

## Supporting Information for

### Alkynyl bridged cyclometalated Ir<sub>2</sub>M<sub>2</sub> clusters: Impact of the heterometal in the photo- and electro-luminescent properties

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## Experimental Section

**General Remarks.** All reactions were carried out under Ar atmosphere using Schlenk tube techniques. Solvents were obtained from a solvent purification system (M-BRAUN MB SPS-800). IR spectra were recorded on a FT-IR Nicolet Nexus spectrometer as Nujol mulls between polyethylene sheets and NMR spectra were recorded on either a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ( $\text{SiMe}_4$ ) and coupling constants in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 CHNS/O microanalyzer. Mass spectra were recorded on a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol as matrix. Cyclic voltammetry were carried out in 0.1 M  $\text{NBu}_4\text{PF}_6$  solutions as supporting electrolyte, using a three-electrode configuration (Pt disk as working electrode, Pt-wire counter electrode, Ag/AgCl reference electrode) on a Voltalab PST 050. The ferrocene/ferrocenium couple served as internal reference (+0.58 V vs Ag/AgCl). The optical absorption spectra were recorded using a Hewlett-Packard 8453 (solution) spectrophotometer in the visible and near-UV range. Diffuse reflectance UV-vis (DRUV) data of pressed powder diluted with KBr were recorded on a Shimadzu (UV-3600 spectrophotometer with a Harrick Praying Mantis accessory) and recalculated following the Kubelka-Munk function. Excitation and emission spectra were obtained on a Jobin-Yvon Horiba Fluorolog 3-11 Tau-3 spectrofluorimeter. The lifetime measurements were performed in a Jobin Yvon Horiba Fluorolog operating in the phosphorimeter mode (with an F1-1029 lifetime emission PMT assembly, using a 450W Xe lamp) or with a Datastation HUB-B with a nanoLED controller and software DAS6. The nanoLEDs employed for lifetime measurements were of 390 nm with pulse lengths of 0.8–1.4 ns. The lifetime data have been fitted using the Jobin-Yvon software package. Quantum yields were measured using a F-3018 Integrating Sphere mounted on a Fluorolog 3-11 Tau-3 spectrofluorimeter. The starting materials  $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$ ,<sup>1</sup>  $[\text{M}\equiv\text{CC}_6\text{H}_4\text{OMe-3}]_n$  (M= Cu, Ag)<sup>2</sup> was prepared as reported in the literature and the spectroscopic properties matched those reported. Alkynes were purchased from Aldrich.

**Preparation of  $[\text{Ir}(\text{ppy})_2(\mu\text{-}\kappa\text{C}^\alpha\text{:}\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})]_2$  (1).** To a fresh (-20°C) solution of  $\text{LiC}\equiv\text{CC}_6\text{H}_4\text{OMe-3}$  (1.68 mmol) in THF (20 ml),  $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})]_2$  (0.300 g, 0.280 mmol) was added. The mixture was stirred at this temperature for 1 hour, and then was allowed to reach room temperature (48 h). The resulting yellow suspension was evaporated to dryness, and the final residue was treated with  $\text{CH}_2\text{Cl}_2$  (~ 40 ml). The

orange solution was filtered under N<sub>2</sub> through Celite, and the filtrate was evaporated to dryness. Addition of cold EtOH (~ 5 ml) afforded as a dark yellow solid (0.216 g, 82%). Anal. Calc. for C<sub>62</sub>H<sub>46</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>2</sub> (1263.49): C, 58.93; H, 3.67; N, 4.43. Found: C, 59.36; H, 3.71; N, 4.36 %. IR:  $\nu(\text{C}\equiv\text{C})$  1997cm<sup>-1</sup>. MALDI-TOF (+):  $m/z$  (%): 501 [Ir(ppy)<sub>2</sub>]<sup>+</sup> (84%), 632 [Ir(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)]<sup>+</sup> (100%), 763 [Ir(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>2</sub>]<sup>+</sup> (57%), 977 [Ir<sub>2</sub>(ppy)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)]<sup>+</sup> (27%), 1108 [Ir<sub>2</sub>(ppy)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>2</sub>]<sup>+</sup> (18%), 1148 [Ir<sub>2</sub>(ppy)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)(OH)]<sup>+</sup> (6%). <sup>1</sup>H NMR (400.1 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K):  $\delta$  = 9.41 (d,  $J$  = 5.5, 4H, H<sup>2</sup><sub>ppy</sub>), 8.00 (d,  $J$  = 7.3, 4H, H<sup>5</sup><sub>ppy</sub>), 7.83 (t,  $J$  = 7.3, 4H, H<sup>4</sup><sub>ppy</sub>), 7.50 (d,  $J$  = 7.3, 4H, H<sup>6</sup><sub>ppy</sub>), 6.93 (t,  $J$  = 6.5, 4H, H<sup>3</sup><sub>ppy</sub>), 6.62 (t,  $J$  = 6.5, 4H, H<sup>7</sup><sub>ppy</sub>), 6.51 (m, 6H, H<sup>8</sup><sub>ppy</sub>, H<sup>5</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 6.27 (dd, <sup>3</sup> $J$  = 8.1 Hz, <sup>4</sup> $J$  = 2.1 Hz, 2H, H<sup>6</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 5.92 (d,  $J$  = 7.5, 4H, H<sup>9</sup><sub>ppy</sub>), 5.77 (d,  $J$  = 7.6, 2H, H<sup>4</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 5.73 (s, 2H, H<sup>2</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 3.39 (s, 6H, -OMe). <sup>13</sup>C {<sup>1</sup>H} NMR (100.62 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K):  $\delta$  = 169.8 (s, C<sup>12</sup><sub>ppy</sub>), 161.3 (s, C<sup>11</sup><sub>ppy</sub>), 159.1 (s, C<sup>3</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 151.7 (s, C<sup>2</sup><sub>ppy</sub>), 144.6 (s, C<sup>10</sup><sub>ppy</sub>), 137.3 (s, C<sup>4</sup><sub>ppy</sub>), 131.0 (s, C<sup>9</sup><sub>ppy</sub>), 129.8 (s, C<sup>8</sup><sub>ppy</sub>), 128.3 (s, C<sup>5</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 124.4 (s, C<sup>6</sup><sub>ppy</sub>), 123.7 (s, C<sup>4</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 122.6 (s, C<sup>3</sup><sub>ppy</sub>), 121.3 (s, C<sup>7</sup><sub>ppy</sub>), 119.9 (s, C<sup>5</sup><sub>ppy</sub>), 115.6 (s, C<sup>2</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 112.2 (s, C<sup>6</sup><sub>C<sub>6</sub>H<sub>4</sub></sub>), 103.0 (s, C <sub>$\beta$</sub> ), 80.2 (s, C <sub>$\alpha$</sub> ), 55.0 (s, C-OMe).

