Supporting Information

Realization of High-Power-Efficiency White Electroluminescence from A Single

Polymer by Energy-Level Engineering

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Materials	Year	V _{on} (V)	PE	EQE	CIE (x,y)	Ref.
			(Im W ⁻¹)	(%)		
			Maximum value/at 100 cd m ⁻² /at 1000 cd m ⁻²			
Small molecules	2004	_ ^a	26.0/-/11.0	12.0/-/-	0.43, 0.45	[1]
	2006	-	28.9/-/-	24.7 ^b /-/-	0.39, 0.45	[2]
	2007	-	29.0/-/-	18.0/-/-	0.46, 0.47	[3]
	2009	-	44.9/-/-	21.6/-/-	-	[4]
	2010	3.1	42.7/37.8/25.2	19.1/19.1/17.4	0.38, 0.44	[5]
	2011	5.1	53.8/53.0/45.0	45.7/45.5/45.0 ^b	0.40, 0.44	[6]
	2012	2.4	67.2/52.1/33.5	26.6/24.8/21.2	0.46, 0.44	[7]
	2013	-	63.2/-/50.1	24.0 /-/22.8	0.38, 0.49	[8]
	2014	-	69.4/69.4/55.0	24.6/24.6/23.6	0.36, 0.48	[9]
	2015		65.8/65.8/53.0	24.6/24.6/23.2	0.36, 0.47	[10]
	2016	2.4	75.3/-/63.1	20.0/-/19.5	0.42, 0.51	[11]
	2017	2.5	105.0/82.5/59.5	28.1/24.0/21.5	0.40, 0.48	[12]
Polymer blends	2004	-	1.6/-/-	_/_/-	0.32, 0.36	[13]
	2005	-	5.5/-/-	-	0.33,0.33	[14]
	2006	-	16.0/15.3/-	6.0/-/-	0.36,0.40	[15]
	2008	-	10.0/-/-	13.8/-/-	0.31, 0.47	[16]
	2009	4.8	23.4/18.5/-	14.2/12.6/-	0.38, 0.38	[17]
	2011	-	33.7/-/21.4	_/_/-	0.29, 0.49	[18]
	2013	-	31.4/28.0/23.0	_/_/-	0.32,0.48	[19]
SWPs	2004	-	2.8/-/-	-	0.26,0.36	[20]
	2005	5.8	0.83/-/-	-	0.31, 0.34	[21]
	2006	3.5	5.8/-/-	3.8/-/-	0.35,0.34	[22]
	2007	3.5	8.5/-/-	5.4/-/-	0.31, 0.36	[23]
	2008	3.5	4.4/-/-	-/-/-	0.35, 0.39	[24]
	2009	3.0	3.39/-/-	1.45/-/-	0.28, 0.39	[25]
	2010	-	11.4/-/-	6.7/-/-	0.37,0.42	[26]
	2011	5.8	9.85/-/-	6.77/-/-	0.39, 0.45	[27]
	2012	5.8	8.5/-/-	7.1/-/-	0.31, 0.43	[28]
	2013	3.6	2.3/-/-	-	0.38, 0.33	[29]
	2014	3.0	8.7/-/-	4.2/-/-	0.44, 0.53	[30]
	2015	-	4.13/-/-	-	0.33, 0.34	[31]
	2016	-	4.2/-/-	-	0.32, 0.37	[32]
	2017	2.9	32.8/4.7/-	10.4/2.6/-	0.37, 0.38	[33]
	2018	2.8	52.1/41.0/27.3	18.0/17.2/14.4	0.417, 0.448 (@1000 cd m ⁻²)	this work

Table S1. Summary of device performance for organic white-emitting materials in the past decades.

^a Not reported. ^bObtained for the tandem structured devices.

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Figure S1. Chemical sturctures and photophysical properties of polymer hosts with different $E_{\rm T}$ s. The UV-visible absorption was tested in dichloromethane and the PL spectra were recorded in toluene at 298 K. The phosphorescent spectra were measured in toluene at 77 K with a delay time of 0.2 ms. The $E_{\rm T}$ s of PH1, PH4 and PH5 determined according to the phosphorescent spectra at 77 K were 2.85 eV, 2.70 eV, and 2.45 eV, respectively.



Figure S2. Time depandent density functional theory (TD-DFT) simulation for polymer PH1, PH4 and PH5. (a) Chemical structures of the repeating unit of the polymer mainchain and the optimized geometric configuration of their lowest triplet state. Owing to the steric methyl groups, PH1 shows larger twisting angle (45.0°) between the triphenylphosphine oxide unit and the linkage than PH4 does (31.7°). (b) Calculated hole/particle distrubution of the natural transition orbitals (NTOs) and the energy levels of the lowest triplet states according to TD-DFT computation on the B3LYP/6-31G(d) level. The hole/particle orbitals are more delocalized as the saturated oxygen atoms and the steric methyl groups are removed from the linkages, with the cacluated $E_{\rm T}$ s decreasing gradually from 2.91 eV to 2.74 eV and 2.45 eV, which is in accordance with with the experimental results (2.85 eV, 2.70 eV and 2.45 eV, respectively).



