

Supporting Information

Two green iridium(III) complexes containing the electron-transpotting group of 4-phenyl-4*H*-1,2,4-triazole for highly efficient OLEDs

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1. Materials and Measurements. ¹H NMR spectra were measured on a Bruker AM 400 spectrometer. Mass spectrometry (MS) spectra were obtained on an electrospray ionization (ESI) mass spectrometer (LCQ fleet, Thermo Fisher Scientific) for ligands and high-resolution electrospray mass spectra (HRMS) was measured on G6500 from Agilent for complexes. Elemental analyses for C, H, and N were performed on an Elementar Vario MICRO analyzer. TG-DSC measurements were carried out on a DSC 823e analyzer (METTLER). Absorption and photoluminescence spectra were measured on a UV-3100 spectrophotometer and a Hitachi F-4600 photoluminescence spectrophotometer, respectively. The decay lifetimes were measured with an Edinburgh Instruments FLS-920 fluorescence spectrometer in degassed CH₂Cl₂ solution at room temperature. The luminescence quantum efficiencies were calculated by comparison of the emission intensities (integrated areas) of a standard sample (*fac*-Ir(ppy)₃) and the unknown sample.¹

2. The synthesis of main ligands (TN₃T and TN₄T). A stirred solution of 2,6-bis-(trifluoromethyl)pyridine (0.215 g, 10mmol) in diethyl ether (20mL) was cooled to -78 °C. LDA (lithium diisopropylamide, 6.0 mL, 10 mmol) was added over 20 min and stirred for 1 h, and then B(OPr-i)₃ (2.89mL, 12.4 mmol) was added. The mixture was warmed to room temperature

and stirred for another 1 h. The pH was adjusted to 10 by the slow addition of 10% aqueous NaOH solution (20 mL). After 1 hour, the organic phase was acidified to pH = 4 by the dropwise addition of 3 N HCl. The extraction with ethyl acetate and evaporation of the organic phase gave the crude corresponding aryl boronic acids. 2-Bromopyridine (1 mL, 10 mmol) and tetrakis(triphenylphosphine)palladium⁰ (0.34 g, 0.3 mmol) and the boronic acids were added in 50 mL THF. After 20 mL of aqueous 2 N K₂CO₃ was delivered, the reaction mixture was heated at 70 °C for 1 day under an nitrogen atmosphere. The mixture was poured into water and extracted with CH₂Cl₂ (10 mL×3 times). Finally, silica column purification (n-hexane : EtOAc = 7 : 1 as eluant) gave the colorless liquid 2',6'-bis(trifluoromethyl)-2,3'-bipyridine (**TN₃T**) and white solid 2',6'-bis(trifluoromethyl)-2,4'-bipyridine (**TN₄T**).

TN₃T. 10% Yield. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 4.2 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.46-7.38 (m, 1H). ESI-MS, *m/z*: Calcd for C₁₂H₆F₆N₂, 292.18 [M]; found 293.25 [M + H]⁺.

TN₄T. 30% Yield. ¹H NMR (400 MHz, CDCl₃) δ 8.87-8.77 (m, 1H), 8.54 (s, 2H), 7.99-7.91 (m, 2H), 7.49 (ddd, *J* = 6.6, 4.7, 2.0 Hz, 1H). ESI-MS, *m/z*: Calcd for C₁₂H₆F₆N₂, 292.18 [M]; found 293.33 [M + H]⁺.

3. X-ray Crystallography. The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT² on all observed reflections. Data were collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS³ supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on *F*² using the program SHELXS-97.⁴ The positions of metal atoms and their first coordination spheres were located from direct-methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of Uiso.

