

## SUPPORTING INFORMATION

### **A Highly Selective Sulfur-Free Iridium (III)-Complex-Based Phosphorescent Chemodosimeter For Detection of Mercury(II) Ion**

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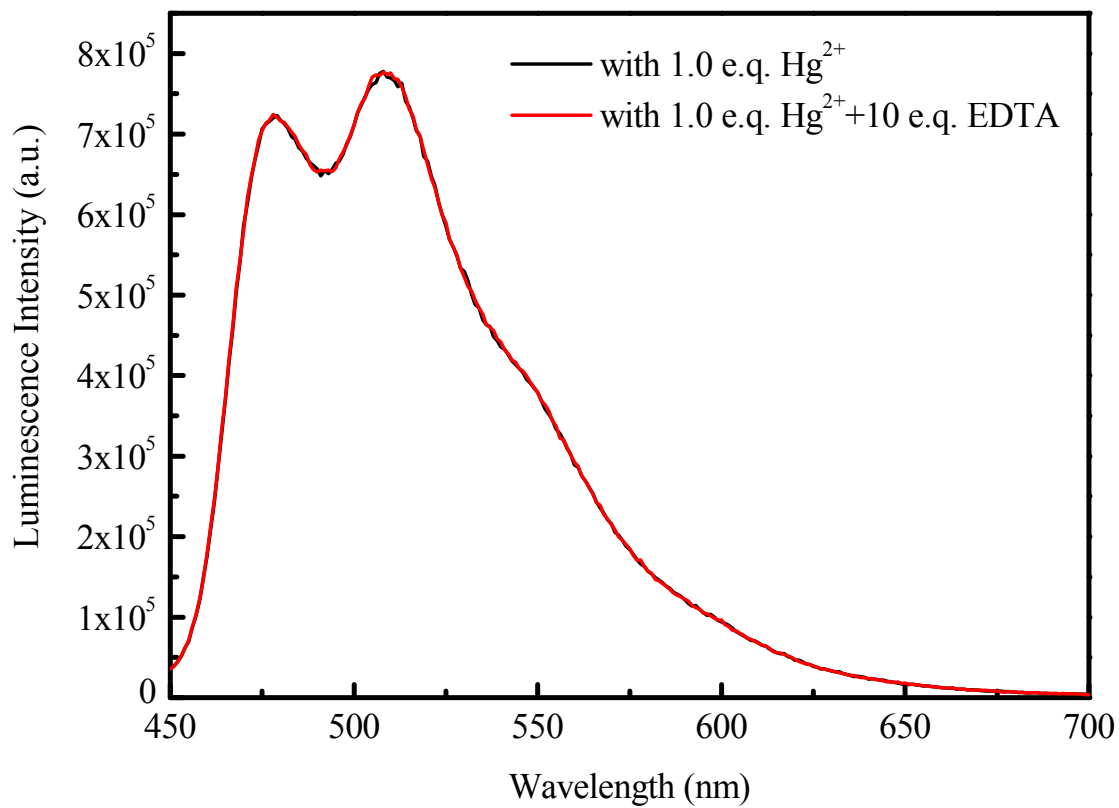
### Synthesis and characterization of Ir(pbi)<sub>2</sub>(acac)

Synthesis of 1,2-diphenyl-1*H*-benzo[*d*]imidazole (Hpbi). 0.1 mol of 2-nitro-*N*-phenylaniline, 40 mL of benzoyl chloride, 0.01 mol of anhydrous zinc chloride and 100 mL of anhydrous benzene were added to a round-bottom flask, then the mixture was refluxed for 3h. After cooled down, the solvent was evaporated, and the residue was recrystallized from ethanol to afford *N*-(2-nitrophenyl)-*N*-phenylbenzamide as yellow crystal with yield of 60%. This intermediate (3 mmol) and iron powder (0.5 g) were mixed and refluxed in 10 mL acetic acid for 2h, then the reaction mixture was filtered, and the filtrate was diluted with water, neutralized with saturated NaHCO<sub>3</sub> solution and then extracted four times with dichloromethane. The combined organic layer was dried over anhydrous sodium sulfate, then the solvent was evaporated to afford Hpbi as white solid in yield of 90 %. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz, δ/ppm): 7.79 (d, *J*=7.6 Hz, 1H, ArH), 7.56-7.53 (t, 5H, ArH), 7.41-7.26 (m, 7H, ArH), 7.23-7.21(d, *J*=8 Hz, 1H, ArH).

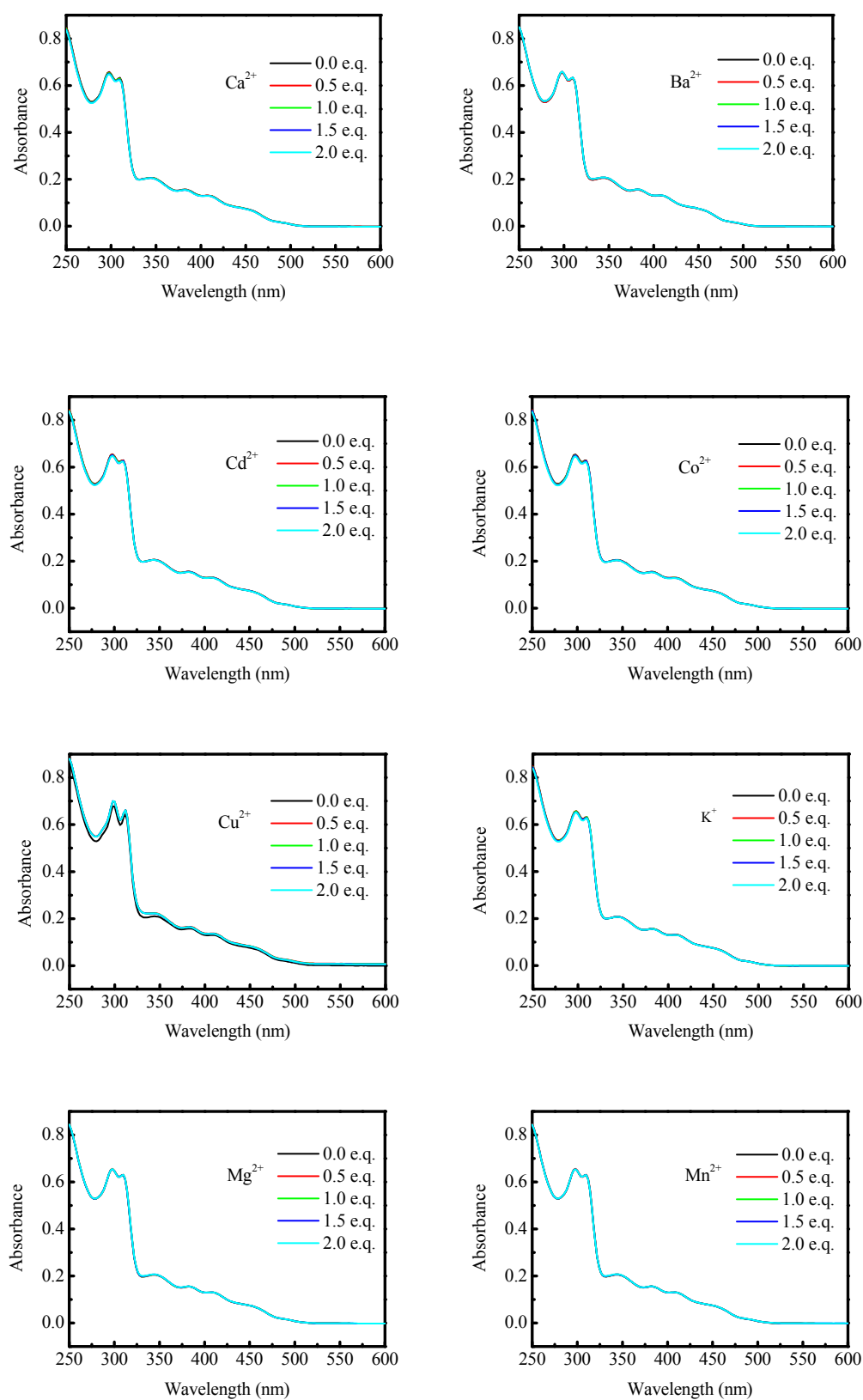
Synthesis of bis(1,2-diphenyl-1*H*-benzimidazolato-*N,C*<sup>2'</sup>)iridium(III) (acetylacetonate) [Ir(pbi)<sub>2</sub>(acac)]. Hpbi (2.4 mmol) and IrCl<sub>3</sub>·*n*H<sub>2</sub>O (1 mmol) were refluxed in a 40 mL mixture of 2-ethoxyethanol and water (3:1 v/v) under argon for 48 h, and the olive chloride-bridged dimer was isolated through filtration with yield of 61%. Then 0.1 mmol of this dichloro-bridged complex, 0.3 mmol of acetylacetonate, and 1 mmol of sodium carbonate were mixed with 10 mL of 2-ethoxyethanol and refluxed under argon for 15 h. After cooled down, the precipitate was filtered and washed with water and methanol, followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol

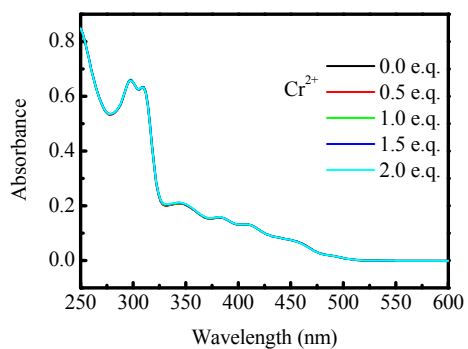
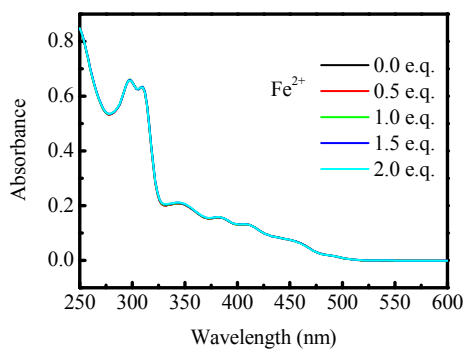
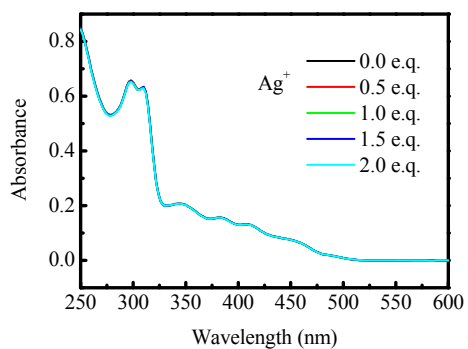
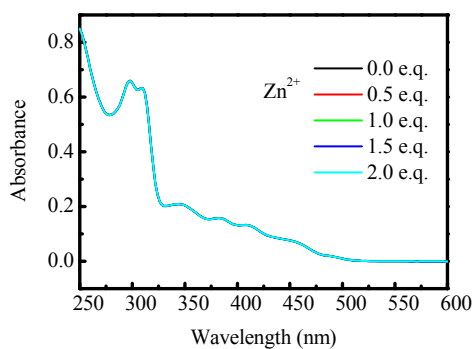
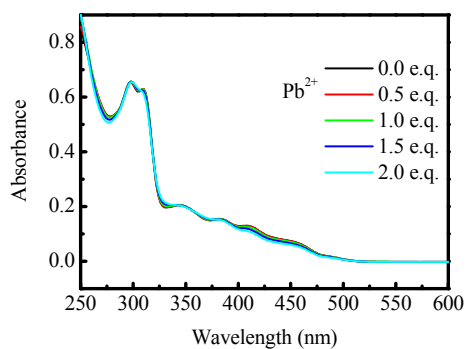
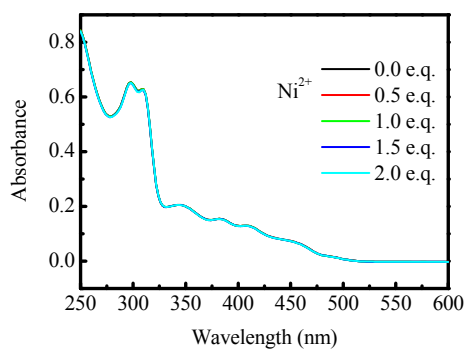
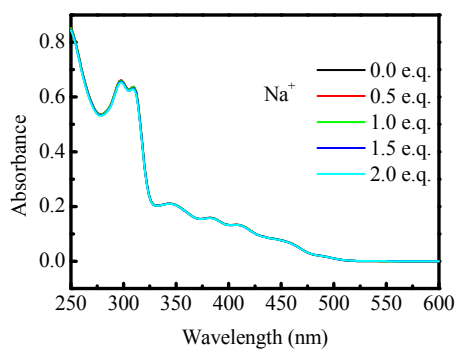
for three times to afford target compounds as bright yellow crystals with yield of 65%, purity (determined by HPLC, vide Figure S14): 99.6%. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3434, 3062, 3038, 1585, 1500, 1452, 1422, 1267, 1027, 746.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $\delta/\text{ppm}$ ): 7.72-7.75 (m, 2H), 7.63-7.67 (m, 8H), 7.58-7.6 (m, 2H), 7.3-7.31 (m, 4H), 7.13-7.15 (m, 2H), 6.53-6.58 (m, 4H), 6.44-6.48 (m, 4H), 5.26 (s, 1H), 1.86 (s, 6H). ESI-MS:  $m/z$  853.2130 ( $M + \text{Na}^+$ ) $^+$ ; Calcd for  $M_w + \text{Na}^+$ : 853.2176.

**Figure S1.** Phosphorescence emission spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})\text{-Hg}^{2+}$  complex in the absence and presence of 10 e.q. EDTA in acetonitrile solution ( $\lambda_{\text{ex}} = 384 \text{ nm}$ ).