Figure S3. Chemical sturctures, photophysical and electrochemical properties of polymer hosts with different HOMO levels. The UV-visible absorption was test in dichloromethane and the PL spectra were recorded in toluene. The cyclic voltammetry (CV) curves were recorded in dichloromethane using ferrocene as the reference and n-Bu₄NClO₄ as the supporting electrolyte. The HOMO levels obtained from oxidation curves is -5.37 eV, -5.20 eV and -5.64 eV for PH1, PH2 and PH3, respectively, according to the equation E_{HOMO} (or E_{LUMO}) = -e [$E_{\text{onset, ox}}$ (or $E_{\text{onset, red}}$) + 4.8V], where $E_{\text{onset, ox}}$ and $E_{\text{onset, red}}$ were the onset of the oxidation and reduction potential, respectively.



Figure S4. Comparison of CV curves for FIrpic and FIrOBu. The oxidation curves were recorded in dichloromethane, while the reduction curves were recorded in tetrahydrofuran, both using ferrocene as the reference and n-Bu₄NClO₄ as the supporting electrolyte. The HOMO levels obtained from the onset of the oxidation curves is -5.64 eV and -5.28 eV for FIrpic and FIrOBu, respectively. The LUMO levels obtained from the onset of the reduction curves is -2.62 eV and -2.24 eV for FIrpic and FIrOBu, respectively.



Figure S5. Current density versus voltage (a) and luminance versus voltage (b) characteristics of SWP1-FIrpic and SWP1-FIrOBu based devices with configuration of ITO (130 nm)/PEDOT:PSS (30 nm)/ SWPs (40 nm)/ SPPO13 (55 nm)/LiF (1 nm)/Al (100 nm)



Figure S6. EL characteristics of blue devices with PH1:1 \sim 30 wt% FIrpic (a–c) or PH1:1 \sim 30 wt% FIrOBu films (d–f). (a) and (d), Current density – voltage characteristics. (b) and (e), Luminance –voltage characteristics. (c) and (f), Power efficiency – luminance characteristics. The device configuration is ITO(130 nm)/PEDOT:PSS (30 nm)/ PH1:FIrpic or FIrOBu (40 nm)/ SPPO13 (55 nm)/LiF (1 nm)/Al (100 nm). The FIrpic-devices show decreased current density at the same voltage as the doping concentratin increases from 1 wt% to 30 wt%, however, an opposite trend is observed for the FIrOBu-devices. This observation is consistent with the statement that hole scattering occurs in the PH1: FIrpic emissive layer, but not in the PH1: FIrOBu layer.



Figure S7. Transient EL decay of the blue devices based on PH1 doped with 5 wt% and 30 wt% FIrpic or FIrOBu. The device configuration is ITO (130 nm)/PEDOT:PSS (30 nm)/ PH1:FIrpic/FIrOBu (40 nm)/ SPPO13 (55 nm)/LiF (1 nm)/Al (100 nm). Regardless of the doping concentration, there is a distinct overshoot upon the turn-off of the voltage for the FIrpic-based devices, but no overshoot is observed for the FIrOBu-based ones.



Figure S8. EL characteristics and PL decay curves of polymer host (PH1, PH4, PH5):15 wt% FIrpic films. (a) Current density – voltage characteristics. (b) EQE – luminance characteristics. The device configuration is ITO (130 nm)/PEDOT:PSS (30 nm)/polymer host:15 wt% FIrpic (40 nm)/ SPPO13 (55 nm)/LiF (1 nm)/Al (100 nm). (c) Phosphorescence decay of the polymer host:15 wt% FIrpic films. The phosphorescence lifetimes of the films are caculated to be 1.05 μ s, 0.87 μ s and 0.086 μ s for the PH1, PH4 and PH5 films, respectively, according to the double exponential fitting. This observation indicates that the excitons on the blue phophors can be quenched as the $E_{\rm T}$ of the polymer host decreases, which accounts for the decreased EQE from PH1 (11.5%) to PH4 (9.3%) and PH5 (0.5%) (at a luminance of 100 cd cm⁻²).



Figure S9. Luminous efficiency – luminance (a, c) and EQE –luminance (b, d) characteristics of the polymer devices. The device configuration is ITO (130 nm)/PEDOT:PSS (30 nm)/SWPs (40 nm)/SPPO13 (55 nm)/LiF (1 nm)/Al (100 nm).



Figure S10. EL performance of SWP2-FIrOBu devices with different ETLs. (**a**) Energy leves of the materials used for the devices. (**b**)–(**d**) Current density – voltage, luminance – voltage characteristics and EQE – current density characteristics. The device configuration is ITO (130 nm)/PEDOT:PSS (30 nm)/SWP2-FIrOBu (40 nm)/ ETM (55 nm)/LiF (1 nm)/Al (100 nm). (**e**) Chemical structures of the ETMs.

Synthesis and Characterization

General Information: All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. TPCz (3,6-bis(diphenylphosphoryl)-9-(4-(diphenylphosphoryl)phenyl)-9H-carbazole), FIrOBu and FIrpic were prepared in our lab. The synthesis of **3**, **S7** and **S8** have been described in previous reports (*Chem. Commun.* **2017**, *53*, 180.; *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1859.). ¹H NMR spectra were recorded with a Bruker Avance 400 NMR spectrometer. Elemental analysis was performed using a Bio-Rad elemental analysis system. MALDI-TOF mass spectra were performed on an AXIMA CFR MS apparatus (COMPACT). Molecular weight of the SWPs and the polymer hosts were measured by gel permeation chromatography (GPC) on a Waters 410 at 25 °C using polystyrene as the standard and tetrahydrofuran as solvent with a flow rate of 1 mL/min.