**Preparation of [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>( $\mu$ -C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>4</sub>] (2).** *Method i:* To a yellow solution of [Ir(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)]<sub>2</sub> (0.1 g, 0.080 mmol) in THF (60 ml) was added [AgC≡CC<sub>6</sub>H<sub>4</sub>OMe-3]<sub>n</sub> (0.04 g, 0.160 mmol) at room temperature and the mixture was stirred for 24 h protected from the light. The resulting suspension was evaporated to dryness, the residue treated with CH<sub>2</sub>Cl<sub>2</sub>(~40 ml) and filtered under N<sub>2</sub> through Celite. The solvent was eliminated from the filtrate and treated with cold n-hexane (~5 ml) to afford **2** as a yellow solid (0.130g, 93% yield). *Method ii:* [AgC≡CC<sub>6</sub>H<sub>4</sub>OMe-3]<sub>n</sub> (0.089 g, 0.373 mmol) was added to a yellow solution of [Ir(ppy)<sub>2</sub>( $\mu$ -Cl)]<sub>2</sub> (0.1 g, 0.094 mmol) in THF (60 ml) and the mixture stirred for c.a. 72 h. protected from the light. The obtained AgCl was filtered off and the resulting yellow filtrate was evaporated to dryness. Addition of cold Et<sub>2</sub>O (~5 ml) afforded **2** as a yellow solid (0.115 g, 75%).

Anal. Calc. for C<sub>80</sub>H<sub>60</sub>Ag<sub>2</sub>Ir<sub>2</sub>N<sub>4</sub>O<sub>4</sub> (1741.53): C, 55.17; H, 3.47; N, 3.22 . Found: C, 54.87; H, 3.50; N, 3.57%. IR:  $\nu(\text{C}\equiv\text{C})$  1990, 1964 cm<sup>-1</sup>. MALDI-TOF (+):  $m/z$  (%): 501 [Ir(ppy)<sub>2</sub>]<sup>+</sup> (85%), 632 [Ir(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)]<sup>+</sup> (53%), 739 [IrAg(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)]<sup>+</sup>, 763 [Ir(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>2</sub>]<sup>+</sup> (100%), 979 [IrAg<sub>2</sub>(ppy)<sub>2</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>2</sub>]<sup>+</sup> (33%), 1455 [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>3</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>3</sub>]<sup>+</sup> (68%), 1480 [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>2</sub>]<sup>+</sup> (26%), 1609 [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>3</sub>]<sup>+</sup> (41%), 1742 [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>(C≡CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>4</sub>]<sup>+</sup>

(8%), 1849  $[\text{Ir}_2\text{Ag}_3(\text{ppy})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]^+$  (37%), 2089  $[\text{Ir}_2\text{Ag}_4(\text{ppy})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_5]^+$  (34%).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  = 9.91 (d,  $J$  = 5.7 Hz, 4H,  $\text{H}^2_{\text{ppy}}$ ), 7.98 (d,  $J$  = 8.3 Hz, 4H,  $\text{H}^5_{\text{ppy}}$ ), 7.67 (d,  $J$  = 8.1 Hz, 4H,  $\text{H}^6_{\text{ppy}}$ ), 7.63 (t,  $J$  = 8.0 Hz, 4H,  $\text{H}^4_{\text{ppy}}$ ), 7.11 (t,  $J$  = 6.8 Hz, 4H,  $\text{H}^3_{\text{ppy}}$ ), 6.97 (t,  $J$  = 8.0 Hz, 4H,  $\text{H}^5_{\text{C}_6\text{H}_4}$ ), 6.76 (m, 8H,  $\text{H}^{7,8}_{\text{ppy}}$ ), 6.69 (dd,  $^3J$  = 8.3 Hz,  $^4J$  = 1.7 Hz, 4H,  $\text{H}^6_{\text{C}_6\text{H}_4}$ ), 6.38 (m, 8H,  $\text{H}^9_{\text{ppy}}$ ,  $\text{H}^4_{\text{C}_6\text{H}_4}$ ), 6.33 (s, 4H,  $\text{H}^2_{\text{C}_6\text{H}_4}$ ), 3.52 (s, 12H, -OMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  = 169.0 (s,  $\text{C}^{12}_{\text{ppy}}$ ), 159.3 (s,  $\text{C}^{11}_{\text{ppy}}$ ,  $\text{C}^3_{\text{C}_6\text{H}_4}$ ), 152.4 (s,  $\text{C}^2_{\text{ppy}}$ ), 144.2 (s,  $\text{C}^{10}_{\text{ppy}}$ ), 136.5 (s,  $\text{C}^4_{\text{ppy}}$ ), 130.6 (s,  $\text{C}^9_{\text{ppy}}$ ), 129.5, 128.9 (s,  $\text{C}^8_{\text{ppy}}$ ,  $\text{C}^5_{\text{C}_6\text{H}_4}$ ), 127.1 (s,  $\text{C}^1_{\text{C}_6\text{H}_4}$ ), 123.8 (s,  $\text{C}^6_{\text{ppy}}$ ), 123.6 (s,  $\text{C}^4_{\text{C}_6\text{H}_4}$ ), 122.6 (s,  $\text{C}^3_{\text{ppy}}$ ), 120.8 (s,  $\text{C}^7_{\text{ppy}}$ ), 119.3 (s,  $\text{C}^5_{\text{ppy}}$ ), 116.5 (s,  $\text{C}^2_{\text{C}_6\text{H}_4}$ ), 112.9 (s,  $\text{C}^6_{\text{C}_6\text{H}_4}$ ), 54.6 (s,  $\text{C}_{\text{-OMe}}$ ).

