Blue emitting iridium(III) phosphors with functional imidazo[4,5-b]pyridin-2-ylidene cyclometalates: designs aimed for greater steric encumbrance

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**General information and materials.** All reactions were conducted under N<sub>2</sub> atmosphere. Commercially available reagents were used without further purification and solvents were dried prior to use. <sup>1</sup>H NMR spectra were measured with Bruker Avance III 400 MHz NMR instrument. The highresolution mass spectra were obtained on Sciex X500R Q-TOF, whereas acetonitrile was applied as the solvent.

**Photophysical measurements**: UV-Vis spectra were recorded on a HITACHI UH-4150 spectrophotometer. The steady-state emission spectra were measured with Edinburgh FS 980. Both wavelength-dependent excitation and emission responses of the fluorimeter were calibrated. The lifetime studies were performed by a time-correlated single photon counting system (TCSPC). Spectral grade solvents (Merck) were used as received. To determine the photoluminescence quantum yield in solution, samples were degassed using at least three freeze-pump-thaw cycles. The solution quantum yields are calculated using the standard sample which has a known quantum yield.

**Electrochemistry**: Cyclic voltammetry was conducted on a CHI621A Electrochemical Analyzer. The oxidation and reduction potentials were measured using a glassy carbon working electrode with 0.1 M of  $NBu_4PF_6$  in  $CH_3CN$ . The potentials were referenced externally to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple.

**Single X-Ray Structural Determination**. The single crystals suitable for X-ray diffraction study were obtained by recrystallization indicated in the experimental section. Single crystal X-ray diffraction data were recorded on a Bruker D8 Venture Photon II diffractometer with microfocus X-ray sources using phi and omega scans mode (APEX3) at 233 K. All deposited data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: <u>deposit@ccdc.cam.ac.uk</u>).

**Computational details of theoretical investigations**: The geometries, electronic structures, and electronic excitations of the studied Ir(III) complexes were investigated by methods based on DFT<sup>1</sup> and TD-DFT<sup>2</sup> using the B3LYP<sup>3</sup> functional with Gaussian 16 set of programs.<sup>4</sup> The polarizable continuum model (PCM)<sup>5</sup> was used to include solvent effects of toluene. The 6-31G(d,p)<sup>6</sup> basis set was used for light elements such as hydrogen, carbon, and nitrogen, while the LANL2DZ<sup>7</sup> basis set

with the Los Alamos National Laboratory (LANL) effective core potentials (ECPs) was used for iridium. The ground state (S<sub>0</sub>) geometries for compounds **f-ct3ax / bx** and **f-ct9ax / bx** were optimized based on their X-ray structural data.<sup>8</sup> Subsequently, the low-energy excited states were computed for the optimized ground state geometries using the TD-DFT method. Electronic orbitals were visualized using Avogadro software<sup>9</sup>. Metal contribution to the orbitals was obtained by applying orbital composition analysis with the Hirshfeld method<sup>10</sup> using Multiwfn software<sup>11</sup>. Further, the integral of the overlap of the norm of the orbitals was analyzed with Multiwfn software.

**OLED fabrication and measurement:** The vacuum-deposited OLEDs were fabricated on patterned ITO substrates with a sheet resistance of 15  $\Omega$  per square. Before device fabrication, ITO substrates were cleaned with tetrahydrofuran, deionized water and isopropanol in sequence, dried in an oven for at least 2 hours, treated with UV-ozone for 20 min, and finally loaded into a deposition chamber with a basic pressure less than  $4 \times 10^{-6}$  Torr. After completing the device fabrication, characterization was carried out at room temperature. EL spectra, luminescent and current density–voltage–luminance characteristics were recorded using a constant source Keithley 2400 sourcemeter and Photo Research PR 655 spectrophotometer. Luminescence quantum yields were measured with a Hamamatsu C11347 absolute photo-luminescence quantum yield measurement system.

