Electronic supplementary information

Light-emitting platinum(II) complexes supported by tetradentate dianionic bis(N-Heterocyclic carbene) ligands: towards robust blue electrophosphors

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Table of contents

Synthesis and characterization	S2
Computational method	S11
OLED fabrication and characterization	S15
Table S1 Crystal data for 2-B and 2-F	S6
Table S2 Selected bond distance and angles of 2-B and 2-F	S7
Table S3 UV-Vis absorption and emission data of 4 in different solvents	S 8
Table S4 Calculated transition energies of 2 , 5 , and 6 at optimized S_0 and T_1 geometries	S13
Table S5 Device performances of the blue OLEDs with various doping concentrations of 4	S16
Table S6 Device performances of the near white OLEDs with various doping levels ofcomplex 4 and yellow Pt(II) phosphor (Pt-Y)	S16
Chart S1 Chemical structures used in OLEDs fabrication and device architecture.	S15
Fig. S1 Powder X-ray diffraction patterns of pseudo-polymorphs 2-B, 2-F, and 2-VD.	S5
Fig. S2 Excitation and emission spectra of 3 in solid-state at 298 K.	S9
Fig. S3 Emission spectra of 4 in a variety of states.	S9
Fig. S4 Emission spectra of 5 in the solid state at 298 K and 77 K and in frozen DMF at 77 K.	S10
Fig. S5 fs-TRF and ns-TRE spectra and decay profiles recorded at the various delay times after 355 nm excitation of 2 in DMF.	S10
Fig. S6 Optimized S_0 and T_1 geometry of 3 and selected bond distances and angles.	S11
Fig. S7 Plots of calculated frontier orbitals of 6 based on optimized S_0 and T_1 geometries.	S12
Fig. S8 Current density-luminance-voltage characteristics and Current efficiency-power efficiency-voltage characteristics of blue OLEDs doped with 2%, 6% and 8% of 4 .	S17
Fig. S9 EL spectra of devices with 2%, 6% and 8% of 4 at driving voltages 6–11 V.	S18
Fig. S10 Current density-luminance-voltage characteristics and Current efficiency-power efficiency-voltage characteristics of white OLEDs.	S19
Fig. S11 EL spectra of Devices W1–W3 at luminances of 100, 1000, and 10000 cd/m^2 .	S20
Fig. S12 Emission spectra of $1-4$ in 5% DMF/THF (v/v) showing FWHM.	S21

Synthesis and characterization

All starting materials were used as received from commercial sources. Complexes 1-4 were prepared according to the procedure reported in our previous communication.¹ The solvents used for photophysical measurements were of HPLC grade. Elemental analyses were performed by the Institute of Chemistry at the Chinese Academy of Sciences, Beijing. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. ¹H (300 MHz or 400 MHz) NMR spectra were recorded on DPX300 and Avance400 Bruker FT-NMR spectrometers. UV-vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer. Steady-state emission and excitation spectra at 298 K and photoluminescence of films on quartz substrate were obtained on a Spex 1681 Flurolog-2 Model F111 spectrophotometer equipped with a Hamamatsu R928 PMT detector. All solutions for photophysical measurements, except stated otherwise, were degassed in a high-vacuum line with at least four freeze-pump-thaw cycles. Emission lifetimes were measured with a Quanta-Ray Q-switch DCR-3 Nd:YAG pulsed laser system. Emission quantum yields of solutions were measured using a solution of quinine hemisulfate salt monohydrate in 0.5 M H_2SO_4 ($\phi_r = 0.546$) (for the blue-emitting complexes 1–4) or a degassed acetonitrile solution of $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2'-bipyridine) ($\phi_r = 0.062$) (for complex 5) as the standard and calculated by $\phi_s = \phi_r (B_r/B_s) (n_s/n_r)^2 (D_s/D_r)$, where the subscripts s and r refer to the sample and reference standard solution respectively, n is the refractive index of the solvents, D is the integrated intensity, and ϕ is the luminescence quantum yield. The quantity B is calculated by $B = 1 - 10^{-AL}$, where A is the absorbance at the excitation wavelength and L is the optical path length. Errors for wavelength values (1 nm) and ϕ (10%) are estimated. Briefly, the fs-TRF and ns-TRE measurements were performed based on a commercial Ti:Sapphire regenerative amplifier laser system (800 nm, 40 fs, 1 kHz, and 3.5 mJ/pulse). The 355 nm pump pulse was generated from TOPAS-C pumped by the 800 nm fundamental laser pulse. The fs-TRF was measured by employing the Kerr-gate technique.² A Kerr device composed of a 1 mm thick Kerr medium (benzene contained in a guartz cell) equipped within a crossed polarizer pair was driven by the 800 nm laser to function as an ultrafast optical shutter to sample transient fluorescence spectra at various selected pump/probe delays. For fs-TRF, the temporal delay of probe to pump pulse was controlled by an optical delay line. The fs-TRF signals were collected by a monochromator and detected with a liquid nitrogen cooled CCD detector. The instrument response function (IRF) of fs-TRF is wavelength-dependent. As detection wavelength varies from 600 to 280 nm, the IRF varies from ~0.5 to ~2 ps for TRF. For the ns-TRE measurement, an intensified CCD (ICCD) detector, which was synchronized to the fs laser system, was used to detect transient emission spectra with the controlled pump/probe time delay covering from ~2 ns and afterwards. To eliminate the effect of rotational diffusion, the polarization direction of the pump laser was set at the magic angle in relative to that of probe for all the measurements. The measurements were done at room temperature and atmospheric pressure with the samples of ~15 mL