1

Diethylphosphite (1.5 mL, 11.7 mmol) was added dropwise to a solution of 4bromophenylmagnesium iodide in tetrahydrofuran which was prepared from *p*bromoiodobenzene (4.5 mL, 35.3 mmol) and magnesium (0.85 g, 35.3 mmol) at 0 °C. The mixture was aged for 30 minutes at 0 °C, then stirred at 25 °C for 16 hours. After the mixture was cooled again to 0 °C, 75 mL aqueous NH₄Cl (1 mol/L) was added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with brine, which was then dried over Na₂SO₄. After the solvent was completely removed, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 1/1 as eluent to give the product as a white powder in 65% yield. ¹H NMR (300 MHz, CDCl₃, δ) 8.02 (d, *J* = 487 Hz, 1H), 7.65 (dd, *J* = 8.3, 2.2 Hz, 4H), 7.53 (dd, *J* = 13.2, 8.3 Hz, 4H).



Br-Cz

bis(4-bromophenyl)phosphine oxide (1) (0.38 g, 1.05 mmol), 9-(4-iodophenyl)-3,6-di-*tert*butyl-carbazole (2) (0.48 g, 1.0 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), 1,4bis(diphenylphosphino)butane (dppb) (21.3 mg, 0.05 mmol) and (*i*-Pr)₂NEt (0.33 ml, 2 mmol) was added consecutively to 10 mL toluene under argon. The mixture was then heated at 100 °C for 2 h. After cooling to room temperature, the obtained suspension was directly applied to a silica gel column using petroleum ether/ethyl acetate=2/1 as eluent to give the crude product. Crystallizing from a mixture of hexane and CH₂Cl₂ gave the pure product as white crystal in a yield of 77%. ¹H NMR (300 MHz, CDCl₃) δ 8.13 (d, *J* = 1.8 Hz, 2H), 7.83 (dd, *J* = 11.5, 8.3 Hz, 2H), 7.74 - 7.67 (m, 6H), 7.62 (dd, *J* = 11.2, 8.5 Hz, 4H), 7.46 (dd, *J* = 8.7, 1.8 Hz 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 1.46 (s, 18H). ¹³C NMR (75 MHz, CDCl₃) δ : 143.8, 142.3, 138.4, 133.6, 132.2, 132.1, 131.5, 130.5, 127.7, 126.2, 126.1, 123.9, 116.4, 109.1, 34.7, 31.9. ³¹P NMR (CDCl₃, 295K, δ): 27.14. MALDI-TOF MS: calcd for C₃₈H₃₆Br₂NOP: 713.1. found: 714.1 [M+H]⁺. Anal. calcd for C₃₈H₃₆Br₂NOP: C, 63.97; H, 5.09; N, 1.96; found: C, 63.79; H, 4.98; N, 1.90.



Br-DtBu

A mixture of bis(4-bromophenyl)phosphine oxide (1) (0.38 g, 1.05 mmol), 3,3",6,6"-tetra-tertbutyl-9'-(4-iodophenyl)-9,3':6',9"-tercarbazole (3) (0.92 g, 1.0 mmol), palladium acetate (Pd(OAc)₂) (11.2 mg, 0.05 mmol), dppb (21.3 mg, 0.05 mmol) and N,Ndiisopropylethylamine ((*i*-Pr)₂NEt) (0.33 ml, 2 mmol) was added to 15 mL toluene under argon. The mixture was then heated at 100 °C for 2 h. After cooling to room temperature, the mixture was applied to a silica gel column using petroleum ether/ethyl acetate=2/1 as eluent to give the crude product as white power. The powder was further crystallized from a mixture of hexane and CH₂Cl₂ to afford the pure product as white crystal in a yield of 82%. ¹H NMR $(400 \text{ MHz}, \text{CDCl}_3) \delta 8.25 \text{ (d, } J = 1.5 \text{ Hz}, 2\text{H}), 8.17 \text{ (d, } J = 1.3 \text{ Hz}, 4\text{H}), 7.99 \text{ (dd, } J = 11.3, 8.4 \text{H})$ Hz, 2H), 7.92 (dd, J = 8.6, 2.1 Hz, 2H), 7.75 – 7.68 (m, 8H), 7.69 – 7.61 (m, 4H), 7.46 (dd, J = 8.6, 1.6 Hz, 4H), 7.33 (d, J = 8.6 Hz, 4H), 1.47 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 142.70, 141.25, 140.00, 139.59, 134.02, 133.54, 132.30, 132.19, 131.63, 127.90, 126.92, 126.80, 126.17, 124.54, 123.60, 123.19, 119.44, 116.26, 111.04, 109.00, 34.72, 32.03. ³¹P NMR (162 MHz, CDCl₃) δ 27.20 (s, 1P). MALDI-TOF MS: calcd for C₇₀H₆₆Br₂N₃OP: 1153.3. found: 1153.3 [M]⁺. Anal. calcd for C₇₀H₆₆Br₂N₃OP: C, 72.72; H, 5.75; N, 3.63; found: C, 72.61; H, 5.68; N, 3.57.