#### Preparation of cyano modified carbene chelates



**Scheme S1**. Synthesis of 5-cyano-3*H*-imidazo[4,5-*b*]pyridinium chelate; experimental condition: (i) NEt<sub>3</sub>, isopropanol/THF, reflux; (ii) Fe(s), HCO<sub>2</sub>H, reflux; (iii) Zn(CN)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, DMF, 120 °C; (iv) (4-<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>I<sup>+</sup>Mes)(OTf<sup>-</sup>), Cu<sub>2</sub>O, DMF, 110 °C.

### Synthesis of G1



2,6-Dibromo-3-nitropyridine (22.82 g, 10 mmol) was dissolved in a mixture of isopropanol and THF (100 mL, 1/1, v/v) in a 250 mL flask. After then, 4-(2,6-dimethylphenyl)aniline (2.16 g, 11 mmol) was added and the mixture was heated to reflux with stirring for 3 hours, during which the reaction mixture turned from yellow to red. After cooled to RT, Et<sub>3</sub>N (2.02 g, 20 mmol) was added dropwise, and the mixture was heated to reflux for another 3 hours. After cooled to RT, the mixture was

concentrated to dryness and dissolved in ethyl acetate. The solution was washed with distilled water (100 mL  $\times$  3) and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The crude product was further purified via silica gel column chromatography using hexane/ethyl acetate (20/1, v/v) as eluent to attain an orange red solid (**G1**) (3.4 g, 85 %).

Selected spectroscopic data of **G1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.37 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 2.07 (s, 6H).

#### Synthesis of H1



Red solid of **H1** (3.8 g, 95%) can be attained following the same approach reported for its analogue **G1**.

Selected spectroscopic data of **H1**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.19 (s, 1H), 8.68 (d, *J* = 2.4 Hz, 1H), 8.55 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H ), 7.19 (m, 3H), 7.12 (d, *J* = 7.2 Hz, 2H), 2.08 (s, 6H).

### Synthesis of G2



A mixture of 6-bromo-*N*-(2',6'-dimethyl-[1,1'-biphenyl]-4-yl)-3-nitropyridin-2-amine (3.98 g, 10 mmol), and iron powder (3.36 g, 60 mmol) in formic acid (40 mL) was heated to reflux for 24 hours. After then, formic acid was removed under vacuum. Ethyl acetate was added to dissolve the residue.

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The solution was washed with distilled water (100 mL ×3). The organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and concentrated to dryness. The crude product was further purified via silica gel column chromatography using hexane/ethyl acetate (2/1, v/v) as eluent to afford a white solid (**G2**, 2.3 g, 61%).

Selected spectroscopic data of **G2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.53 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 2.10 (s, 6H).

## Synthesis of H2



White solid of **H2** (2.9 g, 78%) can be attained following the same approach reported for its analogue **G2**.

Selected spectroscopic data of **H2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.55 (d, *J* = 1.8 Hz, 1H ), 8.43 (s, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 2.09 (s, 6H).

### Synthesis of G3



5-Bromo-3-(2',6'-dimethyl-[1,1'-biphenyl]-4-yl)-3*H*-imidazo[4,5-*b*]pyridine (2.3 g, 6.1 mmol), zinc cyanide (0.78 g, 6.7 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.35 g, 0.3 mmol) were dissolved in anhydrous DMF (30 - S6 -

mL) in a 100 mL flask. The mixture was heated at 120 °C overnight. DMF was removed under reduced pressure and, the residue was dissolved in  $CH_2CI_2$ . This solution was washed with  $Na_2CO_3$  solution (100 mL × 2), followed by distilled water (100 mL × 2). The organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and concentrated to dryness. The crude product was purified by flash chromatography to attain white solid (**G3**, 1.8 g, 90%).

Selected spectroscopic data of **G3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 2.10 (s, 6H).

# Synthesis of H3



White solid of **H3** (2.5 g, 92%) can be attained following the same approach reported for its analogue **G3**.

Selected spectroscopic data of **H3**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (d, *J* = 1.8 Hz, 1H ), 8.59 (s, 1H), 8.49 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 2.09 (s, 6H).