4. Details of cyclic voltammetry measurements and theoretical calculations. Cyclic voltammetry measurements were conducted on a MPI-A multifunctional electrochemical and chemiluminescent system (Xi'an Remex Analytical Instrument Ltd. Co., China) at room temperature, with a polished Pt plate as the working electrode, platinum thread as the counter electrode and Ag-AgNO₃ (0.1 M) in CH₂Cl₂ as the reference electrode, *tetra*-n-butylammonium perchlorate (0.1 M) was used as the supporting electrolyte, using Fc⁺/Fc as the internal standard, the scan rate was 0.1 V/s. We perform theoretical calculations employing Gaussian09 software with B3LYP function.⁵ The basis set of 6-31G(d, p) was used for C, H, N, O, and F atoms while the LanL2DZ basis set was employed for Ir atoms.⁶ The solvent effect of CH₂Cl₂ was taken into consideration using conductor like polarizable continuum model (C-PCM).⁷

5. OLEDs fabrication and measurement. All OLEDs were fabricated on the pre-patterned ITO-coated glass substrate with a sheet resistance of 15 Ω/sq. The deposition rate for organic compounds is 1-2 Å/s. The phosphor and the host TCTA or 2,6DCzPPy were co-evaporated to form emitting layer from two separate sources. The cathode consisting of LiF / Al was deposited by evaporation of LiF with a deposition rate of 0.1 Å/s and then by evaporation of Al metal with a rate of 3 Å/s. The characteristic curves of the devices were measured with a computer which controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. On the basis of the uncorrected PL and EL spectra, the Commission Internationale de l'Eclairage (CIE) coordinates were calculated using a test program of the Spectra scan PR650 spectrophotometer.

6. Table S1. The crystallographic data of **Ir-TN₃T** and **Ir-TN₄T**.

	Ir-TN₃T	Ir-TN₄T
Formula	C ₈₈ H ₄₈ F ₂₄ IrN ₁₄ O ₂	C ₄₄ H ₂₄ F ₁₂ IrN ₇ O
Formula weight	2173.80	1086.90
T (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ /c
<i>a</i> (Å)	15.012(2)	13.884(3)
<i>b</i> (Å)	16.240(2)	24.698(5)
<i>c</i> (Å)	20.022(3)	12.797(2)
<i>α</i> (deg)	97.891(3)	90.00
<i>β</i> (deg)	90.762(3)	112.176
<i>γ</i> (deg)	115.608(3)	90.00
<i>V</i> (Å ³)	4345.7(11)	4063.9(13)
<i>Z</i>	2	4
ρ_{calcd} (g/cm ³)	1.661	1.776
μ (Mo K α) (mm ⁻¹)	3.167	3.387
<i>F</i> (000)	2120	2120
Range of transm factors (deg)	1.408-25.009	1.584-25.010
Reflns collected	24550	29845
Unique(R _{int})	15223(0.0447)	7175(0.1800)
<i>R</i> _I ^a , <i>wR</i> ₂ ^b [I > 2s(I)]	0.0615, 0.1585	0.0502, 0.1213

R_I^a , wR_2^b (all data)	0.0964, 0.1851	0.0591, 0.1383
GOF on F^2	1.034	0.979

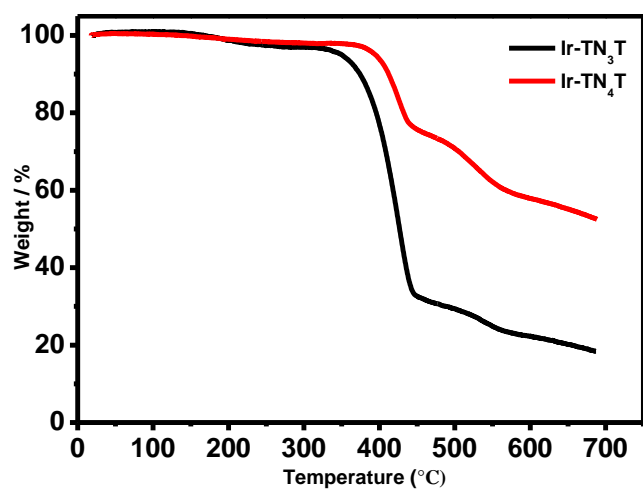
$$R_I^a = \Sigma||F_o| - |F_c||/\Sigma F_o|. \quad wR_2^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}.$$