S3

A mixture of 3,6-dibutoxy-carbazole (**S1**) (10.0 g, 32.1 mmol), 3,6-diiodo-9-tosyl-carbazole (**S2**) (7.67 g, 13.4 mmol), and copper(I) iodide (CuI) (0.51 g, 2.68 mmol), *cis*-1,2-diaminocyclohexane (0.31 g, 2.68 mmol), K₃PO₄ (11.4 g, 53.6 mmol) in dimethylbenzene (30 mL) was stirred at 125 °C under nitrogen for 24 hr. After cooling to room temperature, dichloromethane was added to the mixture, which was then filtered. The filtrate was concentrated and then precipitated in methanol to give a white powder. This powder was then disolved in a mixed solvent of dimethyl sulfoxide (DMSO, 30 ml), tetrahydrofuran (THF, 60 ml) and water (10 ml) under nitrogen. Subsequently, 7.8 g KOH was added. The mixture was stirred at 80 °C for 1 h. After cooling, the mixture was filtered, and the filter residue was washed successively with water, methanol and dichloromethane to give the product **5** as a white powder with a total yield of 82%. ¹H NMR (400 MHz, DMSO-*d*⁶) δ 11.48 (s, 1H), 8.36 (s, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.75 (s, 4H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 4H), 4.12 (t, *J* = 6.4 Hz, 8H), 1.82 – 1.75 (m, 8H), 1.56 – 1.49 (m, 8H), 1.00 (t, *J* = 7.4 Hz, 12H).

4

A mixture of **S3** (15.0 g, 19.1 mmol), *p*-diiodobenzene (37.8 g, 114.5 mmol), and CuI (0.55 g, 2.87 mmol), K₂CO₃ (8.03 g, 59.0 mmol) in 1,3-dimethyl-2-imidazolidinone (DMI, 30 mL) was stirred at 180 °C under nitrogen for 24 h. After cooling to room temperature, the mixture was poured to water and then filtered. The filter residue was collected and washed by water. The solid was then purified by column chromatography on silica gel using petroleum ether/ dichloromethane =2/1 as eluent to afford the product as a white powder with yield of 76%. ¹H NMR (400 MHz, CDCl₃) δ 8.26 (s, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.62 – 7.58 (m, 6H), 7.32 (dd, *J* = 6.6, 2.2 Hz, 2H), 7.29 – 7.27 (m, 2H), 7.05 (dd, *J* = 8.8, 2.2 Hz, 4H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.13 (t, *J* = 6.5 Hz, 8H), 1.89 – 1.82 (m, 8H), 1.64 – 1.51 (m, 8H), 1.04 (t, *J* = 7.4 Hz, 12H).

Br-DOBu

A mixture of **4** (1.98 g, 2.0 mmol) and **1** (0.72 g, 2.0 mmol), Pd(OAc)₂ (22.4 mg, 0.1 mmol), dppb (42.6 mg, 0.1 mmol) and (*i*-Pr)₂NEt (0.44 ml, 4.0 mmol) was added to 40 mL toluene under argon. The mixture was then heated at 100 °C for 2 h. After cooling to room temperature, the mixture was applied to a silica gel column. The column was eluented first with an mixed solvent of toluene/petroleum ether/ethyl acetate = 30/20/1 to remove the unreacted **4**, and then petroleum ether/ethyl acetate=5/2 to afford the product as a white power. This powder was crystallized from a mixture of hexane and ethyl acetate to give a fibrous crystal in a yield of 80%. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 1.8 Hz, 2H), 7.99 – 7.95 (m, 2H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.73 – 7.62 (m, 10H), 7.60 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.57 (d, *J* = 2.4 Hz, 4H), 7.27 (d, *J* = 8.6 Hz, 4H), 7.02 (dd, *J* = 8.6, 2.4 Hz, 4H), 4.10 (t, *J* = 6.5 Hz, 8H), 1.86 – 1.79 (m, 8H), 1.62 – 1.49 (m, 8H), 1.01 (t, *J* = 7.4 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 153.44, 141.20, 139.57, 137.13, 134.01, 133.58, 133.47, 132.31, 132.18, 131.72, 127.89, 126.90, 126.78, 126.22, 124.51, 123.50, 119.46, 115.79, 111.07, 110.35, 104.17,

68.86, 31.60, 19.36, 13.93.³¹P NMR (162 MHz, CDCl₃) δ 27.21 (s, 1P). MALDI-TOF MS: calcd for $C_{70}H_{66}Br_2N_3O_5P$: 1217.3. found: 1217.3 [M]⁺. Anal. calcd for $C_{70}H_{66}Br_2N_3O_5P$: C, 68.91; H, 5.45; N, 3.44; found: C, 68.80; H, 5.36; N, 3.36.



S4

A mixture of *p*-iodoanisole (0.59 g, 2.5 mmol) and **1** (0.72 g, 2.0 mmol), Pd(OAc)₂ (22.4 mg, 0.1 mmol), dppb (42.6 mg, 0.1 mmol) and $(i-Pr)_2NEt$ (0.44 ml, 4.0 mmol) was added to 20 mL toluene under argon. The mixture was then heated at 100 °C for 2 h. After cooling to room temperature, the mixture was applied to a silica gel column using petroleum ether/ethyl acetate=1/1 as eluent to give the crude product as white power in a yield of 85%. ¹H NMR (300 MHz, CDCl₃) δ 7.63 (dd, *J* = 8.4, 2.3 Hz, 4H), 7.59 – 7.49 (m, 6H), 7.00 (dd, *J* = 8.4, 2.3 Hz, 2H), 3.87 (s, 3H).

