Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information

A Simple and Broadly Applicable Synthesis of Fluorene-Coupled D-σ-A Type Molecules: Towards High-Triplet-Energy Bipolar Hosts for Efficient Blue Thermally-Activated Delayed Fluorescence

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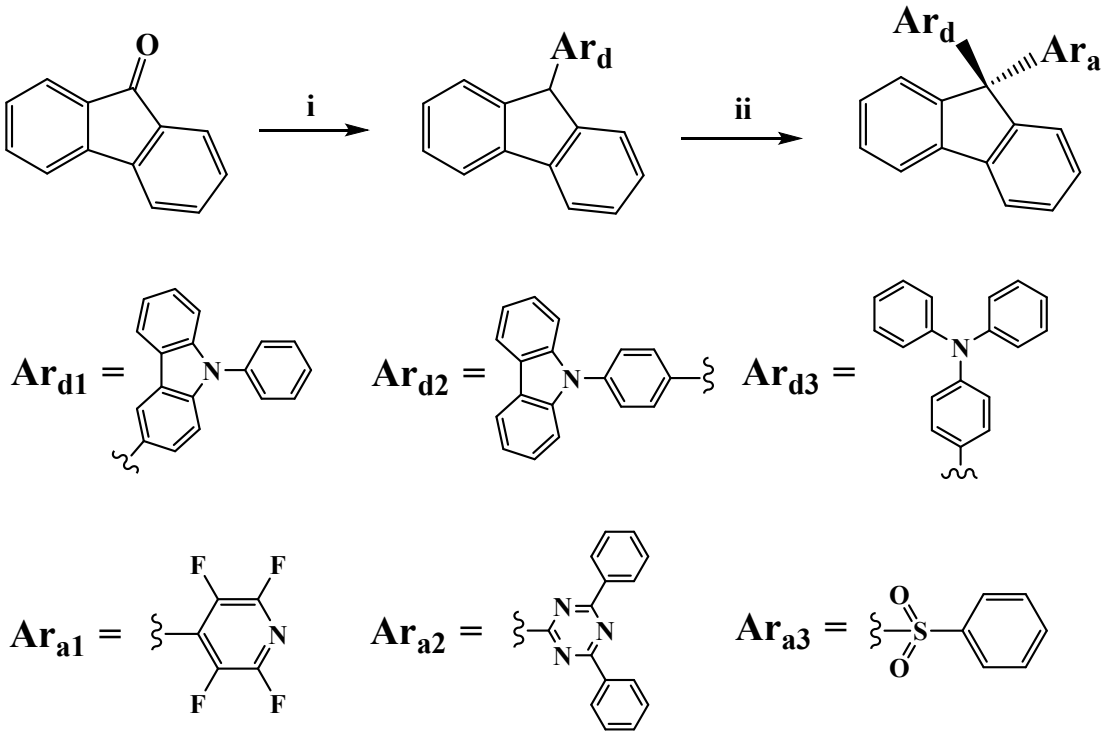

Scheme S1. Syntheses of 3CzFTFP, 9PhFTFP, 3CzFDPhTz, 9PhFDPhTz, and TPAFBSO. i) a) toluene, p-toluenesulfonyl hydrazide, 80 °C, 2 h; b) K_2CO_3, $ArdB(OH)_2$, 110 °C, 5 h; ii) anhydrous THF, -78 °C, *n*-BuLi, 2 h, pentafluoropyridine (or 2-chloro-4,6-diphenyl-1,3,5-triazine, or benzenesulfonyl chloride), room temperature, 3 h.