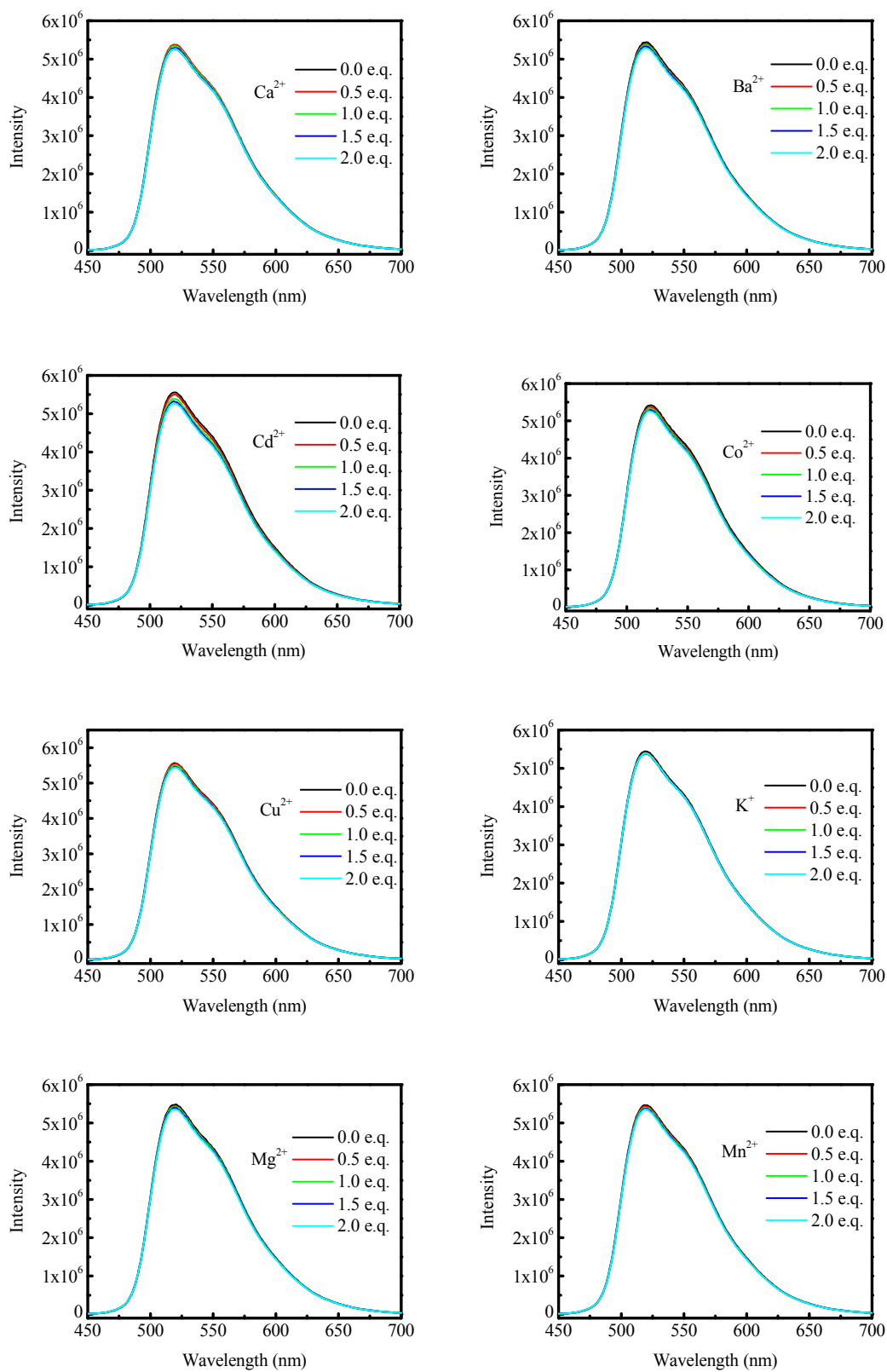


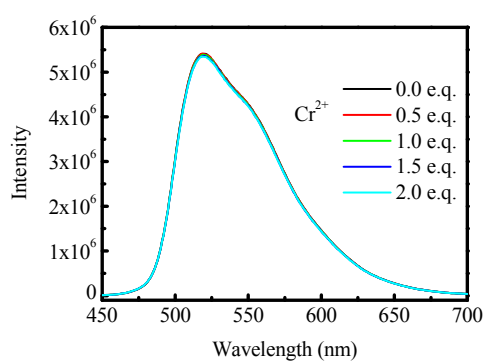
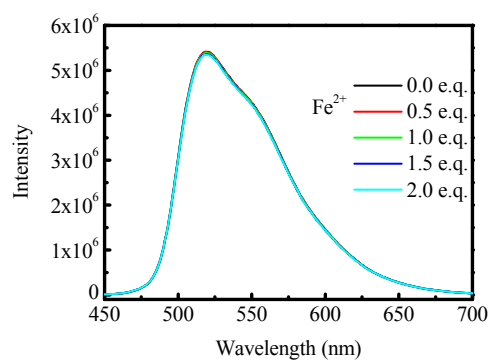
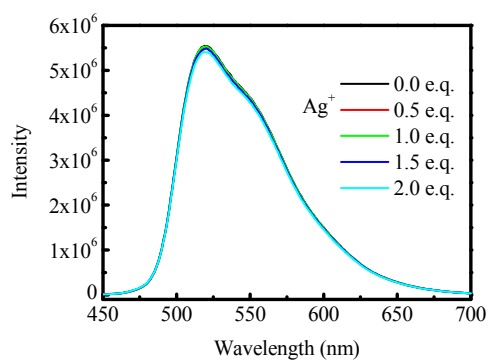
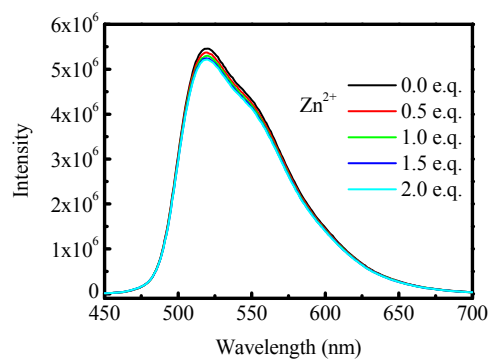
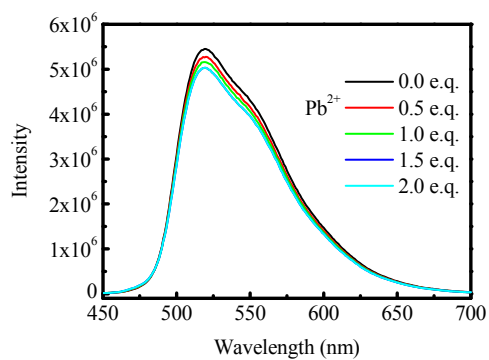
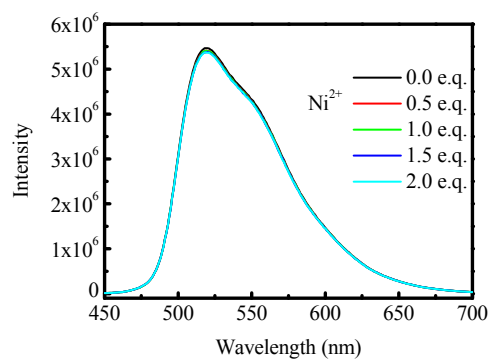
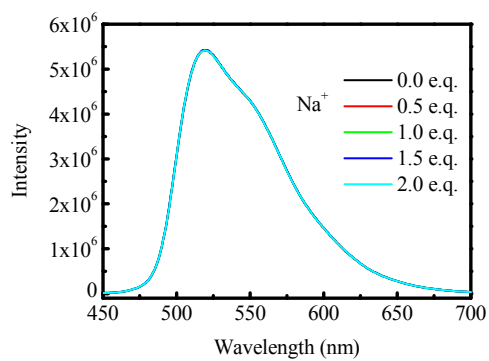
**Figure S2.** Response of UV-vis absorption spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})$  ( $20 \mu\text{M}$ ) in acetonitrile solution to various amounts of metal ions.





