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Synthesis of cyclometalated platinum(II) complexes with benzoayrl-pyridines

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<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic procedure of the organic compound and EL results for the devices except for the optimized ones.

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### ABSTRACT

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series of (C^N)Pt(acac)-type complexes have been successfully synthesized with benzo[b]furan, benzo[b]thiophene, benzo[b]selenophene and benzo[b]tellurophene groups in their benzoayrl-pyridine ligands, respectively. With X-ray crystallography, the chemical structures for the complexes with benzo[b]selenophene and benzo[b]tellurophene groups have been clearly revealed. Photophysical, electrochemical and electroluminescent (EL) behaviors of these (C^N)Pt(acac)-type complexes have been fully characterized. Furthermore, both time-dependent functional theory (TD-DFT) and natural transition orbital (NTO) theoretical results have been obtained to gain insight into their absorption and emission features. It has been shown that both their absorption bands with the lowest energy and phosphorescent emission behaviors are dominated by their benzoayrl-pyridine cyclometalating ligand. Importantly, the effect of the atoms in group VIA on the properties of these (C^N)Pt(acac)-type complexes has been revealed. Owing to the rareness of the (C^N)Pt(acac)-type complexes with benzo[b]selenophene and benzo[b]tellurophene groups, their EL abilities have been characterized by solution-processed organic light-emitting diodes (OLEDs). The optimized red OLEDs with complex bearing benzo[b]selenophene unit can show maximum external quantum efficiency ( $\eta_{ext}$ ) of 6.3%, current efficiency ( $\eta_{L}$ ) of 10.5 cd A<sup>-1</sup> and power efficiency ( $\eta_{P}$ ) of 9.1 Im  $W^{-1}$ , while the EL device with complex bearing benzo[b]tellurophene unit can give deep-red emission at *ca*. 636 nm with  $\eta_{ext}$  of 6.3%,  $\eta_{L}$  of 6.5 cd A<sup>-1</sup> and  $\eta_{P}$  of 5.8 lm W<sup>-1</sup>. This research not only provides novel (C^N)Pt(acac)-type complexes, but also furnishes critical information for the photophysical and EL behavior of these new complexes.

Generally, Pt(II) complexes with C^N-type ligands can exhibit strong phosphorescent emission,<sup>1</sup> which furnishes their crucial application in various fields, such as sensors,<sup>2</sup> photosensitizers,<sup>3</sup> photooxidants,<sup>4</sup> bioimaging<sup>5</sup> and electroluminescent (EL) emitters<sup>6-10</sup> *etc.* It had been observed that the nature of their phosphorescent emission can be affected by the cyclometalating C^N-type ligand strongly through modifying their C^N-type ligand with electron-donating and -withdrawing substituents.<sup>11</sup> Hence, in the C^N-type ligands, more polarizable atoms such as sulfur and nitrogen can significantly influence the features of phosphorescent emission from the (C^N)Pt(acac)-type complexes.<sup>12</sup> For the atoms in group VIA, oxygen and sulfur are frequently incorporated into the C^N-type ligands to develop phosphorescent (C^N)Pt(acac)-type complexes, showing high EL efficiencies.<sup>12</sup> More importantly, sulfur-containing groups can be converted into sulfonyl groups, which can offer electron injection/transporting (EI/ET) ability to the phosphorescent (C^N)Pt(acac)-type complexes bearing these groups.<sup>12</sup> Clearly, the atoms in group VIA can show great potential in tuning and optimizing properties of the (C^N)Pt(acac)-type complexes.

However, introducing oxygen and sulfur atoms to the C^N-type ligands is more prevail. For example, benzo[*b*]furan,<sup>13, 14</sup> dibenzo[*b*]furan,<sup>15, 16</sup> thiophene,<sup>17, 18</sup> benzo[*b*]thiophen,<sup>19, 20</sup> dibenzo[*b*]thiophene,<sup>21</sup> oxazole,<sup>22</sup> benzo[*b*]oxazole,<sup>23</sup> thiazole<sup>24, 25</sup> and benzo[*b*]thiazole<sup>26, 27</sup> moieties have been employed as building blocks for constructing the C^N-type ligands. However, groups containing selenium and tellurium atoms have been rarely adopted to synthesize phosphorescent emitters. One C^N-type Ir(III) complex with selenophene group had been prepared.<sup>28</sup> Recently, we have synthesized a series of unsymmetrical phosphorescent Ir(III) complexes with selenophene as well as aryl selenide groups to show high EL efficiencies.<sup>29</sup>

Arsenvan et al. reported two (C^N)Pt(acac)-type complexes with benzoselenophenylpyridine ligands and characterized their photophysical and electroluminescent properties.<sup>30</sup> In addition, novel Ir(III) complexes with benzoselenophenylpyridine as C<sup>N</sup>-type ligand have also been synthesized with different auxiliary ligands by Arsenvan et al.<sup>31</sup> These phosphorescent emitter can furnish deep-red EL with nice efficiencies. All these encouraging results have indicated research interest in exploring potential of the atoms in group VIA for offering unique optoelectronic properties to the phosphorescent complexes. In view of the critical role played by the atoms in group VIA, systematical investigation their effect on the properties of the (C^N)Pt(acac)-type complexes should be very necessary. On this basis, a series of (C^N)Pt(acac)-type complexes bearing the benzoayrl-pyridine ligand with benzo[b]furan, benzo[b]thiophene, benzo[b]selenophene and benzo[b]tellurophene groups have been synthesized, respectively. In addition, their photophysical, thermal, electrochemical and EL properties have been studied in detail. Obviously, for the first time, the reported results should reveal an overall picture for the effect of the atoms in group VIA on the properties of the (C^N)Pt(acac)-type complexes.

# Experimental

### **General information**

Commercially available chemicals were used directly for synthesis without further purification. All solvents for the reactions were dried and distilled in a proper way. The reactions were monitored with thin layer chromatography (TLC) purchased from Merck & Co., Inc. Silica gel used for flash column chromatography and preparative TLC plates were purchased from Shenghai Qingdao (300-400 mesh).

### Physical measurements

### **Dalton Transactions**

 $^{1}$ H and  $^{13}$ C NMR spectra were measured in CDCl<sub>3</sub> solvent with a Bruker AXS 400MHz<sub>3</sub> MDR<sub>02224A</sub> spectrometer. Chemical shifts were quoted to the solvent residual peak at  $\delta$  7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C NMR spectra, respectively. UV-vis spectra were recorded with a PerkinElmer 950 spectrophotometer. The photoluminescent (PL) properties Lambda of these (C^N)Pt(acac)-type complexes were measured with an Edinburgh Instruments FLS920 fluorescence spectrophotometer. The lifetimes for the excited states were measured by a single photon counting spectrometer from Edinburgh Instruments FLS920 with a 360 nm picosecond LED lamp as the excitation source. The phosphorescent quantum yields ( $\Phi_P$ ) were determined in CH<sub>2</sub>Cl<sub>2</sub> solutions at 293 K against *fac*-[Ir(ppy)<sub>3</sub>] ( $\Phi_P = 97\%$ ).<sup>32</sup> The absolute  $\Phi_P$  data for the doped TCTA (4,4',4"-tri(9-carbazoyl)triphenylamine) films were measured with an integrated sphere on Edinburgh Instruments FLS920 spectrometer. The differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were acquired on a NETZSCH DSC 200 PC unit and a NETZSCH STA 409C instrument, respectively. Cyclic voltammetry (CV) were conducted with a Princeton Applied Research model 273A at a 100 mV s<sup>-1</sup> scan rate. All the CV experiments were conducted with a three-electrode compartment cell possessing a Pt-sheet counter electrode, a glassy carbon working electrode and an Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M acetonitrile solution of [*n*Bu<sub>4</sub>N]BF<sub>4</sub> with ferrocene as internal reference. The data of elemental analyses were obtained on a Flash EA 1112 elemental analyzer. Mass spectrometry data were obtained on a Waters I-class Vion IMS QTof micro-spectrometer.