### Synthesis of (ct3x)H<sub>2</sub><sup>+</sup>



3-(2',6'-Dimethyl-[1,1'-biphenyl]-4-yl)-3*H*-imidazo[4,5-*b*]pyridine-5-carbonitrile (0.97 g, 3 mmol), (4-<sup>*t*</sup>BuC<sub>6</sub>H<sub>4</sub>I<sup>+</sup>Mes)(OTf<sup>-</sup>) (1.74 g, 3.3 mmol) and Cu<sub>2</sub>O (21 mg, 0.15 mmol) in anhydrous DMF (20 mL) was heated at 110 °C for 8 h. After cooled to RT, DMF was removed under reduced pressure and the residue was triturated with deionized water (50 mL). The resulting precipitate was collected, washed with n-hexane, and dried under vacuum to provide a grey solid. It was further purified by recrystallization with acetone and hexane to give white solid. (**ct3xH<sub>2</sub><sup>+</sup>**, 1.4 g, 77%).

Selected spectroscopic data of **(ct3x)H<sub>2</sub>**<sup>+</sup>: <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.13 (s, 1H), 8.89 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.25 (t, *J* = 7.6, 1H), 7.20 (d, *J* = 7.6 Hz, 2H), 2.07 (s, 6H), 1.40 (s, 9H). <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ –77.77 (s, 3F).

Synthesis of (ct9x)H<sub>2</sub>+



White solid of  $(ct9x)H_2^+$  (2.4 g, 72%) can be attained following the same approach reported for its analogue  $(ct3x)H_2^+$ .

Selected spectroscopic data of  $(ct9x)H_2^+$ : <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  11.10 (s, 1H), 9.37 (d, J = 1.6 Hz, 1H), 9.36 (d, J = 1.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.28 – 7.16 (m, 3H), 2.07 (s, 6H), 1.42 (s, 9H). <sup>19</sup>F NMR (376 MHz, DMSO- $d_6$ )  $\delta$  –77.78 (s, 3F).

	abs $\lambda_{\max}^{a,b}$ (nm)	em $\lambda_{max}^{a}$ (nm)	FWHM <sup>c</sup> (nm)	PLQY <sup>d</sup> (%)	τ <sub>obs</sub> (μs)	τ <sub>rad</sub> (μs)	k <sub>r</sub> (10 <sup>5</sup> s <sup>-1</sup> )	k <sub>nr</sub> (10 <sup>5</sup> s <sup>-1</sup> )
<i>f</i> -ct3ax	301 (4.6), 398 (1.7)	502	83	76	1.35	1.78	5.63	1.78
<i>f</i> - ct3bx	303 (3.5), 394 (1.6)	499	79	72	2.30	3.19	3.13	1.22
f-ct9ax	320 (3.7), 384 (2.2)	474	77	95	0.98	1.03	9.69	0.51
f- ct9bx	321 (3.5), 385 (1.9)	487	76	88	1.30	1.48	6.77	0.92

Table S1. Photophysical data of the studied Ir(III) complexes in CH<sub>2</sub>Cl<sub>2</sub> at RT.

<sup>a</sup> Extinction coefficient ( $\epsilon$ ) is given in parentheses with a unit of 10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup>.

 $^{\rm b}$  Recorded in degassed  $\rm CH_2\rm Cl_2$  at a conc. of 10  $^{-5}$  M at RT

<sup>c</sup> Full width at half maximum.

<sup>d</sup> Coumarin 102 (C102) in methanol (QY = 87% and  $\lambda_{max}$  = 480 nm) was employed as standard.

abs  $\lambda_{max}^{a}$  (nm) em  $\lambda_{max}^{b}$  (nm) FWHM<sup>c</sup> (nm) PLQY <sup>d</sup> (%)  $\tau_{obs}$  (µs)  $|\tau_{rad}$  (µs) |k<sub>r</sub> (10<sup>5</sup> s<sup>−1</sup>) k<sub>nr</sub> (10<sup>5</sup> s<sup>-1</sup>) **f-ct3a** 293 (3.6), 342 (2.7), 396 (1.7) 467 1.55 69 89 1.74 5.74 0.71 **f-ct3b** 297 (3.5), 342 (2.7), 395 (1.9) 469 65 2.58 2.97 3.37 0.50 87 **f-ct9a** 298 (4.3), 322 (4.0), 386 (3.2) 448 59 81 0.87 1.07 9.3 2.18 **f-ct9b** 298 (4.5), 324 (4.3), 386 (2.9) 464 67 88 1.04 1.18 8.5 1.15

Table S2. Photophysical data of Ir(III) complexes *f*-ct3a / b and *f*-ct9a / b in toluene at RT.

