Supporting Information

Doubling the Efficiency of Solution-Processed Blue Phosphorescent Organic Light-Emitting Diodes via Modified PEDOT:PSS Hole-Injection Layers

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I. Experimental Section

1. Materials. PEDOT:PSS (Clevios P VP. Al 4083), TCTA (4,4",4"-Tris(carbazol-9-yl)triphenylamine), POPH ((5-Terphenyl-1,3-phenylene)bis(diphenylphosphine oxide)), FIr6 (Bis(2,4-difluorophenylpyridinato)tetrakis(1-pyrazolyl)borate iridium(III)), TmPyPB (1,3,5-Tri[(3-pyridyl)-phen-3-yl]benzene), PVK(Poly (9-vinylcarbazole)) and LiF were purchased from Luminescence Technology Corp. and used directly. PEDOT:PSS (CH 8000), VB-FNPD (9,9-Bis[4-[(4-ethenylphenyl)methoxy]phenyl]-N^2,N^7-di-1-naphthalenyl-N^2,N^7-diphenyl-9H-fluorene-2,7-diamine), x-DCDPA (N,N-Diphenyl-3,5-bis(2-((4-vinylbenzyl)oxy)-9H-carbazol-9-yl)aniline) were purchased from FRST Technology Co., Ltd (Changchun, China) and used directly. PSSNa (average molecular weight = 70000) and PSSA (average molecular weight = 75000, 18 wt% in H_2O) were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China); $PSSNH_4$ (average molecular weight = 200000, 30 wt% in H_2O) was purchased from Shanghai Macleans Biochemical Technology Co., Ltd. (Shanghai, P, R. China).

2. Preparation of Modified PEDOT:PSS Solutions. PSSNa powder, PSSA, and $PSSNH_4$ solutions were dissolved in deionised water to achieve concentrations of 20 mg/mL, 40 mg/mL, 60 mg/mL, 80 mg/mL, and 100 mg/mL for PSSNa and PSSA, and 20 mg/mL, 30 mg/mL, 40 mg/mL, 50 mg/mL, and 60 mg/mL for $PSSNH_4$, respectively. Subsequently, these solutions were mixed with PEDOT:PSS (Clevios P VP. Al 4083) at a 1:1 volume ratio. The mixture was ultrasonicated for 5 minutes and then filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter before use.

3. Fabrication and Measurement of OLEDs. The solution-processed blue devices were fabricated with a configuration of ITO/PEDOT:PSS or modified PEDOT:PSS (30 nm)/TCTA:20 wt% FIr6 (20 nm)/POPH (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (100 nm). The ITO substrates were decontaminated with detergent, rinsed in ultra-purified water, dried at 120 ℃ for 1 h in oven, and then treated with ambient UV-ozone for 20 min. PEDOT:PSS was spin-coated onto ITO substrates at the speed of 3000 rpm, m-PEDOT:PSS with 60 mg/mL PSSNa at the speed of 5000 rpm, m-PEDOT:PSS with 40 mg/mL $PSSNH_4$ at the speed of 4000 rpm, m-PEDOT:PSS with 80 mg/mL PSSA at the speed of 8000 rpm and annealed at 120 ℃ for 20 min, after which they were transferred into inert-atmosphere glove box. In addition, x-DCDPA in toluene (5 mg/mL) was spin-coated at the speed of 2000 rpm for 30 s and baked at 220 ℃ for 40 min to form a cross-linked HTL. VB-FNPD dissolved in toluene (10 mg/mL) was spin-coated at 4000 rpm for 40 s and baked at 100 ℃ for 30 min to remove the solvent, followed by a second baking at 220 ℃ for 60 min to form a cross-linked HTL. PVK in chlorobenzene (10 mg/mL) was spin-coated at the speed of 3000 rpm for 30 s and baked at 150 ℃ for 40 min to form a cross-linked HTL. Subsequently, the 20 nm EML was spin-coated from a chlorobenzene solution onto the hole injection layer (or hole transfer layer) and annealed at 70 ℃ for 30 min. Then, they were transferred into vacuum chamber to deposit POPH and TmPyPB layers ($\leq 1.0 \times 10^{-5}$ Pa). Finally, LiF and Al layers were deposited in another vacuum chamber ($\leq 8.0 \times 10^{-4}$ Pa). The EL spectra, current efficiencies, external quantum efficiencies

and current density-brightness-voltage characteristics were tested with Brightness Light Distribution Characteristics Measurement System C9920-11. The electron-only and hole-only devices were fabricated with structure of Glass/Al (50 nm)/TCTA:20 wt% FIr6 (20 nm)/POPH or TmPyPB (20 nm) /TmPyPB (40 nm)/LiF (1 nm)/Al (150 nm) and ITO/PEDOT: PSS or modified PEDOT:PSS (30 nm)/TCTA:20 wt% FIr6 (20 nm)/TAPC (15 nm)/Al (100 nm), respectively. (TAPC (20 nm) for hole-only devices with cross-linkable hole transport materials.)

