

## Supporting Information

# **Blue electrophosphorescent organoplatinum(II) complexes with dianionic tetradentate bis(carbene) ligands**

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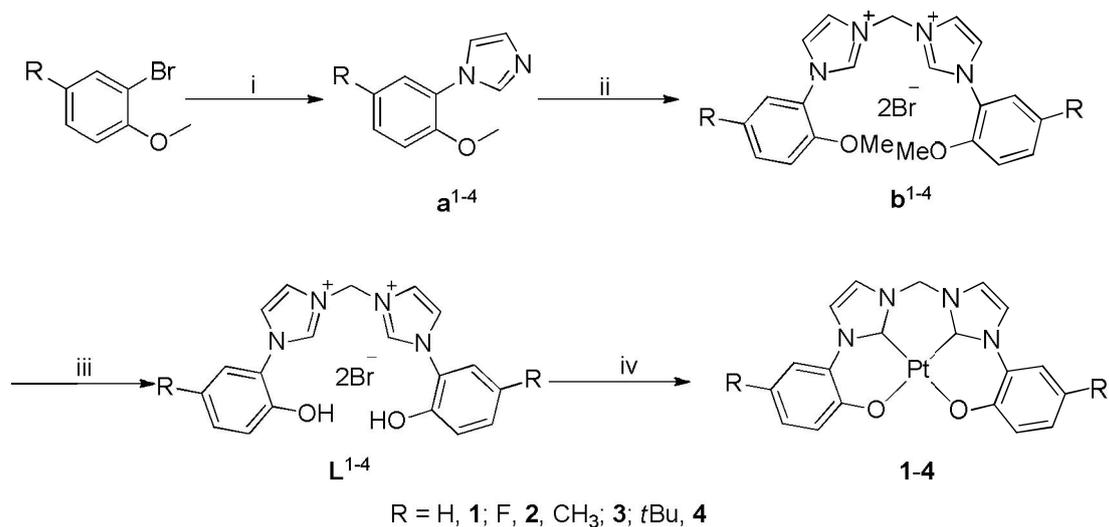
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## Synthesis and Characterization

All starting materials were used as received from commercial sources. 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.  $^1\text{H}$  (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 Fluorolog-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 degassed acetonitrile solution of  $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$  (bpy = 2,2'-bipyridine) as the standard ( $\phi_r = 0.062$ ) 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  $\phi$  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  $\phi$  (10%) are estimated. For measuring absolute solid-state emission quantum yield, an integrating sphere F-3018 (HORIBA JOBIN YVON) was equipped to the Spex 1681 Fluorolog-2 Model F111 spectrophotometer.





i imidazole, Cu<sub>2</sub>O, KOH, DMSO, N<sub>2</sub>, 140 °C, 24 hrs

ii CH<sub>2</sub>Br<sub>2</sub>, THF, 110 °C, 48 hrs

iii HBr (48 wt. % aq.), HOAc, 120 °C, 48 hrs

iv Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N, EtOH, 80 °C, 6 hrs

4-Methyl-2-bromoanisole and 4-(tert-butyl)-2-bromoanisole were prepared from 4-Methyl-2-bromophenol and 4-(tert-butyl)-2-bromophenol by reaction with MeI under the base of K<sub>2</sub>CO<sub>3</sub> following literature procedure.<sup>1</sup> Copper-catalyzed coupling reaction was used for preparing 1-(2-methoxyphenyl)-1H-imidazole and its substituted derivatives.<sup>2</sup>

**4-Methyl-2-bromoanisole:** Yield: 84%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm) 7.36 (d, J=2.1 Hz, 1H), 7.05 (dd, J=8.3 Hz, 2.1 Hz, 1H), 6.79 (d, J=8.3 Hz, 1H), 3.86 (s, 3H), 2.28 (s, 3H)

**4-(tert-butyl)-2-bromoanisole:** Yield: 97%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm) 7.54 (d, J=2.2 Hz, 1H), 7.27 (dd, J=8.6 Hz, 2.2 Hz, 1H), 6.83 (d, J=8.6 Hz, 1H), 3.87 (s,

<sup>1</sup> B. Lygo, *Tetrahedron Lett.*, 1999, **40**, 1389–1392.

<sup>2</sup> Y. Z. Huang, H. Miao, Q. H. Zhang, C. Chen and J. Xu, *Catal. Lett.*, 2008, **122**, 344–348.

3H), 1.28 (s, 9H).

