

# Conversion from ILCT to LLCT/MLCT Excited State by Heavy Metal Ion Binding in Iridium(III) Complexes with Functionalized 2,2'-Bipyridyl Ligands

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Iridium(III) complexes with two ppy (ppy = 2-phenylpyridine) and one functionalized 2,2'bipyridyl ligand containing a bidentate or terdentate binding group were synthesized, and their photophysical and luminescence sensing properties to heavy metal ions were studied. Complex 1 was also structurally characterized by single-crystal X-ray crystallography. These complexes display a low-energy absorption band with the maximum at 410-430 nm ascribed to an intraligand charge transfer (ILCT) transition from the HOMO ( $\pi$ ) residing on the fragment C=C-C<sub>6</sub>H<sub>4</sub>-R to the LUMO  $(\pi^*)$  localized on the 2,2'-bipyridyl (bpy) in the functionalized 2,2'-bipyridyl ligand bpyC=C-C<sub>6</sub>H<sub>4</sub>-R, as revealed from DFT calculations. Upon irradiation at 350 nm  $< \lambda_{ex} < 430$  nm, they show weak emission at ca. 618 nm since <sup>3</sup>ILCT transition is the lowest lying excited state. The ion-binding properties of these iridium(III) complexes to heavy metal ions were investigated by UV-vis and emission spectroscopy. Upon complexation with metal ions through the binding sites in the functionalized 2,2'-bipyridyl ligand, the absorption band at 410-430 nm is significantly blue-shifted to 350-390 nm, resulting most likely from a conversion of ILCT to LLCT/MLCT transition as the lowest energy excited state, as verified from DFT calculations. Interestingly, a significant luminescence enhancement was detected in these iridium(III) complexes upon binding to specific metal ions due to a conversion of the lowest energy state from <sup>3</sup>ILCT to the highly emissive <sup>3</sup>LLCT/<sup>3</sup>MLCT triplet excited state. The sensing properties of these iridium(III) complexes to heavy metal ions were modulated by modifying the binding sites in the functionalized 2,2'-bipyridyl ligand.

## Introdution

In recent years, studies on chemosensors using transitionmetal complexes as luminescence signal groups have attracted considerable interest because of their advantages such as significant Stoke shifts, long emissive lifetimes, and large emission shifts from changes in the local environment compared with those of organic emitters.<sup>1</sup> Transition-metal complexes including those of platinum(II), ruthenium(II), and rhenium(I) have been extensively utilized as probes for anions, metal ions, and biomolecules.<sup>2</sup> It has been well demonstrated that the luminescence properties of iridium(III) complexes can be fine-tuned by ligand substituents, resulting in distinct emission color tuning so that they are adapt to highly sensitive chemosensors for anion,<sup>4</sup> oxygen,<sup>5</sup> and biological labeling reagents<sup>6</sup> have been described, the chemosensors to heavy metal ions are still less explored.<sup>7</sup> On the other hand, heavy metal ions play a vital role in various domains such as

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analytical chemistry and biological and environment sciences.<sup>8</sup> It is well known that  $Zn^{2+}$ ,  $Fe^{3+}$ , and  $Cu^{2+}$  are the three most abundant essential heavy metal ions in the human body and participate in diverse biological processes.  $Hg^{2+}$  and  $Cd^{2+}$  are also considered as significant pollutants, which can cause serious environmental and health problems.<sup>9</sup> Therefore, the design and development of potential chemosensors for the detection of heavy metal ions are very important.

Aiming at exploring the responses toward various heavy metal ions, we designed four iridium(III) complexes (Scheme 1) with two ppy (ppy = 2-phenylpyridine) and one functionalized 2,2'-bipyridyl ligand, where the cyclometalated Ir(ppy)<sub>2</sub>(bpy) chromophore served as a signal emitter and the pyridyl/thiophene-containing moiety as a binding receptor for the metal ion. Absorption and luminescence sensing behavior of these iridium(III) complexes can be modulated by variations in the binding sites of the functionalized 2,2'-bipyridyl ligand. These iridium(III) complexes exhibit a lower energy absorption band arising from intraligand change transfer (ILCT) centered on the functionalized 2,2'-bipyridyl ligand.<sup>7a,10</sup> Upon binding to specific metal ions through the binding sites possessing pyridyl/thiophene donors, the absorption band at 410-430 nm is blue-shifted to 350-390 nm. Meanwhile, the weakly emissive lowest energy <sup>3</sup>ILCT excited state changes to  ${}^{3}[\pi(ppy) \rightarrow \pi^{*}(bpyC \equiv CC_{6}H_{4}-R)]$ 

<sup>3</sup>LLCT and <sup>3</sup>[d(Ir) $\rightarrow \pi^*(bpyC \equiv CC_6H_4 \cdot R)$ ] <sup>3</sup>MLCT triplet states, which are highly luminescent, inducing a remarkable luminescence enhancement. Most interestingly, complex **3** shows an emissive off–on–off effect to copper(II) ion.

#### **Experimental Section**

**General Procedures and Materials.** The manipulations were carried out under an argon atmosphere using Schlenk techniques and vacuum-line systems. The solvents were dried, distilled, and degassed prior to use, except that those for spectroscopic measurements were of spectroscopic grade. (Trimethylsilyl)acetylene (Me<sub>3</sub>SiC=CH), copper(I) iodide (CuI), 4-iodophenylamine, 4-chloromethylpyridine hydrochloride, 2-thenyl chloride, thiophen-2-ylacetaldehyde, hexadecytrimethylammonium chloride, and hydrate iridium(III) chloride (IrCl<sub>3</sub>·6H<sub>2</sub>O) were commercially available and used as received. 5-Ethynyl-2,2'-bipyridine (bpyC=CH)<sup>11</sup> and Ir<sub>2</sub>(ppy)<sub>4</sub>Cl<sub>2</sub><sup>12</sup> were synthesized by the literature procedures. Metal salts of perchlorate hydrate were all purchased from Alfa Aesar.

Caution: Perchlorate salts are potentially explosive. All compounds containing perchlorates should be handled with great care and in small amounts.