4. Measurements and characterization. Ultraviolet-visible (UV-vis) absorption spectra were obtained by using a UV-vis spectrophotometer (TU-9201, Puxi, China). The PL spectra and the PL decay curves were measured on a steady state and time-resolved fluorescence spectrometer equipped with 450 W xenon lamp and EPL-375/470 picosecond pulsed diode laser as the excitation sources (FLSP-920, Edinburgh Instruments, UK). The low temperature phosphorescence spectra were measured by using Fluorescence Spectrophotometer (F-7000). The transient EL characteristics spectra were acquired using McScience M6200. The surface morphology of the films was measured using an atomic force microscopy (AFM, Bruker, Dimension Icon). Element compositions were analyzed by using X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA MK II Thermo Avantage V 3.20 analyzer) with a mono X-ray excitation source (Al Kα, hυ=1486 eV). The work function were analyzed by using Ultraviolet Photoelectron Spectroscopy (UPS, Thermo SCIENTIFIC Nexsa) with a UV source (He Iα, hυ=21.22 eV).

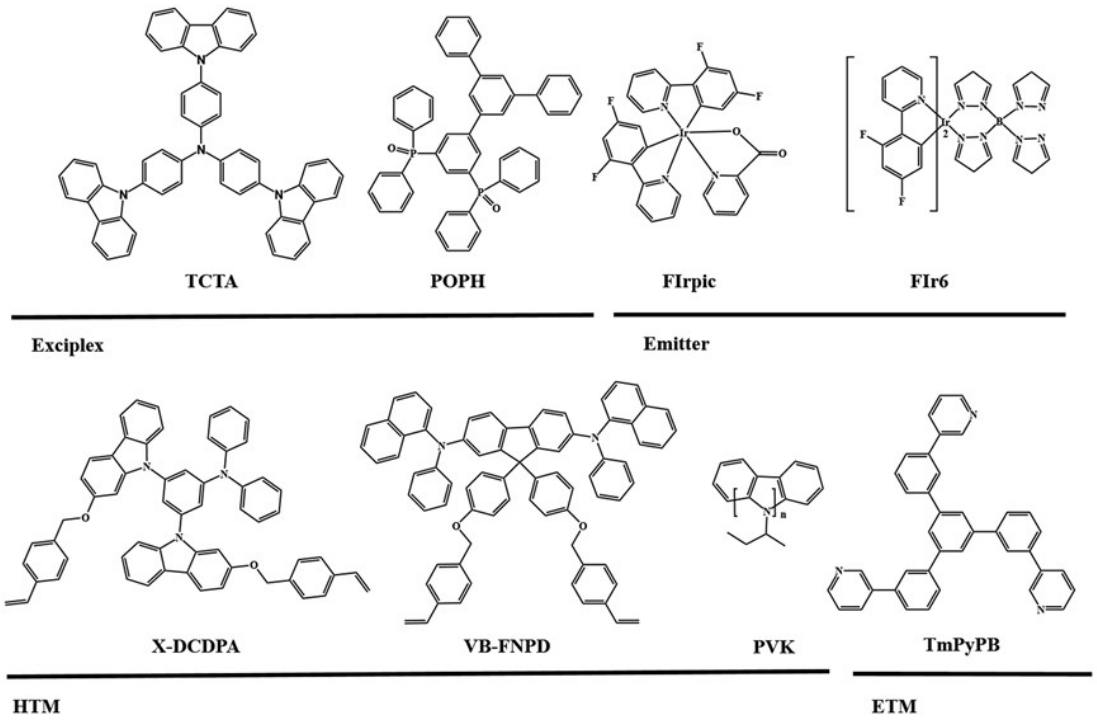
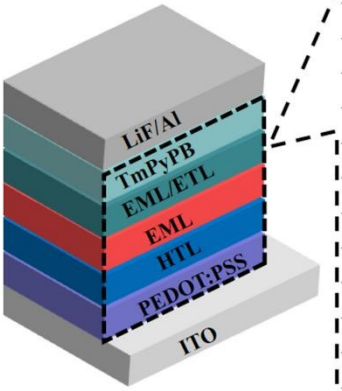


Figure S1. The chemical structures of the materials used here.



B0	PEDOT:PSS/TCTA:FIr6/TmPyPB (60 nm)	
B1	PEDOT:PSS	TCTA:FIr6 /POPH (20 nm) /TmPyPB (40 nm)
B1-Na	PEDOT:PSS-PSSNa (60 mg/mL)	
B1-NH_4	PEDOT:PSS-PSSNH_4 (40 mg/mL)	
B1-H	PEDOT:PSS-PSSA (80 mg/mL)	
B1-V	PEDOT:PSS/VB-FNPD	
B1-P	PEDOT:PSS/PVK	
B1-X	PEDOT:PSS/x-DCDPA	
B2	PEDOT:PSS (CH 8000)	
B3	PEDOT:PSS	TCTA:FIrpic /POPH (20 nm) /TmPyPB (40 nm)
B3-Na	PEDOT:PSS-PSSNa (60 mg/mL)	
B3-NH_4	PEDOT:PSS-PSSNH_4 (40 mg/mL)	
B3-H	PEDOT:PSS-PSSA (80 mg/mL)	
B3-V	PEDOT:PSS/VB-FNPD	
B3-P	PEDOT:PSS/PVK	
B3-X	PEDOT:PSS/x-DCDPA	

Figure S2. Structures of the devices used in this work.