# **Computational details**

DFT calculations were conducted with B3LYP method for all these (C^N)Pt(acac)-type complexes. The 6-31G (d, p) basis set was applied for C, H, N, O, S, Se and Te atoms, while effective core potentials employed for Pt atoms were a LanL2DZ basis set.<sup>33, 34</sup> Excitation

Dalton Transactions Accepted Manuscript

behaviors were acquired by the TD-DFT calculation on the basis of the optimized ground/state) geometries. Additionally, the natural transition orbital (NTO) based on the first triplet state (T<sub>1</sub>) geometries optimized by UB3LYP was analyzed for  $S_0 \rightarrow T_1$  excitation. All the calculations were performed using the *Gaussian 09* program.<sup>35</sup>

X-ray crystallography. Single crystals of Platinum(II) (2-2'-(4',5'-benzo)selenophenyl)pyridinato- $N,C^{3'}$ ) (2,4-pentanedionato-*O*,*O*) (Pt-Se) and Platinum(II) (2-2'-(4',5'-benzo)tellurophenyl)pyridinato-N,C<sup>3'</sup>) (2,4-pentanedionato-O,O) (Pt-Te) that were suitable for X-Ray diffraction studies were successfully grown through slow diffusion of hexane into their chloroform solutions. Single crystal data were collected on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073$  Å) in  $\Phi$  and  $\omega$  scan modes at 293 K. The molecular structure was solved by direct methods followed by difference Fourier syntheses and then refined by full-matrix least-squares techniques against  $F^2$  using SHELXL-97 program.<sup>36</sup> The positions of hydrogen atoms were calculated and refined isotopically using a riding model. All other non-hydrogen atoms were refined isotopically. Absorption corrections were applied using SADABS.<sup>37</sup>

### Synthesis

Synthetic details for ((2-bromophenyl)ethynyl)trimethylsilane (1), 2-(trimethylsilylethynyl)pyridine (5), 2-ethynylpyridine (6) 2-(benzo[*b*]furan-2-yl)pyridine (L-O) and 2-(benzo[*b*]thiophen-2-yl)pyridine (L-S) are provided in the Electronic Supplementary Information (ESI).

(*Z*)-(1-bromo-2-(2-bromophenyl)vinyl)trimethylsilane (2). Diisobutylaluminum hydride (DIBAL-H) (1.00 M in hexane, 13.0 mL, 13.0 mmol) was added dropwise with stirring to a solution of ((2-bromophenyl)ethynyl)trimethylsilane (1) (3.00 g, 11.9 mmol) in hexane (40.0

mL) under a nitrogen atmosphere at room temperature. After stirring for overnight NBS ( $2^{12}$   $2^{1$ 

2-(trimethylsilyl)benzo[b]selenophene (3). Under  $N_2$ atmosphere, а (Z)-(1-bromo-2-(2-bromophenyl)vinyl)trimethylsilane (2) (3.00 g, 9.04 mmol) was dissolved in t-Butyl methyl ether (30 mL), then n-BuLi (2.50 M in hexane, 9.00 mL, 21.7 mmol) was added dropwise at 0 °C. The mixture was warned to room temperature and stirred for 2 h. Then, at 0 °C, selenium powder (0.86 g, 10.8 mmol) was added slowly. The reaction mixture was warned to room temperature and stirred for overnight. Water (10.0 mL) was added and extracted with  $CH_2Cl_2$  (3 × 20.0 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated in vacuo. The residue was chromatographed on a silica column using petroleum ether as the eluent to give **3** as oily liquid (2.07 g, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.94 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.74 (s, 1H), 7.52 (td, J = 7.4, 1.2 Hz, 1H), 7.25 (td, J = 7.4, 1.2 Hz, 1H), 0.37 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 147.19, 144.50, 143.73, 134.51, 125.44, 125.22, 124.32, 124.29, 0.01; FAB-MS (m/z): 254 [M]+; Anal. Calcd for C<sub>11</sub>H<sub>14</sub>SeSi: C, 52.16; H, 5.57; found: C, 52.07; H, 5.51%.

2-bromobenzo[b]selenophene (4). To a solution of 2-(trimethylsilyl)benzo[b]selenophene (3)

(1.00 g, 3.94 mmol) in chloroform (20.0 mL), NBS (0.700 g, 3.94 mmol) was added. at From 2224A temperature and stirred for 3 h. Water (20.0 mL) was added to the solution and the solution was extracted with dichloromethane (3 × 10.0 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with petroleum ether as the eluent to give **4** as white solid (0.820 g, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.76 (d, *J* = 8 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.53 (s, 1H), 7.34-7.24 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ (ppm) 141.0, 139.6, 126.6, 124.7, 124.5, 122.7, 121.6, 115.4; FAB-MS (m/z): 260, 262 [M]<sup>+</sup>; Anal. Calcd for C<sub>8</sub>H<sub>5</sub>BrSe: C, 36.96; H, 1.94; found: C, 36.88; H, 1.89%.

2-(Benzo[b]selenophen-2-yl)pyridine (L-Se). Under nitrogen atmosphere, а 2-bromobenzo[b]selenophene (4) (0.20 g, 0.77 mmol), 2-(tributylstannyl)pyridine (0.34 g, 0.92 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.03 mmol) were added to degassed toluene (15 mL). The reaction mixture was heated to 110 °C and stirred for 16 h. After cooling to room temperature, the mixture was extracted with  $CH_2Cl_2$  (3  $\times$  30 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:15, v/v) as the eluent. The product was obtained as a white solid (0.17 g, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.59 (ddd, J = 4.9, 1.6, 1.0 Hz, 1H), 8.01 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.82-7.80 (m, 2H), 7.72 (td, J = 7.4, 1.6 Hz, 1H), 7.36 (td, J = 7.5, 1.2 Hz, 1H), 7.28 (td, J = 7.6, 1.2 Hz, 1H), 7.20 (ddd, J = 7.4, 4.9, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 153.81, 149.66, 148.88, 143.23, 142.00, 136.52, 125.89, 125.70, 125.11, 124.72, 124.12, 122.58, 118.61.; FAB-MS (m/z): 259 [M]<sup>+</sup>; Anal. Calcd for C<sub>13</sub>H<sub>9</sub>NSe: C, 60.48; H, 3.51; N, 5.43 found: C, 60.36; H, 3.43; N, 5.33%.