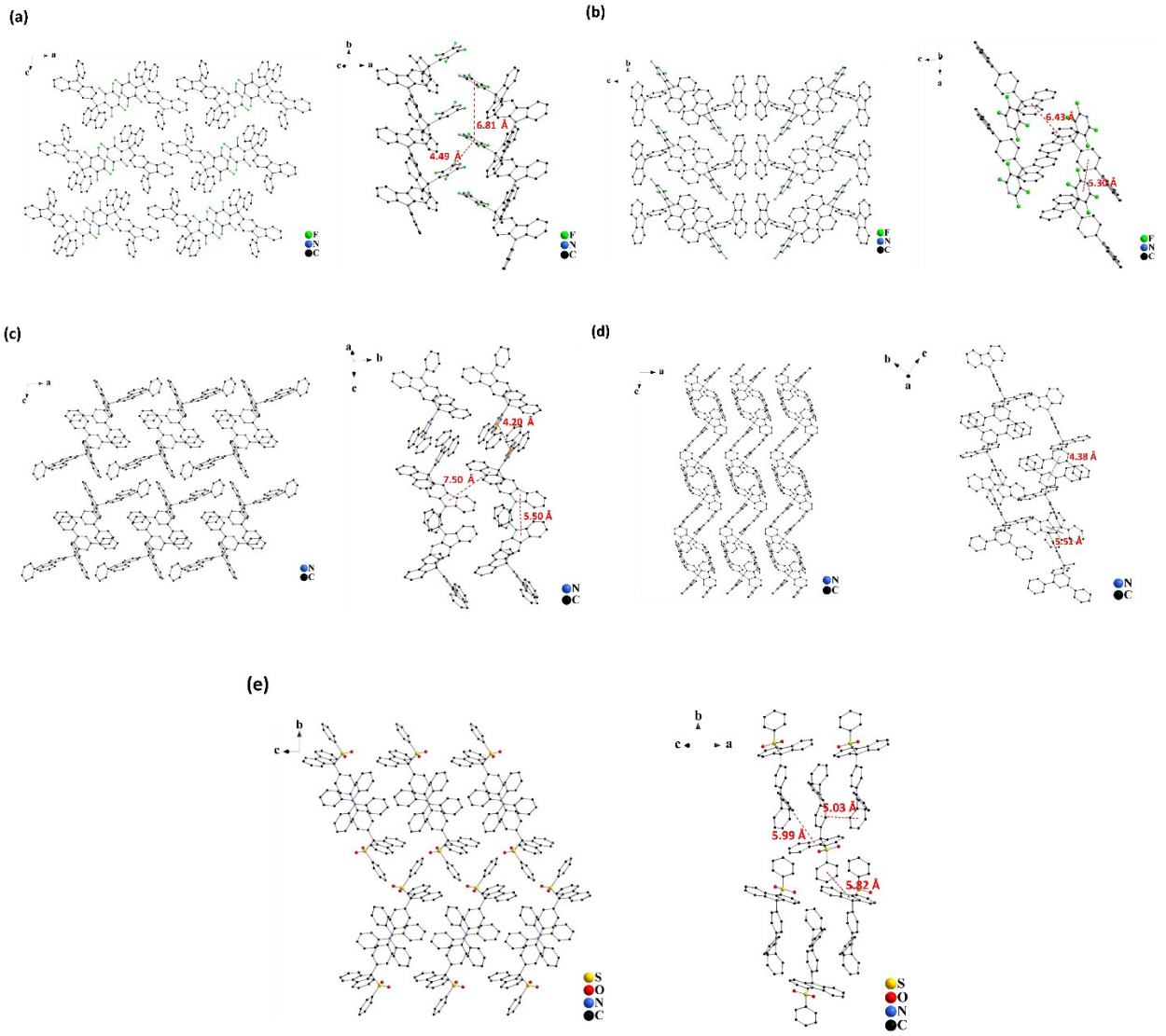

Figure S1. Spatial arrangement of molecules in the single crystals of **3CzFTFP**, **9PhFTFP**, **3CzFDPhTz** and **9PhFDPhTz** (The left one was marked with space distances between aromatic planes from two neighboring molecules).