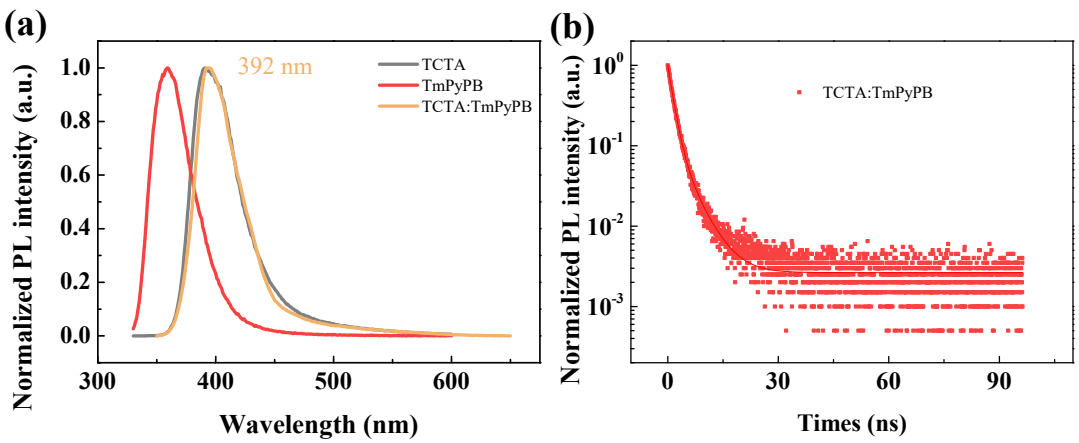


Figure S3. (a) The PL spectra of TCTA, TmPyPB, and TCTA:TmPyPB films. (b) Transient PL decay curve of TCTA:TmPyPB film under 300 nm excitation.

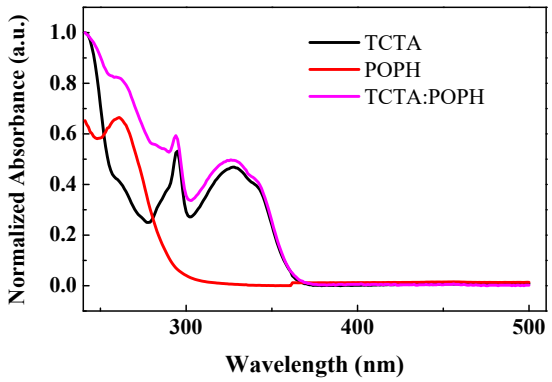


Figure S4. Absorption spectra of TCTA, POPH, and TCTA:POPH films.

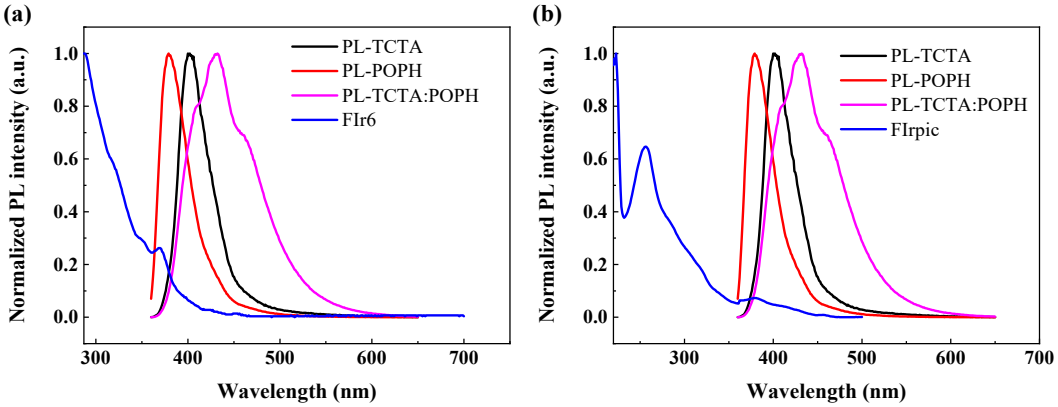


Figure S5. (a) Absorption spectrum of FIr6 and PL spectra of TCTA, POPH, and TCTA:POPH films. (b) Absorption spectrum of FIrpic and PL spectra of TCTA, POPH, and TCTA:POPH films.