S5

Into a 50 mL flask were added **S4** (10.00 g, 21.4 mmol) and dry CH₂Cl₂ (50 mL). The stirred mixture was cooled to 0 °C and then boron tribromide (4.0 ml, 42.8 mmol) was added dropwise. After warming to room temperature, the reaction mixture was poured into cold water. The mixture was then extracted with ethyl acetate and the organic layer was washed with NaHCO₃ aqueous and brine. After drying, the organic layers was concentrated and applied to a silica gel column using ethyl acetate as eluent to give the product in a yield of 90%. ¹H NMR (300 MHz, DMSO- d^6) δ 10.31 (s, 2H), 7.76 (dd, *J* = 8.4, 2.2 Hz, 4H), 7.52 (dd, *J* = 11.3, 8.4 Hz, 4H), 7.41 (dd, *J* = 11.3, 8.4 Hz, 2H), 6.92 (dd, *J* = 8.4, 2.2 Hz, 2H).

S6

A mixture of **S5** (2.50 g, 5.5 mmol), 1, 8-dibromooctane (5.1 ml, 27.6 mmol), K_2CO_3 (2.10 g, 15 mmol) and acetone (30 mL) were added into a 50 mL flask and stirred at flux for 12 h. After cooling to room temperature, the mixture was filtrated and the filter residue was washed with CH_2Cl_2 . The combined filtrate was concentrated and chromatographed by silica gel column using petroleum ether/ethyl acetate = 2/3 as eluent to give the product in a yield of

88%. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, J = 8.3, 1.9 Hz, 4H), 7.55 – 7.48 (m, 6H), 6.96 (dd, J = 8.3, 1.9 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.92 – 1.73 (m, 4H), 1.54 – 1.29 (m, 8H).

Br-FIrpic

A mixture of bis(2-(2,4- difluorophenyl)pyridine) (3-hydroxypicolinate)iridium(III) (**S7**) (0.30 g, 0.37 mmol), **S6** (0.32 g, 0.50 mmol), Cs_2CO_3 (1.21 g, 3.7 mmol) was added to DMF (10 mL) and heated at 40 °C for 8 h. After cooling to room temperature, the mixture was poured into water and then filtered. After the filter residue is dried in vaccum, it was purified by column chromatography using CH₂Cl₂/ethyl acetate = 10:1 as eluent to afford the product as green powder in a yield of 35%. ¹H NMR (400 MHz, CDCl₃) δ 8.81 (dd, *J* = 5.8, 0.9 Hz, 1H), 8.27 (d, *J* = 8.6 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.54 – 7.46 (m, 6H), 7.46 – 7.41 (m, 2H), 7.38 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.20 – 7.11 (m, 1H), 6.99 – 6.92 (m, 3H), 6.49 – 6.34 (m, 2H), 5.80 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.18 – 4.04 (m, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.82 – 1.73 (m, 2H), 1.58 – 1.34 (m, 8H). ³¹P NMR (162 MHz, CDCl₃) δ 27.88 (s, 1H). ¹⁹F NMR (376 MHz, DMSO-*d*⁶) δ -107.60 (d, *J* = 9.8 Hz, 1F), -108.42 (d, *J* = 9.8 Hz, 1F), -109.62 (d, *J* = 10.1 Hz, 1F), -110.18 (d, *J* = 10.1 Hz, 1F). MALDI-TOF MS: calcd for C₅₄H₄₃Br₂F₄IrN₃O₅P: 1271.1. found: 1272.1 [M+H]⁺.

Br-FIrOBu

A mixture of tri(2-(2,4-difluorophenyl)-4-hydroxyl-pyridine) iridium(III) (**S8**) (0.30 g, 0.37 mmol), 1-bromobutane (0.079 ml, 0.74 mmol), Cs₂CO₃ (1.21 g, 3.7 mmol) was added to DMF (10 mL) and heated at 40 °C for 8 h. Then **S6** (0.24 g, 0.37 mmol) was added to the mixture and reacted for another 8 h. After cooling to room temperature, the mixture was poured into water and then filtered. After the filter residue is dried in vaccum, it was purified by column chromatography using CH₂Cl₂/ethyl acetate = 10:1 as eluent to afford the product as green powder in a yield of 35%.¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 3H), 7.61 (d, *J* = 7.1 Hz, 4H), 7.55 – 7.48 (m, 6H), 7.28 – 7.24 (m, 3H), 6.96 (d, *J* = 7.1 Hz, 2H), 6.51 – 6.45 (m, 3H), 6.40 – 6.32 (m, 3H), 6.25 (d, *J* = 8.9 Hz, 3H), 4.06 (t, *J* = 6.4 Hz, 6H), 4.00 (t, *J* = 6.4 Hz, 2H), 1.85 – 1.75 (m, 8H), 1.54 – 1.35 (m, 8H), 0.98 (t, *J* = 7.3 Hz, 6H), 0.89 (t, *J* = 6.5 Hz, 4H). ³¹P NMR (162 MHz, CDCl₃) δ 27.55 (s, 1P). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.25 – 109.45 (m, 3F), -110.10 – -111.34 (m, 3F). MALDI-TOF MS: calcd for C₆₇H₆₁Br₂F₆IrN₃O₅P: 1483.2. found: 1483.2 [M]⁺.