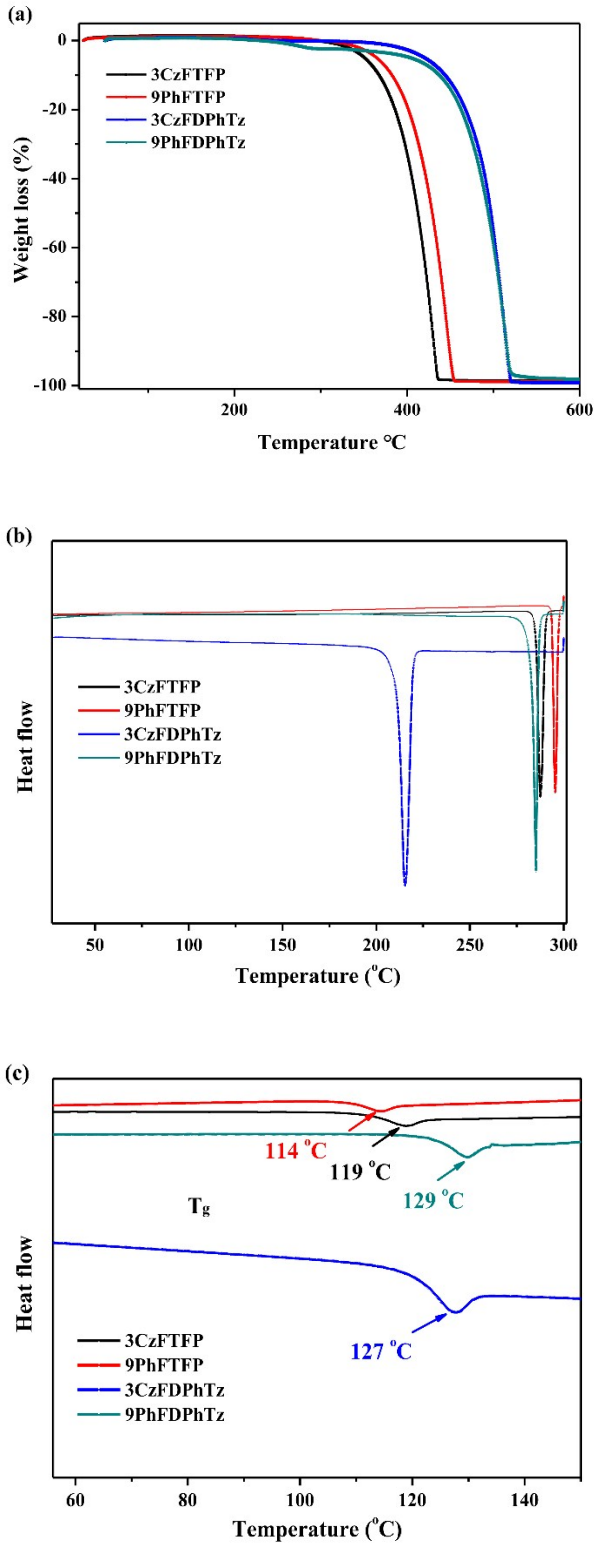

Figure S2. (a) TGA, (b) first-cycle, and (c) second-cycle DSC curves of **3CzFTFP**, **9PhFTFP**, **3CzFDPhTz**, and **9PhFDPhTz**.

