Supporting Information

Blue electroluminescence and hyperluminescence facilitated by Ir(III) phosphors with 5cyano-imidazo[4,5-b]pyridin-2-ylidene cyclometalates

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General information and materials. All reactions were conducted under N₂ atmosphere. Commercially available reagents were used without further purification and solvents were dried prior to use. ¹H NMR spectra were measured with Bruker Avance III 400 MHz NMR instrument. The high-resolution 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. Ag/Ag⁺ (0.01 M AgNO₃) electrode was employed as reference electrode. The oxidation and reduction potentials were measured using a glassy carbon working electrode with 0.1 M of NBu₄PF₆ in CH₃CN. The potentials were referenced externally to the ferrocenium/ferrocene (Fc⁺/Fc) couple.

geometries using the TD-DFT method. Electron orbitals were visualized using Avogadro software⁹. Metal contribution to the orbitals was obtained by applying orbital composition analysis with the Hirshfeld method¹⁰ using Multiwfn software¹¹. Further, the integral of the overlap of the norm of the orbitals was analyzed with Multiwfn software.

Preparation of cyano modified carbene pro-chelate (ct3H₂⁺)

Synthesis of L1

 NO_2

2,6-Dibromo-3-nitropyridine (5.64 g, 20 mml) was dissolved in a mixture of isopropanol and THF (100 mL, 1/1, v/v) in a 250 mL flask. After then, aniline (2.08 g, 22 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, Et₃N (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 with ethyl acetate. The solution was washed with distilled water (100 mL × 3) and the organic layer was dried over anhydrous Na₂SO₄, 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 (L1) (4.1 g, 75 %).

Selected spectroscopic data of **L1**: ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H).

Synthesis of L2

A mixture of 6-bromo-3-nitro-*N*-phenylpyridin-2-amine (6.3 g, 21.43 mmol), and iron powder (7.17 g, 128.6 mmol) in formic acid (60 mL) was heated at 105 °C for 12 hours. After then, formic acid was removed under vacuum. Ethyl acetate was added to dissolve the residue. The solution was washed with distilled water (100 mL ×3). The organic layer was dried over anhydrous Na₂SO₄, 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 (**L2**, 2.65 g, 45.1%).

Selected spectroscopic data of L2: ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.59 (t, *J* = 8.0 Hz, 2H), 7.50 – 7.42 (m, 2H).

Synthesis of L3



5-Bromo-3-phenyl-3*H*-imidazo[4,5-*b*]pyridine (2.19 g, 8 mmol), zinc cyanide (1.13 g, 9.6 mmol) and Pd(PPh₃)₄ (554 mg, 0.48 mmol) were dissolved in anhydrous DMF (30 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_2Cl_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 (L3, 1.41 g, 80.1%).

Selected spectroscopic data of L3: ¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H).

Synthesis of 1-(4-(*tert*-butyl)phenyl)-5-cyano-3-phenyl-3*H*-imidazo[4,5-b]pyridin-1-ium (ct3H₂⁺) trifluoromethylsulfonate



3-Phenyl-3*H*-imidazo[4,5-*b*]pyridine-5-carbonitrile (1.32 g, 6 mmol) (4-^tBuC₆H₄I⁺Mes)(OTf⁻) (3.48 g, 6.6 mmol) and Cu₂O (43 mg, 0.3 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. (**ct3H₂**⁺, 2.35 g, 78%).

Selected spectroscopic data of $ct3H_2^+$: ¹H NMR (400 MHz, DMSO- d_6) δ 11.04 (s, 1H), 8.85 (d, J = 8.4 Hz, 1H), 8.52 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.89 – 7.83 (m, 4H), 7.81 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.6 Hz, 1H), 1.39 (s, 9H). ¹⁹F NMR (376 MHz, DMSO- d_6) δ –77.78 (s, 3F).