S10

2-(9-ethyl-9H-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S9**) (9.00 g, 28.1 mmol), 2-chloro-5-(trifluoromethyl)pyridine (6.64 g, 36.6 mmol), Pd(PPh₃)₄ (1.30 g, 1.1 mmol), aqueous K₂CO₃ (2 M, 50 mL), and toluene (50 mL) were mixed in a flask and then refluxed for 24 h under an argon atmosphere. After cooling to room temperature, the organic layer was separated and washed with brine. After evaporation of the solvent, the residue was purified via chromatography over silica gel with petroleum ether/CH₂Cl₂ = 5: 1 to give a crude product. Recrystallizing the crude product from a mixed solvent of hexane/CH₂Cl₂ gave the pure product as a colorless crystal in a yield of 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.97 (s, 1H), 8.25 (s, 1H), 8.05 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.01 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 (dd, *J* = 6.6, 1.2 Hz, 1H), 7.55 (dd, *J* = 7.2, 0.9 Hz, 1H), 7.43 – 7.34 (m, 2H), 4.08 (t, *J* = 5.5 Hz, 1H), 2.22 – 2.17 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H).

S13

S13 was obtained according to a low-temperature synthetic route for facial tris-cyclometalated iridium(III) complexes reported by McGee, K. A. et. Al (*Inorg. Chem.* **2007**, *46*, 7800). A mixture of 2-(9,9-diethyl-fluoren-2-yl)-5-(trifluoromethyl) pyridine (**S11**) (10.00 g, 27.2 mmol), IrCl₃-3H₂O (4.17 g, 11.83 mmol), 2-ethoxyethanol (240 mL) and water (80 mL) was refluxed under argon for 24 h. After cooling to room temperature, the chloro-bridged iridium dimer **S12** was collected by filtration, washed with water and dried in vacuo. The dimer (0.5 g, 0.26 mmol) was then dissolved in 5 mL of dry acetonitrile under argon. A 3-mL-solution of silver trifluoromethanesulfonate (CF₃SO₃Ag, 0.134 g, 0.52 mmol) in acetonitrile was added. The mixture was heated in dark at 60 °C for 2 h until a gray precipitate appeared. The reaction mixture was filtered to separate a red solution from the precipitate. The solution was concentrated in vacuo to give a red powder. Successively, a mixture of the red powder and **S10** (0.20 g, 0.59 mmol) was heated in 3 mL *o*-dichlorobenzene at 110 °C for 72 h. After

cooling to room temperature, the solvent was removed by evaporation. The residue was purified via chromatography over silica gel with petroleum ether/CH₂Cl₂ =10 : 1 to give the pure product as a red powder in yield of 10%. ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.06 (m, 3H), 7.89 – 7.77 (m, 6H), 7.76 – 7.65 (m, 3H), 7.30 – 7.24 (m, 3H), 7.21 – 7.11 (m, 9H), 7.04 – 6.97 (m, 3H), 3.97 – 3.90 (m, 1H), 2.16 – 1.96 (m, 10H), 0.50 – 0.25 (m, 15H).

Br-IrCF3

A mixture of **S13** (0.20 g, 0.16 mmol), 1,8-dibromooctane (0.062 ml, 0.32 mmol), KOH (0.027 g, 0.48 mmol) and DMSO (2 mL) were stirred at 25 °C for 8 h. Then the mixture was poured into water and then extracted with diethyl ether (150 mL × 3). The combined organic layer was washed with brine and dried over anhyfrous Na₂SO₄. After the solvent was removed, the residue was applied to a silica gel column with petroleum ether/CH₂Cl₂ =50/3 as eluent to give a red powder. The powder was then mixed with **S5** (0.072 g, 0.16 mmol), K₂CO₃ (0.044 g, 0.32 mmol) and acetone (10 mL) under argon. After stirring under reflux for 8 h, the mixture was filtrated and the filter residue was washed with CH₂Cl₂. The combined filtrate was concentrated and chromatographed by silica gel column using hexane/ethyl acetate = 1/1 as eluent to give the product in a total yield of 62%. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.0 Hz, 3H), 7.88 – 7.75 (m, 6H), 7.72 – 7.65 (m, 3H), 7.64 – 7.55 (m, 4H), 7.55 – 7.45 (m, 6H), 7.30 – 7.20 (m, 6H), 7.19 – 7.08 (m, 6H), 7.04 – 6.97 (m, 3H), 6.94 – 6.86 (m, 2H), 4.00 – 3.82 (m, 2H), 2.16 – 1.95 (s, 12H), 1.46 – 1.00 (m, 12H), 0.56 – 0.22 (m, 15H). ³¹P NMR (162 MHz, CDCl₃) δ 27.75 (s, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.48 – 62.52 (m, 9F). MALDI-TOF MS: calcd for C₉₃H₈₀Br₂F₉IrN₃O₂P: 1823.4. found: 1823.4 [M]⁺.

PH1

Α mixture of **Br-DtBu** (0.4624g, 0.40 mmol), 2,2'-(oxybis(2-methyl-4,1phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5** (0.1801 g, 0.40 mmol), 1.5 mg, 0.0016 mmol), 2tris(dibenzylideneacetone)dipalladium $(Pd_2(dba)_3)$, dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 5.3 mg, 0.0128 mmol), K₂CO₃ (0.55 g, 4.00 mmol), toluene (6 mL) and water (2 mL) was heated at 95°C for 24 h under an argon atmosphere. Then a solution of benzeneboronic acid (100 mg) in 3ml toluene were added and the mixture was strired for 4 h. Subsequently, 0.2 ml bromobenzene were added and the mixture was strired for another 4 h. Finally a solution of sodium diethyldithiocarbamatetrihydrate (1g) in water (10 mL) were added into the mixture. The mixture was kept at 80 °C with vigorous stirring under argon for 24 h. After cooling, the organic layer was washed three times with deionized water. After dring with anhydrous sodium sulfate, the organic phase was concentrated to an appropriate volume (~2 mL) and then precipitated in methanol. The precipitate was extracted with acetone and then redisolved in dichloromethane. After concentration, the solution was reprecipitated in methanol to produce the polymer as a white fiber in yield of 80 %. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s. 2H), 8.19 – 8.10 (m, 6H), 7.98 – 7.86 (m, 6H), 7.73 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.7 Hz,