(4-Iodophenyl)pyridin-2-ylmethylamine. This compound was synthesized by modification of the literature procedures.<sup>13</sup> To an aqueous (5 mL) solution of 4-chloromethylpyridine hydrochloride (1.64 g, 10 mmol) were added 4-iodophenylamine (1.75 g, 8 mmol), NaOH (5 M, 4 mL), and hexadecytrimethylammonium chloride (20 mg). After stirring at ambient temperature for 12 h, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, which was washed with H<sub>2</sub>O and dried with MgSO<sub>4</sub>. The product was then purified by silica gel column chromatography using dichloromethane–ethyl acetate (v/v = 5:1) as eluent. Yield: 70%. ESI-MS (*m/z*): 310.2 [M]<sup>+</sup>. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.51 (d, *J* = 6.2 Hz, 1H), 7.76 (t, *J* = 10.5 Hz, 1H), 7.35 (d, *J* = 11.4 Hz, 2H), 7.2 (d, *J* = 7 Hz, 1H), 7.45 (t, *J* = 7 Hz, 1H), 6.44 (d, *J* = 11.5 Hz, 2H), 5.36 (s, 1H), 4.36 (s, 2H).

(4-Iodophenyl)bispyridin-2-ylmethylamine. To a solution of (4-iodophenyl)pyridin-2-ylmethylamine (310 mg, 1 mmol) in dry THF (40 mL) were added NaH (96 mg, 4 mmol) and 2-chloromethylpyridine (152 mg, 1.2 mmol). After the mixture was refluxed for 6 h, ethanol (5 mL) was added to quench the reaction. The solvents were removed in vacuo, and the residue was then poured into 100 mL of water, which was extracted with dichloromethane and dried with MgSO<sub>4</sub>. The product was purified by chromatography on a silica gel column using dichloromethane–acetone (v/v = 5:1) as eluent. Yield: 82%. ESI-MS (*m/z*): 402.4 ([M + H]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.56 (d, *J* = 8 Hz, 2H), 7.70 (t, *J* = 3.2 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 7.24 (t, *J* = 4 Hz, 2H), 6.52 (d, *J* = 7.6 Hz, 2H), 4.83 (s, 4H).

(4-Iodophenyl)thiophen-2-ylmethylamine. A mixture of 4-iodophenylamine (219 mg, 1 mmol) and thiophen-2-ylacetaldehyde (126 mg, 1 mmol) in ethanol (30 mL) was refluxed for 5 h, producing a yellow precipitate after cooling down. The solid was filtered off and washed with cold ethanol. The residue was redissolved in ethanol (30 mL), followed by addition of NaBH<sub>4</sub> with stirring for 4 h. After the solvent was removed, the product was purified by chromatography on a silica gel column using dichloromethane–acetone (v/v = 10:1) as eluent. Yield: 70%. ESI-MS (m/z): 315.2 ([M]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 7.41 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8 Hz,

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1H), 7.03 (t, J = 8.2 Hz, 1H), 6.98 (d, J = 3.2 Hz, 1H), 6.51 (d, J = 8 Hz, 2H), 5.13 (s, 1H), 4.50 (s, 2H).

(4-Iodophenyl)pyridin-2-ylmethylthiophen-2-ylmethylamine. To a solution of (4-Iodophenyl)pyridin-2-ylmethylamine (310.2 mg, 1 mmol) in dry toluene (40 mL) was added sodium amide (39 mg, 1 mmol). After the mixture was refluxed for 2 h, a toluene (10 mL) solution of 2-thenyl chloride (132 mg, 1 mmol) was dropwise added. The mixture was refluxed for 4 h and then the solvent evaporated in vacuo. The residue was dissolved in dichloromethane and chromatographed on a silica gel column using dichloromethane–acetone (v/v = 10:5) as eluent to give the product as a yellow solid. Yield: 79%. ESI-MS (*m*/*z*): 406.9 ([M]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.55 (d, *J* = 8 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 4 Hz, 1H), 7.22 (d, *J* = 9.6 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8 Hz, 1H), 6.62 (d, *J* = 8 Hz, 2H), 4.89 (s, 2H), 4.69 (s, 2H).

(4-[2,2']Bipyridinyl-5-ylethynylphenyl)pyridin-2-ylmethylamine (L1). (4-Iodophenyl)pyridin-2-ylmethylamine (310 mg, 1 mmol) and bpyC=CH (180 mg, 1 mmol) were dissolved in dry THF (45 mL) and triethylamine (15 mL) with stirring. To the solution were then added Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3 mol %) and CuI (1 mol %). After refluxing for 1 day, the mixture was filtered and the filtrate evaporated to dryness. The residue was dissolved in dichloromethane and chromatographed on the silica gel column using dichloromethane-acetone (v/v = 2:1) to give a yellow product. Yield: 50% ESI-MS (m/z): 363.3  $([M + H]^+)$ . <sup>1</sup>H NMR (400 MHz, d-DMSO, 298 K): 8.92 (s, 1H), 8.70 (d, J = 4 Hz, 1H), 8.55 (d, J = 3.2, 1H), 8.43 (d, J = 4 Hz, 1H), 8.40 (d, J =2.8 Hz, 1H), 8.01 (d, J = 3.2 Hz, 1H), 7.97 (t, J = 4 Hz, 1H), 7.77 (t, J = 3.6 Hz, 1H), 7.48 (d, J = 4 Hz, 1H), 7.40 (t, J = 1.6 Hz,1H), 7.34 (t, J = 3.2 Hz, 2H), 7.28 (t, J = 4 Hz, 1H), 6.95 (s, 1H), 6.63 (d, J = 8.8 Hz, 2H), 4.42 (s, 2H). IR (KBr, cm<sup>-1</sup>): 2209m (C≡C).

(4-[2,2']Bipyridinyl-5-ylethynylphenyl)bispyridin-2-ylmethylamine (L2). Synthetic procedures of this compound were the same as that of (4-[2,2']bipyridinyl-5-ylethynylphenyl)pyridin-2-ylmethylamine (L1) except for the use of (4-iodophenyl)bispyridin-2-ylmethylamine instead of (4-iodophenyl)pyridin-2-ylmethylamine. Yield: 52%. ESI-MS (m/z): 454.2 ([M + H]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, 298 K): 8.74 (s, 1H), 8.73 (d, J = 0.8Hz, 1H), 8.57 (d, J = 4.4, 2H), 8.39 (d, J = 1.2 Hz, 1H), 8.37 (d, J = 1.6 Hz, 1H), 7.98 (t, J = 8.8 Hz, 2H), 7.96 (s, 1H), 7.76 (t, J = 1.6 Hz, 2H), 7.46 (t, J = 3.2 Hz, 1H), 7.33 (d, J = 4 Hz, 2H), 7.31 (d, J = 1.6 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 6.70 (d, J = 8.8Hz, 2H), 4.902 (s, 4H). 1R (KBr, cm<sup>-1</sup>): 2208m (C=C).

