## **Supporting information for**

## Achieving near-

# infrared electroluminescence around 780 nm based on butte rfly-shaped dinuclear platinum(II) complexes

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#### Materials and methods

All chemicals and materials, unless otherwise stated, were commercially available and used as received without further purification. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX 400 or Bruker DRX 500 spectrometer using tetramethylsilane as a reference in deuterated chloroform solution at 298 K. MALDI-TOF mass spectrometric measurements were performed on Bruker Bifiex III MALDI-TOF. Thermogravimetric analysis (TGA) was conducted under a dry nitrogen gas flow at a heating rate of 10°C·min<sup>-1</sup> on a Perkin-Elmer TGA 7. The UV/Vis absorption and photoluminescent spectra are measured with a Varian Cray 50 absorption spectrometer and Perkin-Elmer LS50B luminescence spectrometer, respectively. The photoluminescence lifetime was measured using Fluo Time 300 Spectrometer. Cyclic voltammetry (CV) was performed on a CHI 600E electrochemical work station with a scan rate of 100 mV·S<sup>-1</sup> at room temperature under argon, in which a glassy carbon, Pt plate, and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. The oxidation and reduction processes were measured in dichloromethane, with 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was measured under the same conditions. Single crystal of Pt2 was obtained by solvent diffusion from chloroform/n-hexane to its concentrated chloroform solutions which undergoes slow diffusion. X-ray diffractions of Pt2 were recorded on a Bruker D8 Venture diffractometer using CuK $\alpha$  radiation ( $\lambda$ =1.54178 Å). The crystal was kept at 193.00 or 173.00 K during data collection. Full crystallographic information in CIF format has been deposited at the Cambridge Crystallographic Data Center (CCDC) under deposition number 2157705. Quantum chemical calculations were carried out by DFT (PBE1PBE/6-31G) method except Pt atom using Lanl2dz level to further explore geometry. All electronic structure calculations were performed with the Gaussian 09 program package. The results were analyzed further with GaussView.

#### Device fabrication and characterization

First, the ITO (indium tin oxide)-coated glass substrate was washed with acetone and ethanol in an ultrasonic bath. After treatment with ultraviolet ozone for 20 minutes, PEDOT:PSS [poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate)] was sequentially coated on the substrate as a hole injection layer. PVK:OXD-7(Poly(N-vinyl carbazole): 2,2'-(1,3-phenylene)bis[5-(4-tert-butyl- phenyl)-1,3,4oxadiazole]) or CBP (4,4'-bis(Ncarbazolyl)-1,1'- biphenyl) is used as the host, and X wt% represents the doping rate for platinum complexes. In Device I and II, a mixture of PVK: OXD-7 and phosphor in chlorobenzene solution was spin coated at 50 nm on top of PEDOT:PSS; in Device III, a mixture of CBP and phosphor in chlorobenzene solution was spin coated at 55 nm. Then, the electron transport layer (TmPyPB: 1,3,5-Tri[(3-pyridyl)-phen-3-yl]benzene), the electron injection layer (CsF) and Al cathode were consecutively evaporated in the vacuum chamber. The device was sealed with curable UV resin in N<sub>2</sub>-filled glove-box. The EL properties of the devices were measured in the ambient air after after encapsulation. A PR-735 SpectraScan Spectroradiometer (Photo Research) combined with a Keithley 2400 SourceMeter unit was controlled with a customized software to simultaneously determine the current-voltage-luminous intensity characteristics and the EL spectra.

### **Figures and Tables**

Figure S1 TGA curve of the platinum(III) complexes under a stream of nitrogen at a scanning rate of 10 °C  $\cdot$  min<sup>-1</sup>.

**Figure S2** X-ray crystal structure of Pt2: (a) top view; (b) side view; (c) molecular stacking and intermolecular interactions.

Figure S3 UV-vis absorption and PL spectra of Pt1 and Pt2 in solid films at RT.

Figure S4 The PL spectra of Pt1 and Pt2 in their doped films at RT.

Figure S5 The PL decay characteristics of Pt1 and Pt2 in degassed CHCl<sub>3</sub> at RT.

Figure S6 Energy-level diagrams of related materials in Device II and Device III.

Figure S7 Normalized EL spectra of Pt1-doped OLEDs of (a) Device I, (b) Device II,

(c) Device III and (d) Pt2-doped OLEDs of Device III.

Figure S8 EQE-J curves of Pt1-doped OLEDs of (a) Device I, (b) Device II, (c)

Device III and (d) Pt2-doped OLEDs of Device III.

**Figure S9** *J-V-R* characteristics of Pt1-doped OLEDs of (a) Device I, (b) Device II, (c) Device III and (d) Pt2-doped OLEDs of Device III.

**Figure S10** (a) Normalized EL spectra of Pt1-doped OLEDs at different dopant concentrations from 1.0 to 16.0 wt%. (b) *EQE-J* curves of Pt1-doped OLEDs at 1.0 to 16.0 wt% in Device I.

Figure S11 <sup>1</sup>H NMR, <sup>13</sup>C NMR and MALDI-TOF MS of compounds.