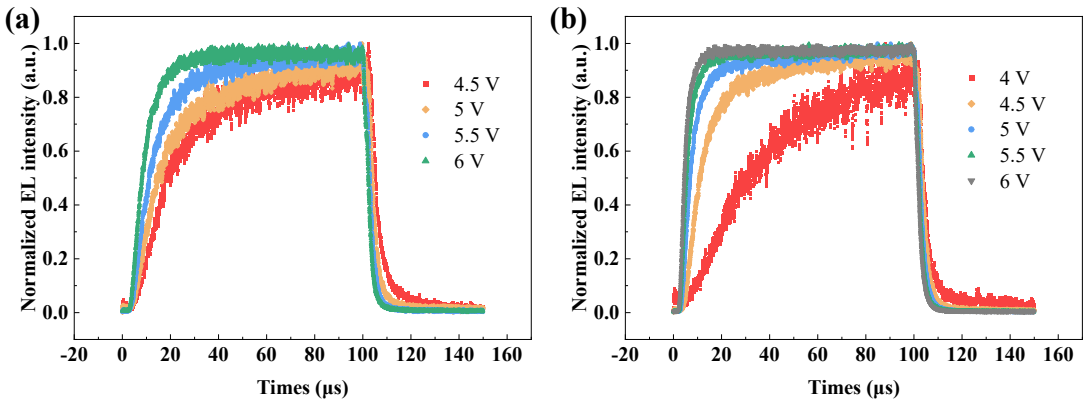


Figure S6. Transient EL decay curves at different voltage for devices with different PEDOT:PSS films. (a) pristine PEDOT:PSS films. (b) PSSNa-modified PEDOT:PSS films.

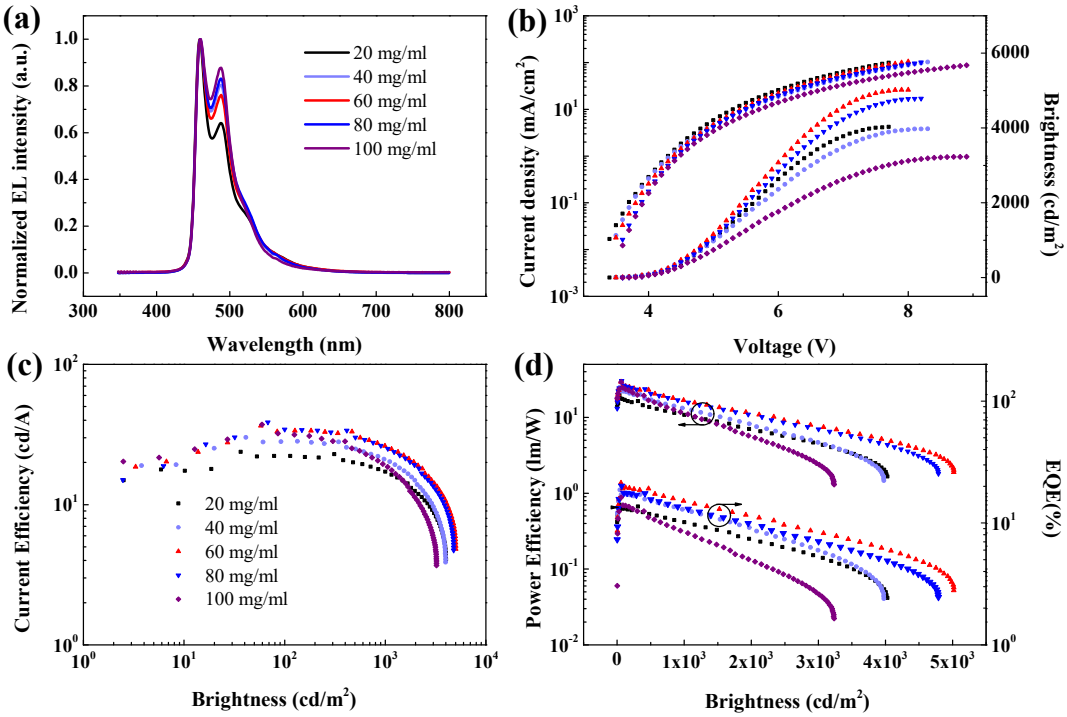


Figure S7. Performances of FIr6-based blue PhOLEDs with different PSSNa incorporation in PEDOT:PSS films. (a) EL spectra of the devices operating at 10 mA/cm^2. (b) Current density-voltage-brightness characteristics of the devices. (c) CE-brightness characteristics of the devices. (d) PE-brightness-EQE characteristics of the devices.