(4-[2,2']Bipyridinyl-5-ylethynylphenyl)thiophen-2-ylmethylamine (L3). Synthetic procedures of this compound were the same as that of (4-[2,2']bipyridinyl-5-ylethynylphenyl)pyridin-2-ylmethylamine (L1) except for the use of (4-iodophenyl)thiophen-2-ylmethylamine instead of (4-iodophenyl)pyridin-2ylmethylamine. Yield: 48%. ESI-MS (m/z): 368.2 ([M + H]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, d-DMSO, 298 K): 8.76 (s, 1H), 8.70 (d, J =8 Hz, 1H), 8.40 (d, J = 8 Hz, 1H), 8.38 (d, J = 8 Hz, 1H), 8.00 (d, J = 4 Hz, 1H), 7.96 (t, J = 8 Hz, 1H), 7.47 (t, J = 4.8 Hz, 1H), 7.39 (d, J = 1.2 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.06 (d, J =4 Hz, 1H), 6.98 (d, J = 4 Hz, 1H), 6.87 (t, J = 4 Hz, 1H), 6.68 (d, J = 8 Hz, 2H), 4.51 (s, 2H). IR (KBr, cm<sup>-1</sup>): 2208m (C=C).

(4-[2,2']Bipyridinyl-5-ylethynylphenyl)pyridin-2-ylmethylthiophen-2-ylmethylamine (L4). Synthetic procedures of this compound were the same as that of (4-[2,2']bipyridinyl-5-yl-ethynylphenyl)pyridin-2-ylmethylamine (L1) except for the use of (4-iodophenyl)pyridin-2-ylmethylthiophen-2-ylmethylamine instead of (4-iodophenyl) pyridin-2-ylmethylthiophen-2-ylmethylamine instead of (4-iodophenyl) pyridin-2-ylmethylamine. Yield: 55%. ESI-MS (m/z): 459.5 ([M + H]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, *d*-DMSO, 298 K): 8.76 (s, 1H), 8.70 (d, J = 4 Hz, 1H), 8.58 (d, J = 4 Hz, 1H), 8.40 (d, J = 1.2 Hz, 1H), 8.38 (d, J = 1.2 Hz, 1H), 8.01 (d, J = 8 Hz, 1H), 7.98 (t, J = 1.2 Hz, 1H), 7.74 (t, J = 2 Hz, 1H), 7.45 (t, J = 0.8 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.36 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.29 (t, J = 4 Hz, 1H), 7.24 (d, J = 8 Hz, 1H), 7.24 (d

1H), 7.09 (d, J = 1.2 Hz, 1H), 7.01 (t, J = 3.6 Hz, 1H), 6.82 (d, J = 9.2 Hz, 2H), 4.99 (s, 2H), 4.76 (s, 2H). IR (KBr, cm<sup>-1</sup>):  $\nu$  2209m (C=C).

[Ir(ppy)<sub>2</sub>(L1)]PF<sub>6</sub> (1). A mixture of Ir<sub>2</sub>(ppy)<sub>4</sub>Cl<sub>2</sub> (267.7 mg, 0.25 mmol) and L1 (181.6 mg, 0.5 mmol) in methanoldichloromethane (30 mL, v/v = 1:2) was refluxed with exclusion of light for 4 h. After cooling to ambient temperature, to the solution was added a methanol solution (2 mL) of potassium hexafluorophosphate (93 mg) with stirring for 30 min. The solution was evaporated to dryness and the residue was dissolved in dichloromethane (5 mL). The solution was then chromatographed on a silica gel column using dichloromethane-methanol (v/v = 2:1) as eluent to give an orange product. Yield: 82%. Anal. Calcd for C46H34IrN6F6P: C, 54.81; H, 3.40; N, 8.34. Found: C, 54.51; H, 3.15; N, 8.56. ESI-MS (m/z): 863.3  $([M - PF_6]^+)$ . <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.61 (s, 1H), 8.50 (t, J = 4.2 Hz, 2H), 8.07–8.17 (m, 5H), 7.94 (d, J = 2 Hz, 1H), 7.93 (s, 1H), 7.82–7.88 (m, 5H), 7.72–7.74 (m, 3H), 7.63 (d, J = 9.6 Hz, 1H), 7.50 (t, J = 1.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.064–7.091 (m, 4H), 6.94–6.96 (m, 2H), 6.64 (d, J = 12 Hz, 2H), 6.33 (d, J = 12 Hz, 2H), 4.47 (s, 2H), 4.06(s, 1H). IR (KBr,  $cm^{-1}$ ): 2213m (C=C).

[Ir(ppy)<sub>2</sub>(L2)]PF<sub>6</sub> (2). This compound was prepared by the same synthetic procedures as that of 1 except using L2 instead of L1. Yield: 82%. Anal. Calcd for C<sub>52</sub>H<sub>39</sub>IrN<sub>7</sub>F<sub>6</sub>P: C, 56.82; H, 3.58; N, 8.82. Found: C, 56.40; H, 3.57; N, 8.72. ESI-MS (*m*/*z*): 954.2 ([M – PF<sub>6</sub>]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.60 (d, *J* = 4.2 Hz, 2H), 8.50 (t, *J* = 3.2 Hz, 2H), 8.07–8.15 (m, 4H), 7.98 (d, *J* = 5.2 Hz, 1H), 7.91 (s, 1H), 7.81–7.87 (m, 7H), 7.71 (d, *J* = 4.8 Hz, 1H), 7.61 (d, *J* = 8 Hz, 1H), 7.50 (t, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 8 Hz, 2H), 7.33 (t, *J* = 3.2 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.06–7.19 (m, 5H), 6.94 (t, *J* = 4 Hz, 2H), 6.30 (m, 2H), 4.89 (s, 4H). IR (KBr, cm<sup>-1</sup>): 2213m (C≡C).

[Ir(ppy)<sub>2</sub>(L3)]PF<sub>6</sub> (3). This compound was prepared by the same synthetic procedures as that of 1 except using L3 instead of L1. Yield: 75%. Anal. Calcd for C<sub>45</sub>H<sub>33</sub>IrN<sub>5</sub>F<sub>6</sub>PS: C, 53.35; H, 3.28; N, 6.91. Found: C, 53.10; H, 3.15; N, 7.21. ESI-MS (*m*/*z*): 868.0 ([M – PF<sub>6</sub>]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.47 (d, *J* = 3.2 Hz, 2H), 8.09–8.12 (m, 4H), 7.94 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 4.2 Hz, 1H), 7.84–7.88 (m, 4H), 7.74–7.76 (m, 2H), 7.63–7.65 (m, 2H), 7.50 (t, *J* = 4 Hz, 1H), 7.30 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.04–7.09 (m, 5H), 6.99 (d, *J* = 2 Hz, 1H), 6.66 (d, *J* = 8 0.8 Hz, 2H), 6.30 (m, 2H), 5.56 (s, 1H), 4.09 (s, 2H). IR (KBr, cm<sup>-1</sup>): 2213m (C≡C).