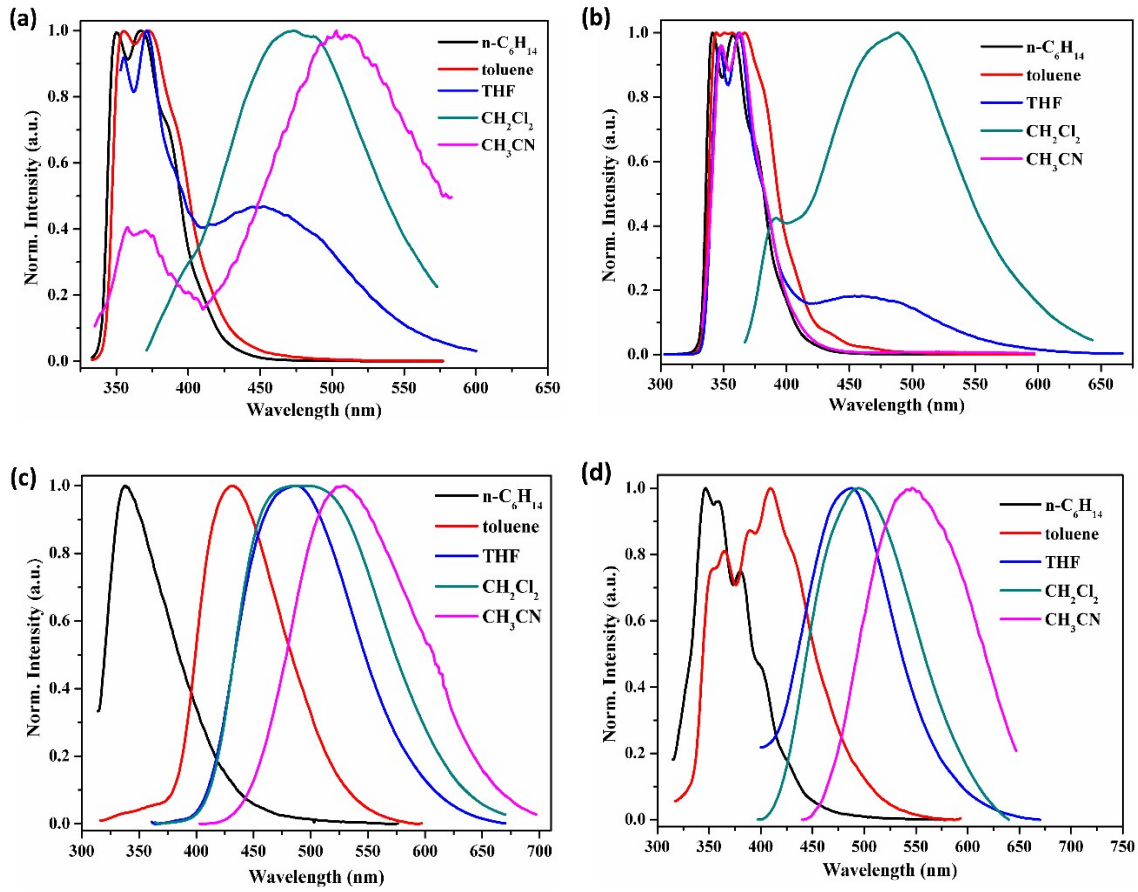

Figure S3. The fluorescence spectra of **3CzFTFP** (a), **9PhFTFP** (b), **3CzFDPhTz** (c) and **9PhFDPhTz** (d) in different solvents.

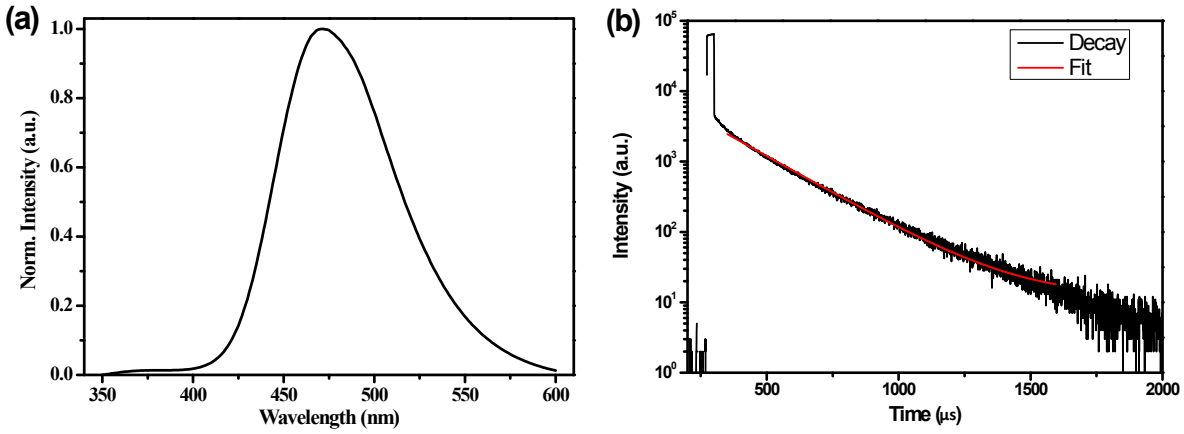

Figure S4. The photoluminescence (PL) spectrum (a) and transient PL decay curve (b) of 5 wt% **2CzPN**-doped **3CzFTFP** thin film (20 nm thick) at room temperature.