**Preparation of  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (**3**).** To a yellow solution of  $[\text{Ir}(\text{ppy})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_2]$  (0.1 g, 0.080 mmol) in THF (60 ml) was added  $[\text{CuC}\equiv\text{CC}_6\text{H}_4\text{OMe-3}]_n$  (0.03 g, 0.160 mmol) at room temperature and the mixture was stirred for 72 h. The resulting suspension was evaporated to dryness, the residue treated with  $\text{CH}_2\text{Cl}_2$  (~40 ml) and filtered under  $\text{N}_2$  through Celite. The solvent was eliminated from the filtrate and treated with cold n-hexane (~5 ml) to afford **2** as an orange solid (0.120 g, 91% yield). Anal. Calc. for  $\text{C}_{80}\text{H}_{60}\text{Cu}_2\text{Ir}_2\text{N}_4\text{O}_4$  (1652.25): C, 58.10; H, 3.66; N, 3.39. Found: C, 57.81; H, 3.75; N, 3.69%. IR:  $\nu(\text{C}\equiv\text{C})$  1952  $\text{cm}^{-1}$ . MALDI-TOF (+):  $m/z$  (%): 501  $[\text{Ir}(\text{ppy})_2]^+$  (25%), 632  $[\text{Ir}(\text{ppy})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})]^+$  (30%), 763  $[\text{Ir}(\text{ppy})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_2]^+$  (28%), 826  $[\text{IrCu}(\text{ppy})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_2]^+$  (24%), 1212  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_3]^+$  (10%), 1367  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_3(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_3]^+$  (100%), 1499  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_3(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]^+$  (19%), 1521  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_3]^+$  (10%), 1652  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]^+$  (6%), 1715  $[\text{Ir}_2\text{Cu}_3(\text{ppy})_4(\text{C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]^+$  (22%).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  = 9.82 (d,  $J$  = 5.6 Hz, 4H,  $\text{H}^2_{\text{ppy}}$ ), 7.81 (d,  $J$  = 7.9 Hz, 4H,  $\text{H}^5_{\text{ppy}}$ ), 7.61 (m, 8H,  $\text{H}^{6,4}_{\text{ppy}}$ ), 7.12 (t,  $J$  = 6.6 Hz, 4H,  $\text{H}^3_{\text{ppy}}$ ), 6.96 (t,  $J$  = 7.7 Hz, 4H,  $\text{H}^5_{\text{C}_6\text{H}_4}$ ), 6.77 (m, 8H,  $\text{H}^{7,8}_{\text{ppy}}$ ), 6.69 (dd,  $^3J$  = 8.5 Hz,  $^4J$  = 1.7 Hz, 4H,  $\text{H}^6_{\text{C}_6\text{H}_4}$ ), 6.48 (d,  $^3J$  = 7.6 Hz, 4H,  $\text{H}^4_{\text{C}_6\text{H}_4}$ ), 6.35 (s, 4H,  $\text{H}^2_{\text{C}_6\text{H}_4}$ ), 6.32 (d,  $J$  = 7.3 Hz, 4H,  $\text{H}^9_{\text{ppy}}$ ), 3.37 (s, 12H, -OMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.62 MHz,  $\text{CD}_3\text{COCD}_3$ , 298 K):  $\delta$  = 168.6 (s,  $\text{C}^{12}_{\text{ppy}}$ ), 162.5 (s,  $\text{C}^{11}_{\text{ppy}}$ ), 159.3 (s,  $\text{C}^3_{\text{C}_6\text{H}_4}$ ), 152.6 (s,  $\text{C}^2_{\text{ppy}}$ ), 144.1 (s,  $\text{C}^{10}_{\text{ppy}}$ ), 136.3 (s,  $\text{C}^4_{\text{ppy}}$ ), 130.4 (s,  $\text{C}^9_{\text{ppy}}$ ), 128.9 (s,  $\text{C}^8_{\text{ppy}}$ ), 128.8 (s,  $\text{C}^5_{\text{C}_6\text{H}_4}$ ), 127.9 (s,  $\text{C}^1_{\text{C}_6\text{H}_4}$ ), 123.8 (s,  $\text{C}^6_{\text{ppy}}$ ), 123.3 (s,  $\text{C}^4_{\text{C}_6\text{H}_4}$ ), 122.3 (s,  $\text{C}^3_{\text{ppy}}$ ), 120.9 (s,  $\text{C}^7_{\text{ppy}}$ ), 119.1 (s,  $\text{C}^5_{\text{ppy}}$ ), 116.5 (s,  $\text{C}_{\alpha\beta}$ ), 115.7 (s,  $\text{C}^2_{\text{C}_6\text{H}_4}$ ), 113.2 (s,  $\text{C}^6_{\text{C}_6\text{H}_4}$ ), 107.6 (s,  $\text{C}_{\alpha\beta}$ ), 54.0 (s,  $\text{C}_{\text{-OMe}}$ ).