**a<sup>1</sup>**: To a degassed DMSO (20 mL) solution of imidazole (1.0 g, 15 mmol) was added 2-bromoanisole (1.25 mL, 10 mmol), KOH (1.12 g, 20 mmol) and Cu<sub>2</sub>O (280 mg, 2 mmol) under nitrogen atmosphere. The resulting mixture was stirred at 140 °C for 24 hrs under N<sub>2</sub>. After cooling to room temperature, the mixture was poured into EA (50 mL) and was filtered. The filtrate was washed with water (50 mL ×3) and dried over anhydrous magnesium sulphate. After rotary evaporated, the crude oil was purified via column chromatography on silica gel with eluent of EA/MeOH (9/1, v/v), affording light yellow liquid product (50%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm) 7.79 (s, 1H), 7.36 (t, J=7.8 Hz, 1H), 7.28 (d, J=7.8 Hz, 1H), 7.21 (s, 1H), 7.17 (s, 1H), 7.05 (m, 2H), 3.85 (s, 3H).

**a<sup>2</sup>**: Following the procedure for preparing **a<sup>1</sup>**, **a<sup>2</sup>** was obtained as light yellow oil with yield of 47%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm) 7.82 (s, 1H), 7.21 (m, 1H), 7.17 (m, 1H), 7.07 (m, 2H), 7.00 (m, 1H), 3.84 (s, 3H).

**a<sup>3</sup>**: Following the procedure for preparing **a<sup>1</sup>**, **a<sup>3</sup>** was obtained as light yellow solid with yield of 57%. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ(ppm) 7.78 (s, 1H), 7.16 (m, 3H), 7.09 (d, J=1.8 Hz, 1H), 6.94 (d, J=8.4 Hz, 1H), 3.81 (s, 3H), 2.33 (s, 3H).

**a<sup>4</sup>**: Following the procedure for preparing **a<sup>1</sup>**, **a<sup>4</sup>** was obtained as light yellow oil with yield of 47%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm) 7.77 (s, 1H), 7.37 (dd, J<sub>1</sub>= 8.6 Hz, J<sub>2</sub>=2.4 Hz, 1H), 7.27 (d, J=2.4 Hz, 1H), 7.21 (1H), 7.17 (1H), 6.99 (d, J=8.6 Hz, 1H), 3.82 (s, 3H), 1.32 (s, 9H).

**b<sup>1</sup>**: A solution of **a<sup>1</sup>** (0.82 g, 4.7 mmol) and dibromomethane (1 mL, 14 mmol) in THF (5 mL) was refluxed at 110 °C for 48 hrs. After cooling to room temperature, the resulting white precipitates was collected by filtration with suction, washed with THF and air-dried (0.9g, 73%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm) 10.01 (s, 2H), 8.30 (m, 2H), 8.22 (m, 2H), 7.64 (m, 4H), 7.41 (d, J=8.3 Hz, 2H), 7.22 (t, J=7.7 Hz, 2H), 6.90 (s, 2H), 3.90 (s, 6H).

**b<sup>2</sup>**: Following the procedure for preparing **b<sup>1</sup>**, **b<sup>2</sup>** was obtained as a white solid with yield of 70%. <sup>1</sup>H-NMR (400 MHz, MeOD) δ(ppm) 8.33 (d, J=2.1 Hz, 2H), 8.11 (d, J=2.1 Hz, 2H), 7.66 (m, 2H), 7.40 (m, 4H), 7.11 (s, 2H), 3.98 (s, 6H). Note: the imidazole NCHN signal do not appeared in MeOD solvent.

**b<sup>3</sup>**: Following the procedure for preparing **b<sup>1</sup>**, **b<sup>3</sup>** was obtained as white solid with yield of 70%. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) δ(ppm) 9.93 (s, 2H), 8.26 (m, 2H), 8.20 (m, 2H), 7.47 (d, J=1.6 Hz, 2H), 7.44 (dd, J<sub>1</sub>=8.6 Hz, J<sub>2</sub>=1.6 Hz, 2H), 7.31 (d, J=8.6 Hz, 2H), 6.86 (s, 2H), 3.88 (s, 6H), 2.33 (s, 6H).

**b<sup>4</sup>**: Following the procedure for preparing **b<sup>1</sup>**, **b<sup>4</sup>** was obtained as white solid with yield of 74%. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm) 10.00 (s, 2H), 8.31 (m, 2H), 8.24 (m, 2H), 7.64 (m, 4H), 7.33 (d, J=8.8 Hz, 2H), 6.89 (s, 2H), 3.89 (s, 3H), 1.28 (s, 18H).