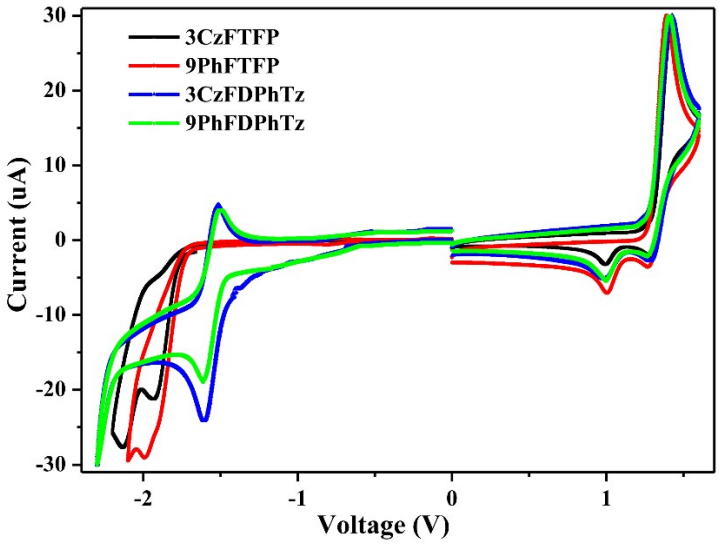

Figure S5. Cyclic voltammograms of **3CzFTFP**, **9PhFTFP**, **3CzFDPhTz** and **9PhFDPhTz** measured in CH_2Cl_2 (anodic scan) and DMF (cathodic scan) at room temperature with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte and a scan rate of 100 mV s^{-1}.

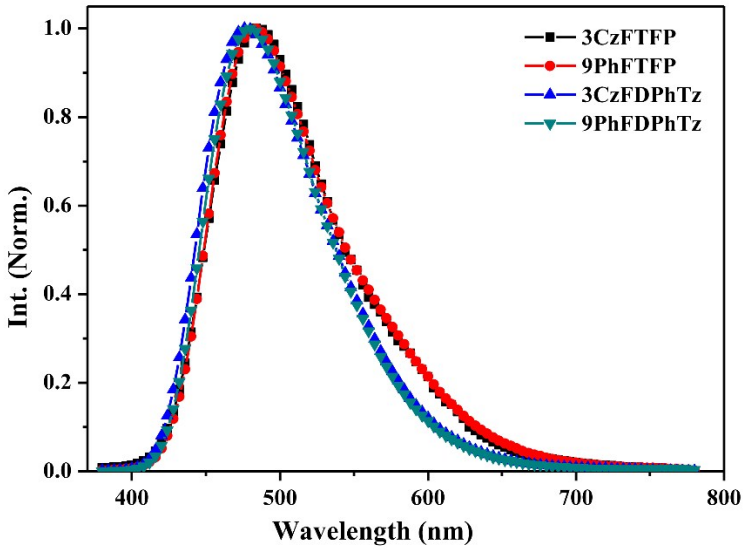

Figure S6. EL spectra of the **2CzPN**-based blue TADF devices using **3CzFTFP**, **9PhFTFP**, **3CzFDPhTz** and **9PhFDPhTz** as the hosts.

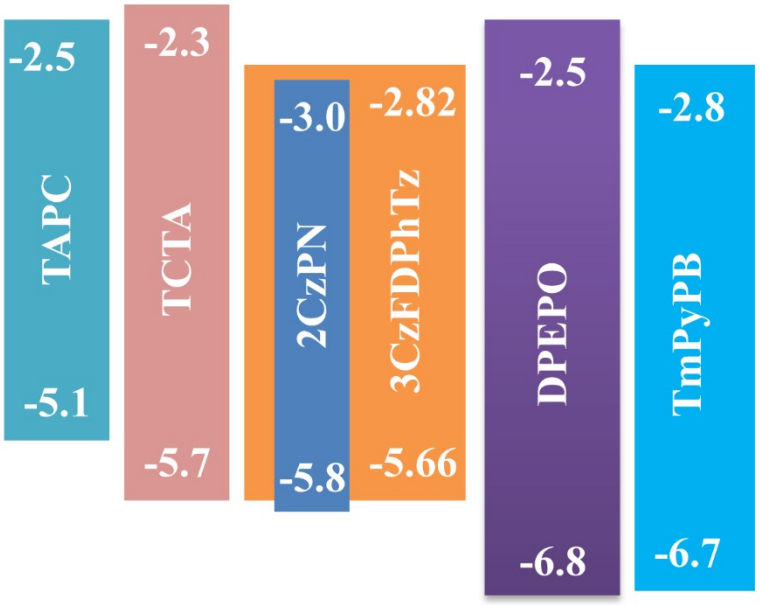

Figure S7. FMO energy level alignment of device C based on **3CzFDPhTz**.