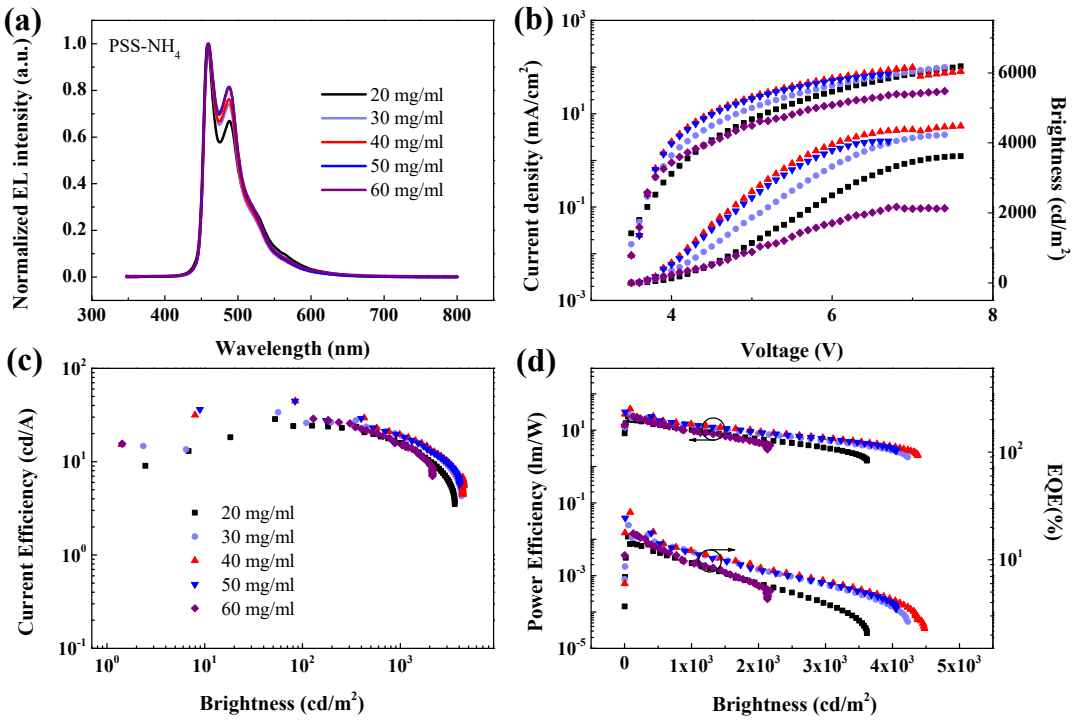


Figure S8. Performances of FIr6-based blue PhOLEDs with different $PSSNH_4$ incorporation in PEDOT:PSS films. (a) EL spectra of the devices operating at 10 mA/cm^2. (b) Current density-voltage-brightness characteristics of the devices. (c) CE-brightness characteristics of the devices. (d) PE-brightness-EQE characteristics of the devices.

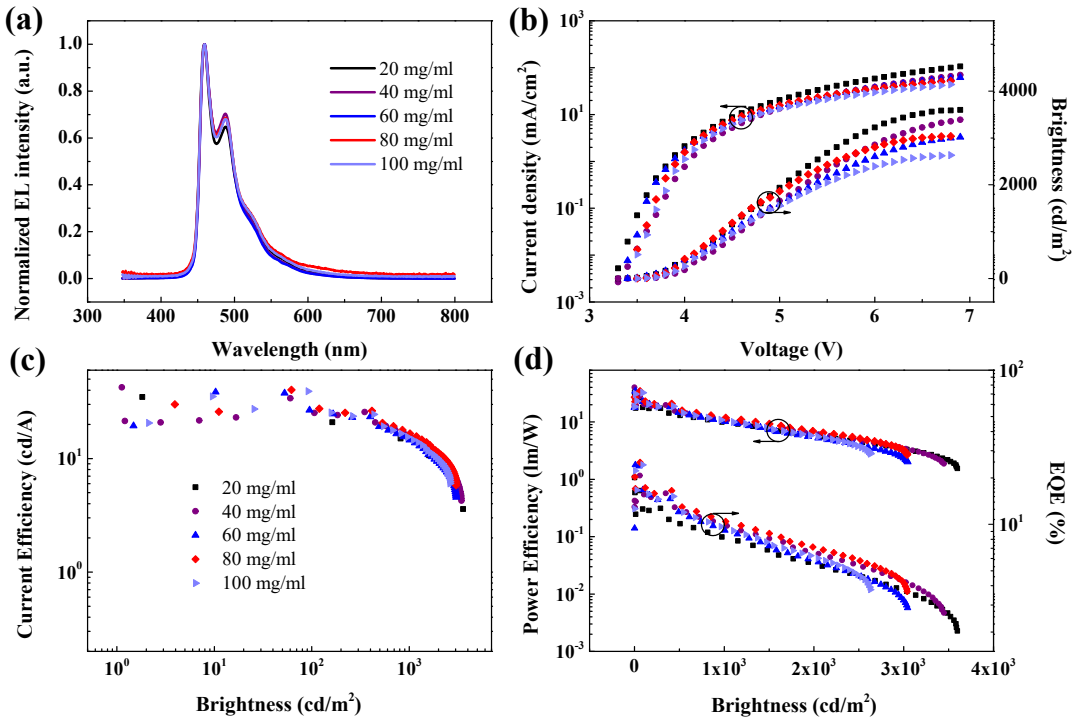


Figure S9. Performances of FIr6-based blue PhOLEDs with different PSSA incorporation in PEDOT:PSS films. (a) EL spectra of the devices operating at 10 mA/cm^2. (b) Current density-voltage-brightness characteristics of the devices. (c) CE-brightness characteristics of the devices. (d) PE-brightness-EQE characteristics of the devices.

