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Supporting Information

Two platinum(II) complexes with the 4-phenyl-4*H*-1,2,4-triazole derivative as ancillary ligand for efficient green OLEDs

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[#]Lu and [#]Tu have the same contributions to this paper.

1. Materials and Measurements. All reagents and chemicals were purchased from commercial sources and used without further purification. ^{1}H 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 CH_2Cl_2 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. Synthesis of the main ligand TN$_3$T. [2] A stirred solution of 2,6-bis-(trifluoromethyl)pyridine (0.215 g, 10 mmol) in diethyl ether (20 mL) was cooled to -78 ℃. LDA (lithium diisopropylamide, 6.0 mL, 10 mmol) was added over 20 min and stirred for 1 h, and then B(OPr-i)$_3$ (2.89 mL, 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)palladium^0 (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 ℃ for 1 day under an nitrogen atmosphere. The mixture was poured into water and extracted with CH_2Cl_2 (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 (**TN$_3$T**, 10% Yield). ^{1}H NMR (400 MHz, $CDCl_3$) 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 $C_{12}H_6F_6N_2$, 292.18 [M]; found 293.25 $[M + H]^+$.

3. X-ray Crystallography. The single crystals of complexes were carried out on a Bruker SMART CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Cell parameters were retrieved using SMART software and refined using SAINT [3] 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 SADABS [4] supplied by Bruker. The structures were solved by direct methods and refined by full-matrix least-squares on $F2$ using the program SHELXS-97.[5] 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-$AgNO_3$ (0.1 M) in CH_2Cl_2 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.[6] 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.[7] The solvent effect of CH_2Cl_2 was taken into consideration using conductor like polarizable continuum model (C-PCM).[8]

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.

1. **Table S1**. The crystallographic data of **(4tfmppy)Pt(dptp).**

	(4tfmppy)Pt(dptp)
Formula	$C_{32}H_{21}F_3N_4OPt$
FW	729.62
T (K)	153(2)
Wavelength (Å)	0.71073
Cryst syst	Monoclinic
Space group	*P2(1)/n*
a (Å)	6.4865(17)
b (Å)	33.878(9)
c (Å)	24.134(7)
α (deg)	90
β (deg)	94.039(6)
γ (deg)	90
V (Å^3)	5290(2)
Z	8

ρ_{calcd} (g/cm^3)	1.832
μ (Mo Kα) (mm^{-1})	5.360
F (000)	2832
Range of transm factors (deg)	2.405-23.256
Reflns collected	24010
Unique	7592
GOF on F^2	1.111
R_1^a, wR_2^b (I>2σ(I))	0.0802, 0.1531
R_1^a, wR_2^b(all data)	0.1587, 0.1864
CCDC NO.	1832372

$R_1^a = \Sigma||F_o| - |F_c||/\Sigma F_o|$. $wR_2^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

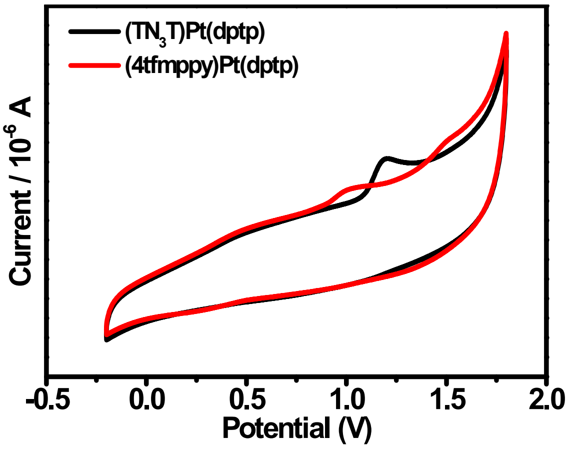
2. **Table S2**. Selected bond lengths and angles of **(4tfmppy)Pt(dptp).**