[Ir(ppy)<sub>2</sub>(L4)]PF<sub>6</sub> (4). This compound was prepared by the same synthetic procedures as that of 1 except using L4 instead of L1. Yield: 79%. Anal. Calad for C<sub>51</sub>H<sub>38</sub>IrN<sub>6</sub>F<sub>6</sub>PS: C, 55.48; H, 3.47; N, 7.61. Found: C, 55.10; H, 3.15; N, 7.86. ESI-MS (*m/z*): 959.2. ([M – PF<sub>6</sub>]<sup>+</sup>). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K): 8.51 (d, *J* = 4.6 Hz, 2H), 8.49 (t, *J* = 5.6 Hz, 2H), 8.07–8.13 (m, 5H), 7.99 (d, *J* = 5.2 Hz, 1H), 7.93 (s, 1H), 7.82–7.86 (m, 6H), 7.72 (d, *J* = 5.2 Hz, 1H), 7.62 (d, *J* = 5.6 Hz, 1H), 7.50 (t, *J* = 3.6 Hz, 1H), 7.30 (t, *J* = 1.2 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.05–7.09 (m, 4H), 6.95 (t, *J* = 4 Hz, 1H), 6.93 (d, *J* = 6.4 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.30 (m, 2H), 4.79 (s, 2H), 4.98 (s, 2H). IR (KBr, cm<sup>-1</sup>): 2214m (C≡C).

**Physical Measurements.** <sup>1</sup>H NMR spectra were measured on a Bruker Avance III (400 MHz) spectrometer with SiMe<sub>4</sub> as the internal reference. Electrospay ion mass spectra (ESI-MS) were performed on a Finnigan LCQ mass spectrometer using dichloromethane-methanol as the mobile phase. Elemental analyses (C, H, N) were recorded on a Perkin-Elmer model 240C automatic instrument. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 25 UV-vis spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellets. Emission and excitation spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer with a R928 red-sensitive photomultiplier. The cyclic voltammograms (CV) were made with a potentiostat/galvanostat model 263A in acetonitrile solutions containing 0.1 M  $(Bu_4N)PF_6$  as the supporting electrolyte. The CV was performed at a scan rate of 200 mV s<sup>-1</sup>. Platinum and glassy graphite were used as the counter and working electrodes, respectively, and the potential was measured against a Ag/AgCl reference electrode.

**Crystal Structural Determination.** Crystals of 1 were obtained by diffusion of *n*-pentane into a dichloromethane solution of 1. Data collection was performed on a SATURN70 CCD diffractometer using the  $\omega$  scan technique at room temperature using graphite-monochromated Mo K $\alpha$  (k = 0.71073 Å) radiation. Absorption corrections by SADABS were applied to the intensity data. The structures were solved by direct methods. The heavy atoms were located from E-maps, and the rest of the nonhydrogen atoms were found in subsequent Fourier maps. All non-hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on  $F^2$ by full-matrix least-squares methods using the SHELXTL-97 program package. The crystallographic data are summarized in Table 1.

Theoretical Calculations. The computational method used was the density functional theory (DFT),<sup>14</sup> where the gradientcorrected correlation functional PBE1PBE<sup>15</sup> was employed for the calculations. The geometry structures of complex 1 and  $Zn^{2+}$ binding species  $1/Zn^{2+}$  were optimized as isolated molecules from the solvent phase at the DFT level of theory. We performed geometry optimization from initial geometry of  $C_1$  symmetry at first from the X-ray structure. Therefore, 60 singlet absorptions and six triplet emissions were obtained to determine the vertical excitation energies for 1 and the simplified  $Zn^{2+}$  binding species  $1/Zn^{2+}$  in acetonitrile using the time-dependent DFT  $(TD-DFT)^{16}$  calculations, respectively. The polarized continuum model method  $(CPCM)^{17}$  with acetonitrile as solvent was used to calculate all the electronic structures in solution. In the calculations, a "double- $\xi$ " quality (SDD) basis set consisting of effective core potentials (ECPs) for the iridium(II) atom proposed by Hay and Walt<sup>18</sup> was used to precisely describe the molecular properties. One additional f-type polarization function is implemented for the iridium(III) atom ( $\alpha$  = 0.938),<sup>19</sup> and the 6-31G(p,d) basis set was used for the remaining

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Table 1. Crystallographic Data for 1

empirical formula	C46H34F6IrN6P
temp, K	293(2)
space group	$P2_1/n$
a, Å	17.081(5)
b, Å	12.896(4)
<i>c</i> , Å	18.368(5)
$\beta$ , deg	98.918(5)
V, Å <sup>3</sup>	3997(2)
Ź	4
$\rho_{\rm calcd}$ , g/cm <sup>-3</sup>	1.675
$\mu, \text{mm}^{-1}$	3.451
radiation $(\lambda, \dot{A})$	0.71073
$R1(F_0)^a$	0.0562
$wR2(F_0)^b$	0.1473
GOF	1.136
${}^{a}$ R1 = $\sum  F_{o} - F_{c}  / \sum F_{o}$ . ${}^{b}$ wR2 =	$\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]^{1/2}.$

atoms. All calculations were performed using the Gaussian 03 program package.  $^{20}$ 

### **Results and Discussion**

Preparations and Characterization. Syntheses of (4-iodophenyl)bispyridin-2-ylmethylamine and (4-iodophenyl)pyridin-2-ylmethylthiophen-2-ylmethylamine need the use of strong bases such as NaNH2 and NaH because of the difficulty in removal of the amino proton of aniline when one proton in N-aniline is substituted by a 2-methylpyridine group. The functionalized 2,2'-bipyridyl ligands L1-L4 were prepared by reaction of 5-ethynyl-2,2'-bipyridine with 4-iodophenylamine derivatives according to the Sonogashira-Hagihara crosscoupling method.<sup>21</sup> Cyclometalated iridium(III) complexes were synthesized by reaction of the corresponding functionalized 2,2'-bipyridyl ligand (L1-L4) with  $Ir_2(ppy)_4Cl_2$  in  $CH_2Cl_2-CH_3OH$  (v/v = 2:1) under reflux, followed by metathesis with  $\text{KPF}_{6}^{22}$  The desired iridium(III) complexes 1–4 (Scheme 1) were obtained as deep orange solids in good yields through chromatographic purification on silica gel columns. They were characterized by elemental analyses, positive ion ESI-MS spectrometry, and <sup>1</sup>H NMR and IR spectroscopy, and by X-ray crystallography for complex 1.