### **Dalton Transactions**

**2-((2-bromophenyl)ethynyl)pyridine (7)**. Under a N<sub>2</sub> atmosphere, 1-bromo-2<sub>3</sub>iodobeitZeBC<sub>2224A</sub> (2.00 g, 7.07 mmol), 2-ethynylpyridine (6) (0.66 g, 6.36 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (50 mg, 0.07 mmol) and copper(I) iodide (27 mg, 0.14 mmol) were mixed in triethylamine (50 mL) and the reaction mixture was left with stirring overnight at room temperature. Then the residue of the solvent was filtered and the filtrate was removed under vacuum. The crude product was purified by column chromatography using petroleum ether as the eluent to obtain the product as pale-yellow oil (1.62 g, 99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.63 (d, J = 4.4 Hz, 1H), 7.68 (td, J = 7.7, 1.5 Hz, 1H), 7.63-7.57 (m, 3H), 7.29 (td, J = 7.6, 1.0 Hz, 1H), 7.25-7.18 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 150.3, 143.3, 136.3, 133.9, 132.6, 130.2, 127.7, 127.2, 126.0, 124.6, 123.2, 92.9, 87.7; FAB-MS (m/z): 257, 259 [M]<sup>+</sup>; Anal. Calcd for C<sub>13</sub>H<sub>8</sub>BrN: C, 60.49; H, 3.12; N, 5.43 found: C, 60.41; H, 3.01; N, 5.36%.

**2-(Benzo[b]tellurophen-2-yl)pyridine (L-Te)**. Under a nitrogen atmosphere, tellurium powder (0.30 g, 2.35 mmol) and NaBH<sub>4</sub> (0.11 g, 2.82 mmol) were dissolved in degassed DMF (15 mL), then the mixture was heated to 100 °C and stirred for 0.5 h approximately until no more bubbles. At this point, the solution turned purple, indicating that NaTeH was generated. Then 2-((2-bromophenyl)ethynyl)pyridine (7) (0.50 g, 1.95 mmol) was added and stirred for overnight at 100 °C. After cooling to room temperature, the mixture was extracted with ethyl acetate (3 × 10 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. Then, the residue was purified by column chromatography over silica gel using ethyl acetate/petroleum ether (1:15, v/v) as the eluent. The product was obtained as a white solid (0.33 g, 55%).

**Dalton Transactions Accepted Manuscript** 

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 8.49 (ddd, J = 4.9, 1.4, 1.0 Hz, 1H), 8.32 (s, 1H), 7.93 (d, J = 8 Hz, 1H), 7.84-7.79 (m, 2H), 7.69 (td, J = 7.6, 1.6 Hz, 1H), 7.36 (td, J = 7.6, 1.0 Hz,

# General synthetic procedure for the (C^N)Pt(acac)-type complexes

Under a nitrogen atmosphere, ligands (1.1 equiv) and  $K_2PtCl_4$  (1.0 equiv) were added in a mixture of 2-ethoxyethanol and water (3:1, v/v). The mixture was heated to 80-90 °C and stirred for 16 h. Then the reaction mixture was cooled to room temperature, and water was added. The colored precipitate of dimer complex was collected by filtration and dried under vacuum. After that, *t*-BuOK (2.5 equiv) and acetylacetone (3.0 equiv) were added in dry CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 0.5 h under N<sub>2</sub> at room temperature. Then, the dimer complex was added and stirred for overnight. After evaporation of solvent, the crude product was chromatographed on a silica column with mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> to give a pure colored product.

Platinum(II) (2-2'-(4',5'-benzo)furanyl)pyridinato-*N*,*C*<sup>3'</sup>) (2,4-pentanedionato-*O*,*O*) (Pt-O). CH<sub>2</sub>Cl<sub>2</sub>:PE = 1:1(v/v); Yield: 22%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.86 (d, J = 6.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.73 (td, J = 7.8, 1.6 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 7.36-7.30 (m, 2H), 7.23 (td, J = 7.6, 0.8 Hz, 1H), 6.96 (t, J = 6.8 Hz, 1H), 5.54 (s, 1H), 2.06 (s, 3H), 2.03 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 184.90, 183.51, 159.47, 156.55, 156.52, 147.77, 138.85, 133.28, 125.36, 123.72, 122.77, 119.04, 116.56, 116.29, 111.09, 102.46, 28.09, 26.34; MS (m/z): 488 [M]<sup>+</sup>; Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>Pt: C, 44.27; H, 3.10; N, 2.87 found: C, 44.09; H, 2.93; N, 2.78%.

Platinum(II) (2-2'-(4',5'-benzo)thiophenyl)pyridinato- $N,C^{3'}$ ) (2,4-pentanedionato-O,O) (Pt-S). CH<sub>2</sub>Cl<sub>2</sub>:PE = 1:1(v/v); Yield: 21% <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.92 (d, J = 5.6 Hz, 1H), 8.81-8.78 (m, 1H), 7.82-7.80 (m, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.36-7.30 (m, 3H), 6.97

### **Dalton Transactions**

(t, J = 6.6 Hz, 1H), 5.56 (s, 1H), 2.10 (s, 3H), 2.03 (s, 3H); <sup>13</sup>C NMR (100 MHz): GDGFDDD2224A (ppm) 185.26, 183.42, 164.65, 146.94, 145.36, 142.28, 138.77, 138.69, 138.17, 126.65, 125.37, 124.14, 122.34, 118.84, 118.19, 102.57, 28.10, 26.42; MS (m/z): 504 [M]<sup>+</sup>; Anal. Calcd for  $C_{18}H_{15}NO_2PtS$ : C, 42.86; H, 3.00; N, 2.78 found: C, 42.76; H, 2.89; N, 2.71%.

Platinum(II) (2-2'-(4',5'-benzo)selenophenyl)pyridinato-*N*,*C*<sup>3</sup>) (2,4-pentanedionato-*O*,*O*) (Pt-Se). CH<sub>2</sub>Cl<sub>2</sub>:PE = 1:1(v/v); Yield: 20%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.97 (dd, J = 8.0, 0.8 Hz, 1H), 8.92 (dd, J = 6.0, 0.6 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.71 (td, J = 7.8, 1.5 Hz, 1H), 7.36 (td, J = 7.6, 1.1 Hz), 7.29-7.23 (m, 2H), 6.95 (t, J = 6.6 Hz, 1H), 5.56 (s, 1H), 2.09 (s, 3H), 2.03 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 185.27, 183.34, 166.52, 148.16, 146.44, 143.74, 142.43, 138.81, 137.63, 128.44, 125.51, 125.33, 124.58, 118.99, 118.59, 102.59, 28.08, 26.46; MS (m/z): 551 [M]<sup>+</sup>; Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>PtSe: C, 39.21; H, 2.74; N, 2.54 found: C, 39.11; H, 2.64; N, 2.43%.

Platinum(II) (2-2'-(4',5'-benzo)tellurophenyl)pyridinato-*N*,*C*<sup>3'</sup>) (2,4-pentanedionato-*O*,*O*) (Pt-Te). CH<sub>2</sub>Cl<sub>2</sub>:PE = 1:1(v/v); Yield: 18%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 9.20 (d, J = 8.0 Hz, 1H), 8.88 (d, J = 5.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.64 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.16-7.09 (m, 2H), 6.89 (t, J = 6.8 Hz, 1H), 5.54 (s, 1H), 2.07 (s, 3H), 2.00 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 185.28, 183.16, 170.51, 154.56, 151.96, 145.76, 138.77, 135.66, 131.70, 130.85, 127.57, 125.44, 125.25, 120.09, 118.14, 102.57, 28.04, 26.52; MS (m/z): 601 [M]<sup>+</sup>; Anal. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>PtTe: C, 36.03; H, 2.52; N, 2.33 found: C, 35.91; H, 2.41; N, 2.43%.