**L<sup>1</sup>**: A solution of the **b<sup>1</sup>** (0.81g, 1.55 mmol) in HBr (48 wt. % aq. 6.5 mL)/HOAc (6.5 mL) was heated to reflux at 120 °C for 48 hrs. After reaction, the mixture was rotary evaporated. Acetone was added to the residue to induce precipitation of brown solids, which was collected by filtration and washed with EA. After reprecipitation from

DMF/EA, white solid was obtained (0.52 g, 68%).  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-d}_6$ )  $\delta(\text{ppm})$  11.08 (br s, 2H), 9.99 (s, 2H), 8.29 (s, 2H), 8.22 (s, 2H), 7.57 (d,  $J=7.86$  Hz, 2H), 7.44 (t,  $J=7.77$  Hz, 2H), 7.19 (d,  $J=8.13$  Hz, 2H), 7.06 (t,  $J=7.58$  Hz, 2H), 6.90 (s, 2H).

$\text{L}^2$ : Following the procedure for preparing  $\text{L}^1$ ,  $\text{L}^2$  was obtained as white solid with yield of 84% after reprecipitation from MeOH/EA.  $^1\text{H-NMR}$  (300 MHz, MeOD)  $\delta(\text{ppm})$  9.97 (im NCHN, s, active), 8.23(d,  $J=2.0$  Hz, 2H), 8.13 (d,  $J=2.0$  Hz, 2H), 7.52 (dd,  $J_1=8.4$  Hz,  $J_2=3.0$  Hz, 2H), 7.26 (td,  $J_1=9.0$  Hz,  $J_2=3.0$  Hz, 2H), 7.14 (dd,  $J_1=9.0$  Hz,  $J_2=4.8$  Hz, 2H), 7.00 (s, 2H).

$\text{L}^3$ : Following the procedure for preparing  $\text{L}^1$ ,  $\text{L}^3$  was obtained as white solid with yield of 65% after reprecipitation from MeOH/EA.  $^1\text{H-NMR}$  (300 MHz,  $\text{DMSO-d}_6$ )  $\delta(\text{ppm})$  10.82 (br s, 2H), 9.96 (s, 2H), 8.28 (m, 2H), 8.20 (m, 2H), 7.39 (d,  $J=1.6$  Hz, 2H), 7.25 (dd,  $J_1=8.4$  Hz,  $J_2=1.6$  Hz, 2H), 7.08 (d,  $J=8.4$  Hz, 2H), 6.88 (s, 2H), 2.28 (s, 6H).

(300 MHz, MeOD)  $\delta(\text{ppm})$  9.91 (im NCHN, s, 2H), 8.20 (m, 2H), 8.09 (m, 2H), 7.43 (d,  $J=1.6$  Hz, 2H), 7.28 (dd,  $J_1=8.4$  Hz,  $J_2=1.6$  Hz, 2H), 7.03 (d,  $J=8.4$  Hz, 2H), 6.98 (s, 2H), 2.35 (s, 6H).

$\text{L}^4$ : Following the procedure for preparing  $\text{L}^1$ ,  $\text{L}^4$  was obtained as white solid with yield of 62%.  $^1\text{H-NMR}$  (400 MHz, DMSO)  $\delta(\text{ppm})$  10.85 (s, 2H), 9.91 (s, 2H), 8.24 (m, 4H), 7.48 (m, 4H), 7.11 (d,  $J=8.4$  Hz), 6.84 (s, 2H), 1.29 (s, 18H).

**1**: A mixture of  $\text{L}^1$  (193 mg, 0.39 mmol),  $\text{Pt}(\text{DMSO})_2\text{Cl}_2$  (164 mg, 0.39 mmol) and

Et<sub>3</sub>N (0.325 mL, 6 eq.) in EtOH (20 mL) was heated to 80 °C for 6 hrs. After completion of reaction, the mixture was cooled to room temperature, collected by centrifugation, washed with ethanol, ether and was dried under vacuum, affording pale yellow solids (60%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm) 8.34 (d, J=2.3 Hz, 2H), 7.71 (d, J=2.3 Hz, 2H), 7.69 (d, J=8.35 Hz, 2H), 7.06 (t, J=7.65 Hz, 2H), 6.92 (d, J=8.27 Hz, 2H), 6.57 (t, J=7.57 Hz, 2H), 6.31 (s, 2H) FAB-MS: 526.0 [M+H]<sup>+</sup>. Anal. Calcd. For C<sub>19</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>Pt·H<sub>2</sub>O: C, 41.99; H, 2.97; N, 10.31. Found: C, 42.06; H, 2.88; N, 9.99.