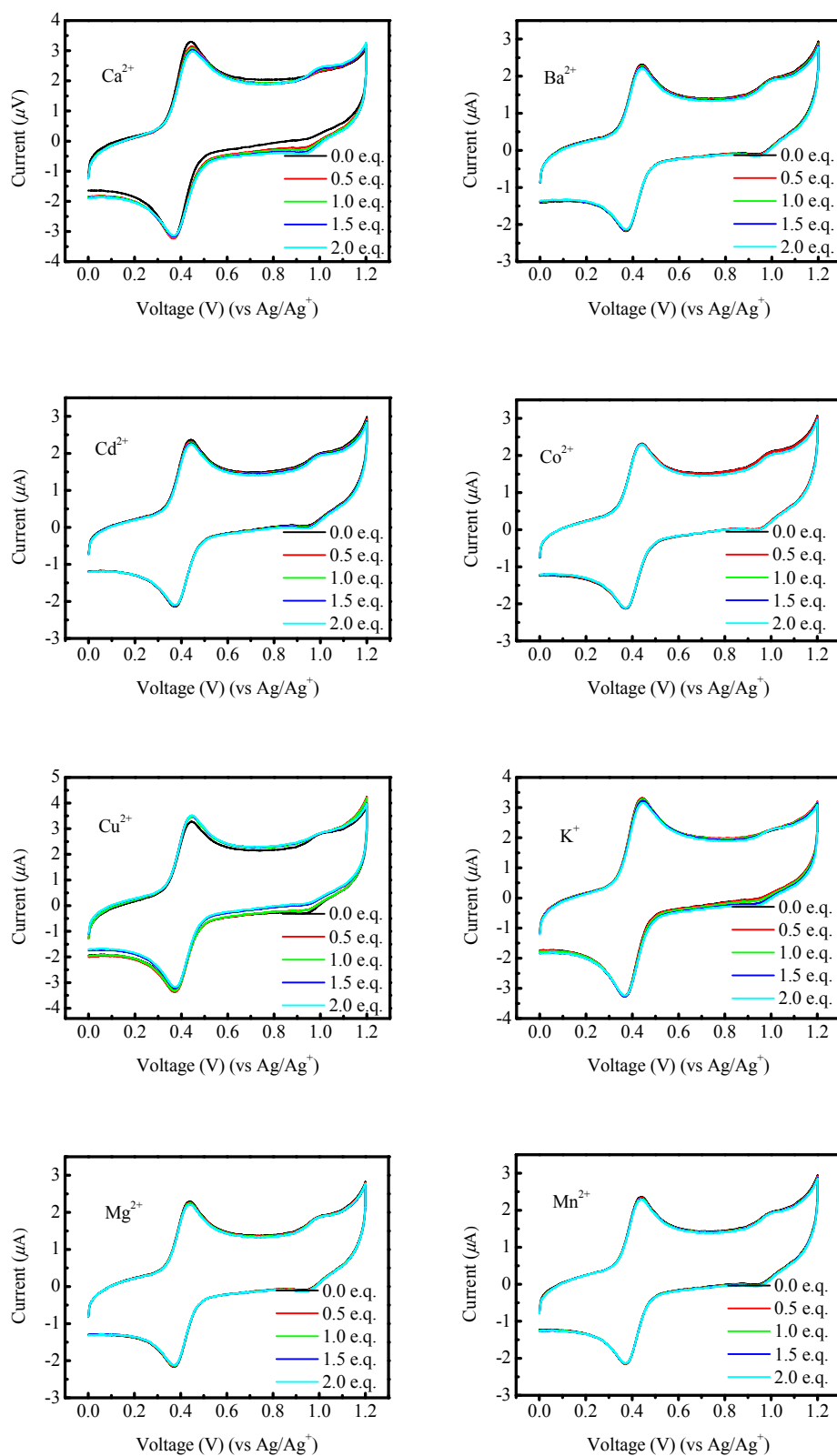
**Figure S3.** Response of phosphorescence spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})$  ( $20 \mu\text{M}$ ) in acetonitrile solution to various amounts of metal ions ( $\lambda_{\text{ex}} = 384 \text{ nm}$ ).

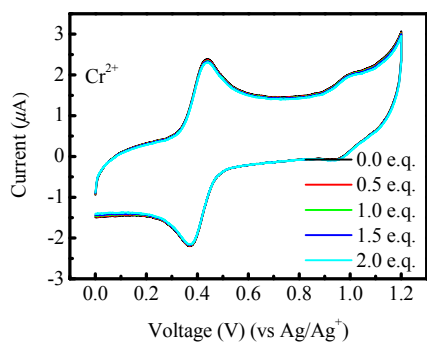
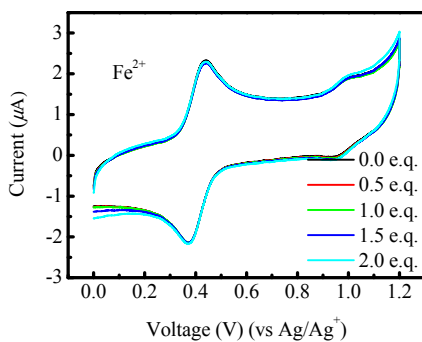
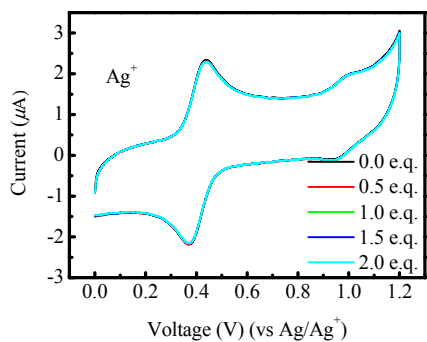
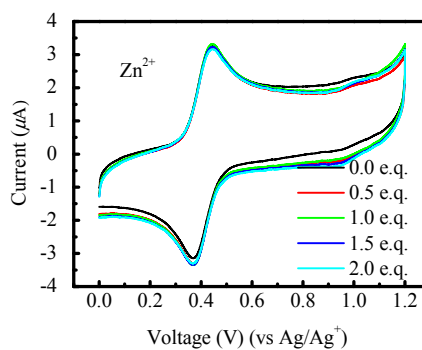
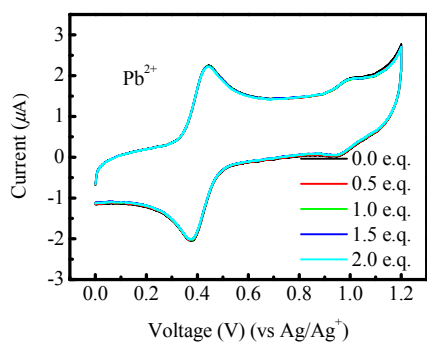
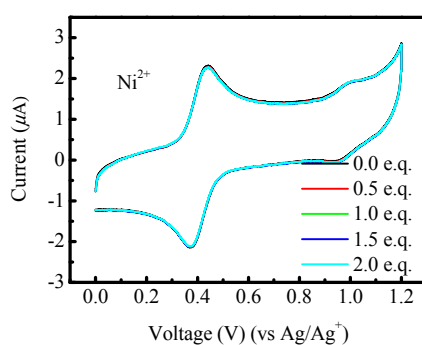
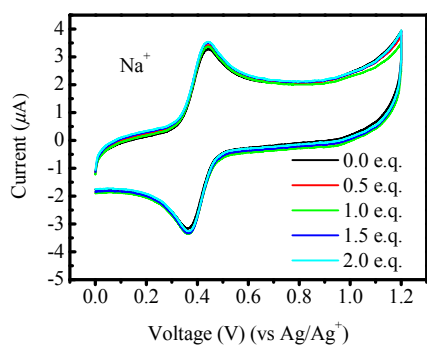