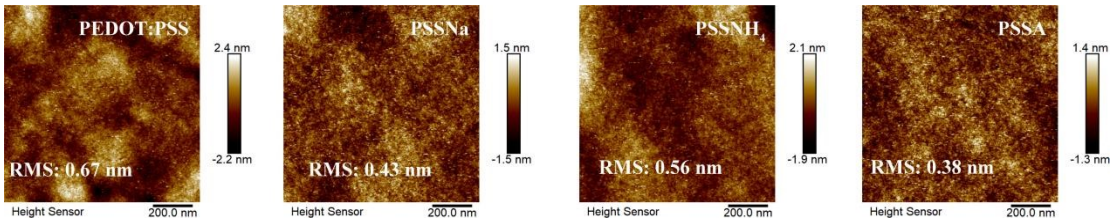


Figure S10. AFM images of FIr6-based films spin-coated on PEDOT:PSS films, and modified PEDOT:PSS films with varied PSS-S, respectively.

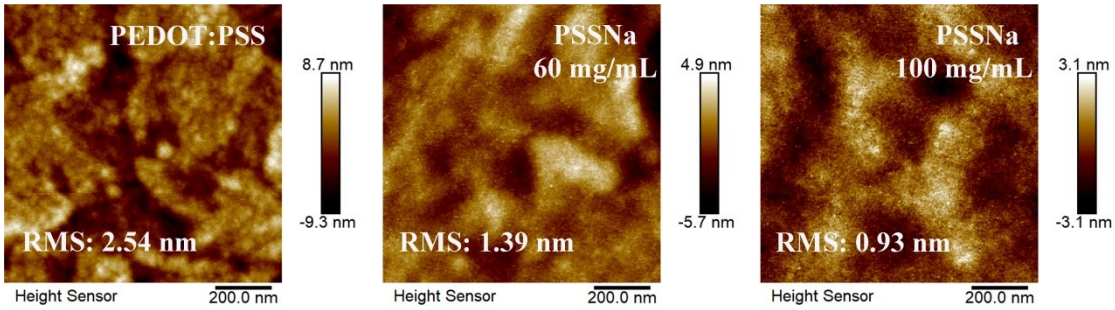


Figure S11. AFM images of PEDOT:PSS films and modified PEDOT:PSS films with varied PSSNa (60 mg/mL and 100 mg/mL), respectively.

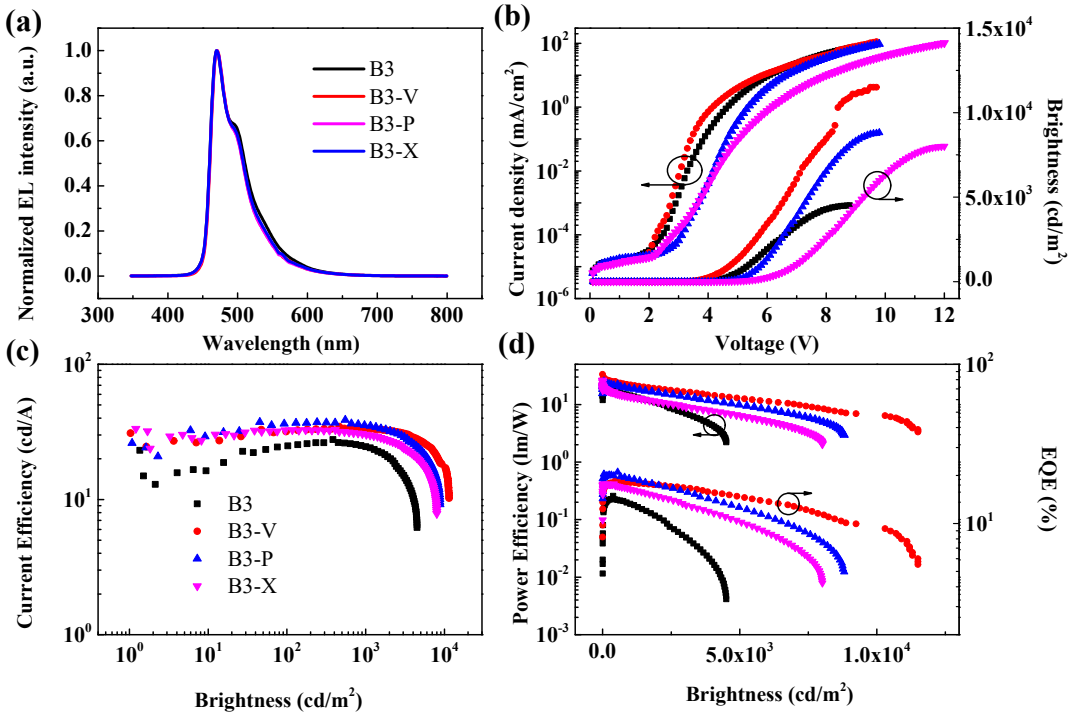


Figure S12. Performances of FIrpic-based device with varied hole transport layers. (a) EL spectra of the devices operating at 10 mA/cm^2. (b) Current density-voltage-brightness characteristics of the devices. (c) CE-brightness characteristics of the devices. (d) PE-brightness-EQE characteristics of the devices.

