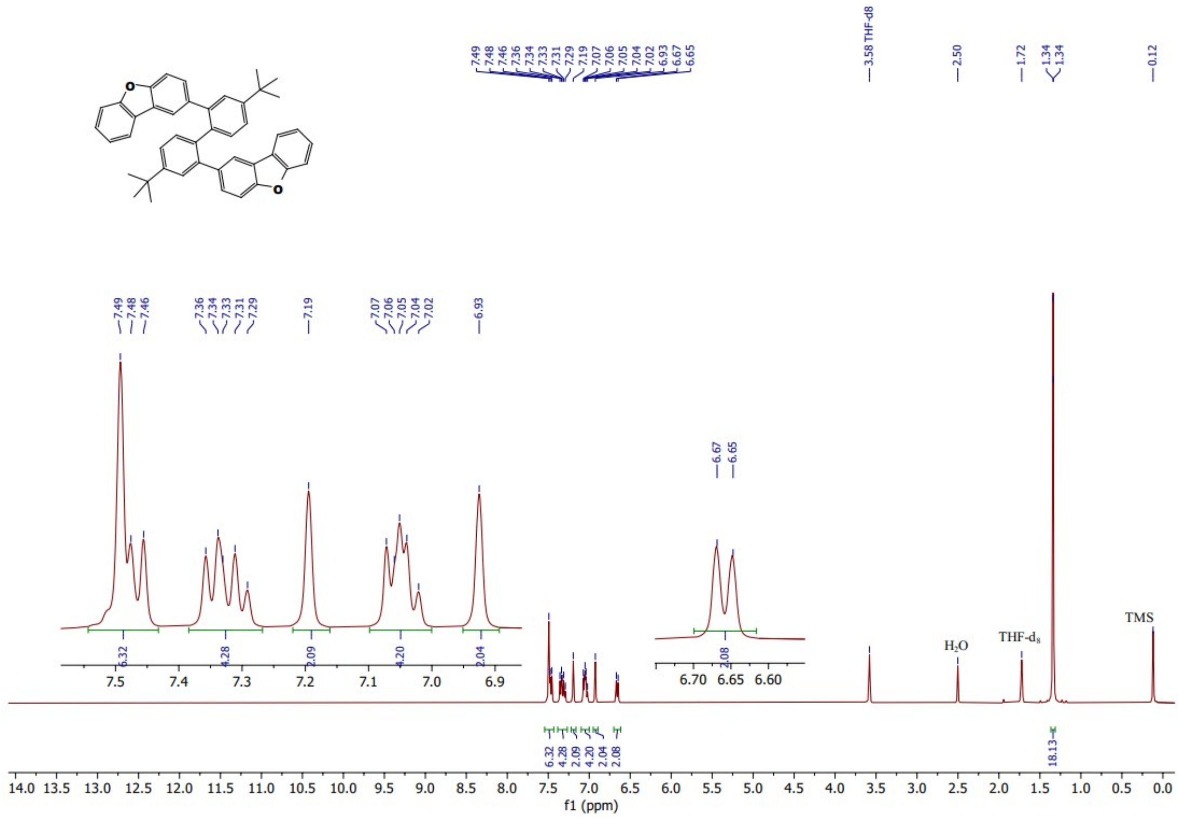


Fig. S17. [1]H NMR spectra of 2,2'-(4,4'-di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF2-BPh(tBu))**