A perspective view of complex 1 is depicted in Figure 1. The iridium(III) center exhibits a distorted octahedral geometry composed of  $C_2N_4$  donors from cyclometalated ppy and chelating 2,2'-bpy ligands. The C donors are cisoriented, whereas the N donors from cyclometalated ppy are trans-arranged, as revealed by previous structural studies on iridium(III) complexes containing ppy ligands.<sup>23</sup> The Ir–N distances [2.152(6) and 2.162(5) Å] for 2,2'-bipyridyl are obviously longer than those [2.017(7) and 2.062(6) Å] for ppy due most likely to the remarkable trans influence of the C donors for the former.

**Photophysical and Electrochemical Properties.** The absorption and emission spectral data of iridium(III) complexes measured in acetonitrile solutions are summarized in Table 2. The UV-vis spectra of **1**-**4** are featured by intense

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**Figure 1.** ORTEP drawing of the cation of **1** with atomic labeling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

Table 2. UV-Vis Absorption and Luminescence Data for 1-4

complex	medium ( <i>T</i> /K)	$\lambda_{abs}/nm \ (\epsilon/dm^3  mol^{-1}  cm^{-1})$	$\lambda_{\rm em}/{\rm nm}$
1	MeCN (298)	254 (44 571), 267 (46 497), 287 (45 869), 416 (25 009)	618
	MeCN (77)		605, 652
	solid (298)		621
	solid (77)		610, 659sh
2	MeCN (298)	259 (43 415), 294 (41 241), 421 (24 643)	616
	MeCN (77)		604, 647
	solid (298)		634
	solid (77)		611, 660sh
3	MeCN (298)	252 (29 510), 267 (30 403), 285 (29 772), 407 (16 760)	617
	MeCN (77)		605, 648sh
	solid (298)		648
	solid (77)		524, 599sh
4	MeCN (298)	255 (48056), 292 (45481), 416 (25902)	617
	MeCN (77)		602, 649sh
	solid (298)		637

absorptions at 255–350 nm together with a low-energy absorption band with the maximum at 410–430 nm. With reference to previous studies on iridium(III) diimine complexes, <sup>24–26</sup> the high-energy bands arise most probably from spin-allowed intraligand transition from ppy and functionalized bpy ligands. The low-energy absorption band with the maximum at 410–430 can be assigned to an intraligand charge transfer (ILCT) character from the HOMO ( $\pi$ ) residing on the fragment C=C-C<sub>6</sub>H<sub>4</sub>-R to the LUMO ( $\pi$ \*) localized on the 2,2'-bipyridyl in the functionalized 2,2'bipyridyl ligand, as confirmed by TD-DFT calculations (vide infra). It has been suggested that the lowest energy absorption of iridium(III) complexes containing two ppy and one diffine ligand with a  $\pi$ -conjugated or amino-substituted system is always dominated by the intraligand  $\pi\pi^*$ transition centered on the diimine ligand.<sup>7a,e,27,28</sup> This lowest energy absorption is quite useful for chemical sensing due to the high sensitivity to ion binding. As presented in Table 2, the corresponding low-energy absorptions of 1-4 exhibit a slight distinction due to the electronic effects of the diverse substituents in the corresponding functionalized bpy ligands L1–L4. In contrast to the iridium(III) complexes, the free ligands L1–L4 display a corresponding ICT band with the maximum around 360 nm (Figure S1, Supporting Information). A red-shift of about 60 nm in the iridium(III) complexes compared with that in the free ligands may be related to the increased electron-accepting properties of the 2,2'-bipyridyl  $\pi^*$  orbitals upon coordination to an iridium-(III) ion.<sup>7e,28a</sup>

The iridium(III) complexes 1-4 display weak emission at 615-650 nm in both the solid state and solution at ambient temperature. Similar patterns of emission spectra of 1-4 suggest that diverse substituents of the corresponding functionalized bpy ligands L1–L4 exert inappreciable influence on the luminescence properties. With reference to previous spectroscopic studies on a series of cyclometalated iridium-(III) complexes with an amino-substituted or  $\pi$ -extended diimine ligands,  $2^{7a,28a,c,d}$  the weak emission in 1–4 is likely due to the lowest energy <sup>3</sup>ILCT exited state, as verified from DFT calculations (vide infra). At 77 K, the emission maxima of 1-4 show a small blue-shift in both the solid state and frozen glasses compared with those measured at ambient temperature, suggesting that the emission originates from <sup>3</sup>ILCT, which was observed in cyclometalated iridium(III) diimine complexes.6a,d

The electrochemical properties of 1-4 were studied by cyclic voltammetry (CV) in acetonitrile solutions, and the data are summarized in Table 3. They have similar eletrochemical behavior independent of the R groups attached to aniline amine (Scheme 1). They exhibit an irreversible oxidation wave in the anodic side and a quasi-reversible reduction wave in the cathodic region. With reference to the previous studies on electrochemical behavior of a series of iridium(III) diimine complexes, <sup>6d,23c,d,29,30</sup> the oxidation wave at ca. +1.0 V vs Fc in the anodic region can be assigned as an iridium-(III)-centered oxidation process, whereas the reduction waves at ca. -1.6 V vs Fc originate likely from reduction of the 2,2'-bipyridyl ligand.

UV-Vis Absorption Response to Metal Ion Binding. The metal ion binding properties of 1-4 were investigated using the corresponding perchlorate salts in acetonitrile solutions.

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Table 3. Cyclic Voltammetric Data for 1–4 in 0.1 M (Bu<sub>4</sub>N)(PF<sub>6</sub>) Acetonitrile Solutions<sup>a</sup>

complex $E_{\rm a}$	(V) $E_{\rm c}^{1/2}$ (V)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{ccc} 97^b & -1.65^c \\ 07^b & -1.66^c \\ 01^b & -1.64^c \\ 08^b & -1.58^c \end{array}$





**Figure 2.** UV-vis spectral changes for complex 1 (20  $\mu$ M) upon addition of Zn<sup>2+</sup> (0–50 equiv) in CH<sub>3</sub>CN. Inset: the Job's plot for determining the stoichiometric ratio between complex 1 and Zn<sup>2+</sup>, where the variations of absorbance at 352 nm were measured as a function of molar ratio  $X_m$  ([Zn<sup>2+</sup>]/[Zn<sup>2+</sup>] + [1])).