# **Results and discussion**

### Synthesis and structural characterization

The synthetic pathways for the C^N-type ligands are shown in Scheme 1. Ligands

2-(benzo[b]furan-2-yl)pyridine (L-O) and 2-(benzo[b]thiophen-2-yl)pyridine (L-S) were 3608H M02224A prepared through Suzuki cross-coupling reaction between 2-bromopyridine and the corresponding arylboronic acid in high yield of over 80% (ESI). However, the synthesis of 2-(benzo[b]selenophen-2-yl)pyridine (L-Se) was started with 1-bromo-2-iodobenzene, which was converted into ((2-bromophenyl)ethynyl)trimethylsilane (1) by Sonogashira cross-coupling reaction at room temperature. After reduction of (1) and followed by treating with NBS, the compound of (Z)-(1-bromo-2-(2-bromophenyl)vinyl)trimethylsilane (2) could be obtained. Through dilithiation in anhydrous *t*-Butyl methyl ether and subsequent addition of selenium powder, we obtained the compound of 2-(trimethylsilyl)benzo[b]selenophene (3), which was converted into 2-bromobenzo[b]selenophene (4) through treating with NBS. By Stille cross-coupling between 2-bromobenzo[b]selenophene (4) and 2-(tributylstannyl)pyridine with Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst, ligand 2-(benzo[b]selenophen-2-yl)pyridine (L-Se) could be successfully synthesized. With 2-bromopyridine as staring material, 2-ethynylpyridine (6) had been prepared in high yield of ca. 90% by Sonogashira cross-coupling reaction followed by removing trimethylsilyl group in methanol with presence of KOH. Again, with Sonogashira cross-coupling reaction between 2-ethynylpyridine (6) and 1-bromo-2-iodobenzene, compound 2-((2-bromophenyl)ethynyl)pyridine (7) was synthesized with a very high yield of ca. 99%. Finally, ligand 2-(benzo[b]tellurophen-2-yl)pyridine (L-Te) has been synthesized by the treatment of compound 7 with NaTeH formed in suit by reduction tellurium powder with NaBH<sub>4</sub>.



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Scheme 1. Synthetic scheme for the organic ligands.

After obtaining all the four C^N-type ligands, the (C^N)Pt(acac)-type complexes had been synthesized by the typical two-step procedure. Firstly, metalation of the corresponding cyclometalating ligand (L-O/L-S/L-Se/L-Te) with  $K_2PtCl_4$  gave the cyclometalated  $Pt^{II}$  $\mu$ -chloro-bridged dimers, which were then converted into the target (C^N)Pt(acac)-type complexes by reaction with potassium(I) acetylacetonate formed in-suit by treating

acetylacetone with *t*-BuOK. In the <sup>1</sup>H NMR spectra of the (C^N)Pt(acac)-type complex  $s_{p}^{View}$  disc online resonance signal peaked at *ca*. 9.0 ppm can be assigned to the proton attached to the aromatic carbon atom adjacent to the nitrogen atoms in pyridyl ring of the C^N-type ligands. The protons on the two methyl groups in the acetylacetone auxiliary ligands split into two sets of a single resonance peak with the chemical shifts at *ca*. 2.0 and 2.1 ppm, respectively.



Scheme 2. Synthetic scheme for the (C^N)Pt(acac)-type phosphorescent complexes.

**X-ray crystallography.** Structures of **Pt-Se** and **Pt-Te** have been investigated by single crystal X-ray crystallography. The ORTEP drawings have been shown in Figure 1 and the detailed structural data are summarized in Table 1 and 2. The molecules of both **Pt-Se** and **Pt-Te** pack in the space to form the crystal system of monoclinic with space group of P2(1)/c. The complex molecules adopt a slightly distorted square planar geometry with *cis*-O<sup>O</sup>O and *cis*-N<sup>O</sup>C chelating disposition (Figure 1).



**Fig. 1** ORTEP drawings of (a) **Pt-Se** and (b) **Pt-Te** with thermal ellipsoids drawn at the 10% probability level. The H atoms are omitted for clarity.

compound	Pt-Se	Pt-Te	
CCDC No.	1918815	1918816	
formula	C <sub>18</sub> H <sub>15</sub> NO <sub>2</sub> PtSe	$C_{18}H_{15}NO_2PtTe$	
Formula weight	551.36	600.00	
Crystal system	monoclinic	monoclinic	
Space group	P2(1)/c	P2(1)/c	
<i>a</i> (Å)	19.364 (4)	19.507 (5)	
<i>b</i> (Å)	11.864 (3)	12.005 (3)	
<i>c</i> (Å)	14.588 (3)	14.592 (4)	
$\alpha$ (deg)	90	90	
$\beta$ (deg)	104.857 (3)	103.877 (3)	
$\gamma(\text{deg})$	90	90	
$V(Å^3)$	3239.3 (12)	3317.4 (15)	
Ζ	8	8	
$D_{calcd}$ (g cm <sup>-3</sup> )	2.261	2.403	
F(000)	2064	2208	
μ (mm <sup>-1</sup> )	10.919	10.191	
$\theta$ range (deg)	4.352-50	4.018-51.23	
diffrn reflns number	22371	19311	
reflns number total	5636	6187	
no. of parameter	419	419	
<i>R</i> 1, <i>wR</i> 2 [ $I > 2.0\sigma(I)$ ] <sup><i>a</i></sup>	0.0247, 0.0559	0.0314, 0.0750	
R1, wR2 (all data)	0.0343, 0.0604	0.0428, 0.0809	
GOF on $F^{2 b}$	1.036	1.033	

Table 1. Crystal and data parameters for structures Pt-Se and Pt-Te.

 ${}^{a}R1 = \Sigma ||F_{0}| - |F_{c}|| / \Sigma |F_{0}|. wR2 = \{ \Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{0}^{2})^{2}] \}^{1/2}. {}^{b} \text{GOF} = [(\Sigma w |F_{0}| - |F_{c}|)^{2} / (N_{\text{obs}} - N_{\text{param}})]^{1/2}.$ 

**Dalton Transactions Accepted Manuscript** 

In both **Pt-Se** and **Pt-Te**, the bond length of Pt1-O1 is longer than that of Pt1-O2 due to the stronger *trans*-effect of the coordinated carbon atom than that of nitrogen atom (Table 2). The bond angle of O-Pt-C in **Pt-Se** and **Pt-Te** is 173.73(18)° and 171.1(2)°, respectively, which that for O-Pt-N is 176.60(17)° for **Pt-Se** and 178.4(2)° for **Pt-Te** (Table 2). The O-Pt-O bond angle in **Pt-Se** and **Pt-Te** is *ca*. 91°, while that of N-Pt-C is about 82° (Table 2). The two C-Se bonds in benzo[*b*]selenophene possess unit bond length of 1.892(6) and 1.898(6) Å, respectively, which are shorter than that of the typical C-Se bond (*ca*. 1.90-1.93 Å).<sup>29</sup> Similarly, the two C-Te bonds (2.088(6) and 2.084(6) Å, respectively) in benzo[*b*]tellurophene unit are shorter than the typical C-Te bond (*ca*. 2.1-2.2 Å) as well.<sup>38</sup> These results should indicate the conjugation effect between Se/Te atom with the two bonded *sp*<sup>2</sup> carbon atoms to form fused aromatic systems

compound	Pt-Se		Pt-Te	
	Pt1-O1	2.079(4)	Pt1-O1	2.071(5)
	Pt1-O2	2.000(3)	Pt1-O2	2.018(4)
bond lengths (Å)	Pt1-N1	2.002(4)	Pt1-N1	1.993(5)
	Pt1-C12	1.980(6)	Pt1-C7	2.004(7)
	Se1-C11	1.892(6)	Te1-C6	2.088(6)
	Se1-C18	1.898(6)	Te1-C13	2.084(6)
	O1-Pt1-O2	91.16(15)	O1-Pt1-O2	91.31(19)
	O1-Pt1-N1	92.12(17)	O1-Pt1-N1	90.3(2)
	O1-Pt1-C12	173.73(18)	O1-Pt1-C7	171.1(2)
angles (°)	O2-Pt1-N1	176.60(17)	O2-Pt1-N1	178.4(2)
	O2-Pt1-C12	95.09(18)	O2-Pt1-C7	96.6(2)
	N1-Pt1-C12	81.6(2)	N1-Pt1-C7	81.8(2)
	C11-Se1-C18	85.5(3)	C6-Te1-C13	80.1(3)