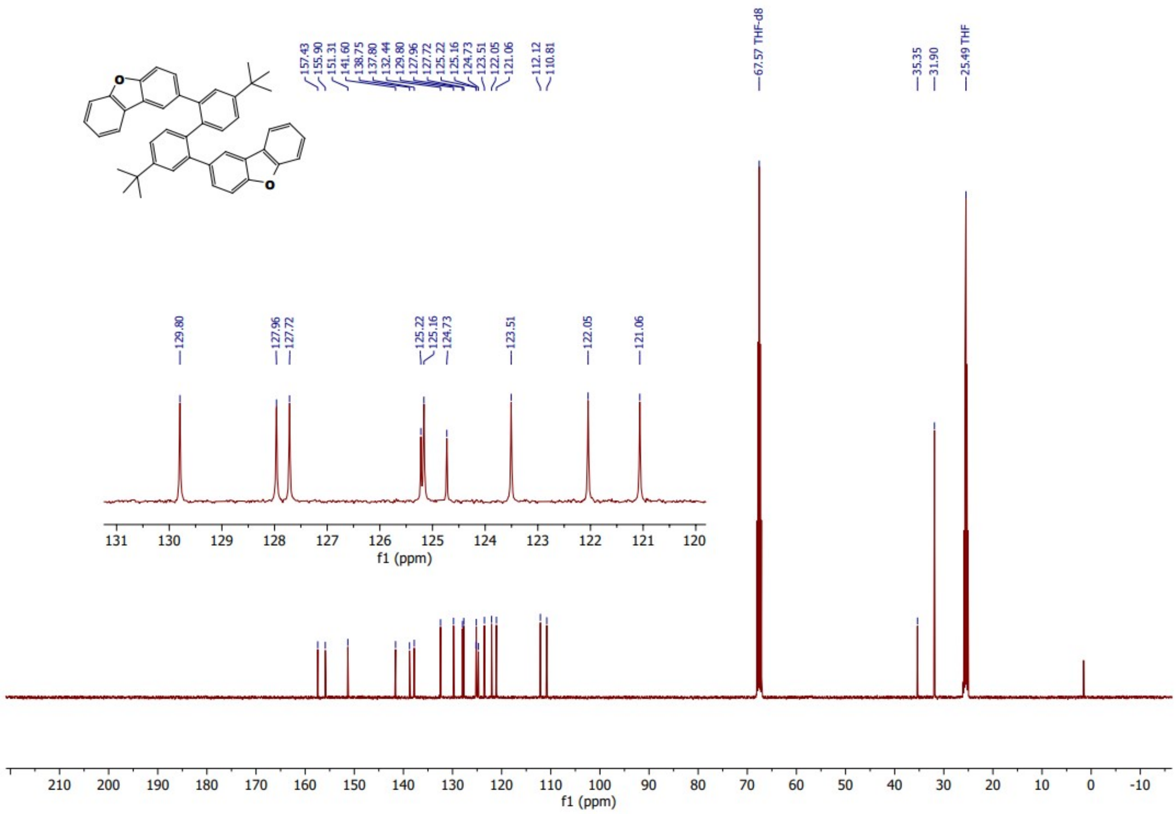


Fig. S18. [13]C NMR spectra of 2,2'-(4,4'-di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF2-BPh(tBu))**