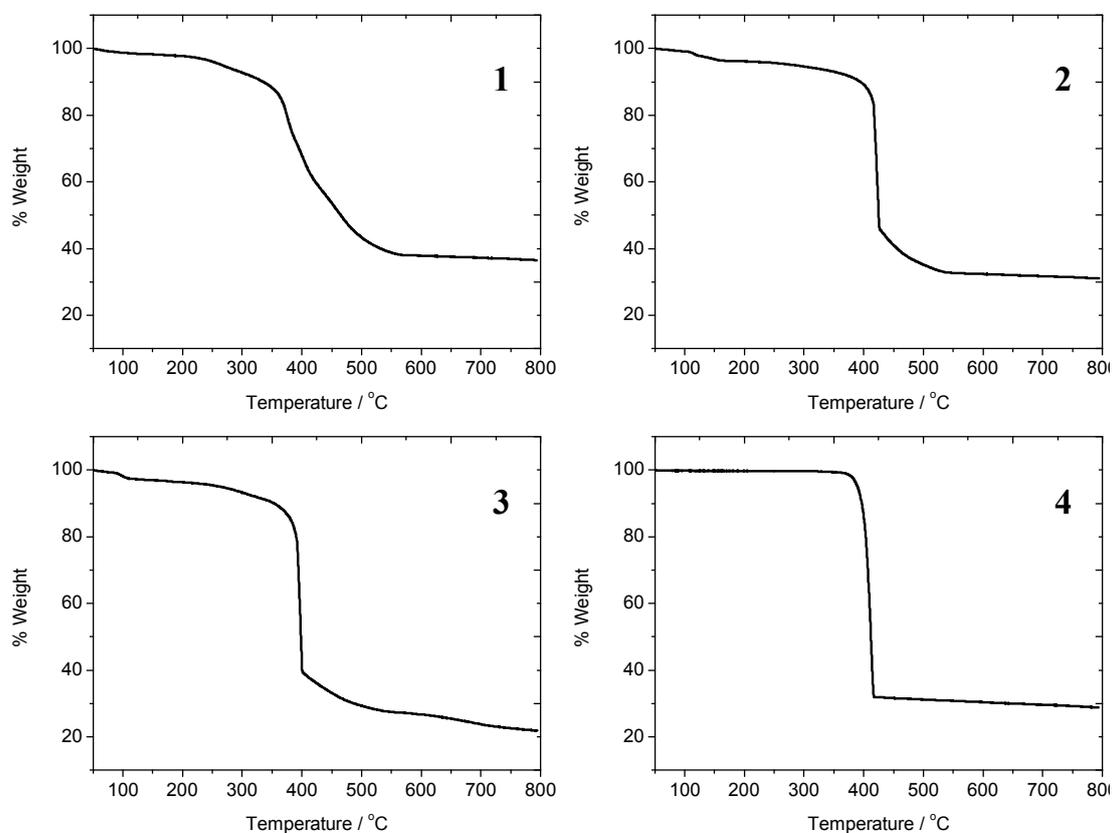
**2:** Following the procedure for prepare **1**, **2** was obtained as white solid with yield of 49%. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm) 8.34 (d, J=1.8 Hz, 2H), 7.72 (d, J=1.8 Hz, 2H), 7.66 (d, J=10.5 Hz, 2H), 6.90 (m, 4H), 6.32 (s, 2H) FAB-MS: 561.0 [M+H]<sup>+</sup>. Anal. Calcd. For C<sub>19</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>Pt·H<sub>2</sub>O: C, 39.38; H, 2.44; N, 9.67. Found: C, 38.77; H, 2.40; N, 9.35.

**3:** Following the procedure for preparing **1**, **3** was obtained as white solid with yield of 56%. <sup>1</sup>H-NMR (300 MHz, DMSO-d<sub>6</sub>) δ(ppm) 8.31 (d, J=2.1 Hz, 2H), 7.69 (d, J=2.1 Hz, 2H), 7.51 (s, 2H), 6.87 (d, J=8.2 Hz, 2H), 6.80 (d, J=8.2 Hz, 2H), 6.29 (s, 2H), 2.25 (s, 6H) FAB-MS: 553.0 [M+H]<sup>+</sup>. Anal. Calcd. For C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>Pt·CH<sub>2</sub>Cl<sub>2</sub>: C, 41.39; H, 3.16; N, 8.78. Found: C, 41.38; H, 3.22; N, 8.82.

**4:** Following the procedure for preparing **1**, **4** was obtained as white solid with yield of 58%. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ(ppm) 8.42 (d, 2.3 Hz, 2H), 7.71 (d, 2.3 Hz, 2H), 7.52 (d, J=2.3 Hz, 2H), 7.08 (dd, J<sub>1</sub>= 8.6 Hz, J<sub>2</sub>=2.3 Hz, 2H), 6.83 (d, J=8.6 Hz,

2H), 6.30 (s, 2H), 1.29 (s, 18H) FAB-MS: 638.2 [M+H]<sup>+</sup>. Anal. Calcd. For

C<sub>27</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>Pt·H<sub>2</sub>O: C, 49.46; H, 4.92; N, 8.55. Found: C, 49.36; H, 4.64; N, 8.46.