Table 2. Selected structural parameters of Pt-Se and Pt-Te.

Thermal and photophysical properties. Under a nitrogen flow, both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) had been employed to characterize

the thermal properties of these (C^N)Pt(acac)-type complexes. All four complexes shows good 2224A thermal stability with their 5% weight-reduction temperature ( $\Delta T_{5\%}$ ) ranging from 250 to 296 °C (Table 3). Clearly, **Pt-Te** possesses the lowest  $\Delta T_{5\%}$ , which might be assigned to the weak C–Te bonds due to the large radius of tellurium atom. The DSC traces reveal a high glass transition temperature ( $T_g$ ) > 120 °C for these (C^N)Pt(acac)-type complexes, which should be attributed to the rigid configuration of their coordination skeleton. The thermal properties of these (C^N)Pt(acac)-type complexes are sufficient for the fabrication of OLEDs with a solution-process technique.

	Absorption (293K) <sup><i>a</i></sup> $\lambda_{abs}$ (nm)	Emission $\lambda_{em}^{a}$ (nm) solution/film <sup>b</sup>	$\Phi_{ m P}(\%)$ solution/film <sup>c</sup>	τ <sup>d</sup> (μs) 293 K/77 K	$\Delta T_{5\%}^{e}$ (°C)	$T_g{}^f$
Pt-O	234(3.21), 259(3.29), 322(3.25), 429(2.82), 441(2.81)	497, 616, 672 /616, 674	7.3/11.1	4.6 ns(497), 0.46 μs(616) /2.06 μs(625)	260	126
Pt-S	235(3.39), 267(3.29), 320(3.28), 428(2.81), 445(2.81)	508, 612, 659 /611, 664	9.1/13.6	3.5 ns(508), 0.34 μs(612) /3.38 μs(622)	281	131
Pt-Se	232(3.42), 271(3.24), 323(3.28), 352(3.08), 431(2.80), 446(2.81)	503, 620, 671 /621, 676	8.3/12.1	3.1 ns(503), 0.40 μs(620) /2.21 μs(631)	296	133
Pt-Te	236(3.51), 258(3.31), 279(3.22), 330(3.24), 364(3.00), 383(2.96), 437(2.77), 457(2.81)	514, 634, 687 /634, 690	5.1/7.4	6.6 ns(514), 0.40 μs(634) /0.97 μs(651)	250	122

Table 3. Photophysical and thermal data of these (C^N)Pt(acac)-type complexes.

<sup>*a*</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> at 10<sup>-5</sup> M and log  $\varepsilon$  values are shown in parentheses. <sup>*b*</sup> Measured in 6 wt% doped PMMA film. <sup>*c*</sup>Measured in a degassed CH<sub>2</sub>Cl<sub>2</sub> solution relative to *fac*-[Ir(ppy)<sub>3</sub>] ( $\Phi_P = 97\%$ ) for the solution and the 8 wt% doped film of TCTA with an integrated sphere. <sup>*d*</sup> Recorded in a degassed CH<sub>2</sub>Cl<sub>2</sub> solution with a 360 nm light source and the wavelengths in parentheses. <sup>*e*</sup>  $\Delta T_{5\%}$  is measured under N<sub>2</sub> flow with a heating rate of 20 K min<sup>-1</sup>. <sup>*f*</sup>Glass transition temperature ( $T_{\varepsilon}$ ) is measured under N<sub>2</sub> flow with a heating rate of 10 K min<sup>-1</sup>.

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Fig. 2 UV-vis absorption spectra for these (C^N)Pt(acac)-type complexes in CH<sub>2</sub>Cl<sub>2</sub> at 293 K.

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Generally, two kinds of absorption bands have been detected in the in the UV-vis absorption spectra of these (C^N)Pt(acac)-type complexes (Figure 2). The intense absorption bands with high energy <400 nm can be safely assigned to the spin-allowed  $\pi \to \pi^*$  transitions of the aromatic segments in the cyclometalating ligands.<sup>11</sup> Clearly, From Pt-O to Pt-Te, all the intense absorption bands exhibit noticeable bathochromic effect (Figure 2 and Table 3). The much weaker absorption bands >400 nm were tentatively assigned to the excitation to both singlet and triplet charge transfer (CT) states.<sup>11</sup>

In order to get a deep insight into the features of the absorption behaviors of these (C^N)Pt(acac)-type complexes, the simulation of their UV-vis spectra (Figure 3) with discrete vertical vibronic transitions and the time-dependent density functional theory (TD-DFT) calculations have been carried out (Figure 4 and Table 4). Based on their optimized  $S_0$ geometries, the distribution patterns of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) mainly corresponding the key  $S_0 \rightarrow S_1$  transition have been shown in Figure 4. As shown in Figure 3, the good resemblance between simulated

### **Dalton Transactions**

and experimental UV-vis spectra in terms of both absorption wavelength and spectra: profile bas)2224A indicated the he validity of the calculation method. Clearly, from oxygen to tellurium, extra-nuclear electrons possess higher energy level to facilitate their contribution to the HOMOs (Figure 4). Hence, the contribution from the group VIA atom in the C^N-type ligand increases from oxygen to tellurium (4.4% for Pt-O, 14.2% for Pt-S, 18.6% for Pt-Se and 31.5% for Pt-Te) (Table 4). Based on their chemical properties, electron-donating ability will enhance from oxygen to tellurium. Obviously, the enhanced electron-donating ability should facilitate electron transition process in the concerned aromatic segments. Hence, the high-energy bands >400 nm corresponding to the electron transitions in the aromatic segments in the C^N-type ligands can show bathochromic effect from L-O to L-Te (Figure 2). Based on the calculation results in Figure 4, the low-energy absorption bands of these (C^N)Pt(acac)-type complexes should be induced mainly by the HOMO  $\rightarrow$  LUMO (H  $\rightarrow$  L) transition. According to the molecular orbital (MO) patterns in Figure 4, the low-energy absorption bands (> 400 nm) of these (C^N)Pt(acac)-type complexes should mainly show intraligand charge transfer (ILCT) feature from  $\pi$  orbitals of the fused-ring units to  $\pi^*$  orbitals of the pyridyl group in the C^N-type ligands. In addition, based on the contribution from the  $d_{\pi}$  orbitals to the front MOs, metal-to-ligand charge transfer (MLCT) can also account for the feature for the low-energy absorption bands of these (C^N)Pt(acac)-type complexes.