**X-Ray Crystallography.** Table S1 reports details of the structural analysis for complexes **1**·2CH<sub>3</sub>COCH<sub>3</sub>, **2**·2CH<sub>2</sub>Cl<sub>2</sub> and **3**. Yellow crystals of **1** and **2** were obtained by slow evaporation of the complexes in acetone (**1**·2CH<sub>3</sub>OCH<sub>3</sub>; room temperature) or in a 1:2 mixture of CH<sub>2</sub>Cl<sub>2</sub>/acetone (**2**·2CH<sub>2</sub>Cl<sub>2</sub>), respectively. Crystals of **3** were prepared by slow diffusion of *n*-hexane into solution of **3** in CH<sub>2</sub>Cl<sub>2</sub>. X-ray intensity data were collected with a NONIUS- $\kappa$ CCD area-detector diffractometer, using graphite-monochromatic Mo-K $\alpha$  radiation, and images were processed using the DENZO and SCALEPACK suite of programs.<sup>3</sup> The structures were solved by Direct Methods using SHELXS-97<sup>4</sup> (**2**·1.5CH<sub>2</sub>Cl<sub>2</sub>) or Patterson and Fourier methods using DIRDIF2008<sup>5</sup> (**1**·2CH<sub>3</sub>OCH<sub>3</sub>, **3**), and refined by full-matrix least squares on  $F^2$  with SHELXL.<sup>6</sup> The absorption corrections were performed using MULTI-SCAN<sup>7</sup> (**1**·2CH<sub>3</sub>OCH<sub>3</sub>, **3**), or X-Abs<sup>8</sup> (**2**·2CH<sub>2</sub>Cl<sub>2</sub>), with the WINGX program suite.<sup>9</sup> For complex **2**, two crystallization CH<sub>2</sub>Cl<sub>2</sub> molecules were observed. One of these molecules is model with occupancy 1. The second could not be adequately modelled and was removed from the model. Examination with PLATON<sup>10</sup> and SQUEEZE.<sup>10,11</sup> revealed the presence of one void of 287 Å<sup>3</sup> in the unit cell, containing 157 e<sup>-</sup>. This fits with the presence of 2 molecules of CH<sub>2</sub>Cl<sub>2</sub> in the unit cell and gives rise to the stoichiometry (**2**·2CH<sub>2</sub>Cl<sub>2</sub>). For **3**, one methoxyphenyl ring is disordered over two positions, A and B, with group occupancies of 0.75 and 0.25, respectively. C17A, C16B, C17B, C18B and O2B atoms were introduced in the refinement isotropically. The rest of non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters of 1.2 times the  $U_{\text{iso}}$  value of their attached carbons for aromatic and methylene hydrogens and 1.5 times for the methyl groups. The structures present some residual peaks greater than 1 e Å<sup>-3</sup> in the vicinity of the metal atoms, solvent molecules, and/or aromatic rings but with no chemical meaning.

**Computational Details.** All DFT and TD-DFT calculations were performed by the Gaussian 09 programs<sup>12</sup> using the range-separated and dispersion-corrected hybrid density functional  $\omega$ B97X-D.<sup>13</sup> The basis set used for the iridium centers was the LanL2DZ effective core potential<sup>14</sup> and 6-31G(d,p) for the ligand atoms. The  $\omega$ B97X-D functional was selected for this study because it contains both long-range exchange and empirical dispersion corrections, which are important for the modeling of structures with weak interactions and localized anionic or strongly electron donating sites.<sup>15</sup> The geometry structures were optimized in gas phase and the solvent effect of the dichloromethane in the TD-DFT calculations was taken in consideration by the

polarizable continuum model (PCM).<sup>16</sup> The GaussSum 2.2 software<sup>17</sup> was used to calculate group contributions to the molecular orbitals. The emission energy was calculated as the difference of the DFT-optimised T<sub>1</sub> geometry for both states (adiabatic electronic transition).

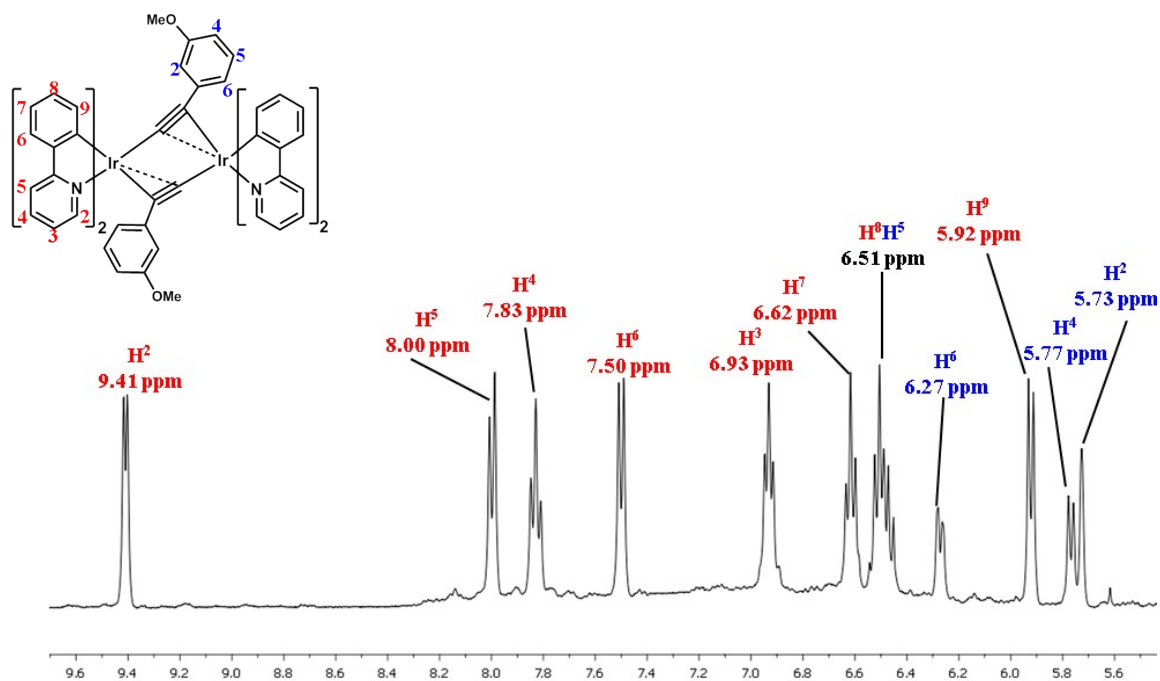
**Device preparation and analysis.** Double layer LECs were fabricated as follows.<sup>18</sup> ITO coated glass plates were patterned by conventional photolithography (Naranjo Substrates). The substrates were cleaned by using sequential ultrasonic baths, namely in water-soap, water, ethanol, and propan-2-ol solvents. After drying, the substrates were placed in a UV–ozone cleaner (Jetlight 42-220) for 8 min. An 100 nm layer of PEDOT:PSS was doctor-bladed onto the ITO-glass substrate to increase the device preparation yield (400  $\mu\text{m}$  substrate distance and a speed of 10 mm/s). The luminescent layer was prepared by depositing a mixture of CBP and the emitter in a mass ratio 80:20 in THF (20 mg/mL). The active layer was deposited by means of spin-coating (700 rpm for 1 min) reaching a thickness of 90-100 nm. These conditions resulted in homogenous thin films with a roughness less than 5 %, having no apparent optical defects. The latter was determined using the profilometer DektakXT from Bruker. Once the active layer was deposited, the samples were transferred into an inert atmosphere glovebox (<0.1 ppm O<sub>2</sub> and H<sub>2</sub>O, Innovative Technology). Aluminum cathode electrode (75 nm) was thermally evaporated using a shadow mask under high vacuum (<1·10<sup>-6</sup> mbar) using an Angstrom Covap evaporator integrated into the inert atmosphere glovebox. Time dependence of luminance, voltage, and current was measured by applying constant and/or pulsed voltage and current by monitoring the desired parameters simultaneously by using Avantes spectrophotometer (Avaspec-ULS2048L-USB2) in conjunction with a calibrated integrated sphere Avasphere 30-Irrad and Botest OLT OLED Lifetime-Test System. Electroluminescence spectra were recorded using the above mentioned spectrophotometer.