**Figure S1** Thermogravimetric analyses (TGA) curves of solid samples of complexes 1–4 under a nitrogen atmosphere with a heating ramp of 10 °C/min.

## Single-Crystal X-ray Diffraction

Single-crystal of **3** suitable for X-ray diffraction analysis was obtained from its dilute solution in dichloromethane in air upon slow evaporation of the solvent.

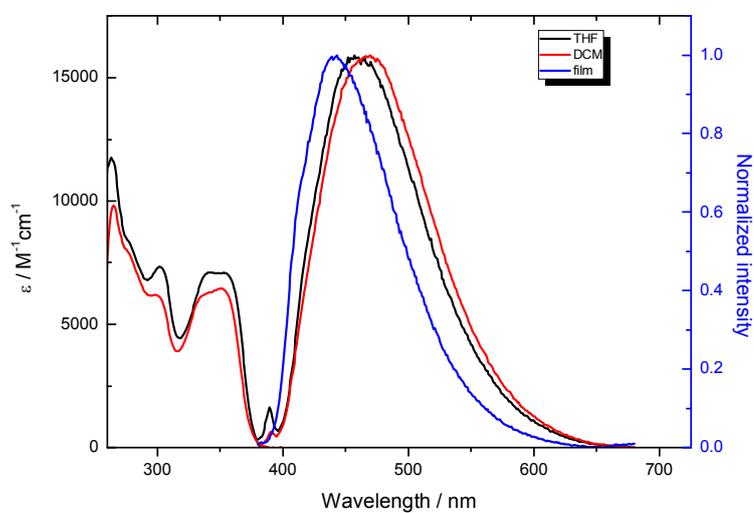
**Table S1.** Crystal Data of complex **3**

formula	C <sub>22</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>3</sub> Pt
fw	656.43
color	colorless
crystal size	0.1×0.02×0.02 mm <sup>3</sup>
crystal system	Orthorhombic
space group	<i>Pnma</i>
<i>a</i> , Å	6.7618(2)
<i>b</i> , Å	24.1817(7)
<i>c</i> , Å	13.4445(4)
$\alpha$ , deg	90
$\beta$ , deg	90
$\gamma$ , deg	90
<i>V</i> , Å <sup>3</sup>	2198.33(11)
<i>Z</i>	4
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.983
$\mu$ , cm <sup>-1</sup>	14.461
<i>F</i> (000)	1272
2 $\theta_{\max}$ , deg	130.81
no. obsd. data	1872
no. unique data	1606
GOF	1.191
for $I > 2\sigma(I)$	
no. variables	155
<i>R</i> (for all data) <sup>a</sup>	0.0517
<i>R<sub>w</sub></i> (for all data) <sup>b</sup>	0.0968
residual $\rho$ , e Å <sup>-3</sup>	1.364, -2.386

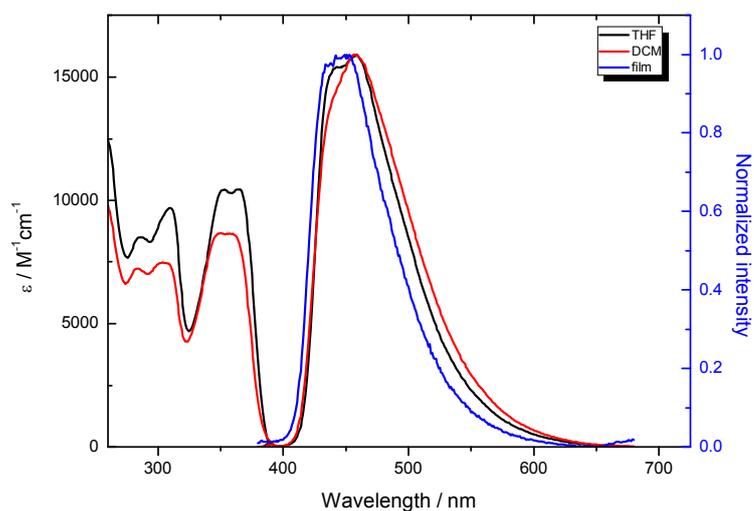
<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ .

## Photophysical Properties

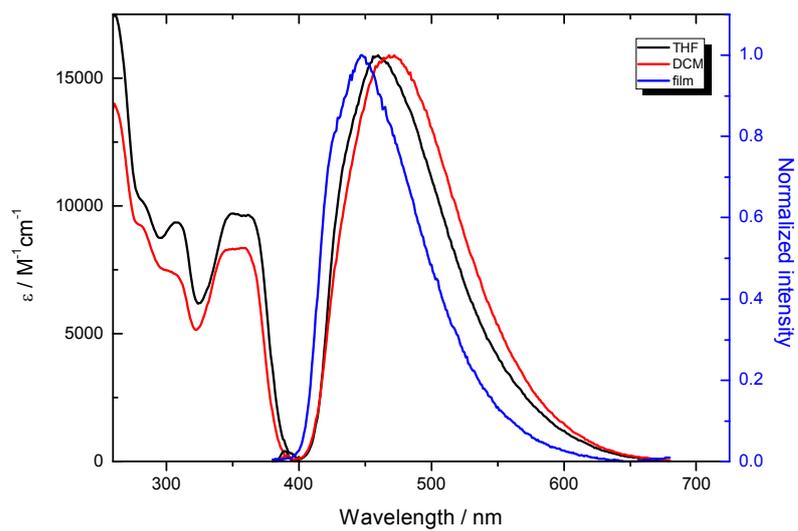
Thin films for photoluminescence studies were obtained by drop-casting a solution of PMMA containing complexes (1 wt%) in dichloromethane/DMF (9:1, v/v) onto a quartz plate. Upon drying with air flow gently, uniform films were obtained. The spectra depict the complex's absorption (left) and room temperature photoluminescence (right) in degassed THF/DMF (19:1, v/v) (black line) solution and DCM/DMF (19:1, v/v) (red line, except for complex 4) (concentration  $\sim 2.0 \times 10^{-5}$  M) and photoluminescence of thin film (blue line) doped with 1 wt% complex at ambient conditions.



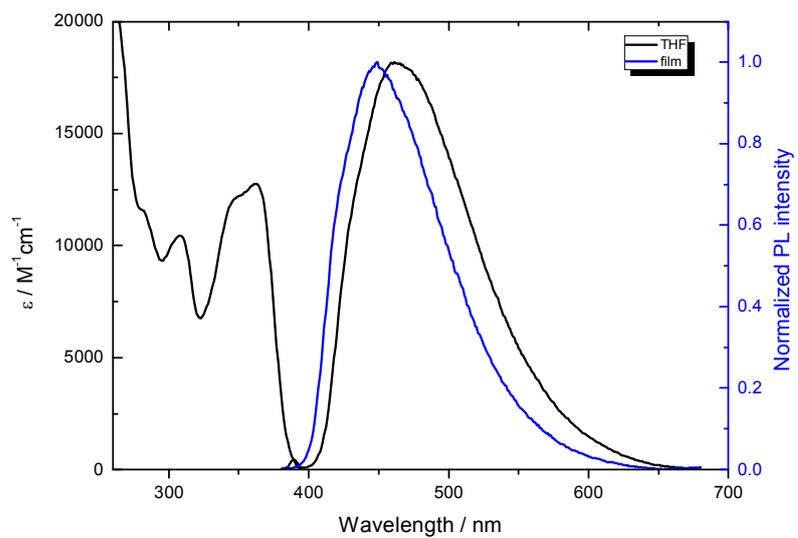
Complex 1



Complex 2



Complex 3



Complex 4

## Computational Method

DFT and TD-DFT calculations on complex **3** were carried out using PBE0 method<sup>3</sup> with basis set of 6-31+G\* for C, H, O, N atoms and pseudopotential Stuttgart/Dresden (SDD)<sup>4</sup> basis set for Pt atom. Geometry optimization of ground state ( $S_0$ ) and the lowest excited triplet state ( $T_1$ ) were firstly performed. TD-DFT calculations based on these optimized geometries were then performed for gaining insight into frontier orbitals involved in the  $S_1 \leftarrow S_0$  and  $T_1 \rightarrow S_0$  transitions. Gaussian 03<sup>5</sup> package was used for all calculation.

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<sup>3</sup> J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

<sup>4</sup> M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1987, **86**, 866–872; D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123–141.