<sup>a</sup> Extinction coefficient ( $\epsilon$ ) is given in parentheses with a unit of 10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup>.

 $^{\rm b}$  Recorded in degassed toluene at a conc. of  $10^{-5}$  M at RT

<sup>c</sup> Full width at half maximum.

<sup>d</sup> Coumarin 102 (C102) in methanol (QY = 87% and  $\lambda_{max}$  = 480 nm) was employed as standard.

Table S3. Electroluminescence data of PhOLED devices with *f*-ct9ax as the emitters in CzSi host with varied doping concentration from 7.5 – 17.5

Departs	V <sub>on</sub>	ELa	CE <i><sup>b</sup></i>	PE <sup><i>b</i></sup>	EQE <sup>b</sup>	L <sub>m</sub>	CIE <sup>a</sup>	FWHM <sup>a</sup>
Dopants	(V)	(nm)	(cd A <sup>-1</sup> )	(lm W <sup>-1</sup> )	(%)	(cd m <sup>-2</sup> )	(x, y)	(nm)
7.5 wt% <b><i>f</i>-ct9ax</b>	3.68	456	20.6/18.1/10.8	17.4/11.2/4.7	22.1/20.2/12.7	1672	0.143, 0.101	57
10 wt% <b>f-ct9ax</b>	3.63	460	24.6/21.7/17.0	21.2/13.7/8.3	23.0/21.6/16.3	2361	0.141, 0.116	57
12.5 wt% <b>f-ct9ax</b>	3.60	460	27.7/24.5/19.5	24.0/16.3/9.8	24.2/22.8/18.7	3246	0.141, 0.127	57
15 wt% <b><i>f</i>-ct9ax</b>	3.55	464	28.9/26.7/21.5	24.2/17.5/11.0	24.2/23.3/19.8	4172	0.141, 0.137	57
17.5 wt% <b><i>f</i>-ct9ax</b>	3.49	468	27.4/26.1/21.8	21.0/18.4/10.9	23.2/22.6/19.6	4103	0.412,0.143	57

wt%.

<sup>*a*</sup> Those are recorded at a current density of 10 mA cm<sup>-2</sup>.

<sup>*b*</sup> Corresponded to the maximum value, and data recorded at 100 and 1000 cd $\cdot$ m<sup>-2</sup>.

**Table S4**.  $EQE_{1000}$  and  $J_{90}$  of the blue OLED devices based on recent reported Ir(III) carbene complexes and the record-setting TADF emitters.