(4tfmppy)Pt(dptp)	
Selected bonds	
Pt1-C1	2.00(2)
Pt1-N1	2.018(15)
Pt1-N2	2.030(16)
Pt1-O1	2.070(14)
Selected angels	
C1-Pt1-N1	81.8(8)
N2-Pt1-O1	89.1(6)
C1-Pt1-O1	170.8(7)
N1-Pt1-N2	177.2(6)
Selected torsion angels	
C1-Pt1-N1-O1	176.511(678)
N1-Pt1-O1-N2	177.427(665)

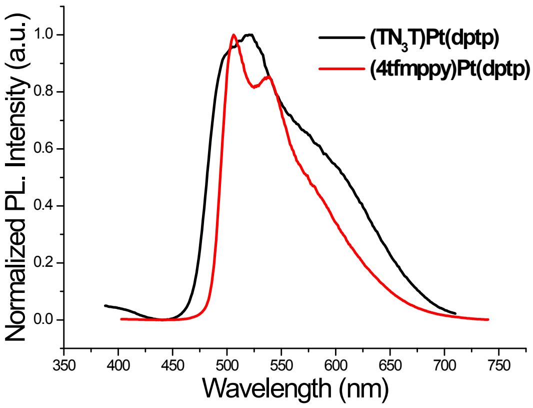
O1-Pt1-N2-C1	176.115(681)

8. **Table S3.** The electronic cloud density distribution.

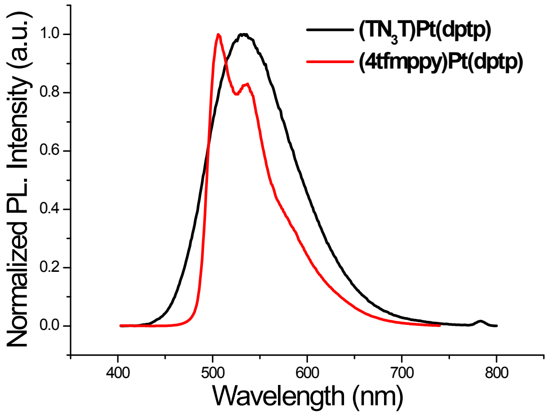
Complex	Orbital	Energy/eV (Calculated)	Energy/eV (Experimental)	Composition (%)		
				Main Ligands	Pt	Ancillary Ligands
(TN$_3$T)Pt(dptp)	HOMO	-5.40	-5.46	4.84	13.22	81.94
	LUMO	-2.23	-2.93	92.43	5.08	2.49
(4tfmppy)Pt(dptp)	HOMO	-5.25	-5.31	7.29	18.02	74.69
	LUMO	-1.89	-2.68	91.28	5.37	3.35



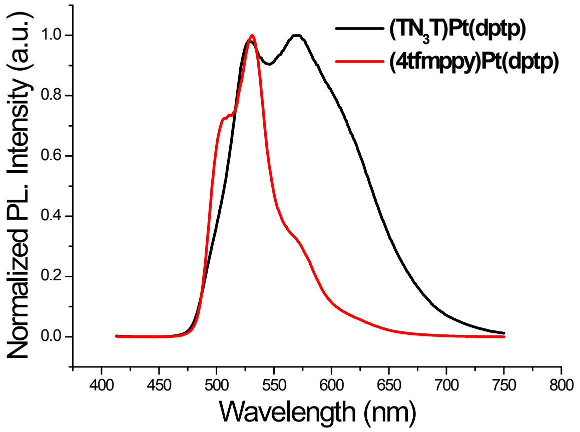
9. **Figure S1**. Cyclic voltammograms of complexes the platinum(II) complexes.



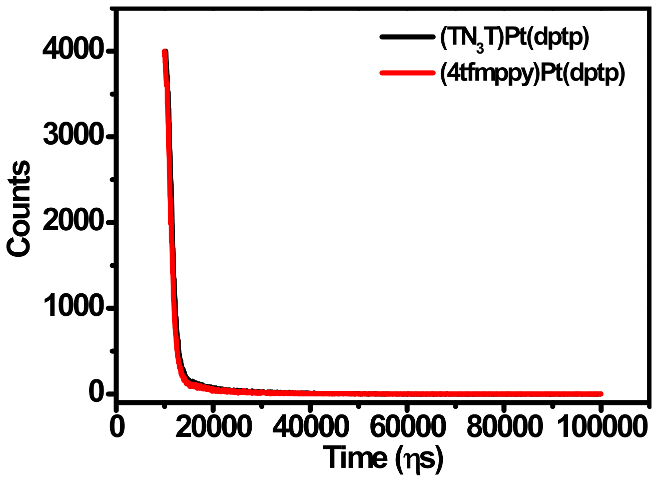
10. **Figure S2.** The emission spectra of Pt(II) complexes doped TCTA films (16 wt%).