Fig. 3 Both simulated (black) and experimental (red) UV–vis absorption spectra with discrete vertical vibronic transitions for these (C^N)Pt(acac)-type complexes (H  $\rightarrow$  L: HOMO  $\rightarrow$  LUMO transition).



Fig. 4 Molecular orbital (MO) patterns for these (C^N)Pt(acac)-type complexes based on their optimized  $S_0$  geometries.

		Contrib	oution of	metal a	$l_{\pi}$ orbitals and $\pi$	Main configuration of $S_0 \rightarrow S_1$	Main configuration of $S_0 \rightarrow T_1$
Complexes	MO	orbitals of ligand to MOs (%)		excitation/ $E_{cal}/\lambda_{cal}/f^a$	excitation/ $E_{cal}/\lambda_{cal}$ <sup>a</sup>		
		Pt	LO	acac	0		
						H→L (93.2%)	H→L (91.9%)
Pt-O	L	7.4	91.6	1.0	1.6	2.945 eV	2.126 eV
						421 nm	583 nm
	Н	17.7	78.5	3.8	4.4	0.170	
		Pt	LS	acac	S		
						H→L (94.0%)	H→L (90.1%)
Pt-S	L	7.6	91.4	1.0	2.9	2.931 eV	2.134 eV
						423 nm	581 nm
	Н	17.1	79.0	3.8	14.2	0.139	
		Pt	LSe	acac	Se		
						H→L (94.2%)	H→L (89.1%)
Pt-Se	L	7.6	91.5	0.9	2.7	2.917 eV	2.108 eV
						425 nm	588 nm
	Н	16.3	80.1	3.6	18.6	0.140	
		Pt	LTe	acac	Те		
						H→L (95.5%)	H→L (85.1%)
Pt-Te	L	7.6	91.4	0.9	2.8	2.844 eV	2.073 eV
						436 nm	598 nm
	Н	13.7	83.5	2.8	31.5	0.120	

**Table 4.** TD-DFT results of these (C^N)Pt(acac)-type complexes on the basis of their optimized  $S_0$  geometries.

<sup>*a*</sup> H $\rightarrow$ L denotes transition from HOMO to LUMO.  $E_{cal}$ ,  $\lambda_{cal}$  and f denote calculated excitation energy, calculated emission wavelength and oscillator strength, respectively. The oscillator strength of S<sub>0</sub> $\rightarrow$ T<sub>1</sub> is zero owing to the spin-forbidden character of singlet-triplet transition under TD-DFT calculation in the Gaussian program with no consideration of spin-orbital coupling.

Photoluminescence (PL) spectra of these (C^N)Pt(acac)-type complexes at 293 K have been collected under excitation at 400 nm. All these complexes can obviously show two PL bands (Figure 5a). The high-energy PL bands centered at *ca*. 490 nm should be fluorescent signals indicated by their short lifetime in the order of nano-second (4.6 ns for **Pt-O**, 3.5 ns for **Pt-S**, 3.1 ns for **Pt-Se** and 6.6 ns for **Pt-Te**) (Table 3). This observation can be ascribed to the small contribution of the Pt(II) centers to the key front molecular orbitals of these (C^N)Pt(acac)-type complexes due to electron-rich and extended  $\pi$ -conjugation of the benzoaryl groups in the

C^N-type ligands.<sup>39, 40</sup> Accordingly, weak spin-orbital coupling (SOC) effect will be induced to 2224A bring too slow efficient inter-system crossing (ISC) process to complete eliminate fluorescent signals. On the contrary, long wavelength emissions in red-color region can be ascribed to the phosphorescent signals, substantiated by their much longer micro-second lifetimes ( $\tau_p$ ) which can be even prolonged at 77 K (Table 3). At both 293 K and 77 K, all four (C^N)Pt(acac)-type complexes show well-structured spectra profile for the phosphorescent bands (Figure 5).



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Fig. 5 PL spectra of these (C^N)Pt(acac)-type complexes at 293 K (a) and 77 K (b) in CH<sub>2</sub>Cl<sub>2</sub>.

With the aim to clearly elucidate the PL behaviors of these (C^N)Pt(acac)-type complexes,

### **Dalton Transactions**

the natural transition orbitals (NTOs) have been obtained based on the optimized  $T_{\Phi l}$  geometries 2224A for their  $S_0 \rightarrow T_1$  transition (Figure 6). Furthermore, contribution from different segments of these  $(C^N)Pt(acac)$ -type complexes to both NTO hole (H) and particle (P) orbitals have been list in Table 5 as well. The NTO patterns have indicated that both H and P orbitals are mainly located on the C<sup>N</sup>-type ligands of these (C<sup>N</sup>)Pt(acac)-type complexes with the contribution > 89% (Table 5). Accordingly, large percentage of  $H \rightarrow P$  transition over 90% should indicate their ligand-centered  $S_0 \rightarrow T_1$  transition with the feature of ILCT in the C^N-type ligand (Figure 6). Hence, the phosphorescent emission in these (C^N)Pt(acac)-type complexes should dominantly exhibit ligand-centered character, which has been indicated by their structured phosphorescent band at both 293 K and 77 K (Figure 5). Owing to their phosphorescent feature of ILCT from the  $\pi$  orbitals of the fused-ring unit to  $\pi^*$  orbitals of the pyridyl group in the C<sup>N</sup>-type ligands (Figure 6), the phosphorescent wavelengths of these (C<sup>N</sup>)Pt(acac)-type complexes from Pt-O to Pt-Te should show bathochromic effect due to the fact that the enhanced electron-donating ability from oxygen to tellurium will facilitate the ILCT process to lower its energy level.

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Fig. 6 Natural transition orbital (NTO) patterns for  $S_0 \rightarrow T_1$  excitation for these  $(C^N)Pt(acac)$ -type complexes based on their optimized T<sub>1</sub> geometries.

C 1	NTO	Contribution percenta	Contribution percentages of metal $d_{\pi}$ orbitals and $\pi$ orbitals of ligand to NTOs						
Complexes	а		(%)						
		Pt	LO	acac					
Pt-O	Н	9.3	89.2	1.4					
	Р	6.9	92.4	0.7					
		Pt	LS	acac					
Pt-S	Н	9.1	89.5	1.4					
	Р	7.1	92.1	0.8					
		Pt	LSe	acac					
Pt-Se	Н	8.6	90.2	1.3					
	Р	7.0	92.2	0.7					
		Pt	LTe	acac					
Pt-Te	Н	7.6	91.3	1.1					
	р	71	92.2	0.7					

**Table 5.** NTO results for these  $(C^N)Pt(acac)$ -type complexes based on their optimized  $T_1$ geo

<sup>a</sup> H and P denote NTO hole and particle orbital, respectively.