Figure S1



Figure S2



(a)



(b)



(c)













Figure S6



Figure S7







Figure S9



Figure S10



## Figure S11

<sup>1</sup>H NMR of **CNpiq** 







## <sup>13</sup>C NMR of (CNpiq)<sub>2</sub>Pt<sub>2</sub>(µ-C<sub>8</sub>PhOXT)<sub>2</sub>



MALDI-TOF of (CNpiq)<sub>2</sub>Pt<sub>2</sub>(µ-C<sub>8</sub>PhOXT)<sub>2</sub>



MALDI-TOF of (CNpiq)<sub>2</sub>Pt<sub>2</sub>(µ-PhOXT)<sub>2</sub>



compound	Pt2
Formula	$C_{48}H_{28}N_8O_2Pt_2S_2$
Formula weight	1203.09
Т (К)	193
Wavelength (Å)	1.54178
Crystal system	triclinic
Space group	P-1
<i>a</i> (Å)	13.5533(3)
<i>b</i> (Å)	19.4177(4)
c (Å)	20.0115(4)
α (°)	106.9470(10)
eta (°)	97.2750(10)
γ (°)	101.9880(10)
$V(Å^3)$	4828.33(18)
Ζ	4
$ ho_{ m calc} d \left( { m g/cm^3}  ight)$	1.983
$\mu (\mathrm{mm}^{-1})$	14.969
F (000)	2768.0
Range of transm	4.712-136.56
Unique (R <sub>int</sub> )	17586(0.0531)
$R_{l}, wR_{2} [I > 2\sigma (I)]$	0.0351, 0.0941
$R_1$ , $wR_2$ (all data)	0.0385, 0.0963
GOF on $F^2$	1.039
CCDC No.	2157705

**Table S1**. Crystal data and structure refinement for Pt2.

Table S2. Selected bond lengths [Å] and angles  $[\circ]$  for Pt2.

Bond lengths (Å)							
Pt1-Pt2	3.0124(3)	Pt1-S1	2.3071(12)				
Pt1-N2	2.122(4)	Pt1-N3	2.033(4)				
Pt1-C014	1.986(5)	Pt2-S2	2.3028(11)				
Pt2-N5	2.133(4)	Pt2-N7	2.037(4)				
Pt2-C016	1.979(5)						
Bond angles (°)							

S1-Pt1-Pt2	91.66(3)	N2-Pt1-Pt2	77.81(11)
N2-Pt1-S1	88.02(12)	N3-Pt1-Pt2	89.84(11)
N3-Pt1-S1	176.55(11)	N3-Pt1-N2	95.33(16)
C014-Pt1-Pt2	105.08(13)	C014-Pt1-S1	96.19(16)
C014-Pt1-N2	174.78(18)	C014-Pt1-N3	80.43(19)
S2-Pt2-Pt1	93.21(3)	N5-Pt2-Pt1	79.93(11)
N5-Pt2-S2	86.65(11)	N7-Pt2-Pt1	87.67(11)
N7-Pt2-S2	176.10(12)	N7-Pt2-N5	97.24(15)
C016-Pt2-Pt1	102.07(13)	C016-Pt2-S2	96.18(14)
C016-Pt2-N5	176.41(18)	C016-Pt2-N7	79.93(17)
C01O-S1-Pt1	104.09(16)	C02B-S2-Pt2	101.81(16)
N1-N2-Pt1	118.2(3)	C02B-N2-Pt1	132.2(3)
C01C-N3-Pt1	121.9(3)	C017-N3-Pt1	115.8(3)
N6-N5-Pt2	120.3(3)	C01O-N5-Pt2	130.6(3)
C01E-N7-Pt2	120.6(3)	C018-N7-Pt2	117.8(3)

Dopants/Ratio (wt%)	Device tpye	$\lambda_{\rm EL}^{max}({\rm nm})$	$EQE_{\max}$ (%)	$V_{\rm on}{}^a({\rm V})$	$R_{\max}^{b}(mW/Sr/m^2)$
Pt1/1.0	Ι	758	0.93	8.8	5878
Pt1/2.0	Ι	768	1.03	14.0	6122
Pt1/4.0	Ι	771	0.81	14.4	5104
Pt1/6.0	Ι	781	0.64	14.4	5175
Pt1/8.0	Ι	788	0.75	14.5	6583
Pt1/10.0	Ι	797	0.52	15.1	5922
Pt1/12.0	Ι	800	0.57	14.6	3597
Pt1/14.0	Ι	805	0.53	14.6	2908
Pt1/16.0	Ι	814	0.33	14.8	2499
Pt1/1.0	II	760	1.16	8.8	6574
Pt1/2.0	II	768	1.78	14.0	5845
Pt1/4.0	II	782	0.66	16.0	6216
Pt1/1.0	III	756	1.47	7.4	1688
Pt1/2.0	III	760	2.73	9.6	5709
Pt1/4.0	III	773	2.14	11.0	7547
Pt2/1.0	III	742	1.94	7.0	2035
Pt2/2.0	III	744	2.62	7.6	4021
Pt2/4.0	III	762	1.29	10.2	10712

 Table S3. The device performance of OLEDs based on Pt1 and Pt2.

<sup>a</sup> Turn-on voltage. <sup>b</sup> Radiance at  $EQE_{max}$ .