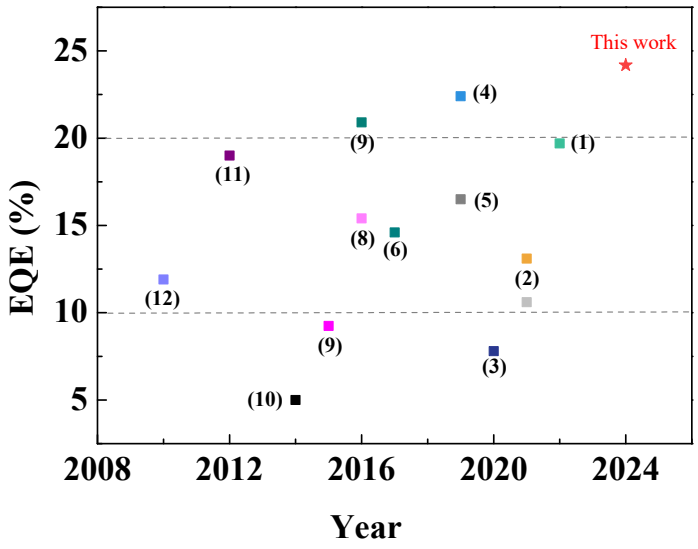


Figure S13. The EQE-Year of high-performance solution-processed FIrpic-based device reported in the literature.

Table S1. The key properties of FIr6-based blue OLEDs with PSSNa-modified PEDOT:PSS.

PSSNa (mg/mL)	V_{on} (V)	CE[a]$_{max/1000}$ (cd/A)	PE[b]$_{max/1000}$ (lm/W)	EQE[c]$_{max/1000}$ (%)	B[d]$_{max}$ (cd/m^2)	EQE Roll-off[e]	CIE
0	3.9	19.94 (16.05)	12.28 (8.55)	11.88 (9.59)	3670	19.28	(0.155, 0.237)
20	3.4	23.79 (17.17)	19.67 (10.79)	14.18 (10.13)	4031	28.56	(0.159, 0.238)
40	3.5	30.14 (21.09)	24.92 (13.25)	18.70 (12.93)	3977	30.86	(0.150, 0.232)
60	3.5	36.48 (26.19)	29.38 (16.79)	21.33 (15.15)	5020	28.97	(0.145, 0.263)
80	3.6	33.08 (22.93)	27.35 (13.10)	19.33 (13.39)	3545	30.73	(0.145, 0.259)
100	3.6	32.13 (18.57)	24.62 (11.00)	16.19 (8.25)	3235	49.04	(0.169, 0.364)

[a] The data for maximum current efficiency and values taken at 1000 cd/m^2 (CE). [b] maximum power efficiency and values taken at 1000 cd/m^2 (PE). [c] maximum external quantum efficiency and values taken at 1000 cd/m^2 (EQE). [d] maximum brightness (B). [e] EQE roll-off = (EQE_{max}-EQE_{1000})/EQE_{max}*100%.

Table S2. The key properties of FIr6-based OLEDs with $PSSNH_4$-modified PEDOT:PSS.

$PSSNH_4$ (mg/mL)	V_{on} (V)	$CE^a_{max/1000}$ (cd/A)	$PE^b_{max/1000}$ (lm/W)	$EQE^c_{max/1000}$ (%)	B^d_{max} (cd/m^2)	EQE Roll-off[e]	CIE
0	3.9	19.94 (16.05)	12.28 (8.55)	11.88 (9.59)	3670	19.28	(0.155, 0.237)
20	3.5	24.27 (15.82)	19.39 (10.15)	14.11 (9.28)	3619	34.23	(0.159, 0.240)
30	3.5	27.56 (18.82)	21.65 (13.14)	17.09 (11.68)	4230	31.66	(0.147, 0.232)
40	3.5	31.58 (19.61)	27.56 (14.67)	18.12 (12.13)	4378	33.06	(0.148, 0.231)
50	3.6	29.01 (19.69)	23.37 (14.73)	17.71 (12.02)	4053	32.13	(0.146, 0.240)
60	3.5	28.87 (15.05)	23.87 (9.27)	17.56 (9.22)	2140	47.49	(0.147, 0.238)

[a] The data for maximum current efficiency and values taken at 1000 cd/m^2 (CE). [b] maximum power efficiency and values taken at 1000 cd/m^2 (PE). [c] maximum external quantum efficiency and values taken at 1000 cd/m^2 (EQE). [d] maximum brightness (B). [e] EQE roll-off = $(EQE_{max}-EQE_{1000})/EQE_{max}*100\%$.