7. Table S2. Selected bond lengths and angles of **Ir-TN₃T** and **Ir-TN₄T**.

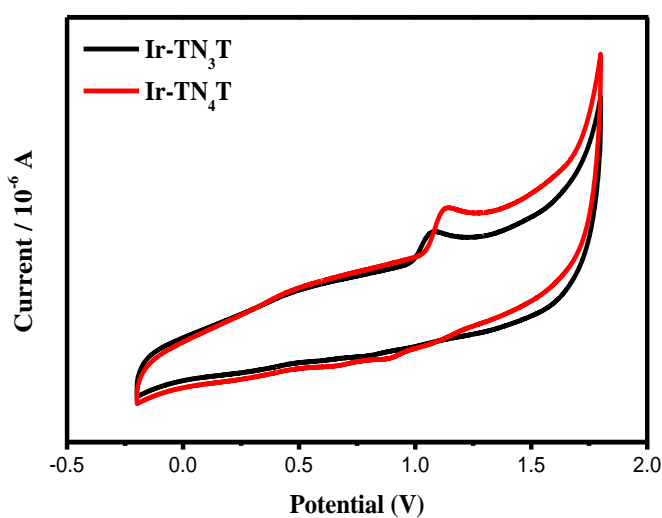
Bond length (Å)	Ir-TN₃T	Ir-TN₄T
Ir-C(1)	1.957(9)	2.032(16)
Ir-C(2)	1.997(9)	2.023(5)
Ir-N(1)	2.017(8)	2.046(5)
Ir-N(2)	2.030(8)	2.058(5)
Ir-N(4)	2.098(7)	2.120(5)
Ir-O(1)	2.139(6)	2.135(4)
Selected angles	(°)	(°)
C(1)-Ir-N(1)	79.5(3)	81.1(2)
C(2)-Ir-N(2)	79.6(3)	80.35(19)
O(1)-Ir-N(4)	82.9(2)	84.94(16)
N(1)-Ir-N(2)	175.2(3)	172.0(2)
N(4)- Ir-C(2)	173.2(3)	169.12(18)
O(1)-Ir-C(1)	174.7(3)	172.13(18)

8. Table S3. The electronic cloud density distributions of the iridium(III) complexes.

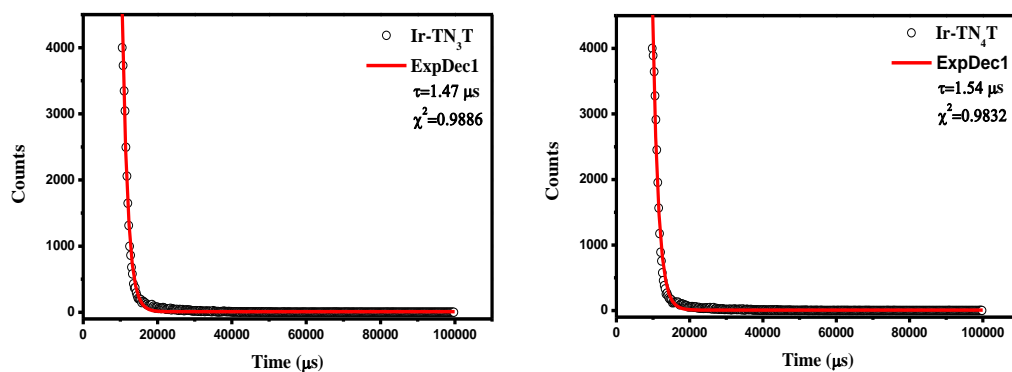
Complex	Orbital	Energy/eV (Calculated)	Energy/eV (Experimental)	Composition (%)		
				Ir	Main ligands	Ancillary Ligands
Ir-TN₃T	HOMO	-5.36	-5.34	13.97	8.20	77.83
	LUMO	-2.18	-2.91	3.45	94.66	1.89
Ir-TN₄T	HOMO	-5.40	-5.40	15.52	6.94	77.54
	LUMO	-2.08	-2.91	3.02	94.18	2.80