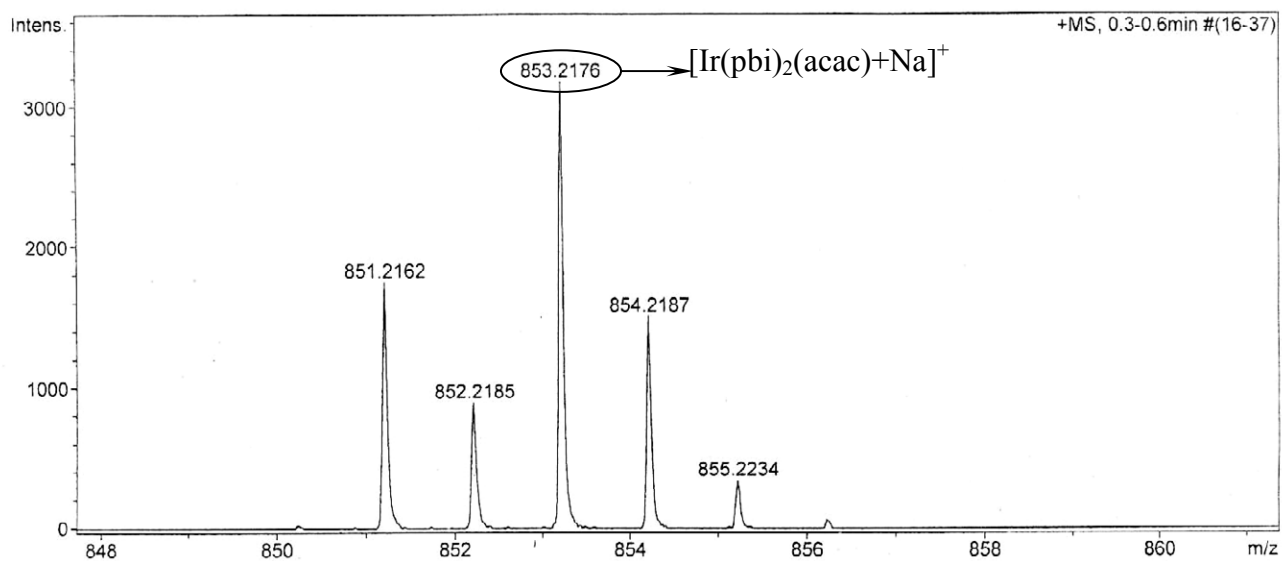


**Figure S4.** Response of cyclic voltammograms of **Ir(pbi)<sub>2</sub>(acac)** (50  $\mu$ M) in acetonitrile solution to various amounts of metal ions.