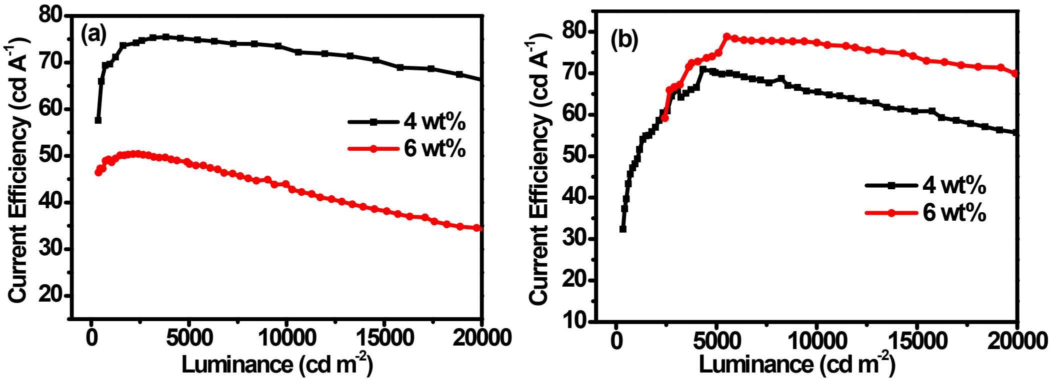
11. **Figure S3.** The emission spectra of Pt(II) complexes doped 2,6DCzPPy films (16 wt%).



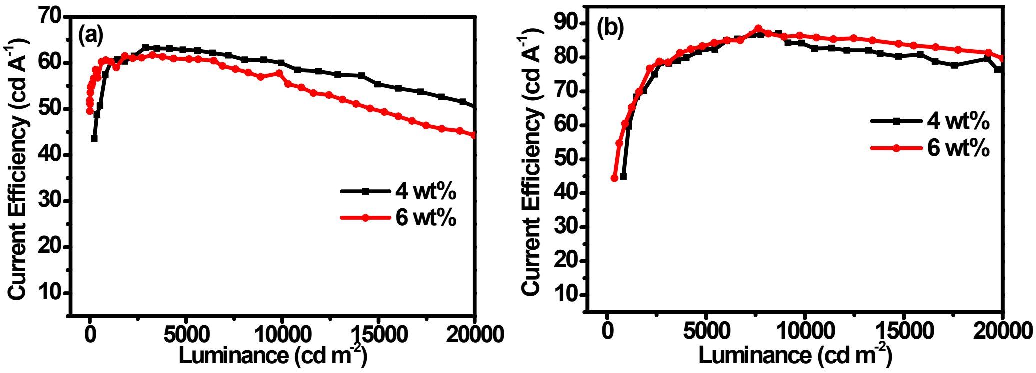
12. **Figure S4.** The emission spectra of Pt(II) complexes in power solid states.



13. **Figure S5.** The selected lifetime curves of the platinum(II) complexes in degassed CH_2Cl_2 solution.



14. **Figure S6.** Current efficiency versus luminance curves of single-layer-emitting devices with diffrerent dopded concentrations: (a) for **(TN$_3$T)Pt(dptp)**; (b) for **(4tfmppy)Pt(dptp)**.



15. **Figure S7.** Current efficiency versus luminance curves of double-layer-emitting devices with diffrerent dopded concentrations: (a) for **(TN$_3$T)Pt(dptp)**; (b) for **(4tfmppy)Pt(dptp)**.

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