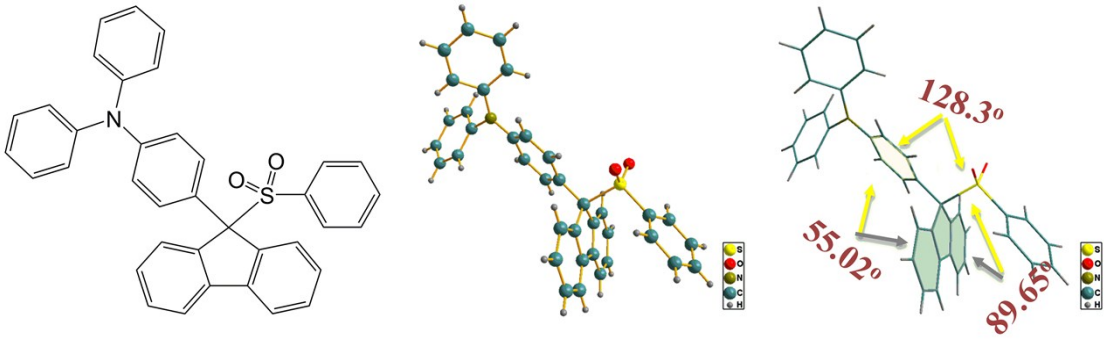

Figure S8. Molecular chemical structures (left), single-crystal ball-and-stick models (middle), and wires/sticks models with marked dihedral angle values (right) of **TPAFBSO**.

Table S1. Summary of the EL performance of devices using **3CzFTFP**, **9PhFTFP**, **3CzFDPhTz**, **9PhFDPhTz**, and other high-E_T compounds reported in the literature as the host, and 2CzPN as the emitter.

Host	V_{on}[a] (V)	CE[a,b] (cd A^{-1})	PE[a,b] (lm W^{-1})	EQE[a,b] (%)	CIE (x, y)	Ref.
3CzFTFP	4.0	38.3, 11.8, -	30.1, 6.5, -	16.9, 4.7, -	(0.21, 0.34)	This work
9PhFTFP	3.6	32.4, 18.7, -	28.3, 11.2, -	13.4, 7.4, -	(0.21, 0.34)	This work
3CzFDPhTz	3.0	33.0, 18.7, 5.6	32.4, 13.7, 4.0	16.4, 7.6, 3.0	(0.19, 0.30)	This work
9PhFDPhTz	3.2	23.3, 18.7, 6.9	20.9, 13.7, 4.1	9.7, 7.7, 3.1	(0.19, 0.31)	This work
***m*-DCz-S**	3.3	26.1, 15.6, 6.5	24.1, 9.9, 3.0	11.4, 6.5, 2.9	(0.17, 0.30)	Ref. 1
***o*-CzCN**	5.1	29.23, -, -	18.36, -, -	14.52, -, -	(0.17, 0.23)	Ref. 2
***m*-CzCN**	4.8	26.37, -, -	16.56, -, -	14.98, -, -	(0.17, 0.26)	Ref. 2
***p*-CzCN**	3.8	14.41, -, -	11.12, -, -	8.10, -, -	(0.17, 0.28)	Ref. 2
mCP/PO15	3.0	45.3, -, 5.5	47.4, -, 3.0	21.8, -, 2.8	-	Ref. 3
CzDPPy	3.4	34.8, 18.9, 1.9	33.1, 10.4, 0.5	16.0, 7.23, 0.9	(0.18, 0.34)	Ref. 4
tCzDPPy	3.9	28.9, 8.7, -	23.3, 4.2, -	11.7, 4.2, -	(0.22, 0.38)	Ref. 4
mCP	6.2	23.87, 15.8, 8.53	-	14.0, 6.5, 4.0	(0.17, 0.32)	Ref. 5
ZDZ	5.0	31.83, 23.2, 10.72	-	18.5, 10.7, 4.9	(0.17, 0.34)	Ref. 5
ZDN	4.7	53.05, 30.8, 14.29	-	25.7, 15.3, 6.0	(0.19, 0.39)	Ref. 5
NDN	4.8	47.74, 26.7, 11.82	-	23.9, 10.7, 4.7	(0.20, 0.42)	Ref. 5
BT-01	3.0	53.0, 40.2, 20.2	47.5, 26.6, 9.0	25.5, 19.5, 10.0	(0.16, 0.31)	Ref. 6
BT-02	3.4	47.5, 30.3, 13.3	42.6, 19.2, 5.9	22.3, 13.9, 6.2	(0.17, 0.31)	Ref. 6
***o*-mCPBI**	3.6	21.4, -, -	17.7, -, -	10.2, 6.5, 5.6	(0.16, 0.30)	Ref. 7
BmPOPB	3.17	35.1, 22.9, 6.6	32.42, 17.44, 3.0	17.4, 11.6, 3.6	(0.16, 0.28)	Ref. 8
BpPOPB	3.20	30.3, 20.3, 5.9	28.0, 14.95, 2.6	15.2,10.19,3.23	(0.16, 0.27)	Ref. 8
TPBi	3.34	21.1, 16.5, 6.8	18.4, 10.81, 2.8	8.6, 7.3, 3.2	(0.20, 0.30)	Ref. 8
PPT/TPBi	-	-	-	13.6, -, -	(0.17, 0.30)	Ref. 9
TmPyPB	4.1	30.1, -, 10.4	27.1, -, 4.1	19.0, -, 6.1	(0.18, 0.36)	Ref. 10
***o*-CzDPz**	4.5	26.2, 14.9, 5.4	16.5, 7.0, 2.6	14.5, 8.2, 3.0	(0.16, 0.28)	Ref. 11