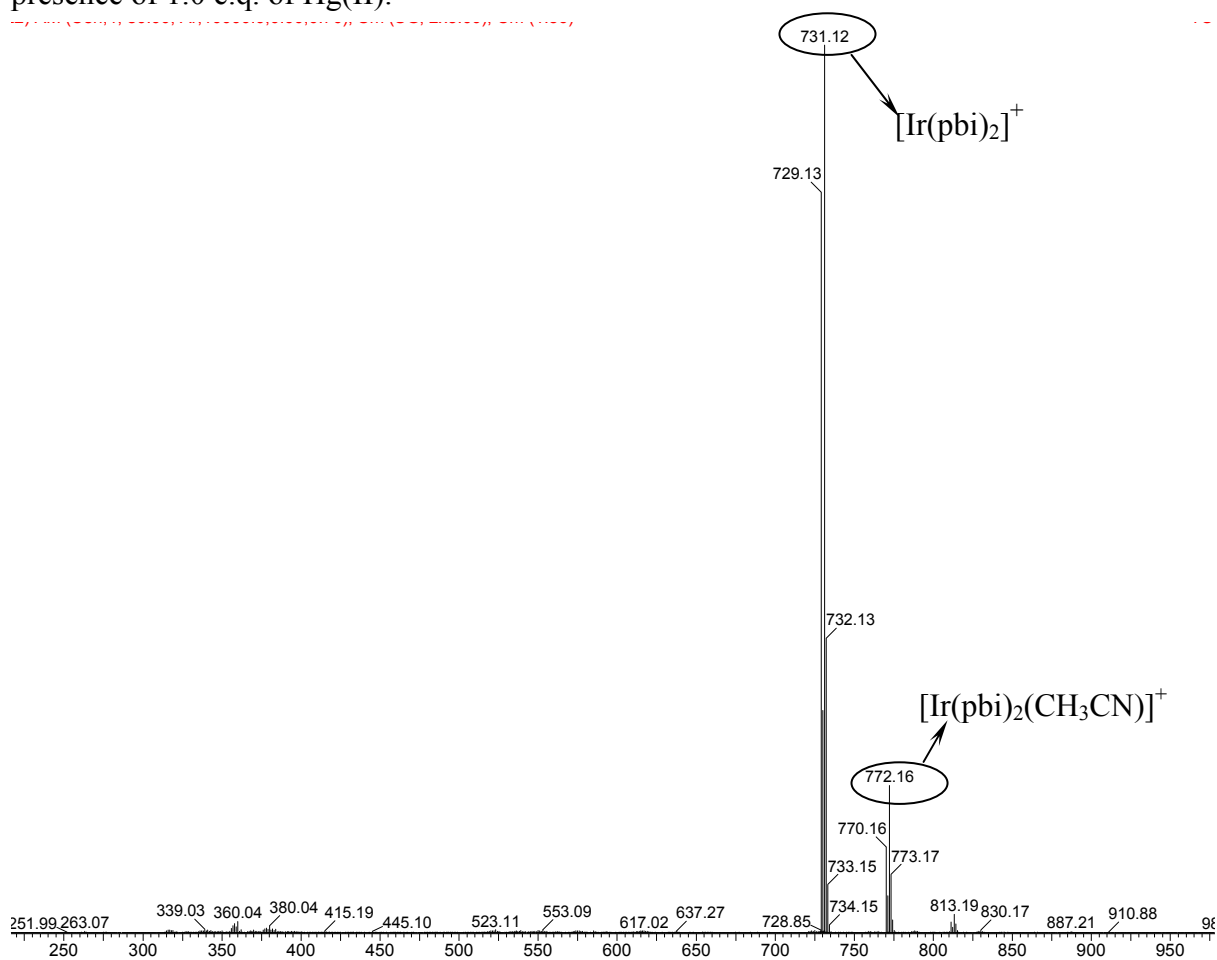




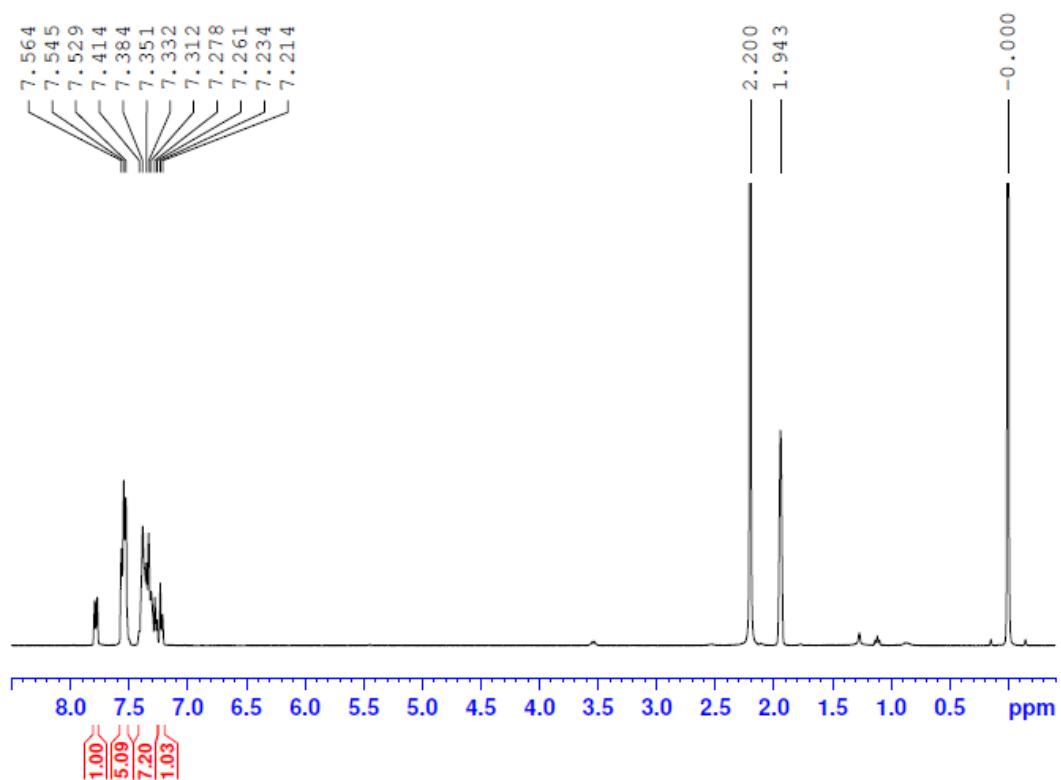
**Figure S5.** ESI-MS spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})$  in acetonitrile solution.



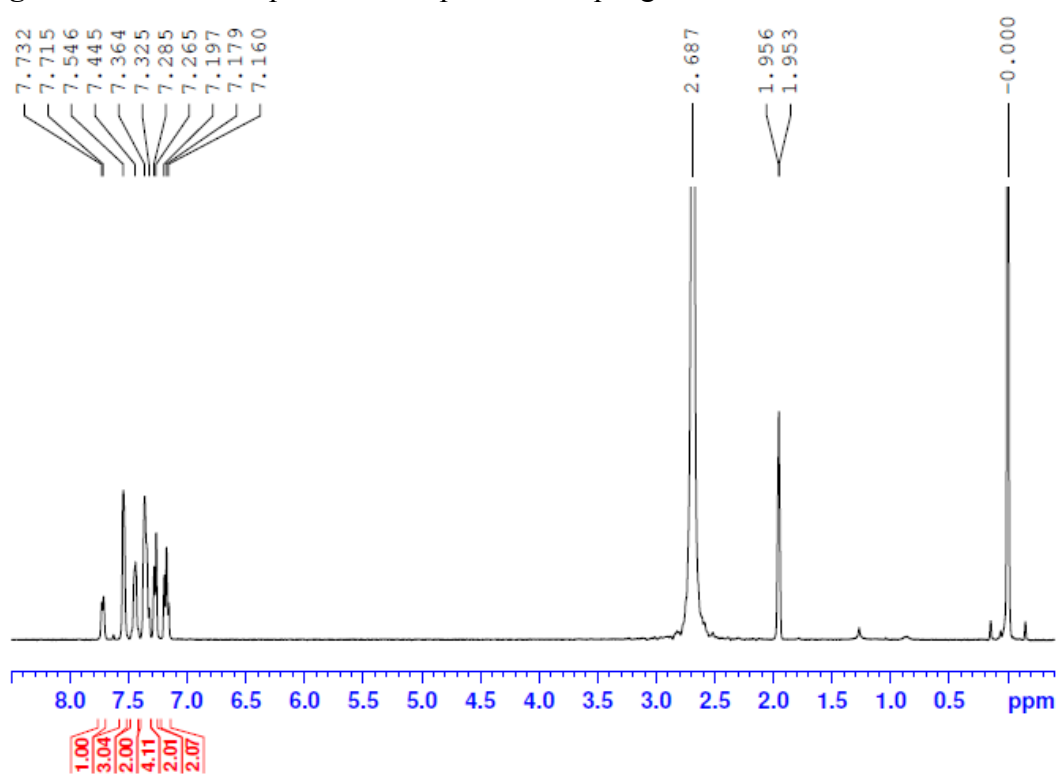
**Figure S6.** ESI-MS spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})$  in acetonitrile solution in the presence of 1.0 e.q. of  $\text{Hg}(\text{II})$ .