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flowed in a cell with 0.5 mm path length. In the ns-TEF, the sample solutions were purged with nitrogen gas to diminish the oxygen quenching effect. The samples were monitored by UV-vis absorption and revealed no degradation after the time-resolved measurement.

a⁵: To degassed solution of imidazole (430 mg, 6.3 mmol) in DMSO (10 mL) was added 2-bromo-3-methyoxynaphthalene (1 g, 4.2 mmol), Cu₂O (150 mg, 1.04 mmol) and KOH (480 mg, 8.6 mmol) under N₂. The mixture was heated to 140 °C under N₂ for 24 hours. After cooling to room temperature, the mixture was poured into 50 mL ethyl acetate and then filtered. The filtrate was then washed with H₂O (50 mL ×3), dried over MgSO₄. After purifying via column chromatography with eluent of ethyl acetate, 510 mg off-white solid was obtained (53.9%).

An alternative but more efficient method:

A mixture of 2-bromo-3-methyoxynaphthalene (1.02 g, 4.3 mmol), imidazole (440 mg, 6.46 mmol), CuI (100 mg, 0.52 mmol), L-proline (105 mg, 0.91 mmol) and K₂CO₃ (1.2 g, 8.70 mmol) in DMSO (10 mL) was degassed by pump-thaw and then stirred at 100 °C for 60 hours under N₂. After cooling to room temperature, the mixture was poured into 30 mL ethyl acetate and then filtered to remove the inorganic salts. The filtrate was washed with water (30 mL ×3) and then dried over Na₂SO₄. After removing solvent, the solid mixture was purified via column chromatography with eluent of ethyl acetate, affording an off-white solid (75%). ¹H-NMR (400 MHz, CDCl₃) δ (ppm) 7.87 (s, 1H), 7.81 (s, 1H), 7.78 (s, 1H), 7.74 (s, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 (s, 2H), 7.21 (s, 1H), 3.97 (s, 3H).

b⁵: A solution of **a**⁵ (419 mg, 1.87 mmol) and dibromomethane (1 mL, 14 mmol) in THF (5 mL) was heated to 110 °C for 48 hours. The mixture was then cooled to room temperature and the white solid was collected by filtration, washed with THF and diethyl ether, and dried under vacuum (520 mg, 90%). ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 10.12 (s, 2H), 8.38 (s, 2H), 8.34 (s, 2H), 8.32 (s, 2H), 7.99 (t, *J* = 7.2 Hz, 4H), 7.80 (s, 2H), 7.66 (t, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 6.99 (s, 2H), 4.03 (s, 6H).

L⁵: A mixture of **b**⁵ (496.5 mg, 0.8 mmol) in HOAc/HBr (12 mL/12 mL) was refluxed for 48 hours. The reaction mixture was then concentrated. The precipitate was collected by centrifugation, washed with H₂O, acetone and diethyl ether, affording a white solid (436.6 mg, 92%). ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm) 11.17 (s, 2H), 9.98 (s, 2H), 8.45 (s, 2H), 8.22 (s, 2H), 8.13 (d, *J* = 9.2 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.59 (t, 2H), 7.46 (m, 6H), 7.00 (s, 2H).