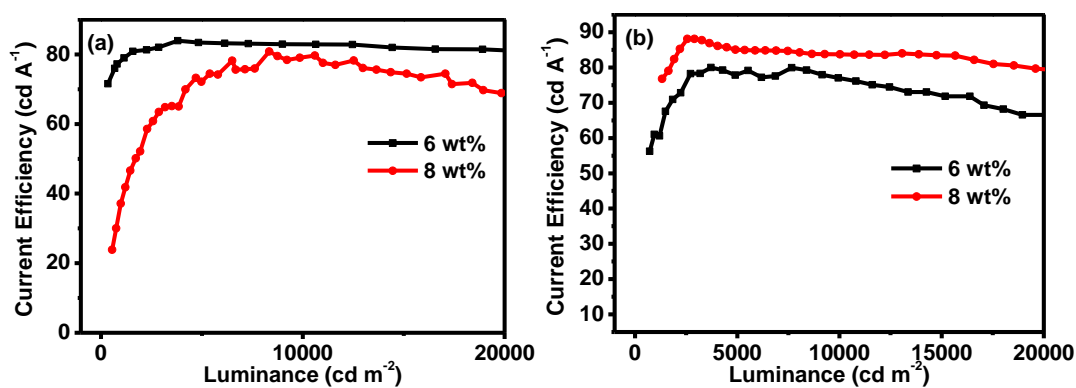
9. Figure S1. The TG curves of the iridium(III) complexes.



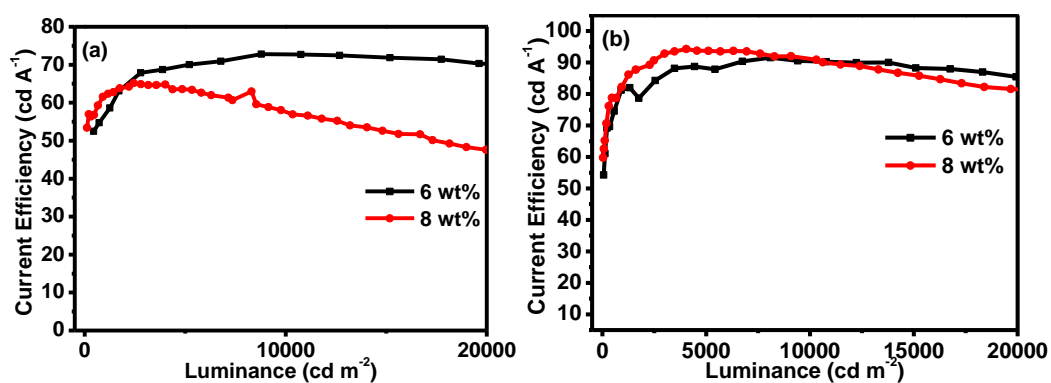
10. Figure S2. Cyclic voltammograms of complexes the iridium(III) complexes.



11. **Figure S3.** The selected lifetime curves of the iridium(III) complexes in degassed CH_2Cl_2 solution.



12. **Figure S4.** Current efficiency versus luminance of different doped concentrations of single-layer-emitting layer devices: (a) for **Ir-TN₃T**; (b) for **Ir-TN₄T**.



13. **Figure S5.** Current efficiency versus luminance of different doped concentrations of double-layer-emitting devices: (a) for **Ir-TN₃T**; (b) for **Ir-TN₄T**.

References:

- (1) D. P. Rillema, D. G. Taghdiri, D. S. Jones, C. D. Keller, L. A. Worl, T. J. Meyer and H. A. Levy, *Inorg. Chem.*, 1987, **26**, 578.
- (2) *SAINT-Plus*, version 6.02, Bruker Analytical X-ray System, Madison, WI, 1999.
- (3) Sheldrick, G. M. *SADABS An empirical absorption correction program*, Bruker Analytical X-ray Systems, Madison, WI, 1996.
- (4) Sheldrick, G. M. *SHELXTL-97*. Universität of Göttingen, Göttingen, Germany, 1997.
- (5) E. Runge and E. K. U. Gross, *Phys. Rev. Lett.*, 1984, **52**, 997.
- (6) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, Revision A.01, Gaussian, Inc., Wallingford, CT, 2009.
- (7) (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299; (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.