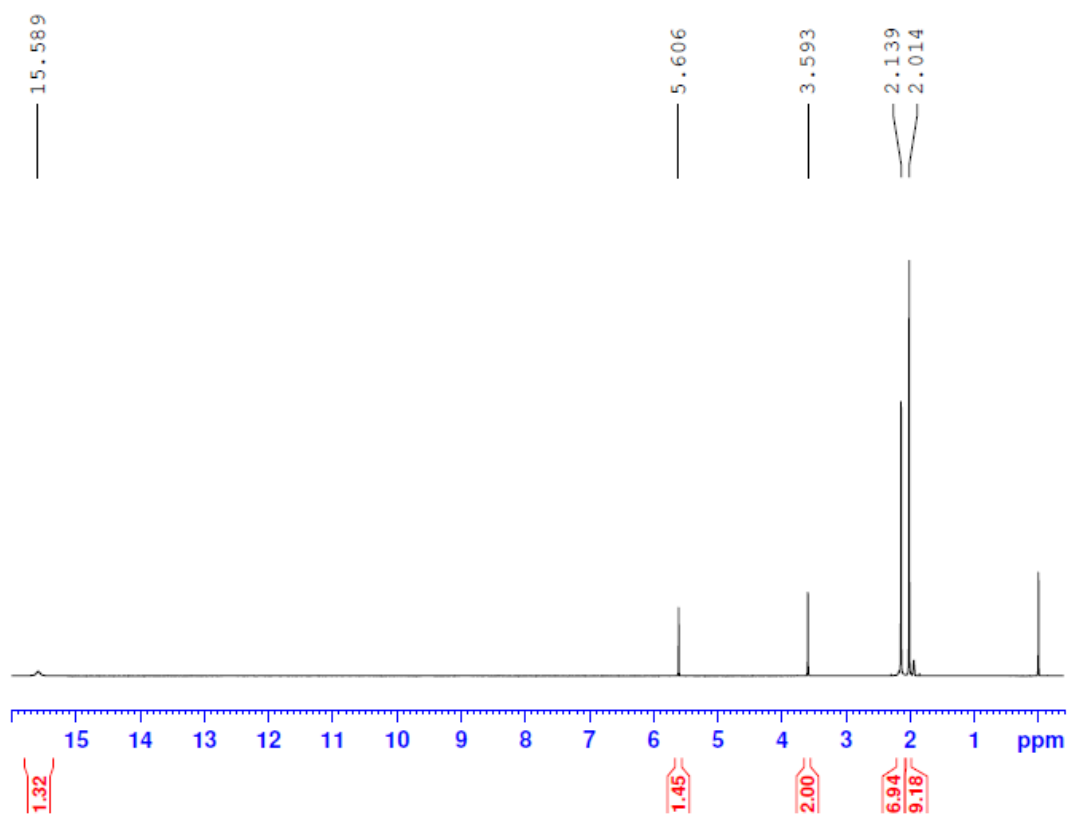
**Figure S7.**  $^1\text{H}$  NMR Spectrum of Hpbi in  $\text{CD}_3\text{CN}$ .



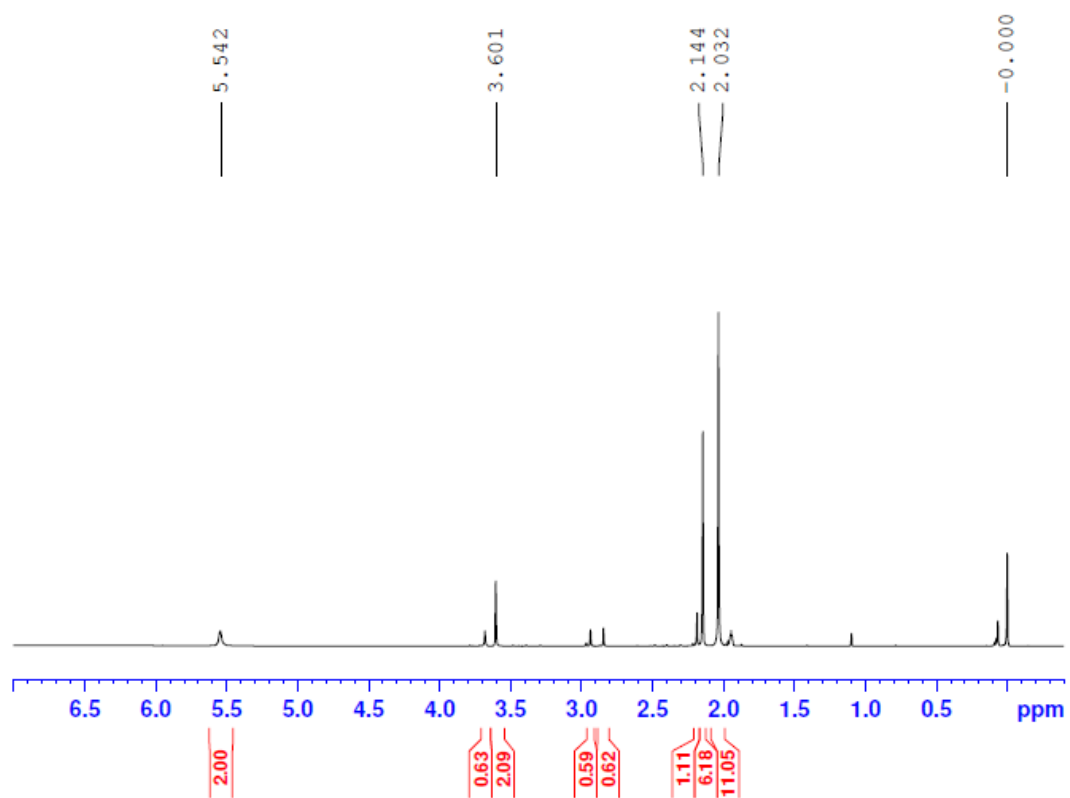
**Figure S8.**  $^1\text{H}$  NMR Spectrum of Hpbi + 1.0 e.q.  $\text{Hg}^{2+}$  in  $\text{CD}_3\text{CN}$ .