## References

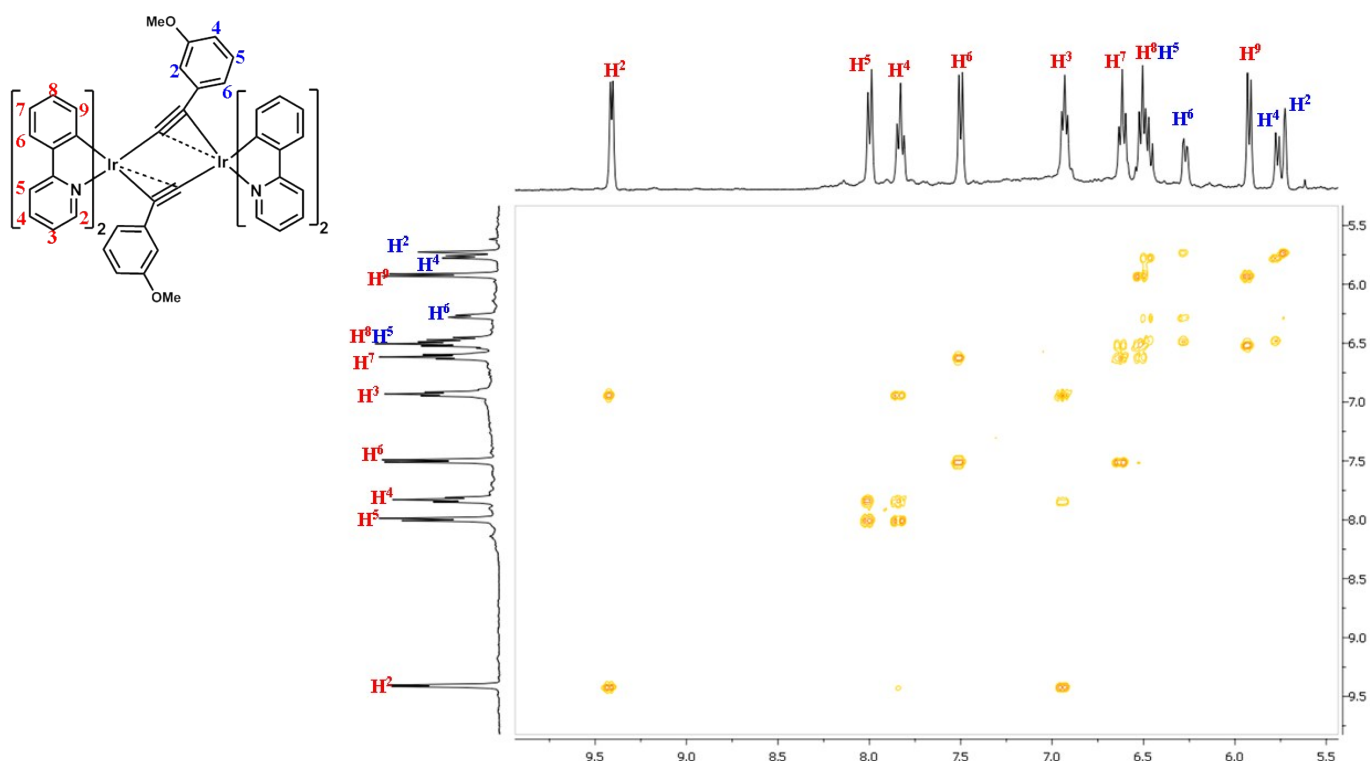
- 1 M. Mauro, G. De Paoli, M. Otter, D. Donghi, G. D'Alfonso and L. De Cola, *Dalton Trans.* 2011, **40**, 12106.
- 2 G. van Koten and J. G. Noltes, In *Comprehensive Organometallic Chemistry, Vol. 2.* (Eds.: Wilkinson, F. G. A. Stone, E. Lebel), Pergamon Press, Oxford: 1982, p 721.
- 3 Z. Otwinowski and W. Minor, In *Methods in Enzymology*, C. V. Carter Jr., R. M. Sweet, Eds. Academic Press: New York, 1997; Vol. 276A, pp 307.