Devices		V _{on} (V) ^a	CE (cd·A⁻¹) ^b	PE (lm·W⁻¹) ^b	EQE (%) ^b	J ₉₀ (mA⋅cm ⁻²) ^c	L _{max} (cd⋅m ⁻²)	CIE (x,y) ^d	EL Peak (nm) ^d	FWHM ^d
f at 2a	7.5 %	3.43	37.6 / 32.4 / 26.1	34.5 / 23.2 / 13.5	24.8 / 21.4 / 17.3	0.1	5353	(0.144, 0.209)	472	58
J-CLSa	10 %	3.29	41.3 / 36.2 / 30.9	39.4 / 26.6 / 16.6	25.5 / 22.4 / 19.3	0.1	7542	(0.147, 0.227)	472	59
(wt%)	12.5 %	3.23	43.2 / 37.0 / 31.3	41.9 / 27.6 / 17.1	25.1 / 21.5 / 18.4	0.1	9491	(0.150, 0.248)	476	60
	15 %	3.18	44.2 / 39.1 / 33.8	43.7 / 30.0 / 19.1	23.7 / 21.3 / 19.0	0.3	11420	(0.152, 0.268)	476	61
f-ct3b conc.	7.5 %	3.55	41.6 / 32.0 / 28.7	37.4 / 25.3 / 14.8	26.4 / 23.4 / 18.3	0.1	5487	(0.141, 0.216)	472	56
	10 %	3.45	45.4 / 41.2 / 34.3	41.3 / 28.3 / 18.4	26.7 / 24.2 / 20.4	0.1	7785	(0.143, 0.242)	476	57
	12.5 %	3.41	47.1 / 43.2 / 38.6	43.3 / 30.3 / 21.4	26.8 / 24.6 / 22.2	0.4	9617	(0.145, 0.263)	476	59
(wt%)	15 %	3.37	49.3 / 46.2 / 40.6	45.8 / 32.8 / 23.0	25.4 / 24.7 / 22.1	1.4	11790	(0.147, 0.275)	480	59

Table S1. Performances of Ph OLEDs with varied concentrations of Ir(III) emitters deposited in CzSi host.

^{*a*} Turn on voltage.

^b Corresponded to the maximum value, and values recorded at 100 cd·m⁻² and 1000 cd·m⁻².

^c Current density at 90% of max. EQE.

^d Data recorded at a current density of 10 mA cm⁻².

Table S2. Performances of Ph OLED and hyper-OLED devices based on exciplex co-host (SiCzCz : SiTrzCz2).^a

dopant	V _{on} (V) ^b	CE (cd·A ^{−1}) ^c	PE (lm·W⁻¹) ^c	EQE (%) ^c	J ₉₀ (mA⋅cm ⁻²) ^d	L _{max} (cd⋅m ⁻²)	CIE (x,y) ^e	EL Peak (nm) ^e	FWHM ^e
12.5 % <i>f</i>-ct3b	2.89	28.5 / 23.9 / 27.5	23.9 / 22.8 / 18.5	13.6 / 12.0 / 13.2	12.7	41200	(0.171, 0.314)	476	76
15 % f-ct3b	2.77	27.8 / 25.3 / 21.4	24.0 / 23.5 / 15.5	12.6 / 10.7 / 11.4	27.2	40610	(0.176, 0.341)	480	78
15 % f-ct3b :	2.67		21 0 / 16 4 / 0 6		0.1	12600	(0,128, 0,178)	470	22
1% v-DABNA	2.07	20.5 / 21.2 / 17.4	31.0/10.4/9.0	21.5 / 10.9 / 13./	0.1	13090	(0.128, 0.178)	472	23

^a OLED devices were fabricated using the architecture: ITO / HAT-CN (10 nm) / BCFN (60 nm) / SiCzCz (5 nm) / SiCzCz : SiTrzCz2 : dopant (20 nm) / mSiTrz (5 nm) / mSiTrz : Liq (35 nm) / Liq (2 nm) / Al (120 nm).

^b Turn on voltage.

^c Corresponded to the maximum value, and values recorded at 100 cd·m⁻² and 1000 cd·m⁻², respectively.

^{*d*} Current density at 90% of max. EQE.

 e Data recorded at a current density of 10 mA cm $^{-2}.$

dopant	λ _{max} (nm) ^a	PLQY (%) ^{a, b}	FWHM (nm)	
<i>f</i> -ct3a	482	80	77	
<i>f</i> -ct3b	480	85	73	
<i>f</i>-ct3a : 1wt% ν-DABNA	468	88	21	
<i>f</i>-ct3b : 1 wt%v-DABNA	468	94	20	

Table S3. Photophysical data of the studied Ir(III) carbene complexes in doped thin films at RT.

^{*a*} Photoluminescent spectra and quantum yield were recorded in doped CzSi thin film at RT (12.5 wt%). ^{*b*}Quantum yield was measured by integrated sphere.