5: A mixture of L^5 (57.6 mg, 0.097 mmol), Pt(DMSO)₂Cl₂ (41.0 mg, 0.097 mmol) and Et₃N (80 µL, 0.57 mmol) in DMF (5 mL) was heated to 80 °C for 6 hours. After completion of reaction, the mixture was cooled to room temperature, filtered and washed with small amount of DMF, ethanol and diethyl ether, affording a greenish-yellow solid (9.1 mg, 15%). ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm) 8.55 (s, 2H), 8.33 (s, 2H), 7.83 (s, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.32 (m, 2H), 7.27 (s, 2H), 7.15 (m, 2H), 6.41 (s, 2H); FAB-MS: 626.1 [M+H]⁺. Anal. Calcd. For C₂₇H₁₈N₄O₂Pt·H₂O: C, 50.39; H, 3.13; N, 8.71. Found: C, 49.53; H, 3.14; N, 8.33.

b⁶: A solution of **a**³ (0.53 g, 2.1 mmol) and 1, 2-dibromoethane (0.12 mL, 1.39 mmol) in THF (6 mL) was refluxed at 110 °C for 48 hours. After cooling to room temperature, the resulting white precipitate was collected by filtration with suction, washed with THF and air-dried (377 mg, 48%). ¹H-NMR (DMSO-d₆, 400 MHz) δ (ppm): 9.57 (s, 2H), 8.13 (s, 2H), 7.90 (s, 2H), 7.40 (4H), 7.26 (d, J = 8.9 Hz, 2H), 4.89 (s, 4H), 3.79 (s, 6H), 2.32 (s, 6H).

L⁶: A solution of the bisimidazolium salt **b**⁶ (0.12g, 0.21 mmol) in HBr (48 wt. % aq. 3 mL)/HOAc (3 mL) was heated to reflux at 120 °C for 48 hours. After reaction, the mixture was rotary evaporated. Acetone was added to the residue to induce precipitation of a brown solid, which was collected by filtration and washed with ethyl acetate. After re-precipitation from methanol/ethyl acetate, white solid was obtained (0.09 g, 79%). ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 10.62 (s, 2H), 9.63 (s, 2H), 8.10 (s, 2H), 7.91 (s, 2H), 7.36 (s, 2H), 7.22 (d, 6.7 Hz, 2H), 7.07 (d, *J* = 7.96 Hz, 2H), 4.92 (s, 4H), 2.28 (s, 6H).

6: A mixture of L^6 (104.6 mg, 0.195 mmol) and Pt(DMSO)₂Cl₂ (83.7 mg, 0.198 mmol) in EtOH (20 mL) in the presence of Et₃N (163 µL) was heated to 80 °C for 6 hours. The reaction mixture was then rotary evaporated to dryness and purified via column chromatography on silica-gel with eluent of DCM/MeOH (20/1, v/v), affording a light yellow solid (58.7 mg, 53%). ¹H-NMR (400 MHz, DMSO-d₆) δ (ppm) 8.04 (d, *J* = 1.7 Hz, 2H), 7.54 (d, *J* = 1.7 Hz, 2H), 7.32 (s, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 4.38 (s, 4H), 2.23 (s, 6H); ¹³C-NMR (300 MHz, DMSO-d₆) δ (ppm) 155.54, 140.13, 128.96, 128.11, 125.32, 123.67, 121.57, 120.85, 118.04, 51.57, 21.59; FAB-MS: 568.1 [M+H]⁺; Anal. Calcd. For C₂₂H₂₀N₄O₂Pt·CH₂Cl₂·H₂O: C, 41.20; H, 3.61; N, 8.36. Found: C, 41.33; H, 3.75; N, 8.40.