Out of expectation, the complex Pt-S does not follow this order, even showing hypochromic effect compared with Pt-O (612 nm for Pt-S vs. 616 nm for Pt-O) (Table 3 and Figure 5). In addition, this unexpected result has been predicted by the TD-DFT results as well (Table 4). From the UV-vis absorption spectra of these (C^N)Pt(acac)-type complexes (Figure 2), it seems

### **Dalton Transactions**

that Pt-S shows slight hypochromic effect in its absorption onset of the long-wavelength view rice Online absorption band with respect to that of other complexes. Reasonably, Pt-S will show phosphorescent emission with the shortest wavelength among all these  $(C^N)Pt(acac)$ -type complexes. This result can be interpreted as follows: As indicated by the NTO results, the phosphorescence of these (C^N)Pt(acac)-type complexes show ILCT feature of from the  $\pi$ orbitals of the fused-ring unit to  $\pi^*$  orbitals of the pyridyl group in the C^N-type ligands. Clearly, among furan, thiophene, selenophene and tellurophene, thiophene shows the highest aromaticity to furnish its higher stability and resistance to oxidation. Hence, benzo[b]thiophene unit should be more reluctant to be excited to transfer electrons to the pyridyl group in **Pt-S**. Accordingly, it will furnish ILCT states in slightly higher energy-level. As a result, Pt-S can show the shortest phosphorescent wavelength. For Pt-O, Pt-Se and Pt-Te, all the fused ring units show weaker aromaticity and energy-level of the ILCT process is mainly up to the electron-donating ability of the group VIA atoms. So, from Pt-O (ca. 616 nm) to Pt-Se (ca. 620 nm) and then to Pt-Te (ca. 634 nm), bathochromic effect can be clearly seen in their phosphorescent wavelength.

These (C^N)Pt(acac)-type complexes exhibit relatively low phosphorescent quantum yield  $(\Phi_{\rm P})$  in dilute solution (Table 3). In order to clarify this result, radiative constant  $(k_{\rm r})$  for each of these (C^N)Pt(acac)-type complexes has been obtained by theoretical calculation (Figure 7). Their  $k_{\rm r}$ s are in the order of *ca*. 10<sup>4</sup>, which is much lower than that associated with analogs. Hence, these (C^N)Pt(acac)-type complexes possess low  $\Phi_{\rm P} < 10\%$  (Table3). In Figure 7, it can be seen clearly that the order of  $k_{\rm r}$ s of these (C^N)Pt(acac)-type complexes follows **Pt-S** > **Pt-O** > **Pt-Te**, which is the same to the order of their  $\Phi_{\rm P}$ s. The experimental  $k_{\rm r}$ s of these (C^N)Pt(acac)-type complexes have been obtained by following the equations of  $1/\tau_{\rm p} = (k_{\rm r} + k_{\rm nr})$ 

Page 26 of 36

and  $\Phi_{\rm p} = k_{\rm r}/(k_{\rm r} + k_{\rm nr})$ , in which  $\tau_{\rm p}$  is phosphorescent lifetime at 293 K,  $k_{\rm r}$  is radiative constant. Despite higher than the theoretical data, the experimental  $k_{\rm r}$ s still fell in the same order of **Pt-S** (*ca.* 2.7 × 10<sup>5</sup> s<sup>-1</sup>) > **Pt-Se** (*ca.* 2.1 × 10<sup>5</sup> s<sup>-1</sup>) > **Pt-O** (*ca.* 1.6 × 10<sup>5</sup> s<sup>-1</sup>) > **Pt-Te** (*ca.* 1.3 × 10<sup>5</sup> s<sup>-1</sup>). So, there is a good consistency between experimental and theoretical results, indicating the validity of the theoretical calculations.



**Fig. 7** Calculated radiation constants ( $k_r$ s) and phosphorescent quantum yields ( $\Phi_P$ s) for these (C^N)Pt(acac)-type complexes.

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**Electrochemical Properties.** The electrochemical properties of these (C^N)Pt(acac)-type complexes had been characterized by cyclic voltammetry (CV) with ferrocene as the internal standard. In the anodic scan, all these (C^N)Pt(acac)-type complexes exhibit two irreversible oxidation processes (Table 6 and Figure S1). The first oxidation process should be induced by the oxidation of the electron-rich benzoayrl groups in the C^N-type ligands. Clearly, **Pt-S** can possess the highest first  $E_{pa}$  ca. 0.30 V (Table 6), which can be ascribed to the enhanced aromaticity associated with thiophene unit to restrain its oxidation. In addition, the first  $E_{pa}$  (ca. 0.16 V) for **Pt-Te** is lowest due to the easiness of oxidation of tellurium atom. The second  $E_{pa}$ s (ca. 0.5 V) of these (C^N)Pt(acac)-type complexes can be assigned to the oxidation of the Pt(II) centers in these complexes.<sup>12</sup> One reversible reduction process had been observed at ca. -2.0 V

for these (C^N)Pt(acac)-type complexes, which can be ascribed to the reduction of the pythemeo2224A rings in the C^N-type ligands (Table 6 and Figure S1).

	1 1			/ / /	
Complex	$E_{\mathrm{pa}}\left(\mathbf{V}\right)$	$E_{\rm pc}\left({ m V} ight)$	$E_{\rm g}({\rm eV})$	$E_{\rm HOMO}~({\rm eV})^{e}$	$E_{\text{LUMO}} (\text{eV})^f$
			$E_{\rm g}^{{\rm opt}c}/E_{\rm g}^{{\rm cv}d}$		
Pt-O	0.27 <sup><i>a</i></sup> , 0.45 <sup><i>a</i></sup>	-2.19 <sup>b</sup>	2.61/2.64	-5.25	-2.61
Pt-S	0.30 <sup><i>a</i></sup> , 0.46 <sup><i>a</i></sup>	-2.19 <sup>b</sup>	2.63/2.64	-5.26	-2.61
Pt-Se	0.28 <sup>a</sup> , 0.57 <sup>a</sup>	<b>-</b> 2.11 <sup>b</sup>	2.61/2.68	-5.37	-2.69
Pt-Te	0.16 <sup><i>a</i></sup> , 0.53 <sup><i>a</i></sup>	-1.95 <sup>b</sup>	2.56/2.48	-5.33	-2.85

**Table 6.** Redox properties of these (C^N)Pt(acac)-type complexes.

<sup>*a*</sup> Irreversible. The value was derived from the anodic peak potential. <sup>*b*</sup> Reversible. The value was set as  $E_{1/2}$ . <sup>*c*</sup>Optical energy gap was calculated from the absorption onset ( $\lambda_{onset}$ , the wavelength at the cross-point between absorption zero line and tangent line of the lowest-energy absorption band) of the UV-vis absorption spectra,  $E_g^{opt} = 1240/\lambda_{onset}$  eV. <sup>*d*</sup> CV energy gap  $E_g^{cv} = LUMO - HOMO$ . <sup>*e*</sup> HOMO levels are calculated according to the equation HOMO =  $-(4.8 + E_{pa})$ . <sup>*f*</sup> Data are obtained from the onset potential of the first reduction wave of the CV data.

Electrophosphorescent OLEDs. For the complexes Pt-Se and Pt-Te, they should represent the unprecedented phosphorescent emitters with benzo[b]selenophene and benzo[b]tellurophene units. Hence, it should be very necessary to characterize their EL ability. With Pt-Se and Pt-Te as emitters, solution-processed OLEDs with the configuration of ITO/PEDOT:PSS (45 nm)/Pt x%:TCTA (ca. 40 nm)/TPBi (45 nm)/LiF(1 nm)/Al (100 nm) (Figure 8) had been constructed. The compound of TCTA (4,4',4"-Tri(9-carbazoyl)triphenylamine) was selected as the host material. The solution of PEDOT:PSS water (poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was used to deposit hole injection layer, while a layer of TPBi (1,3,5-tris[N-(phenyl)-benzimidazole]benzene) served the purpose of electron-transporting as well as hole-blocking. The thin layer of LiF could play the role of electron-injection.