Emitter	λ _{EL} (nm)	CIE (x, y)	EQE _{max} (%)	EQE ₁₀₀₀ (%)	Citation
<i>f</i> -ct3a	476	0.150, 0.248	25.1	18.4	This work
<i>f</i> -ct3b	476	0.145, 0.263	26.8	22.2	This work
f at 0 d	468	0.134, 0.183	16.5	14.9	Adv. Opt. Mater. 2025, 13, 2402332.
J-Cl80					https://doi.org/10.1002/adom.202402332
	466	0.14, 0.22	20.9	20.4	Nat. Commun. 15, 2977 (2024).
PION-ID-DIB					https://doi.org/10.1038/s41467-024-47307-3
	460	0.132, 0.147	26.4	23.7	Nat. Photon. 16, 212–218 (2022).
BD-02					https://doi.org/10.1038/s41566-022-00958-4
DH 4	464	0.134, 0.175	21	18.6	Adv. Opt. Mater. 2024, 12, 2303109.
P14					https://doi.org/10.1002/adom.202303109
CF	474	474 0.14, 0.22	23.6	18.7	Angew. Chem. Int. Ed. 2022, 61, e202203982.
Cu5					https://doi.org/10.1002/anie.202203982

Table S4. EL performances of reported blue emitters and associated OLED devices.

lr1	462	0.16, 0.21	28	21	J. Mater. Chem. C, 2022, 10, 17965–17973.
					<u>https://doi.org/10.1039/D2TC03463H</u>
D1	469	0.19, 0.39	20.6	13.6	J. Mater. Chem. C, 2020, 8, 2551-2557.
DI					https://doi.org/10.1039/C9TC05779J
iDrAu RN	442	0.154, 0.036	14.8%	2%	Angew. Chem. Int. Ed. 2025, 64, e202413536.
IPIAUDIN					https://doi.org/10.1002/anie.202413536
2C-2DDbC-DN	490	0.20, 0.38	25.9	24.7	Nat. Mater. 23, 1523–1530 (2024).
3CZZDPNCZDN					https://doi.org/10.1038/s41563-024-02004-w
	478	0.15, 0.23	27.8	19.9	ACS Appl. Mater. Interfaces 2024, 16, 43786–43794.
PACZICZPADN					https://doi.org/10.1021/acsami.4c09057
	444	0.15, 0.05	15.8	3.9	Angew. Chem. Int. Ed. 2024, 63, e202408522.
Ру-ВМ					https://doi.org/10.1002/anie.202408522
340-0007	464	464 0.13, 0.14	21.5	4.3	Adv. Opt. Mater. 2024, 12, 2400739.
ZTBUPQCZ					https://doi.org/10.1002/adom.202400739



Figure S1. Structure drawing of *f*-ct3a with thermal ellipsoids shown at 30% probability level. Selected bond length (Å): Ir-C(58) = 2.028(2), Ir-C(35) = 2.033(2), Ir-C(12) = 2.040(2), Ir-C(24) = 2.091(4), Ir-C(47) = 2.098(2), Ir-C(1) = 2.107(2). Selected bond angle (°): C(1)-Ir-C(12) = 78.47(9), C(35)-Ir-C(24) = 78.53(9), C(58)-Ir-C(47) = 78.42(10), C(12)-Ir-C(24) = 168.05(9), C(35)-Ir-C(47) = 170.47(9), C(58)-Ir-C(1) = 171.00(10). Hydrogen atoms were omitted for clarity.



Figure S2. Cyclic voltammograms of studied Ir(III) complexes in acetonitrile solution.



Figure S3. Thermogravimetric diagrams of studied Ir(III) complexes measured under N_2 atmosphere.



Figure S4. The device architecture with the energy levels.





Figure S5. Structural drawings of the employed materials in the doped OLED devices.



Figure S6. OLED device performances based on *f*-ct3a and *f*-ct3b with varied doping ratios from 7.5 wt% to 15 wt% in CzSi; EL spectra of (a) *f*-ct3a and (d) *f*-ct3b; EQE vs. luminance diagram of (b) *f*-ct3a and (e) *f*-ct3b; J-V-L curves (c) *f*-ct3a and (f) *f*-ct3b.



Figure S7. Photoluminescence of *f*-ct3a and *f*-ct3b in co-doped CzSi host at 12.5 wt% at RT.



Figure S8. OLED device performances based on *f***-ct3b** with doping ratios of 12.5 wt% and 15 wt% in a 1:1 co-host of SiCzCz and SiTrzCz2; (a) EL spectra; (b) EQE vs. luminance diagram; (c) J-V-L curves.



Figure S9. Spectral overlap between the emission of studied Ir(III) complexes and the absorption of v-DABNA in toluene.



Figure S10. Relative luminance as a function of operational time of *f***-ct3b** based hyper-OLED devices using SiCzCz and SiTrzCz2 exciplex co-host and with $L_0 = 1000 \text{ cd} \cdot \text{m}^{-2}$.



Figure S11. ¹H-NMR spectrum (400 MHz) of *f*-ct3a in CDCl₃ at 298 K.



Figure S12. ¹H-NMR spectrum (400 MHz) of *f*-ct3b in CDCl₃ at 298 K.

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