7: A mixture of **L**³ (105.6 mg, 0.20 mmol), Pd(OAc)₂ (45.6 mg, 0.20 mmol) and Et₃N (0.167 mL, 1.2 mmol) in EtOH (10 mL) was heated to 80 °C for 6 hours. After completion of reaction, the mixture was cooled to room temperature, filtered and washed with ethanol, diethyl ether and dried under vacuum, affording an off-white solid (46 mg, 48.9%). ¹H-NMR (300 MHz, DMSO-d₆) δ (ppm) 8.32 (d, *J* = 2.1 Hz, 2H), 7.80 (d, *J* = 2.1 Hz, 2H), 7.47 (d, *J* = 1.6 Hz, 2H), 6.82 (dd, *J* = 8.3 Hz, 1.6 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.32 (s, 2H), 2.22 (s, 6H); FAB-MS: 464.1 [M+H]⁺. Anal. Calcd. For C₂₁H₁₈N₄O₂Pd·H₂O: C, 52.24; H, 4.18; N,11.60. Found: C, 52.13; H, 4.13; N, 11.25.

8: A mixture of L^3 (42.8 mg, 0.082 mmol), Ni(OAc)₂•4H₂O (20.4 mg, 0.082 mmol) and Et₃N (68.5 µL, 0.49 mmol) in EtOH (5 mL) was heated to 80 °C for 6 hours. After completion of reaction, the mixture was cooled to room temperature, filtered and washed with ethanol, diethyl ether and dried under vacuum, affording a greenish-yellow solid (25.9 mg, 75.7%).¹H-NMR (300 MHz, DMSO-d₆) δ (ppm) 8.25 (s, 2H), 7.74 (s, 2H), 7.44 (s, 2H), 6.74 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.3 Hz, 2H), 6.17 (s, 2H), 2.22 (s, 6H); FAB-MS: 417.1 [M+H]⁺; Anal. Calcd. For C₂₁H₁₈N₄O₂Ni·H₂O: C, 57.97; H, 4.63; N, 12.88. Found: C, 57.14; H, 4.78; N, 12.08.



Fig. S1 A comparison of powder X-ray diffraction patterns of pseudo-polymorphs (2-B, 2-F, and 2-VD) of complex 2.

	2-В	2-F
formula	$C_{19}H_{13}F_2N_4O_2Pt$	$C_{20}H_{14}Cl_{2}F_{2}N_{4}O_{2}Pt \\$
fw	578.42	646.34
color	Colorless	Colorless
crystal size	0.2×0.15×0.10	0.05×0.01×0.01
crystal system	Monoclinic	Monoclinic
space group	<i>P</i> 2 ₁ /m	<i>P</i> 2 ₁ /c
<i>a</i> , Å	6.9645(4)	11.5589(9)
b, Å	25.7559(15)	8.2655(7)
<i>c</i> , Å	9.9824(6)	22.3063(15)
α , deg	90	90
β , deg	99.1520(10)	111.907(4)
γ, deg	90	90
<i>V</i> , Å ³	1767.82(18)	1977.3(3)
Z	4	4
D_c , g cm ⁻³	2.173	2.171
μ , cm ⁻¹	15.322	16.181
<i>F</i> (000)	1100	1232
$2\theta_{\rm max}$, deg	132.14	131.86
no. unique data	3089	3345
no. obsd. data GOF for $I > 2\sigma(I)$	1.076	1.036
no. variables	259	280
R ^a	0.0568	0.0744
Rw ^b	0.1503	0.2377
residual ρ , e Å ⁻³	2.079, -1.906	3.929, -2.074

Table S1 Crystal data

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b $R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$

Crystal 2-B					
Pt(1)-C(9)	1.911(13)	O(1)-Pt(1)-C(9)	90.0(5)	O(1)-Pt(1)-O(1')	88.0(5)
Pt(1)-O(1)	-O(1) 2.026(7) C(9)-Pt(1)-C(9')		91.8(8)	O(1)-Pt(1)-C(9')	175.8(4)
Crystal 2-F					
Pt(1)–C(7)	1.920(10)	Pt(1)-O(2)	2.011(7)	C(11)-Pt(1)-O(2)	92.2(4)
Pt(1)-C(11)	1.935(12)	O(1)-Pt(1)-C(7)	92.1(4)	O(1)-Pt(1)-C(11)	176.1(4)
Pt(1)-O(1)	2.040(9)	C(7)-Pt(1)-C(11)	91.3(5)	O(2)-Pt(1)-C(7)	176.5(4)