Figure 2 shows the changing UV-vis spectroscopic curves of 1 by titration with  $Zn^{2+}$ . Upon addition of up to 50 equiv of  $Zn^{2+}$  to an acetonitrile solution of 1, the absorption bands at 287 and 421 nm decrease gradually with appearance of new absorptions at 267 and 358 nm. Well-defined isosbestic points were observed at 378, 318, and 275 nm, indicating that only one new absorbing species was produced during the titration. Job's equilibrium plot analysis suggested the formation of a stoichiometric ratio of 1:2 between  $Zn^{2+}$  and 1, as shown in the inset of Figure 2. A plot of absorbance versus  $X_{\rm m}$  ([Zn<sup>2+</sup>]/[Zn<sup>2+</sup>] + [1])) shows that the absorbance goes through a maximum at a molar fraction of ca. 0.33. The binding constants log  $K_1$  and log  $K_2$  for 1:1 and 2:1 binding ratios between 1 and  $Zn^{2+}$  were estimated to be  $4.21 \pm 0.16$ and  $4.18 \pm 0.05$ , respectively, by a nonlinear least-squares fitting using the absorbance versus the concentration of the metal ions.<sup>31,32</sup> Analogous to that of Cd<sup>2+</sup>, addition up to 50 equiv of  $Cd^{2+}$  to acetonitrile solutions of 1 gave rise to obvious UV-vis spectroscopic changes (Figure S2, Supporting Information) because of the similar electronic and coordination character between Zn<sup>2+</sup> and Cd<sup>2+</sup>. Binding constants  $\log K_1$  and  $\log K_2$  for 1:1 and 2:1 binding ratios between 1 and  $Cd^{2+}$  are 3.3  $\pm$  0.15 and 3.05  $\pm$  0.03, respectively. They are obviously lower than those between 1 and  $Zn^{2+}$ , suggesting that 1 displays a better selective binding to  $Zn^{2+}$ .



**Figure 3.** UV-vis spectral changes for complex  $2(20 \,\mu\text{M})$  upon addition of Hg<sup>2+</sup> (0–1.0 equiv) in CH<sub>3</sub>CN. Inset: plot of UV-vis titration data (points), showing the fitting to a 1:1 binding isotherm (solid line) at 421 nm.

Complex 2 exhibits remarkable spectroscopic response to  $Zn^{2+}$ ,  $Hg^{2+}$ , and  $Cd^{2+}$  in a similar way to that described for complex 1 to  $Zn^{2+}$  and  $Cd^{2+}$ . Figure 3 shows the UV-vis absorption spectral changes of 2 by addition of up to 1.0 equiv of  $Hg^{2+}$ . With gradual decrease of the absorbance at 421 and 306 nm, a new band at 355 nm appeared and increased progressively. A metal ion binding species with 1:1 complexation ratio was supported by a good agreement of the experimental data with the theoretical fitting (Figure 3, inset). Similar UV-vis spectroscopic changes were also observed by titration of complex  $\hat{2}$  with  $\tilde{Z}n^{2+}$  or  $Cd^{2+}$ (Figures S4 and S5, Supporting Information) in acetonitrile. The binding constants (log K) calculated from the absorbance changes of complex 2 upon addition of  $Zn^{2+}$ ,  $Hg^{2+}$ , and  $Cd^{2+}$  are 8.18  $\pm$  0.04, 8.01  $\pm$  0.1, and 7.6  $\pm$  0.06, respectively.

To further investigate the influence of variations in acceptors on metal ion binding properties of cyclometalated iridium(III) complexes, a thiophene-containing moiety was introduced as the binding sites.<sup>33</sup> As the bonding character of thiophene S donor is quite different from that of the pyridine N donor, it is expected that thiophene-containing complexes 3 and 4 would cause unique sensing properties to some metal ions. With addition of up to 1.5 equiv of Cu<sup>2+</sup> into an acetonitrile solution of complex 3, the absorption band at ca. 410 nm decreased gradually with the appearance of a new band at 385 nm, where well-defined isosbestic points were observed at 273, 315, and 396 nm (Figure 6a). Nevertheless, if more than 1.5 equiv of Cu<sup>2+</sup> was added to an acetonitrile solution of 3, the new absorption band at 385 nm was obviously reduced with gradual addition of up to 50 equiv of  $Cu^{2+}$  (Figure 6b). In order to determine the stoichiometric ratio of the formed species during titration of 3 with  $Cu^{2+}$ , Job's method was also applied to the absorbance versus  $X_{\rm m}$  $([Cu^{2+}]/[Cu^{2+}] + [1])$ . The stoichiometric ratio of the species formed between  $Cu^{2+}$  and complex 3 was estimated as 1:2 (Figure S10, Supporting Information). Due to the abnormal changes in the process of spectroscopic titration, the binding constants could not be exactly estimated by the method mentioned above. The result is consistent with

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the assumption that each  $Cu^{2+}$  is surrounded by a squareplanar  $N_2S_2$  chromophore from two molecules of complex 3, but no new species is formed when more than 1.5 equiv of  $Cu^{2+}$ is added. Distinct UV-vis spectroscopic changes were unobserved upon addition of other metal ions except that Fe<sup>3+</sup> gave rise to a faint effect to the UV-vis spectrum of 3, suggesting that complex 3 displays a highly selective binding to  $Cu^{2+}$ .

The UV-vis spectrum of complex 4, containing both pyridine and thiophene moieties, displayed significant changes upon binding to  $Cu^{2+}$ ,  $Hg^{2+}$ , or  $Fe^{3+}$  ion. By addition of up to 1.0 equiv of  $Cu^{2+}$  ion to an acetonitrile solution of 4, a new band at 375 nm appeared and increased progressively with gradual decrease of the absorbance at 416 and 310 nm (Figure S12, Supporting Information). A plot of the absorbance at 416 nm of 4 versus the concentration of Cu<sup>2+</sup> is consistent with the theoretical fitting and suggests that the stoichiometric ratio of the formed species is 1:1 (Figure S12, inset, Supporting Information). The UV-vis spectroscopic changing curves of 4 in acetonitrile solutions upon titration with  $Hg^{2+}$  or  $Fe^{3+}$  were depicted in Figure S13 or S14 (Supporting Information), respectively. The binding constants (log K) calculated from the absorbance changes of complex 4 upon addition of  $Cu^{2+}$ ,  $Hg^{2+}$ , and  $Fe^{3+}$  are 7.24  $\pm$  $0.35, 7.42 \pm 0.1, \text{ and } 7.5 \pm 0.13, \text{ respectively.}$ 