Emitter	EQE <sub>1000</sub> (%) <sup>a</sup>	J <sub>90</sub> (mA cm <sup>-2</sup> ) <sup>a</sup>	Citations		
<i>f</i> -ct3ax	14.2	1	This work		
<i>f</i> -ct3bx	14.2	2	This work		
<i>f</i> -ct9ax	19.8	4	This work		
<i>f</i> -ct9bx	18.1	2	This work		
<i>f</i> -ct3a	19.0	0.3	J. Mater. Chem. C, 2025,13, 3501-3510 https://doi.org/10.1039/D4TC04498C		
<i>f</i> -ct3b	22.1	1.4	J. Mater. Chem. C, 2025,13, 3501-3510 https://doi.org/10.1039/D4TC04498C		
<i>f</i> -ct9a	20.9	1	Adv. Sci. 2024, 11, 2309389. https://doi.org/10.1002/advs.202309389		
<i>f</i> -ct9b	17.1	1.4	Adv. Sci. 2024, 11, 2309389. https://doi.org/10.1002/advs.202309389		
<i>fac</i> -lr(tpz)3	16	5	Adv. Opt. Mater. 2021, 9, 2001994. https://doi.org/10.1002/adom.202001994		
<i>mer</i> -Ir(pmp)₃	13.3	7	Nat. Mater. 2016, 15, 92–98. https://doi.org/10.1038/nmat4446		
lr(cb)₃	22.3	3	Adv. Funct. Mater. 2018, 28, 1802945. https://doi.org/10.1002/adfm.201802945		
<i>m</i> -2tBu	14.2	0.8	Adv. Photonics Res. 2022, 3, 2100381. https://doi.org/10.1002/adpr.202100381		
<i>f</i> -PhCF3	9.7	0.5	Adv. Optical Mater. 2022, 10, 2201633. https://dx.doi.org/10.1002/adom.202201633		
<i>f</i> -ct1b	13.8	13	Nat. Commun. 2023, 14, 6419. https://doi.org/10.1038/s41467-023-42090-z		
<i>f</i> -ct5mix	20.9	1	Small Methods 2024, 8, 2301555. https://doi.org/10.1002/smtd.202301555		
<i>m</i> -lr(L <sub>6F</sub> B)₃	19.2	15	Synthetic Metals 2024, 308, 117734. https://doi.org/10.1016/j.synthmet.2024.117734		
<i>f</i> -ct7c	22.3	1	Adv. Funct. Mater. 2024, 2311692. https://doi.org/10.1002/adfm.202311692		
<i>f</i> -ct6b	17.1	0.1	Adv. Mater. 2024, 36, 2305273. https://doi.org/10.1002/adma.202305273		
<i>f</i> -Ir(tBpp)₃	14.5	5	Inorg. Chem. Front., 2024, 11, 2413–2426. http://dx.doi.org/10.1039/D4QI00454J		
<i>f</i> -ct8c	15.4	10	Adv. Optical Mater. 2025, 13, 2402332. https://dx.doi.org/10.1002/adom.202402332		

f ct1E	21.4	0.8	Angew. Chem. Int. Ed. 2025, 64, e202421664.		
<i>J</i> -015			https://doi.org/10.1002/anie.202421664		
	16.2	0.3	Adv. Mater. 2022, 34, 2110547.		
ICBNDADPO	10.2		https://doi.org/10.1002/adma.202110547		
	13	0.1	Adv. Mater. 2022, 34, 2207416.		
pop-Dadina-Ivie			https://doi.org/10.1002/adma.202207416		
	17.4	2	Nat. Commun. 2020, 11, 1765.		
TIVICZ-BU			https://doi.org/10.1038/s41467-020-15558-5		
DCDC N1	17	0.3	Angew. Chem. Int. Ed. 2021, 60, 20280.		
D2D2-IN1			https://doi.org/10.1002/anie.202108283		
	20.0	5	Angew. Chem. Int. Ed. 2021, 60, 9598.		
SAC-SUDD			https://doi.org/10.1002/anie.202100423		
	16	1	Nat. Photonics 2017, 8, 326–332.		
DIVIAC-DP3	10		https://doi.org/10.1038/nphoton.2014.12		
	28.7	0.7	Nat. Photonics 2024, 18, 1161–1169.		
UPA-D4			https://doi.org/10.1038/s41566-024-01508-w		
CCO 2	31.3	0.02	Nat. Commun. 2023, 14, 2019.		
0.0-2			https://doi.org/10.1038/s41467-023-37687-3		

<sup>*a*</sup> These data are estimated from the figures in the citations.



**Figure S1**. Structure drawing of *f*-ct3ax with thermal ellipsoids shown at 30% probability level. Selected bond length (Å): Ir-C(38) = 2.011(4), Ir-C(7) = 2.014(4), Ir-C(69) = 2.034(4), Ir-C(63) = 2.049(10), Ir-C(32) = 2.078(4), Ir-C(1) = 2.080(4). Selected bond angle (°): C(69)-Ir-C(63) = 77.7(4), C(38)-Ir-C(32) = 78.34(16), C(7)-Ir-C(1) = 78.70(14), C(7)-Ir-C(63) = 169.1(5), C(69)-Ir-C(32) = 167.97(16), C(38)-Ir-C(1) = 171.71(15). Hydrogen atoms were omitted for clarity.