Table S3. The key properties of FIr6-based blue OLEDs with PSSA-modified PEDOT:PSS.

PSSA (mg/mL)	V_{on} (V)	$CE^a_{max/1000}$ (cd/A)	$PE^b_{max/1000}$ (lm/W)	$EQE^c_{max/1000}$ (%)	B^d_{max} (cd/m^2)	EQE Roll-off[e]	CIE
0	3.9	19.94 (16.05)	12.28 (8.55)	11.88 (9.59)	3670	19.28	(0.155, 0.237)
20	3.3	21.52 (13.93)	17.96 (9.95)	12.56 (8.28)	3597	34.08	(0.158, 0.236)
40	3.3	25.68 (15.68)	20.32 (10.71)	15.91 (9.76)	3447	38.65	(0.150, 0.227)
60	3.5	27.37 (15.14)	23.89 (10.57)	15.78 (9.52)	3053	39.67	(0.150, 0.223)
80	3.5	30.04 (16.59)	26.96 (11.84)	17.29 (10.44)	3038	39.62	(0.148, 0.226)
100	3.5	27.30 (15.50)	23.18 (10.82)	16.66 (9.67)	2630	41.96	(0.152, 0.224)

[a] The data for maximum current efficiency and values taken at 1000 cd/m^2 (CE). [b] maximum power efficiency and values taken at 1000 cd/m^2 (PE). [c] maximum external

quantum efficiency and values taken at 1000 cd/m^2 (EQE). [d] maximum brightness (B). [e] EQE roll-off = (EQE_{max}-EQE_{1000})/EQE_{max}*100%.

Table S4. pH values of the PEDOT:PSS solution doped with PSS-S.

	pH					
Device	0	1	2	3	4	5
PSSNa				2.0-2.2		
$PSSNH_4$	2.0			2.0-2.2		
PSSA				2.0-1.4		

Table S5. TRPL fitting parameters of various FIr6-based films.

FIr6 films	A_1	τ_1 (μs)	A_2	τ_2 (μs)	τ_{ave} (μs)
No HIL	0.57	0.99	0.40	3.42	2.71
PEDOT:PSS	0.40	0.15	0.56	1.64	1.55
PSSNa (60 mg/mL)	0.36	0.36	0.49	2.36	2.16
$PSSNH_4$	0.30	0.24	0.50	2.50	2.38
PSSA	0.38	0.16	0.56	1.59	1.50
PSSNa (100 mg/mL)	0.36	0.09	0.54	2.06	2.00
VB-FNPD	0.87	0.0073	0.13	1.37	1.32
PVK	0.31	0.48	0.37	2.70	2.41
x-DCDPA	0.29	0.32	0.43	1.92	1.76

Table S6. TRPL fitting parameters of various FIrpic-based films.

FIrpic films	A_1	τ_1 (μs)	A_2	τ_2 (μs)	τ_{ave} (μs)
No HIL	0.71	1.08	0.89	2.55	2.18
PEDOT:PSS	0.37	0.23	0.56	1.56	1.44
PSSNa	0.35	0.24	0.50	1.80	1.67
$PSSNH_4$	0.20	0.16	0.50	1.83	1.77
PSSA	0.31	0.092	0.54	1.68	1.63
VB-FNPD	0.70	0.0052	0.30	1.31	1.30
PVK	0.31	0.28	0.55	1.76	1.64
x-DCDPA	0.36	0.10	0.45	1.14	1.07

Table S7 The key performances of solution-processed blue phosphorescent OLEDs based on FIrpic.

Ref	emitter	HIL	EQE^{a}_{max} (%)
This work	TCTA: FIrpic	m-PEDOT:PSS	24.18
[1]	P(DMAC-Ge): 2,6-DCz-PPy: FIrpic	PEDOT:PSS	19.7
[2]	TcTa: FIrpic	PEDOT: PSS:40 v% H_2O	10.6
		PEDOT: PSS: 30 v% acetone	13.1
[3]	BCz-2SO: FIrpic	PEDOT: PSS	7.8
[4]	mCP: FIrpic	PEDOT: PSS: PSSA	22.4
[5]	Ph-O-TCTA: PhPO: FIrpic	PEDOT: PSS	16.5
[6]	TCTA: 2PO: FIrpic	PEDOT: PSS	14.6
[7]	TCTA: 2PTPS: FIrpic	PEDOT: PSS: PFI	20.9
[8]	PVK: OXD-7: FIrpic	MoO_x	15.4
[9]	PmCPSi: FIrpic	PEDOT: PSS	9.24
[10]	BCzTPh: BCzTPA: FIrpic	PEDOT: PSS/TFB	5.0
[11]	PVK: OXD-7: FIrpic	PEDOT: PSS (CH 8000): H_2O	19.0
[12]	PTC: FIrpic	PEDOT: PSS	11.9

[a] maximum external quantum efficiency (EQE).

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