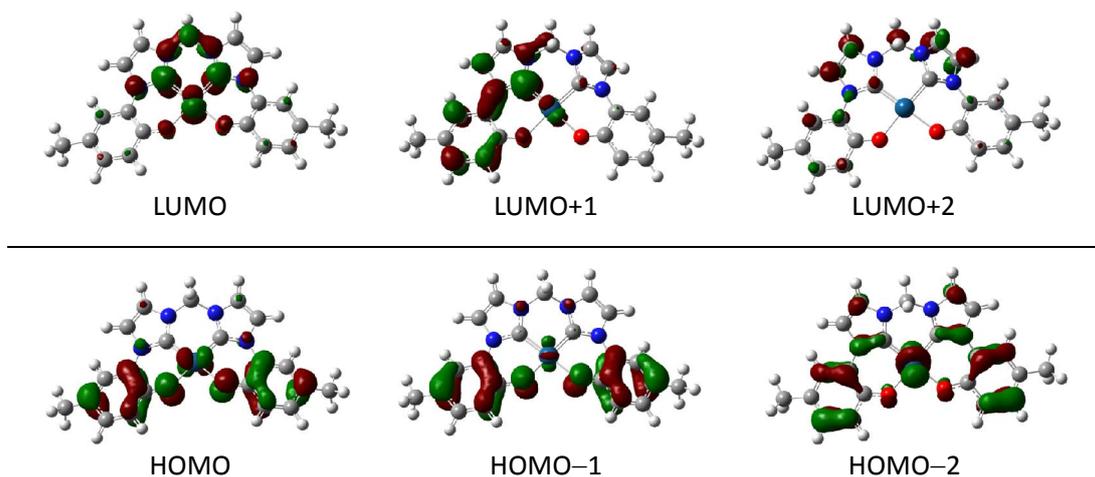
<sup>5</sup> Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

**Table S2** Comparison of structures data of optimized ground state geometry and single-crystal structure of complex **3**

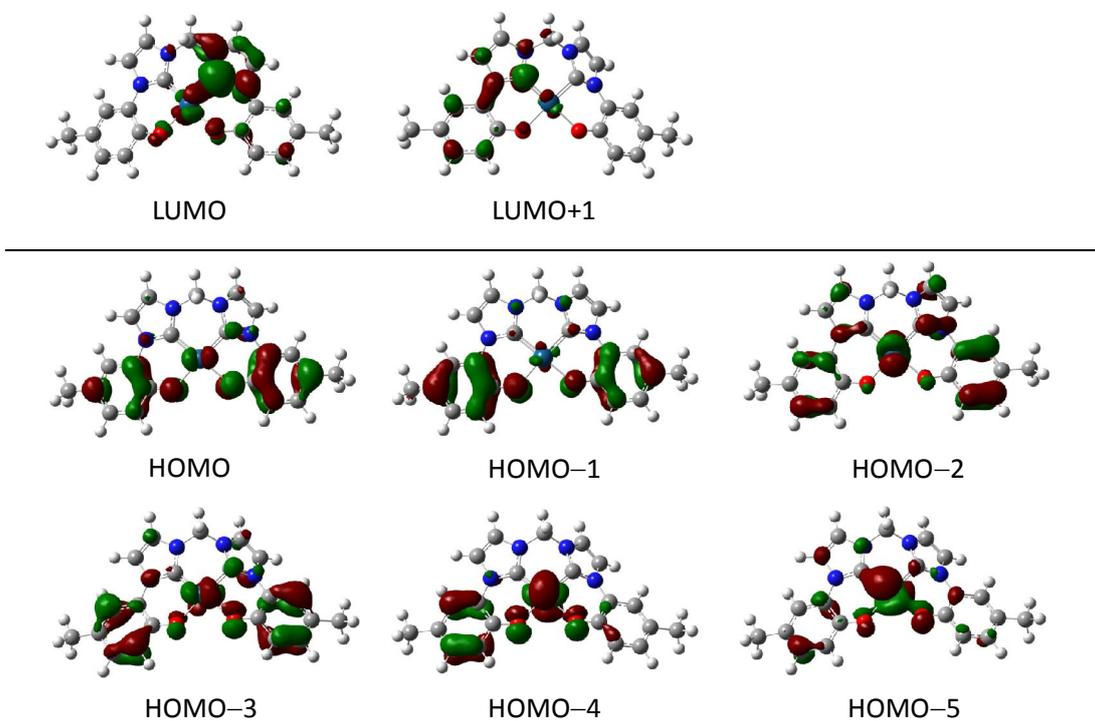
Selected parameters	Optimized	Single-crystal
Pt–O distances	2.042 Å	2.053(5) Å
Pt–C(NHC) distances	1.926 Å	1.933(8) Å
C–Pt–C angles	91.72 Å	91.5(4) <sup>o</sup>
C–Pt–O angles	89.50 <sup>o</sup> / 89.56 <sup>o</sup>	90.3(3) <sup>o</sup>
O–Pt–O angles	89.18 <sup>o</sup>	87.8(3) <sup>o</sup>