***m*-CzDPz**	4.7	19.1, 11.7, 5.6	12.0, 5.6, 2.1	10.5, 6.4, 3.1	(0.16, 0.30)	Ref. 11
3-CzDpz	3.8	26.2, 15.0, 6.8	20.6, 8.6, 2.9	15.8, 9.0, 4.1	(0.16, 0.29)	Ref. 11
mCPDPz	4.8	23.3, 13.3, 7.4	14.6, 6.5, 2.6	10.9, 6.2, 3.5	(0.17, 0.34)	Ref. 11

[a] Von: turn-on voltage, CE: current efficiency, PE: power efficiency, and EQE: external quantum efficiency. [b] In the order of maximum, then values at 100 and 1000 cd m^{-2}.

CCDC 1816870 (**3CzFTFP**), 1816871 (**9PhFTFP**), 1816873 (**3CzFDPhTz**), 1816874 (**9PhFDPhTz**) and 1830678 (**TPAFBSO**) contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement details for **3CzFTFP.**

Empirical formula	**$C_{36}H_{20}F_4N_2$**
Formula weight	556.54
Temperature (K)	120(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	19.0256(7)
b (Å)	6.8065(3)
c (Å)	20.2686(9)
α (˚)	90
β (˚)	102.703(2)
γ (˚)	90
Volume (Å^3)	2560.49(19)
Z	4
Density (calculated) (g·cm^{-3})	1.444
Absorption coefficient (mm^{-1})	0.105
F(000)	1144
Theta range for data collection (˚)	3.17 – 27.51
Limiting indices	-24 ≤ h ≤ 24, -8 ≤ k ≤ 8, -25 ≤ l ≤ 26
R_{int}	0.0455
Reflections collected / unique	9160 / 5842
Goodness-of-fit on F^2	1.076
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	0.0646/0.1499
R indices (all data) [a]	0.1047/0.1699
Largest diff. peak and hole (e Å^{-3})	0.329 and -0.369