Table S2 Selected bond distance (Å) and angles (°) of crystals 2-B and 2-F

Solvent	Absorption	Emission
	λ_{max} / nm (ϵ / 10 ³ M ⁻¹ cm ⁻¹)	λ_{max} / nm
DMF	280 (^a sh, 12.2), 306 (11.0), 345	455
	(12.2), 358 (12.8)	
THF	282 (^a sh, 11.5), 308 (10.5), 352	461
	(12.3), 363 (12.7)	
DCM	281 (^a sh, 11.8), 306 (9.7), 345	470
	(11.6), 358 (12.3)	
Toluene	306 (9.5), 351 (11.7), 362 (12.0)	468

Table S3 UV-Vis absorption and emission data of **4** in different solvents (concentration $\sim 2 \times 10^{-5}$ M)

a sh = shoulder. In all solvents other than DMF, 5% (v/v) DFT is contained.



Fig. S2 Excitation and emission spectra of **3** in solid-state at 298 K (absorption spectrum of **3** in THF/DMF (19:1; v/v) solution is also included for comparison).



Fig. S3 Emission spectra of 4 in a variety of states.



Fig. S4 Emission spectra of 5 in the solid state at 298 K and 77 K and in frozen DMF at 77 K.



Fig. S5 fs-TRF and ns-TRE spectra (a, c) and decay profiles (b, d) recorded at the various denoted delay times after 355 nm excitation of **2** in DMF.

Computational method

DFT and TD-DFT calculations were carried out using PBE0 method³ with basis set of 6-31+G^{*} for C, H, O, N atoms and pseudopotential Stuttgart/Dresden (SDD)⁴ basis set for Pt atom. Geometry optimization of ground state (S₀) and the lowest excited triplet state (T₁) were firstly performed. TD-DFT calculations based on these optimized geometries were then performed for gaining insight into frontier orbitals involved in the S₁ \leftarrow S₀ and T₁ \rightarrow S₀ transitions. Gaussian 09⁵ package was used for all calculation.



Fig. S6 Optimized a) S_0 and b) T_1 geometry of **3** and selected bond distances (Å), bond angles (°) and dihedral angles (°).

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Fig. S7 Plots of calculated frontier orbitals of complex 6 based on optimized S_0 and T_1 geometries.

Complex	Excited state	λ_{max} (f)	Assignments
2	S ₁	379.17 (0.156)	HOMO→LUMO (96%)
	S_2	357.53 (0.0658)	HOMO→LUMO+1 (93%)
	S3	333.72 (0.0003)	HOMO→LUMO+2 (94%)
	T1	688.19 (0.0)	HOMO→LUMO (88%)
			HOMO-1→LUMO (6%)
	T2	463.96 (0.0)	HOMO-1→LUMO (78%)
			HOMO→LUMO+1 (5%)
			HOMO→LUMO (4%)
	Т3	436.67 (0.0)	HOMO→LUMO+1 (54%)
			HOMO-1→LUMO+1 (30%)
5	S_1	407.40 nm (0.1565)	HOMO→LUMO (92%)
			HOMO-1→LUMO+1 (5%)
	S_2	385.00 nm (0.1162)	HOMO→LUMO+1 (63%)
			HOMO-1→LUMO (33%)
	S3	367.37 nm (0.0090)	HOMO-1→LUMO (63%)
			HOMO→LUMO+1 (31%)

Table S4 Calculated transition ene	ergies of 2, 5	, and 6 at optimized	$I S_0$ and T_1 geometries
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	T1 608.04 nm (0.0)		HOMO→LUMO (48%)
			HOMO-1→LUMO+1 (29%)
			HOMO→LUMO+2 (5%)
	T2	601.44 nm (0.0)	HOMO-1→LUMO (41%)
			HOMO→LUMO+1 (31%)
			HOMO-2→LUMO+1 (6%)
	Т3	461.97 nm (0.0)	HOMO→LUMO (39%)
			HOMO-2→LUMO (23%)
			HOMO-3→LUMO+1 (10%)
			HOMO→LUMO+2 (7%)
			HOMO-1→LUMO+1 (5%)
6	S ₁	363.13 nm (0.0932)	HOMO→LUMO (96%)
	S ₂ 335.91 nm (0.1101)		HOMO-1→LUMO (76%)
			HOMO→LUMO+1 (19%)
	S3	324.18 nm (0.0073)	HOMO-1→LUMO (20%)
			HOMO→LUMO+1 (72%)
	T1	659 94 nm (0 0)	HOMO→LUMO (85%)
			HOMO-1→LUMO (6%)
	Т2	478 12 nm (0 0)	HOMO-1→LUMO (75%)
	12	(0.0)	HOMO→LUMO+1 (11%)
			HOMO→LUMO (5%)
	ТЗ	423 33 nm (0.0)	HOMO→LUMO+1 (45%)
			HOMO-2→LUMO (18%)
			HOMO-1→LUMO+1 (11%)
			HOMO-1→LUMO (7%)