2H), 7.56 (d, J = 6.3 Hz, 4H), 7.44 (d, J = 8.6 Hz, 4H), 7.32 (d, J = 8.6 Hz, 4H), 7.28 – 7.22 (m, 2H), 7.05 – 6.93 (m, 4H), 2.32 (s, 6H), 1.45 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 156.76, 145.61, 142.70, 140.90, 140.03, 139.70, 137.27, 135.82, 134.26, 132.12, 132.03, 131.56, 131.07, 129.86, 129.74, 126.82, 126.70, 124.50, 123.59, 123.19, 120.76, 119.44, 116.44, 116.27, 111.11, 109.00, 34.73, 32.03, 20.73. ³¹P NMR (162 MHz, CDCl₃) δ 28.93 (s, 1P). Number average molecular weight (Mn)=97,400 Da; Polymer dispersity index (PDI)=2.47.

PH2

This polymer was obtained as a white fiber in yield of 85 % according to a similar procedure as **PH1** except that **Br-DOBu** (0.4880 g, 0.40 mmol) and **5** (0.1801 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.12 (s, 2H), 7.95 – 7.85 (m, 6H), 7.74 – 7.68 (m, 2H), 7.65 – 7.47 (m, 10H), 7.30 – 7.22 (m, 6H), 7.05 – 6.90 (m, 8H), 4.08 (t, *J* = 6.4 Hz, 8H), 2.31 (s, 6H), 1.90 – 1.74 (m, 8H), 1.56 – 1.50 (m, 8H), 0.99 (t, *J* = 7.3 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 156.72, 153.39, 145.58, 140.81, 139.63, 137.24, 137.10, 135.78, 134.22, 132.08, 131.59, 131.04, 129.83, 129.71, 126.71, 126.15, 124.43, 123.45, 120.72, 119.42, 116.41, 115.76, 111.11, 110.32, 104.11, 68.81, 31.56, 20.70, 19.32, 13.90. ³¹P NMR (162 MHz, CDCl₃) δ 28.48 (s, 1P). Mn=92,400 Da, PDI=2.57.

PH3

This polymer was obtained as a white fiber in yield of 82 % according to a similar procedure as **PH1** except that **Br-Cz** (0.2853 g, 0.40 mmol) and **5** (0.1801 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 2H), 7.98 (dd, *J* = 11.3, 8.4 Hz, 2H), 7.86 (dd, *J* = 11.7, 8.2 Hz, 4H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 4H), 7.49 – 7.43 (m, 4H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 1.6 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 2.30 (s, 6H), 1.45 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 156.74, 155.33, 145.38, 143.67, 142.00, 138.49, 137.28, 135.89, 133.74, 132.07, 131.78, 131.07, 130.06, 129.76, 129.64, 129.51, 129.38, 126.06, 123.88, 123.83, 120.74, 120.00, 118.07, 116.40, 109.23, 34.74, 31.95, 19.73. ³¹P NMR (162 MHz, CDCl₃) δ 28.62 (s, 1P). Mn=46,800 Da, PDI=2.06.

PH4

This polymer was obtained as a white fiber in yield of 78 % according to a similar procedure as **PH1** except that **Br-DtBu** (0.4624 g, 0.40 mmol) and 2,2'-(oxybis(4,1-phenylene))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.1688 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (d, *J* = 1.8 Hz, 2H), 8.15 (d, *J* = 1.6 Hz, 4H), 8.13 – 8.06 (m, 2H), 7.94 – 7.89 (m, 6H), 7.77 (d, *J* = 6.5 Hz, 4H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.67 – 7.59 (m, 6H), 7.44 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.31 (d, *J* = 8.6 Hz, 4H), 7.16 (d, *J* = 8.6 Hz, 4H), 1.44 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 157.33, 144.35, 142.69, 140.89, 140.03, 139.71, 135.08, 134.22, 132.80, 131.54, 131.00, 128.80, 127.23, 127.11, 126.83, 126.71, 126.15, 124.48, 123.59, 123.18, 119.45, 116.27, 111.10, 109.01, 34.72, 32.03. ³¹P NMR (162 MHz, CDCl₃) δ 28.02 (s, 1H). Mn=55,600 Da; PDI=3.98.

PH5

This polymer was obtained as a white fiber in yield of 78 % according to a similar procedure as **PH1** except that **Br-DtBu** (0.4624 g, 0.40 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene (0.1320 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.15 (d, *J* = 1.4 Hz, 4H), 8.14 – 8.07 (m, 2H), 8.00 – 7.89 (m, 6H), 7.86 (d, *J* = 6.0 Hz, 4H), 7.80 – 7.75 (m, 4H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.44 (dd, *J* = 8.7, 1.6 Hz, 4H), 7.31 (d, *J* = 8.6 Hz, 4H), 1.45 (s, 36H). ¹³C NMR (101 MHz, CDCl₃) δ 144.31, 142.70, 141.02, 140.03, 139.70, 134.17, 132.86, 132.81, 132.76, 131.57, 127.96, 127.46, 127.33, 126.80, 126.16, 124.50, 123.59, 123.19, 119.45, 116.28, 111.08, 109.00, 34.73, 32.03. ³¹P NMR (162 MHz, CDCl₃) δ 27.89 (s, 1P). Mn=26,300 Da; PDI=2.78.