**Figure S9.**  $^1\text{H}$  NMR Spectrum of Hacac in  $\text{CD}_3\text{CN}$ .

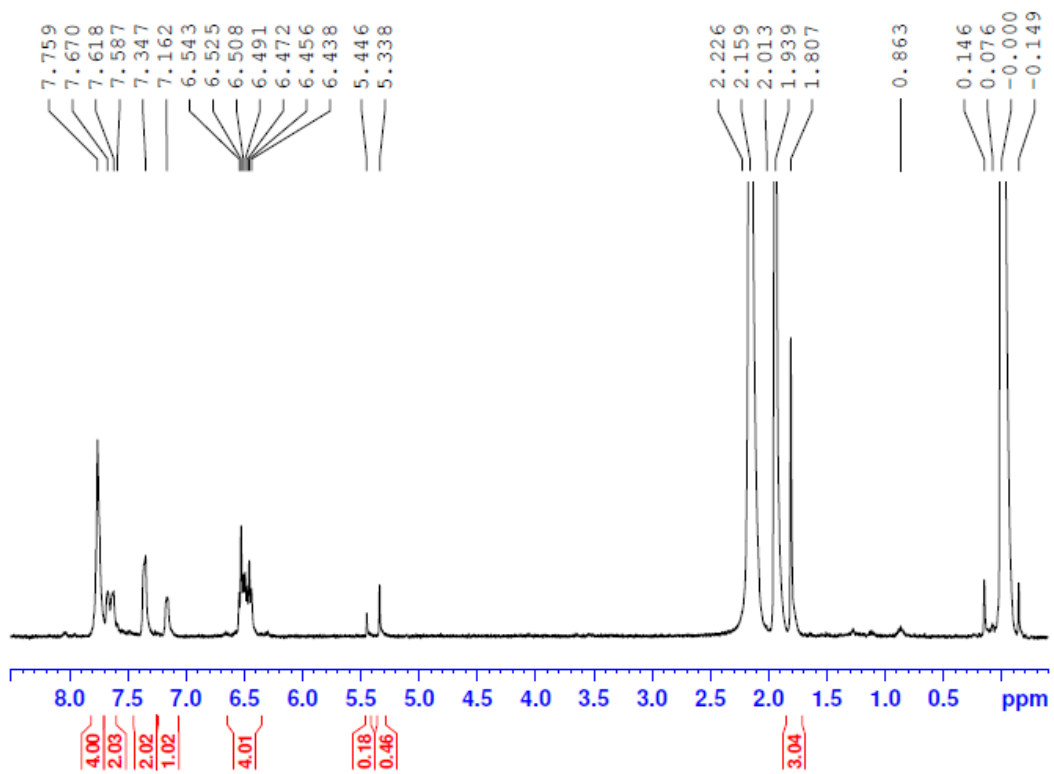


**Figure S10.**  $^1\text{H}$  NMR Spectrum of Hacac + 1.0 e.q.  $\text{Hg}^{2+}$  in  $\text{CD}_3\text{CN}$ .

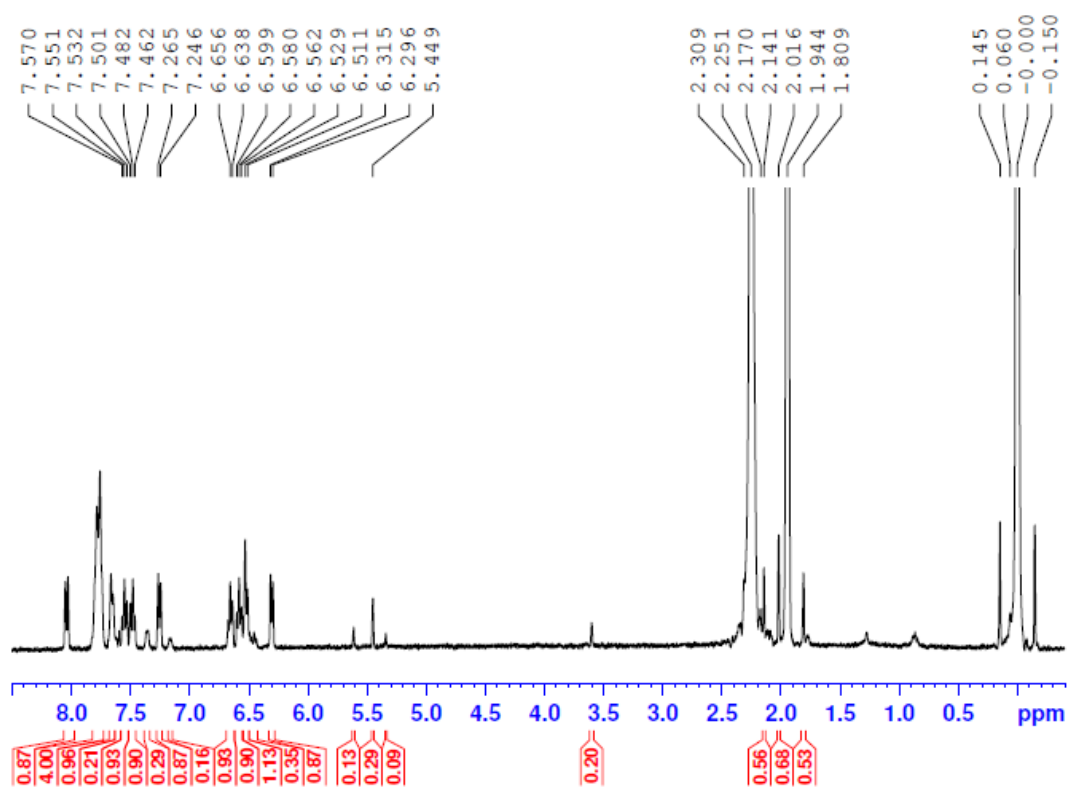




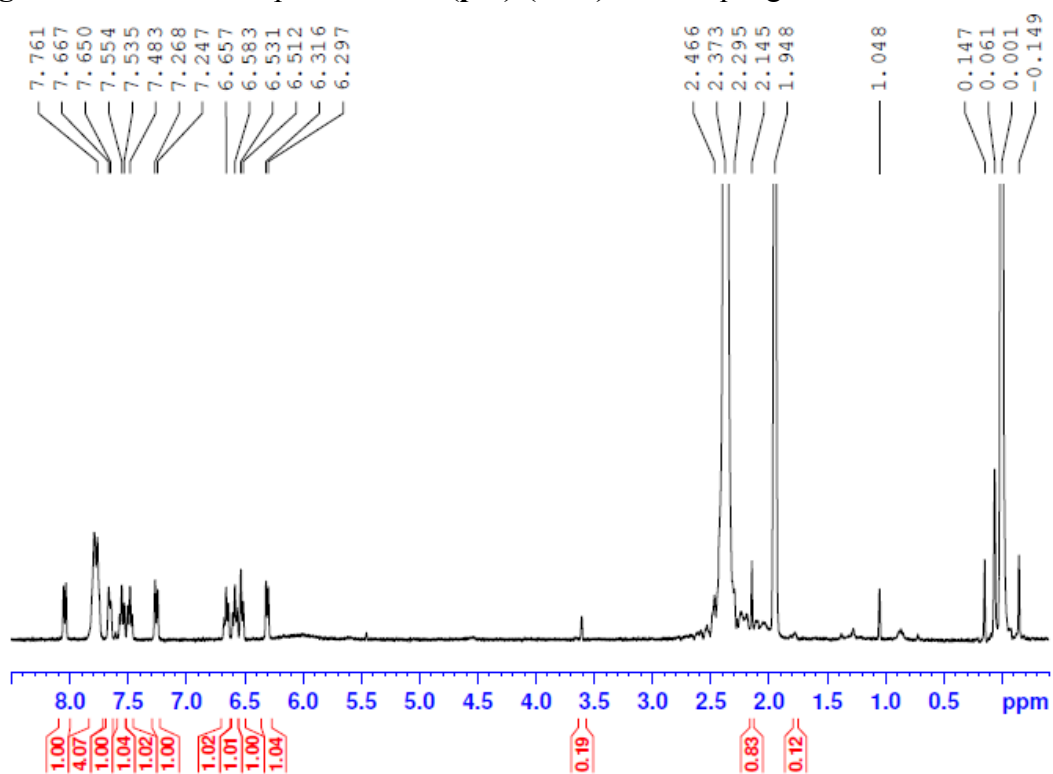
**Figure S11.**  $^1\text{H}$  NMR Spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac})$  in  $\text{CD}_3\text{CN}$ .



**Figure S12.**  $^1\text{H}$  NMR Spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac}) + 0.8 \text{ e.q. Hg}^{2+}$  in  $\text{CD}_3\text{CN}$ .



**Figure S13.**  $^1\text{H}$  NMR Spectrum of  $\text{Ir}(\text{pbi})_2(\text{acac}) + 1.0 \text{ e.q. Hg}^{2+}$  in  $\text{CD}_3\text{CN}$ .



**Figure S14.** High performance liquid chromatogram of **Ir(pbi)<sub>2</sub>(acac)**