Upon binding to specific metal ions, the new observed bands around 350–380 nm in the absorption spectra of iridium(III) complexes 1–4 arise most probably from  $\pi(\text{ppy})\rightarrow\pi^*(\text{bpyC}\equiv\text{CC}_6\text{H}_4\text{-R})$  LLCT and d(Ir) $\rightarrow\pi^*(\text{bpyC}\equiv$ CC<sub>6</sub>H<sub>4</sub>-R) MLCT transitions, whereas the low-energy ILCT band is significantly weakened, as revealed from DFT calculations (vide infra). Once the binding sites in 1–4 are bonded to a specific metal ion, the ILCT process is significantly suppressed, resulting in the LLCT/MLCT transition as the lowest- energy state. In the case of 3, an obvious decrease in the LLCT/MLCT absorption at 385 nm with addition of more than 1.5 equiv of Cu<sup>2+</sup> implies that the LLCT/MLCT absorption band could be perturbed by a paramagnetic Cu<sup>2+</sup> ion with a high concentration.<sup>34</sup>

Luminescence Sensing Properties. The luminescence sensing properties of iridium(III) complexes 1-4 were investigated by emission spectral titration in acetonitrile solutions. With excitation at 350 nm  $\leq \lambda_{ex} \leq 430$  nm, which spans the whole absorption region of both LLCT/MLCT and ILCT states, 1-4 are weakly luminescent at ca. 617 nm because the <sup>3</sup>ILCT transition is mostly populated as the lowest energy excited state. As predicted from TD-DFT calculations (vide infra), once the binding sites are bound to a specific metal ion, highly luminescent <sup>3</sup>LLCT and <sup>3</sup>MLCT states are thus populated as the lowest energy excited states, resulting in a significant luminescence enhancement for 1-4 in response to metal ion binding. The switching behavior from <sup>3</sup>ILCT to  ${}^{3}LLCT/{}^{3}MLCT$  triplet excited state in 1–4 upon binding to a specific metal ion and the corresponding luminescence off-on effect are very helpful for heavy metal ion detection and identification.

Figure 4 depicts the emission spectral changes of complex 1 as well as a naked-eye detectable luminescence response to  $Zn^{2+}$  binding. The luminescence intensity of 1 (20  $\mu$ M) shows a 25-fold ( $I - I_0/I_0$ ) enhancement upon addition of 50 equiv of  $Zn^{2+}$ , where  $I_0$  and I are the emission intensity of complex



**Figure 4.** Emission spectral changes ( $\lambda_{ex} = 360 \text{ nm}$ ) for **1** (20  $\mu$ M) upon addition of Zn<sup>2+</sup> (0–50 equiv) in CH<sub>3</sub>CN. Inset: Luminescence images in CH<sub>3</sub>CN solution before (a) and after (b) addition of 1 equiv of Zn<sup>2+</sup> for complex **1**.



Figure 5. Emission responses of complex 1 (20  $\mu$ M) at 617 nm as a function of various added metal ions (50 equiv).

1 before and after titration with  $Zn^{2+}$ . This luminescence enhancement is well consistent with the corresponding UV-vis spectral changes during titration of 1 with  $Zn^{2+}$ , where the  $Zn^{2+}$  ion binding results in a conversion of the lowest energy excited state from <sup>3</sup>ILCT to <sup>3</sup>LLCT/<sup>3</sup>MLCT triplet character. The emission response behavior at 617 nm for complex 1 (20  $\mu$ M) as a function of 50 equiv of various metal ions is shown in Figure 5, revealing that 1 displays high binding selectivity to  $Zn^{2+}$  and  $Cd^{2+}$  ions.

Titration of complex **2** with 1 equiv of  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  in acetonitrile solutions resulted in a 30-, 27-, and 24-fold increase  $(I - I_0/I_0)$  in emission intensity (Figure S9, Supporting Information), respectively. This indicates that complex **2** displays a remarkable switching on luminescence sensing effect to  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$ . The titration data fit to a 1:1 binding ratio between **2** and the corresponding  $Zn^{2+}$ ,  $Cd^{2+}$ , or  $Hg^{2+}$  ion (Figures S6–S8, Supporting Information), coinciding well to that from UV–vis absorption spectral titration.

As demonstrated in UV-vis spectroscopic titration (Figure 6a and b), complex **3** exhibits specific binding properties to  $Cu^{2+}$  apart from a weak binding to  $Fe^{3+}$ . Figure 7 shows the emission response of complex **3** ( $20 \,\mu$ M) at 617 nm as a function of various added metal ions (1.5 equiv), suggesting that complex **3** exhibits high binding selectivity toward  $Cu^{2+}$ . Addition of up to 1.5 equiv of  $Cu^{2+}$  to an acetonitrile solution of complex **3** induced 7-fold emission enhancements (Figure 6c), but the emission

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**Figure 6.** UV-vis spectral changes of complex **3** (20  $\mu$ M) in CH<sub>3</sub>CN upon addition of 0–1.5 equiv (a) and 1.5–5 equiv (b) of Cu(ClO<sub>4</sub>)<sub>2</sub>, and emission spectral titration of complex **3** (20  $\mu$ M) upon the addition of 0–1.5 equiv (c) and 1.5–5 equiv (d) of Cu(ClO<sub>4</sub>)<sub>2</sub>.



Figure 7. Emission responses of complex 3 (20  $\mu$ M) at 617 nm as a function of various added metal ions (1.5 equiv).

intensity was then gradually reduced when more Cu<sup>2+</sup> was added (Figure 6d). Under UV light irradiation at 365 nm, the luminescence variation of complex 3 in response to different amounts of Cu<sup>2+</sup> was naked-eye detectable, as indicated in Figure S11 (Supporting Information). This luminescence off-on-off behavior during the titration is indeed interesting and can be reasonably elucidated. The luminescence switch-on effect during titration of 3 with Cu<sup>2+</sup> is most likely due to blocking of the quenching pathway upon Cu<sup>2+</sup> binding to the amine N and thiophene S donors. In contrast, when more than 1.5 equiv of  $Cu^{2+}$  is added to the acetonitrile solution of 3, the paramagnetism from excess Cu<sup>2+</sup> would exert severe influence on the <sup>3</sup>LLCT/<sup>3</sup>MLCT emissive state, resulting in some quenching of the luminescence of 3.<sup>34</sup> This explanation was further confirmed by the Job's curve, which indicated that only one species existed during titration of 3 with  $Cu^{2+}$  (Figure S10 Supporting Information).