SWP1-FIrpic

This polymer was obtained as a light yellow fiber in yield of 75 % according to a similar procedure as **PH1** except that **Br-DtBu** (0.3205 g, 0.2772 mmol), **Br-FIrpic** (0.1528 g, 0.12 mmol), **Br-IrCF3** (0.0051 g, 0.0028 mol), and **5** (0.1801 g, 0.40 mmol) are used as the monomers.¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.19 - 8.09 (m, 6H), 7.96 - 7.85 (m, 6H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.65 - 7.50 (m, 6H), 7.44 (d, *J* = 8.6 Hz, 4H), 7.32 (d, *J* = 8.6 Hz, 4H), 7.28 - 7.22 (m, 2H), 7.05 - 6.90 (m, 4H), 4.23 - 3.93 (m, 1.27 H), 2.31 (s, 6H), 1.44 (s, 36H). ³¹P NMR (162 MHz, CDCl₃) δ 29.44 (s, 0.3P), 29.07 (s, 0.7P). ¹⁹F NMR (376 MHz, CDCl₃) δ -107.68 – -107.71 (m, 2F), -110.28 – -110.31 (m, 2F). Mn=8,500 Da, PDI=2.04 (for the soluble part in THF).

SWP1-FIrOBu

This polymer was obtained as a light yellow fiber in yield of 78 % according to a similar procedure as **PH1** except that **Br-DtBu** (0.3205 g, 0.2772 mmol), **Br-FIrOBu** (0.1782 g, 0.12 mmol), **Br-IrCF3** (0.0051 g, 0.0028 mol), and **5** (0.1801 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.15 - 8.10 (m, 6H), 7.96 - 7.85 (m, 6H), 7.76 - 7.72 (m, 2H), 7.65 - 7.50 (m, 6H), 7.44 (dd, *J* = 8.6, 1.7 Hz, 4H), 7.31 (d, *J* = 8.6 Hz, 4H), 7.28 - 7.22 (m, 2H), 7.05 - 6.90 (m, 4H), 4.05 - 3.96 (m, 3.45 H), 2.31 (s, 6H), 1.44 (s, 36H). ³¹P NMR (162 MHz, CDCl₃) δ 28.91 (s, 0.3P), 28.28 (s, 0.7 P). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.28 - -109.54 (m, 3F), -111.15 (dd, *J* = 32.7, 9.6 Hz, 3F). Mn=53,800 Da, PDI=3.56.

SWP2-FIrOBu

This polymer was obtained as a light yellow fiber in yield of 75 % according to a similar procedure as **PH1** except that **Br-DOBu** (0.3373 g, 0.2772 mmol), **Br-FIrOBu** (0.1782 g, 0.12 mmol), **Br-IrCF3** (0.0051 g, 0.0028 mol), and **5** (0.1801 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (s, 2H), 8.08 – 8.15 (m, 2H), 7.96 – 7.85 (m, 6H), 7.74 – 7.66 (m, 2H), 7.63 – 7.45 (m, 10H), 7.05 – 6.90 (m, 8H), 4.08 (t, *J* = 6.4 Hz, 8H),

4.04 – 3.98 (m, 3.75 H), 2.31 (s, 6H), 1.90 – 1.74 (m, 8H), 1.56 – 1.50 (m, 8H), 0.99 (t, J = 7.3 Hz, 12H). ³¹P NMR (162 MHz, CDCl₃) δ 36.23 (s, 0.3P), 30.19 (s, 0.7P). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.21 – -109.53 (m, 3F), -111.15 (dd, J = 35.9, 9.4 Hz, 3F). Mn=34,400 Da, PDI=3.42.

SWP3-FIrOBu

This polymer was obtained as a light yellow fiber in yield of 75 % according to a similar procedure as **PH1** except that **Br-Cz** (0.1978 g, 0.2772 mmol), **Br-FIrOBu** (0.1782 g, 0.12 mmol), **Br-IrCF3** (0.0051 g, 0.0028 mol), and **5** (0.1801 g, 0.40 mmol) are used as the monomers. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 2H), 7.98 (dd, *J* = 11.3, 8.4 Hz, 2H), 7.86 (dd, *J* = 11.7, 8.2 Hz, 4H), 7.78 – 7.70 (m, 2H), 7.52 (d, *J* = 6.4 Hz,4H), 7.49 – 7.43 (m, 4H), 7.28 – 7.20 (m, 2H), 7.01 – 6.90 (m, 4H), 4.06 – 3.98 (m, 3.25H), 2.30 (s, 6H), 1.45 (s, 18H). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.21 – -109.44 (m, 3F), -111.15 (dd, *J* = 34.9, 9.7 Hz, 3F). ³¹P NMR (162 MHz, CDCl₃) δ 30.47 (s, 0.3P), 29.02 (s, 0.7 P). ¹⁹F NMR (376 MHz, CDCl₃) δ -109.21 – -109.44 (m, 3F). Mn=36,600 Da, PDI=3.79.