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

Table S3. Crystal data and structure refinement details for **9PhFTFP.**

Empirical formula	**C_{36} H_{20} F_4 N_2**
Formula weight	556.54
Temperature (K)	120(2) K
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	8.1153(5)
b (Å)	17.5146(11)
c (Å)	36.762(2)
α (˚)	90
β (˚)	90
γ (˚)	90
Volume (Å^3)	5225.2(5)
Z	8
Density (calculated) (g·cm^{-3})	1.415
Absorption coefficient (mm^{-1})	0.103
F(000)	2288
Theta range for data collection (˚)	2.98 – 27.10
Limiting indices	-10 ≤ h ≤ 10, -21 ≤ k ≤ 22, -46 ≤ l ≤ 47
R_{int}	0.0674
Reflections collected / unique	29721 / 5760
Goodness-of-fit on F^2	1.286

Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	0.0842/0.1618
R indices (all data) [a]	0.1134/0.1707
Largest diff. peak and hole (e Å^{-3})	0.292 and -0.376

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

Table S4. Crystal data and structure refinement details for **3CzFDPhTz.**

Empirical formula	**$C_{46}H_{30}N_4$**
Formula weight	638.47
Temperature (K)	120(2) K
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	22.949(2)
b (Å)	9.1637(9)
c (Å)	31.752(3)
α (˚)	90
β (˚)	96.447(3)
γ (˚)	90
Volume (Å^3)	6635.1(11)
Z	8
Density (calculated) (g·cm^{-3})	1.279
Absorption coefficient (mm^{-1})	0.075
F(000)	2672
Theta range for data collection (˚)	2.97 – 27.17
Limiting indices	-29 ≤ h ≤ 28, -11 ≤ k ≤ 11, -36 ≤ l ≤ 40

R_{int}	0.0792
Reflections collected / unique	35141 / 7196
Goodness-of-fit on F^2	1.206
Final R indices [$F_o^2 > 2\sigma(F_o^2)$][a]	0.0955/0.1759
R indices (all data) [a]	0.1392/0.1940
Largest diff. peak and hole (e Å^{-3})	0.342 and -0.389

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

Table S5. Crystal data and structure refinement details for **9PhFDPhTz.**

Empirical formula	**$C_{46}H_{30}N_4$**
Formula weight	638.74
Temperature (K)	120(2) K
Crystal system	Triclinic
Space group	*P*-1
a (Å)	10.0321(13)
b (Å)	11.8164(17)
c (Å)	15.471(2)
α (˚)	90.653(7)
β (˚)	93.450(7)
γ (˚)	113.629(7)
Volume (Å^3)	1675.9 (4)
Z	2
Density (calculated) (g·cm^{-3})	1.266
Absorption coefficient (mm^{-1})	0.075

F(000)	668
Theta range for data collection (˚)	3.18 – 26.45
Limiting indices	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
R_{int}	0.0297
Reflections collected / unique	11156 / 6851
Goodness-of-fit on F^2	1.020
Final R indices $[F_o^2 > 2\sigma(F_o^2)]^a$	0.0461/0.1005
R indices (all data) ^{a}	0.0749/0.1127
Largest diff. peak and hole (e Å^{-3})	0.242 and -0.226

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

Table S6. Crystal data and structure refinement details for **TPAFBSO.**

Empirical formula	**$C_{37}H_{27}NO_2S$**
Formula weight	549.66
Temperature (K)	293(2) K
Crystal system	Triclinic
Space group	*P*-1
a (Å)	8.8671(3)
b (Å)	34.1025(12)
c (Å)	12.0757(3)
α (˚)	90
β (˚)	128.710(2)
γ (˚)	90
Volume (Å^3)	2849.40 (16)

Z	4
Density (calculated) ($g \cdot cm^{-3}$)	1.281
Absorption coefficient (mm^{-1})	0.149
F(000)	1152
Theta range for data collection (˚)	2.93 – 27.14
Limiting indices	-10 ≤ h ≤ 11, -43 ≤ k ≤ 43, -15 ≤ l ≤ 14
R_{int}	0.0241
Reflections collected / unique	33264 / 6259
Goodness-of-fit on F^2	1.110
Final R indices $[F_o^2 > 2\sigma(F_o^2)]^a$	0.0395/0.0964
R indices (all data) ^{a}	0.0436/0.0986
Largest diff. peak and hole (e $Å^{-3}$)	0.333 and -0.438

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$

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