**Figure S2**. Structure drawing of *f*-ct3bx with thermal ellipsoids shown at 30% probability level. Selected bond length (Å): Ir-C(38) = 2.0165(19), Ir-C(7) = 2.0306(18), Ir-C(69) = 2.031(2), Ir-C(49) = 2.0818(18), Ir-C(47) = 2.0955(18), Ir-C(1) = 2.0963(18). Selected bond angle (°): C(38)-Ir-C(49) = 78.24(8), C(7)-Ir-C(1) = 78.50(7), C(7)-Ir-C(63) = 79.96(7), C(7)-Ir-C(49) = 168.23(7), C(69)-Ir-C(1) = 168.29(7), C(38)-Ir-C(63) = 172.97(7). Hydrogen atoms were omitted for clarity.



**Figure S3**. Structure drawing of *f*-ct9ax with thermal ellipsoids shown at 30% probability level. Selected bond length (Å): Ir-C(69) = 2.007(2), Ir-C(7) = 2.025(2), Ir-C(38) = 2.042(2), Ir-C(63) = 2.087(2), Ir-C(32) = 2.091(2), Ir-C(1) = 2.093(2). Selected bond angle (°): C(69)-Ir-C(63) = 78.20(10), C(38)-Ir-C(32) = 78.54(9), C(7)-Ir-C(1) = 78.48(9), C(7)-Ir-C(63) = 172.46(8), C(69)-Ir-C(32) = 169.76(9), C(38)-Ir-C(1) = 176.44(9). Hydrogen atoms were omitted for clarity.



**Figure S4**. Structure drawing of *f*-ct9bx with thermal ellipsoids shown at 30% probability level. Selected bond length (Å): Ir-C(69) = 2.026(3), Ir-C(38) = 2.034(3), Ir-C(7) = 2.038(3), Ir-C(32) = 2.099(3), Ir-C(80) = 2.101(3), Ir-C(1) = 2.113(3). Selected bond angle (°): C(38)-Ir-C(32) = 78.34(12), C(69)-Ir-C(80) = 78.32(12), C(7)-Ir-C(1) = 78.06(11), C(69)-Ir-C(32) = 168.88(12), C(7)-Ir-C(80) = 169.68(12), C(38)-Ir-C(1) = 175.71(11). Hydrogen atoms were omitted for clarity.



Figure S5. Absorption and emission spectra of studied Ir(III) complexes in  $CH_2Cl_2$  at  $10^{-5}$  M at RT.



Figure S6. Cyclic voltammograms of studied Ir(III) complexes in acetonitrile solution.



Figure S7. Thermogravimetric diagrams of studied Ir(III) complexes measured under  $N_2$  atmosphere.



Figure S8. Structural drawings of the employed materials in the doped OLED devices.



**Figure S9**. OLED performances of *f*-ct9ax as phosphor with varied concentration from 7.5% - 17.5 wt%. (a) EL spectra measured at a current density of 10 mA cm<sup>-2</sup>; (b) EQE versus luminance of devices; (c) Corresponding current density-voltage-luminance (J-V-L) characteristics.



**Figure S10**. Relationship between  $EQE_{1000}$  and  $J_{90}$  for selective blue OLED devices fabricated using Ir(III) carbene emitters and the record-setting TADF emitters.



Figure S11. <sup>1</sup>H-NMR spectrum (400 MHz) of *f*-ct3ax in CDCl<sub>3</sub> at 298 K.



Figure S12. <sup>1</sup>H-NMR spectrum (400 MHz) of *f*-ct3bx in CDCl<sub>3</sub> at 298 K.



Figure S13. <sup>1</sup>H-NMR spectrum (400 MHz) of *f*-ct9ax in CDCl<sub>3</sub> at 298 K.



Figure S14. <sup>1</sup>H-NMR spectrum (400 MHz) of *f*-ct9bx in CDCl<sub>3</sub> at 298 K.

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