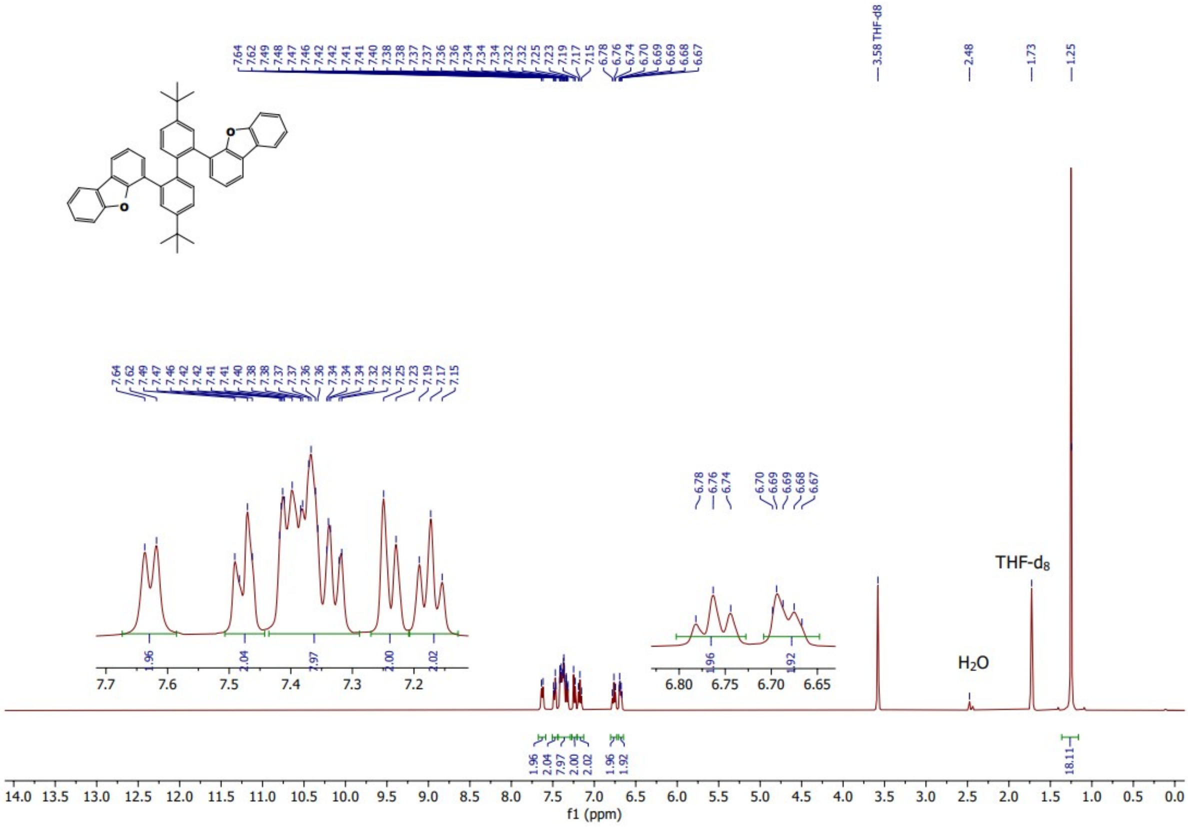


Fig. S19. [1]H NMR spectra of 4,4'-(4,4'-di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF4-BPh(tBu))**

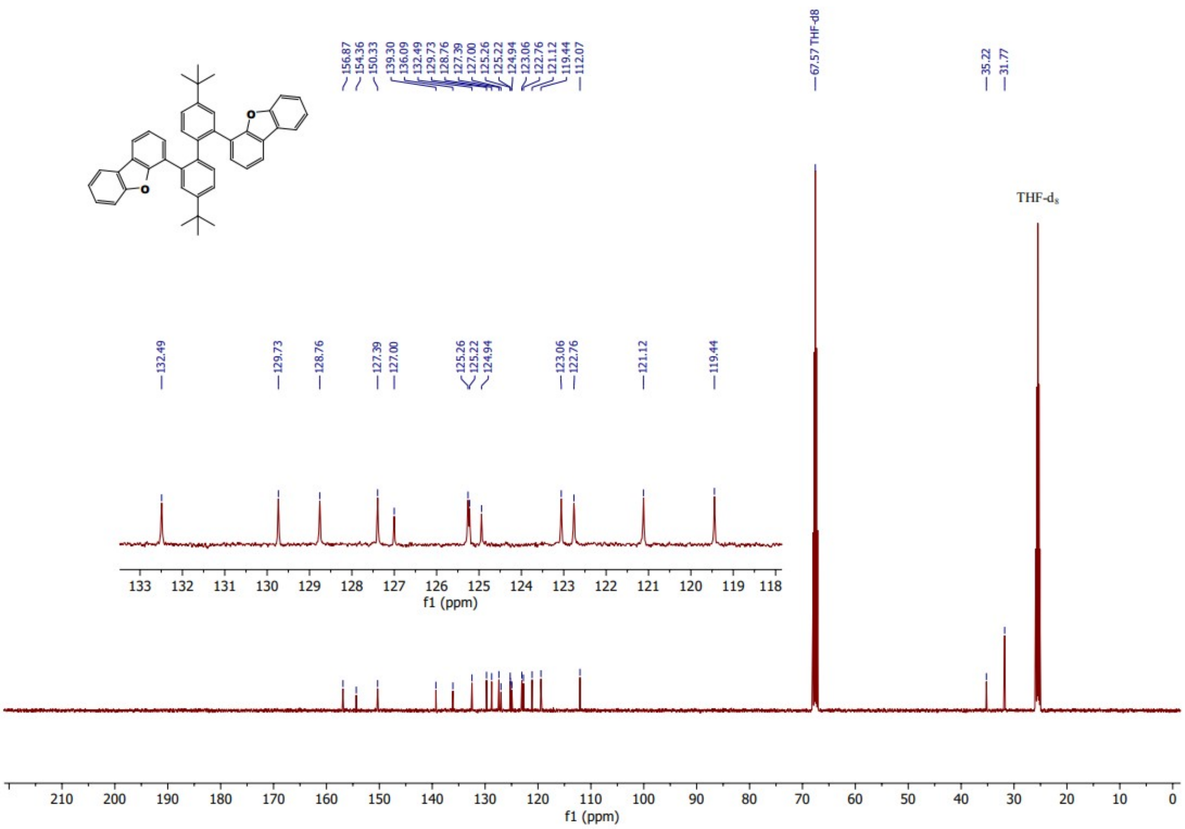


Fig. S20. [13]C NMR spectra of 4,4'-(4,4'-di-*tert*-butyl-[1,1'-biphenyl]-2,2'-diyl)didibenzo[b,d]furan (**DBF4-BPh(tBu))**

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