- 4 G. M. Sheldrick, *SHELX-97, a Program for the Refinement of Crystal Structures*. University of Göttingen: Germany, 1997.
- 5 P. T. Beursken, G. Beursken, R. de Gelder, J. M. M. Smits, S. García-Granda and R. O. Gould, *DIRDIF2008*, Crystallography Laboratory, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands, 2008
- 6 G. M. Sheldrick, *Acta Crystallogr., Sect. C* 2015, **71**, 3.
- 7 R. H. Blessing, *Acta Crystallogr.* 1995, **A51**, 33.
- 8 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Cryst.*, 1995, **28**, 53.
- 9 L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.
- 10 A. L. Speck, *J. Appl. Cryst.*, 2003, **36**, 7.
- 11 (a) A. L. Speck, *Acta Crystallogr., Sect C*, 2015, **71**, 9. (b) A. L. Speck, *Acta Crystallogr.*, 1990, **A46**, C.
- 12 Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- 13 J. D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2008, **10**, 6615.
- 14 W. R. Wadt and P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284.
- 15 (a) F. Jensen, *J. Chem. Theory Comput.* 2010, **6**, 2726; (b) K. S. Thanthiriwatte, E. G. Hohenstein, L. A. Burns and C. D. Sherrill, *J. Chem. Theory Comput.* 2011, **7**, 88.
- 16 V. Barone and M. Cossi, *J. Phys. Chem. A* 1998, **102**, 1995.
- 17 N. M. O'Boyle, A. L. Tenderholt and K. M. Langner, *J. Comp. Chem.* 2008, **29**, 839.
- 18 (a) A. J. Norell Bader, A. A. Ilkevich, I. V. Kosilkin and J. M. Leger, *Nano Lett.*, 2011, **11**, 461; (b) A. Pertegas, N. M. Shavaleev, D. Tordera, E. Orti, M. K. Nazeeruddin and H. J. Bolink, *J. Mat. Chem. C*, 2014, **2**, 1605; (c) G. Qian, Y. Lin, G. Wantz, A. R. Davis, K. R. Carter and J. J. Watkins, *Adv. Funct. Mat.*, 2014, **24**, 4484; (d) S. Tang, H. A. Buchholz and L. Edman, *J. Mat. Chem. C*, 2015, **3**, 8114.