Complex 4, containing N<sub>2</sub>S binding donors, displays a remarkable luminescence response to  $Cu^{2+}$ ,  $Hg^{2+}$ , or  $Fe^{3+}$ . The emission titration data were fitted to a 1:1 binding model, suggesting the metal ion binding to amine N, pyridyl N, and thiopene S donors. Upon titration of complex 4 by addition of equimolar  $Cu^{2+}$ ,  $Hg^{2+}$ , or  $Fe^{3+}$  ion in acetonitrile solutions, the emission intensity exhibits 20-, 18-, or 15-fold



**Figure 8.** Emission spectral changes ( $\lambda_{ex} = 360 \text{ nm}$ ) for **4** (20  $\mu$ M) upon addition of Cu<sup>2+</sup> (0–1.0 equiv) in CH<sub>3</sub>CN. Inset: plot of the fluorescence titration data (points) showing the fit to a 1:1 binding isotherm (solid line) at 421 nm.

enhancement, respectively. Figure 8 depicts the emission spectral changes of complex 4 upon addition of  $Cu^{2+}$ , and the inset shows the changes of the emission intensity as a function of the  $Cu^{2+}$  ion concentration. The enhanced luminescence response for complex 4 at 617 nm as a function of various metal ions is shown in Figure S17 (Supporting Information).

TD-DFT Calculation. To further understand the nature of absorption and emissive transition characters of complexes 1-4 and the effect of metal ion titration on the photophysical properties, calculations based on TD-DFT for 1 and simplified  $Zn^{2+}$  binding species  $1/Zn^{2+}$  were performed. The calculated frontier orbitals for the low-lying transitions revealed dramatic differences between 1 (Tables S1 and S2, Supporting Information) and  $1/Zn^{2+}$  (Tables S3 and S4, Supporting Information). As shown in Figure 9, the HOMO ( $\pi$ ) for 1 mainly resides on the fragment C=C-C<sub>6</sub>H<sub>4</sub>-R and the LUMO ( $\pi^*$ ) is localized on the 2,2'-bipyridyl (bpy) in the functionalized 2,2'-bipyridyl ligand bpyC=C-C<sub>6</sub>H<sub>4</sub>-R. Thus, the calculated lowest singlet at 466 nm is featured by a HOMO→LUMO intraligand charge transfer (ILCT) transition for 1. The calculated absorptions at 378 and 346 nm are from HOMO-2→LUMO and HOMO-1→LUMO states with LLCT/MLCT character (Table S2, Supporting Information). In strikingly contrast, the HOMO (Figure 9) resides on both ppy (51.9%) and Ir(5d) (44.1%) for  $Zn^{2+}$ binding species  $1/Zn^{2+}$  (Table S3, Supporting Information), although the LUMO is still predominately located on 2,2'bipyridyl (79.6%) and the C=C-C<sub>6</sub>H<sub>4</sub>-R fragment (16.4%) of the bpyC=C-C<sub>6</sub>H<sub>4</sub>-R ligand. The HOMO-2 is contributed by the bpyC=C-C<sub>6</sub>H<sub>4</sub>-R ligand (62.6%) and Ir(5d) (25.9%). The HOMO-3 is mainly composed of ppy (47.7%), Ir(5d) (24.5%), and the bpyC=C-C<sub>6</sub>H<sub>4</sub>-R ligand (27.8%). The lowest lying absorption (HOMO→LUMO transition) at 529 nm is typical of a LLCT/MLCT state, but the oscillator strength is too weak (0.0002) to be experimentally detected. The calculated excitations of absorption at 359 nm from HOMO−3→LUMO (54.9% contribution) and HOMO-2→LUMO (30.0% contribution) transitions are thus ascribed as an admixture of LLCT/MLCT/ILCT and ILCT/MLCT character, respectively. The calculation of emission properties of 1 and  $1/2n^{2+}$  was also carried out by TD-DFT. The compositions of frontier orbitals (HOMO and LUMO) are comparable to the character of those from the singlet manifold mentioned above. The emission



Figure 9. Frontrier orbitals of complex 1 and  $Zn^{2+}$  ion binding species  $1/Zn^{2+}$ .

character of 1 changes from <sup>3</sup>ILCT to <sup>3</sup>LLCT/<sup>3</sup>MLCT transition for  $1/Zn^{2+}$  upon  $Zn^{2+}$  ion binding.

#### Conclusions

Four cyclometalated iridium(III) complexes of functionalized 2,2'-bipyridyl ligands with a N,N or N,S, N,N,N, or N, N,S binding donors were synthesized and characterized, and their binding properties to the metal ions investigated. The UV-vis and emission spectral titrations demonstrated that the ion-binding properties of 1-4 could be modulated through modification of the binding sites by introducing one or two pyridyl/thiophene as binding sites. Complexes 1-4 display a low-energy absorption at 410-430 nm, arising from an ILCT transition from the HOMO ( $\pi$ ) residing on the fragment C=C-C<sub>6</sub>H<sub>4</sub>-R to the LUMO ( $\pi^*$ ) localized on the 2,2'-bipyridyl (bpy) in the functionalized 2,2'-bipyridyl ligand  $bpyC \equiv C - C_6 H_4$ -R as revealed from TD-DFT calculations. They are weakly luminescent in both solid state and solution at ambient temperature. Upon binding to specific metal ions, complexes 1-4 displayed remarkable UV-vis and emission spectral changes, arising from a conversion of the lowest energy excited state from ILCT to LLCT and MLCT

character. On the one hand, the low-energy absorption at 410–430 nm in these iridium(III) complexes is significantly blue-shifted to around 360 nm upon metal ion binding. On the other hand, a 9–30-fold luminescence enhancement was detected upon binding to specific metal ions because of the conversion from <sup>3</sup>ILCT excited state to highly emissive <sup>3</sup>LLCT/<sup>3</sup>MLCT triplet state. Complex 1 shows selective luminescence recognition to  $Zn^{2+}$  with a 25-fold luminescence enhancement. Particularly, complex 3 acts as a specific luminescence chemosensor to Cu<sup>2+</sup>, which exhibits an unique off–on–off luminescence switching effect.

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**Supporting Information Available:** Figures giving additional UV–vis and emission spectral titration curves, tables and figures regarding the TD-DFT calculations, and an X-ray crystallographic file in CIF format for the structure determination of compound 1. This material is available free of charge via the Internet at http://pubs.acs.org.