**Fig. 8** Energy diagram of the solution-processed OLEDs together with chemical structures of the materials employed in the fabricated OLEDs.

In order to optimize EL performance, solution-processed OLEDs with different doping levels of **Pt-Se** or **Pt-Te** in emission layer had been fabricated. The doping-levels were set at 6.0 wt%, 8.0 wt% and 10.0wt% and the concerned devices were named as **A1**, **A2** and **A3** with **Pt-Se** as emitter together with **B1**, **B2** and **B3** with **Pt-Te** as emitter (Figure 8). Both **Pt-Se** and **Pt-Te** can furnish the optimized EL performances with a doping level of 8.0 wt%, corresponding to device **A2** and **B2**, respectively (Table 7). When a proper voltage applied, device **A2** and **B2** can emit stable red electrophosphorescence at *ca*. 620 nm for device **A2** and 636 nm for device **B2** (Figure 9). The EL spectra of optimized OLEDs (Figure 9) are similar to the PL spectra of corresponding complexes **Pt-Se** and **Pt-Te** in solution (Figure 5a), indicating efficient energy transfer from the TCTA host to the phosphorescent emitters **Pt-Se** and **Pt-Te**.





Fig. 9 EL spectra for the optimized OLEDs at *ca*. 10V.

Current density-voltage-luminance (*J-V-L*) characteristics and EL efficiency-luminance curves for the solution-processed OLEDs are shown in Figure 10, 11 and ESI (Figure S2 and S3). The corresponding EL data have been tabulated in Table 7. All these devices show a low turn-on voltage *ca*. 4.0 V. For the optimized device **A2** with **Pt-Se** as emitter, EL performances with maximum external quantum efficiency ( $\eta_{ext}$ ) of 6.3%, current efficiency ( $\eta_L$ ) of 10.5 cd A<sup>-1</sup>, and power efficiency ( $\eta_P$ ) of 9.1 lm W<sup>-1</sup> have been achieved for the red-emitting device, showing the highest luminance ca. 6423 cd m<sup>-2</sup> at 16.7 V. Doped with **Pt-Te**, deep-red device **B2** can show  $\eta_{ext}$  of 6.3 %,  $\eta_L$  of 6.5 cd A<sup>-1</sup> and  $\eta_P$  of 5.8 lm W<sup>-1</sup>. Despite of their inferior EL performance compared with the state-of-the-art EL data from the analogs, the EL efficiencies achieved by **Pt-Se** and **Pt-Te** can still show their potential as red phosphorescent emitters for OLEDs. Critically, to the best of our knowledge, the EL results for **Pt-Te** can represent the first EL performances ever achieved by the phosphorescent emitters with benzo[*b*]tellurophene moiety.

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Fig. 10 Current density-voltage-luminance (J-V-L) characteristics for the optimized OLEDs.



Fig. 11 Relationship between EL efficiencies and luminance of the optimized devices: (a) Device A2, (b) Device B2.

Table 7. EL performance of the electrophosphorescent OLEDs.

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Device	dopant	$V_{\text{turn-on}}\left(\mathbf{V}\right)$	Luminance $L_{\text{max}} (\text{cd m}^{-2})^a$	$\eta_{\mathrm{ext}}$ (%)	$\eta_{\rm L}$ (cd A <sup>-1</sup> )	$\eta_{\mathrm{P}} (\mathrm{lm} \mathrm{W}^{-1})$	$\lambda_{\max}(nm)^d$
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				4.9 (5.1) <sup><i>a</i></sup>	8.0 (5.1)	5.8 (4.1)	View Article Online
A1	<b>Pt-Se</b> (6.0 wt%)	4.4	5540 (17.3)	4.4 <sup>b</sup>	7.3	3.1	DOI: 10.9039/D0DT02224A
				3.4 <sup>c</sup>	5.5	1.7	(0.66, 0.33)
				6.3 (4.5)	10.5 (4.5)	9.1 (3.4)	(20)
A2	<b>Pt-Se</b> (8.0 wt%)	3.8	6423 (16.7)	5.8	9.6	4.8	(0, ((, 0, 22)))
				4.3	7.1	2.5	(0.00, 0.33)
				4.8 (4.1)	7.9 (4.1)	6.9 (3.4)	620
A3	<b>Pt-Se</b> (10.0 wt%)	4.1	4272 (16.3)	3.7	6.2	2.6	(0, ((, 0, 22)))
				2.1	3.4	1.1	(0.00, 0.33)
				6.0 (4.5)	6.3 (4.5)	5.3 (3.5)	(2)
B1	<b>Pt-Te</b> (6.0 wt%)	3.9	3829 (17.1)	4.7	4.8	2.0	030
				2.2	2.3	0.6	(0.69, 0.29)
				6.3 (4.4)	6.5 (4.4)	5.8 (3.4)	(2)
B2	<b>Pt-Te</b> (8.0 wt%)	3.8	3886 (17.0)	4.9	5.1	2.2	030
				2.4	2.3	0.6	(0.69, 0.29)
				5.3 (4.4)	5.5 (4.4)	4.7 (3.4)	(2)
<b>B3</b>	<b>Pt-Te</b> (10.0 wt%)	4.1	4302 (17.0)	3.6	3.8	1.5	636
				1.8	1.9	0.5	(0.09, 0.29)

<sup>*a*</sup> Maximum value of the device. Values in the parentheses are the voltages at which they were obtained. <sup>*b*</sup> Values were collected at *ca*. 100 cd m<sup>-2</sup>. <sup>*c*</sup> Values were collected at *ca*. 1000 cd m<sup>-2</sup>. <sup>*d*</sup> Values were collected at 10 V and CIE coordinates (x, y) are shown in parentheses.

# Conclusion

With benzo[*b*]furan, benzo[*b*]thiophene, benzo[*b*]selenophene and benzo[*b*]tellurophene moieties containing VIA group element, a series of (C^N)Pt(acac)-type complexes have been prepared. The relationship between photophysical behaviors of these (C^N)Pt(acac)-type complexes and their chemical structures have been indicated, which should provide new information for the optoelectronic properties of (C^N)Pt(acac)-type complexes. Importantly, red-emitting solution-processed OLEDs can be fabricated with maximum  $\eta_{ext}$  of 6.3%,  $\eta_L$  of 10.5 cd A<sup>-1</sup> and  $\eta_P$  of 9.1 lm W<sup>-1</sup>, representing very impressive EL performances achieved by the (C^N)Pt(acac)-type with benzo[*b*]selenophene and benzo[*b*]tellurophene groups. Not only has this research enriched the family of (C^N)Pt(acac)-type complexes, but also the EL results demonstrate the potential of these complexes in the field of OLEDs.

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# **Conflicts of interest**

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There are no conflicts to declare.

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# TOC

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Synthesis of cyclometalated platinum(II) complexes with benzoayrl-pyridines as C^N ligands for investigating their photophysical, electrochemical and electroluminescent properties

Dezhi Wang, Xi Chen, Hua Yang, Daokun Zhong, Boao Liu, Xiaolong Yang, Ling Yue, Guijiang Zhou, Miaofeng Ma and Zhaoxin Wu

(C^N)Pt(acac)-type complexes with benzo[*b*]furan, benzo[*b*]thiophene, benzo[*b*]selenophene and benzo[*b*]tellurophene moieties and their optoelectronic properties.