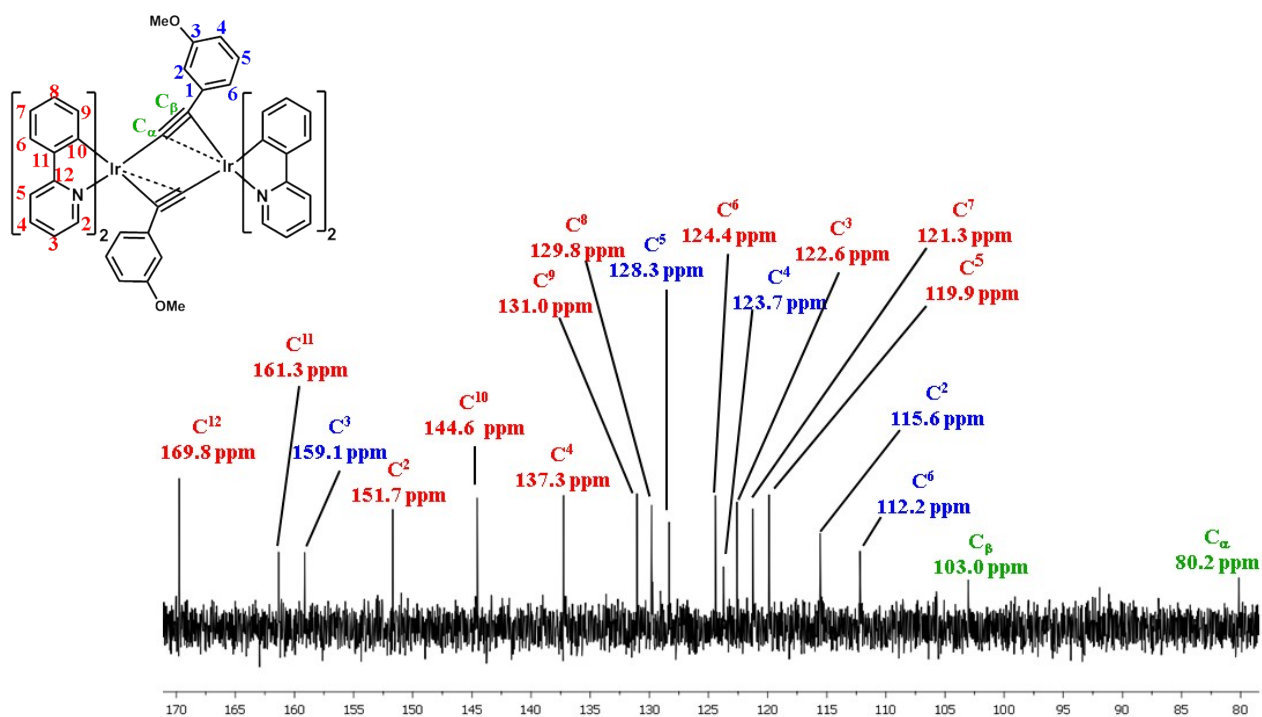




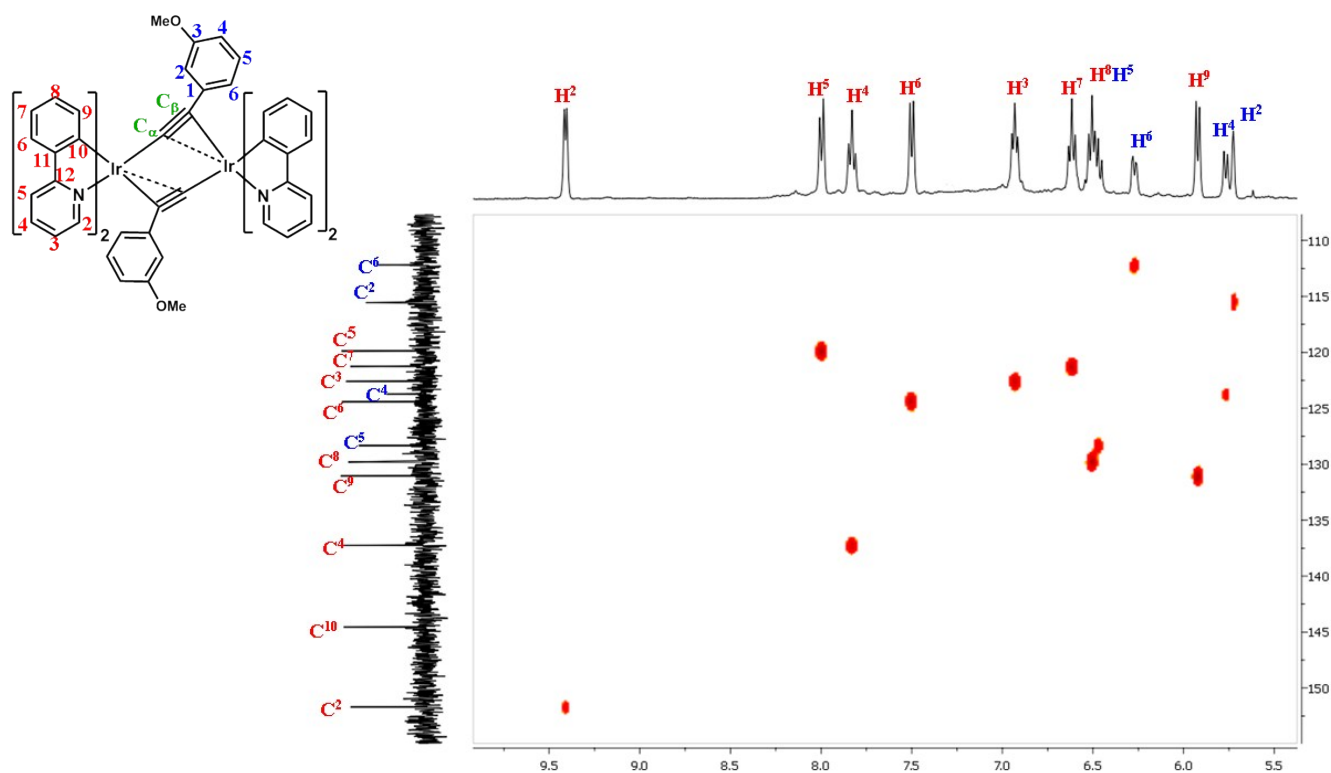
**Fig. S1** Selected region of the  $^1\text{H}$  NMR in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}(\text{ppy})_2(\mu\text{-}\kappa\text{C}^\alpha\text{:}\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})]_2$  (**1**)



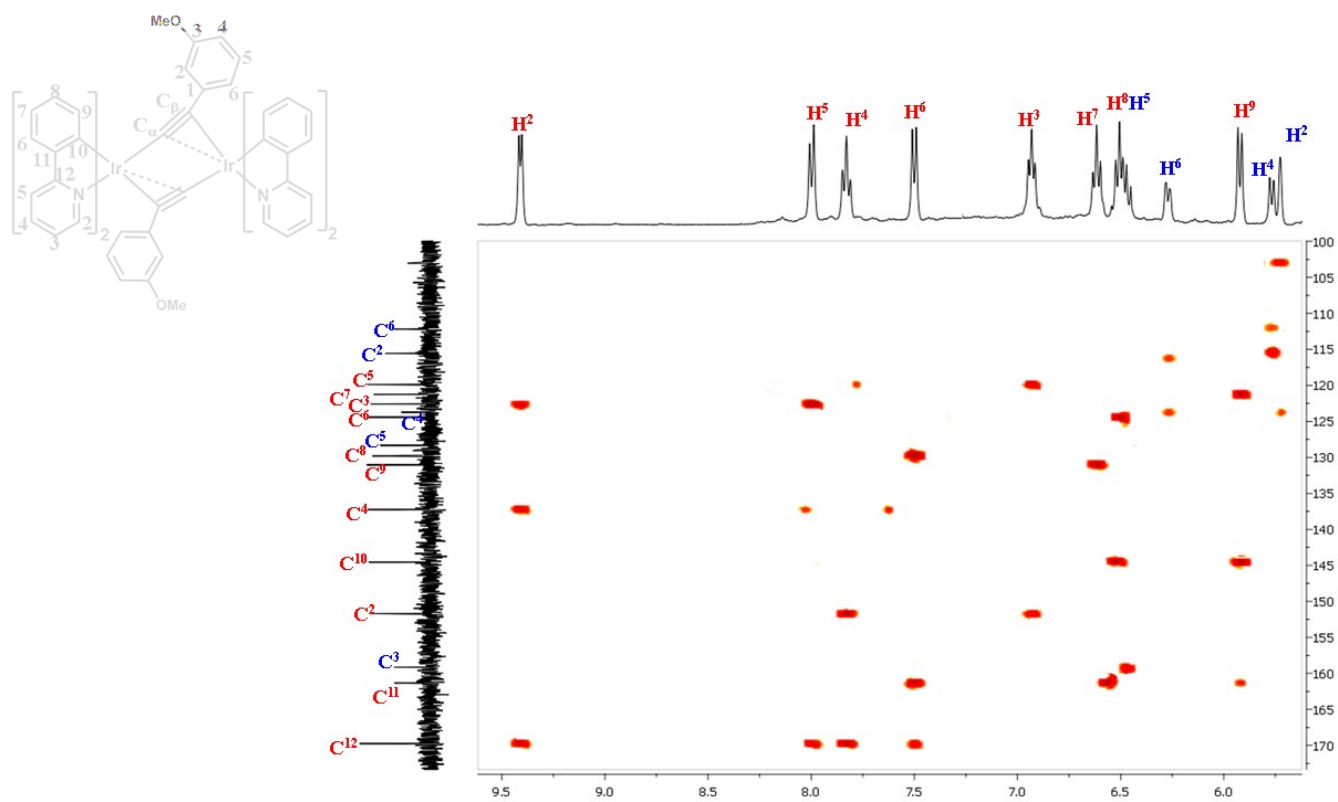
**Fig. S2** Selected region of the  $^1\text{H}$ - $^1\text{H}$  COSY in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}(\text{ppy})_2(\mu\text{-}\kappa\text{C}^\alpha\text{:}\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})]_2$  (**1**)