**Table S3** Calculated transition energies of complex **3** at optimized S<sub>0</sub> and T<sub>1</sub> geometries

Transition	$\lambda_{\max}$ (f)	Assignments
S <sub>0</sub> →S <sub>1</sub>	351.38 nm (0.0599)	HOMO→LUMO+1 (88%)
S <sub>0</sub> →S <sub>2</sub>	334.62 nm (0.0006)	HOMO–1→LUMO (90%)
S <sub>0</sub> →S <sub>3</sub>	329.18 nm (0.0507)	HOMO–1→LUMO+1 (85%) HOMO→LUMO+2 (4%)
S <sub>0</sub> →S <sub>4</sub>	314.65 nm (0.0041)	HOMO–1→LUMO+2 (32%) HOMO→LUMO+4 (57%)
S <sub>0</sub> →S <sub>5</sub>	304.36 nm (0.0343)	HOMO–1→LUMO+1 (85%) HOMO→LUMO+2 (4%)
S <sub>0</sub> →S <sub>6</sub>	304.03 nm (0.0876)	HOMO–1→LUMO+2 (32%) HOMO→LUMO+4 (57%)
T <sub>3</sub> →S <sub>0</sub>	421.19 nm (0.0)	HOMO–3→LUMO (11%) HOMO–2→LUMO (66%) HOMO→LUMO (5%)
T <sub>2</sub> →S <sub>0</sub>	437.49 nm (0.0)	HOMO–2→LUMO (4%) HOMO→LUMO+1 (63%) HOMO–1→LUMO+1 (23%) HOMO→LUMO+2 (6%) HOMO–1→LUMO+2 (4%)
T <sub>1</sub> →S <sub>0</sub>	493.23 nm(0.0)	HOMO–1→LUMO (89%) HOMO→LUMO (5%)



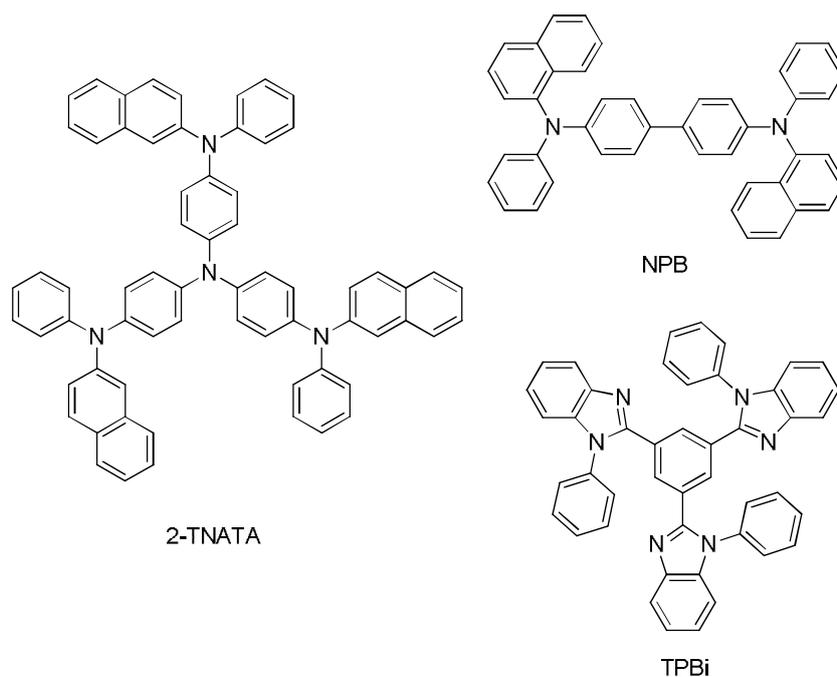
**Figure S2** Frontier orbitals mainly involved in the low-lying transitions of complex **3** based on the structurally optimized geometry in the lowest-lying single state.



**Figure S3** Frontier orbitals mainly involved in the low-lying transitions of complex **3** based on the structurally optimized geometry in the lowest-lying triplet state.

## Device Fabrication and Measurement

Complex **3** was used as phosphorescent dopant in fabricating blue OLEDs. The device configuration is ITO / 2-TNATA (40 nm) / NPB (20 nm) / DP4-Pt 3% (30 nm) / TPBi (40 nm) / LiF (0.5 nm) / Al (100 nm). 2-TNATA, NPB and TPBi were used as hole-injection layer (HIL), hole-transporting layer (HTL) and electron-transporting layer (ETL), respectively. The host DP4 was obtained from Aglaia Tech. Beijing, China, and its chemical structure cannot be revealed due to patent consideration. All materials were thermal-deposited in high vacuum in succession without breaking the vacuum. After finishing the whole deposition, the device was encapsulated with glass cap and tested at ambient conditions. The electroluminescence was recorded by a PR650-spectrometer and K2400 as the voltage source.



### Complex 1