OLED fabrication and characterization

Glass slides with pre-patterned ITO electrodes used as substrates of OLEDs were cleaned in an ultrasonic bath of Decon 90 detergent and deionized water, rinsed with deionized water, and then cleaned in sequential ultrasonic baths of deionized water, acetone, and isopropanol, and subsequently dried in an oven for 1 h. They were then treated in an ultraviolet-ozone chamber before loading into an evaporation chamber. All layers of organic and metal were thermally deposited sequentially in a vacuum deposition system with a base pressure of 10⁻⁸ mBar. All films were sequentially deposited at rates between 0.03–0.1 nm/s without vacuum break. All film thicknesses were determined in-situ by calibrated oscillating quartz-crystal sensors. The doping process in the emitting layer was realized by co-deposition technology. The Commission Internationale de L'Eclairage (CIE) coordinates, luminance-current density-voltage characteristics, and electroluminescence (EL) spectra were measured simultaneously with a programmable Keithley model 2400 source-meter measurement unit and a Photoresearch PR-655 spectrascan spectroradiometer. All devices were characterized at room temperature without encapsulation. External quantum efficiency was calculated by assuming a Lambertian distribution.

Chart S1 Chemical structures used in OLEDs fabrication and device architecture.



(This complex was designed and prepared by our group with structure unreported yet in the literature.)

Chart S1 (continued)



Table S5 Device performances of the blue OLEDs with various doping concentrations (x wt%) of complex 4

Device (x wt.%)	Max. L^a (cd/m ²)	Max. CE^b (cd/A)	Max. PE^{c} (lm/W)	CIE^{d} (a) 100 cd/m ²
B1 (2%)	8700	19.1	13.3	(0.190, 0.211)
B2 (4%)	9500	23.8	16.6	(0.191, 0.217)
B3 (6%)	6500	14.9	13.3	(0.189, 0.198)
B4 (8%)	6200	15.3	10.6	(0.191, 0.207)

^{*a*} Luminance; ^{*b*} Current efficiency; ^{*c*} Power efficiency; ^{*d*} CIE coordinates.

Table S6 Device performances of the near white OLEDs with various doping levels of complex **4** and yellow Pt(II) phosphor (Pt-Y)

Device (CzSi:4:Pt-Y)	Max. L^a	Max. CE^b	Max. PE^c	CIE^{d} (a 1000
	(cd/m)	(cd/A)	(Im/w)	cd/m
W1 (100:10:1)	32000	87.8	55.2	(0.350, 0.458)
W2 (100:10:0.5)	16000	30.0	18.8	(0.303, 0.389)
W3 (100:6:1)	30000	59.6	37.4	(0.365, 0.481)
W4 (100:6:0.5)	26000	47.5	33.2	(0.315, 0.411)

^{*a*} Luminance; ^{*b*} Current efficiency; ^{*c*} Power efficiency; ^{*d*} CIE coordinates.



Fig. S8 (a) Current density-luminance-voltage characteristics and (b) Current efficiency-power efficiency-voltage characteristics of blue OLEDs doped with 2%, 6% and 8% of 4.



Fig. S9 EL spectra of the devices with 2%, 6% and 8% of 4 at driving voltages 6–11 V.



Fig. S10 (a) Current density-luminance-voltage characteristics and (b) Current efficiency-power efficiency-voltage characteristics of white OLEDs.



Fig. S11 EL spectra of Devices W1–W3 at luminances of 100, 1000, and 10000 cd/m^2 .



Fig. S12 Emission spectra of 1–4 in 5% DMF/THF (v/v) showing minimized FWHM of 2 (77 nm) compared with 1 (101 nm), 3 (94 nm), and 4 (100 nm).