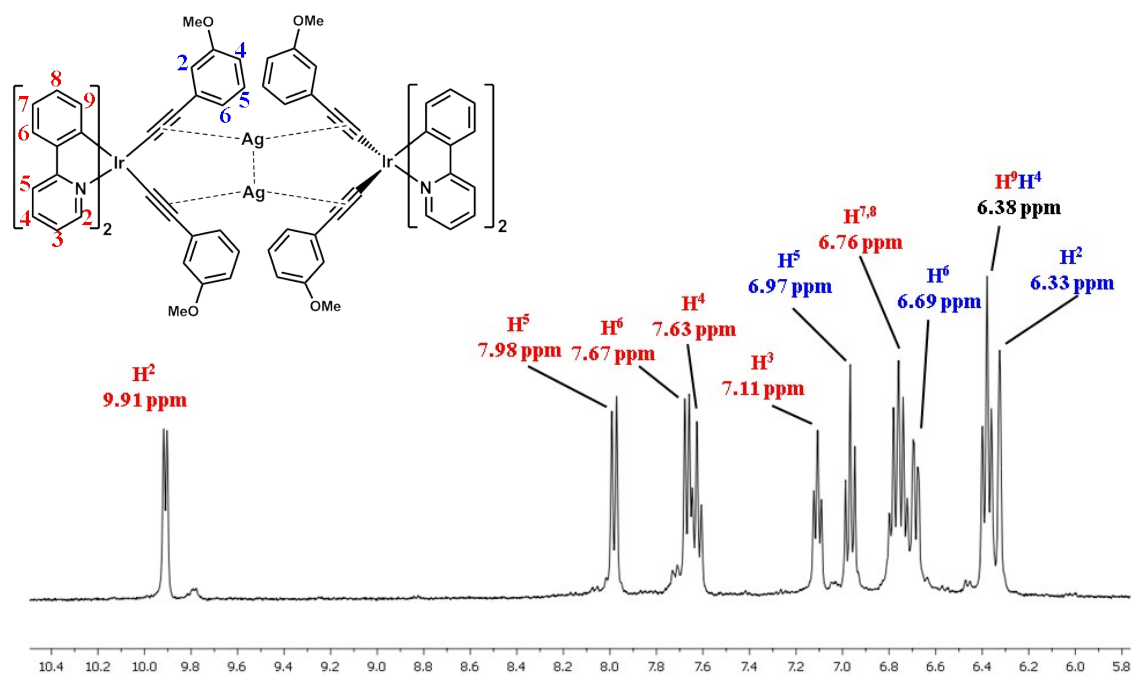
**Fig. S3** Selected region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}(\text{ppy})_2(\mu-\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_2]$  (**1**)



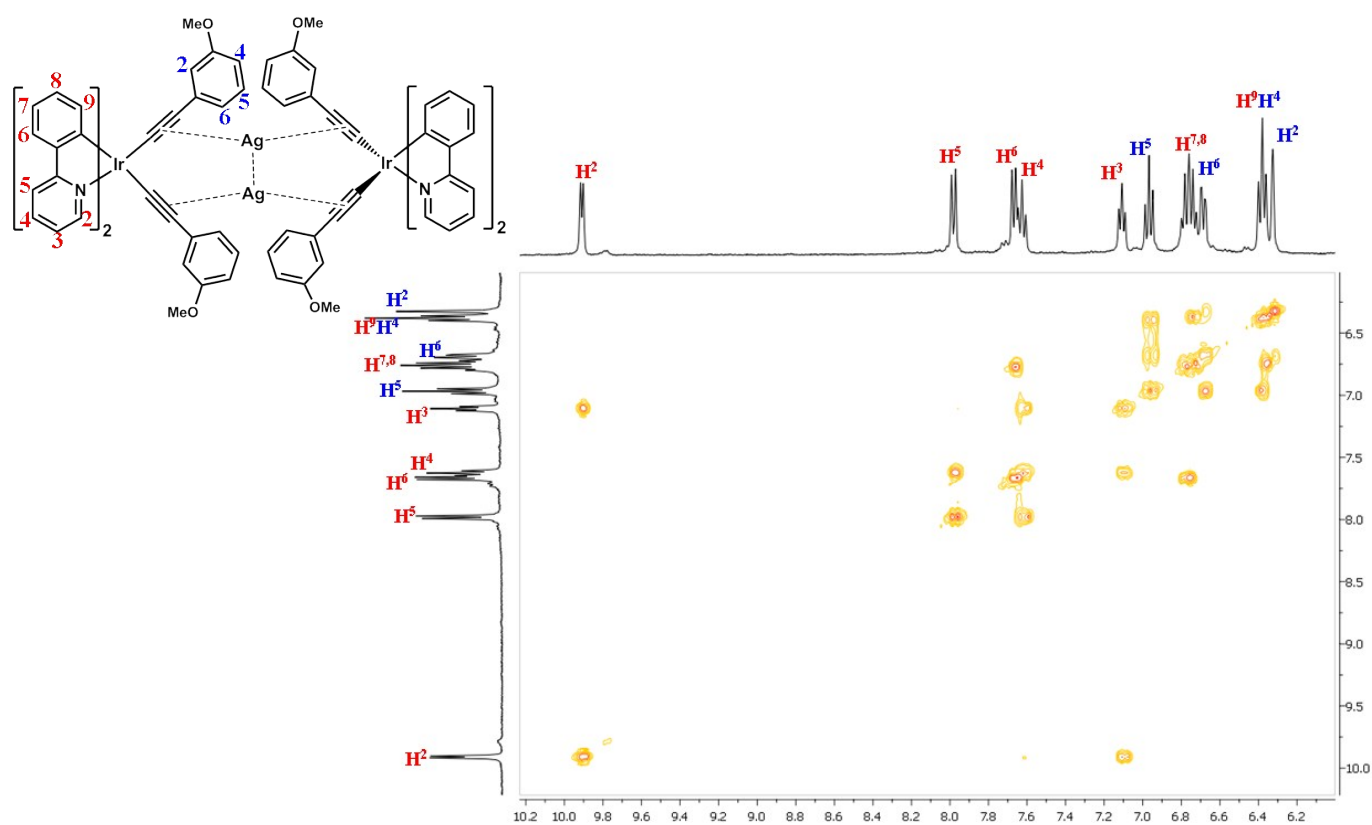
**Fig. S4** Selected region of the HSQC in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}(\text{ppy})_2(\mu-\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_2]$  (**1**)



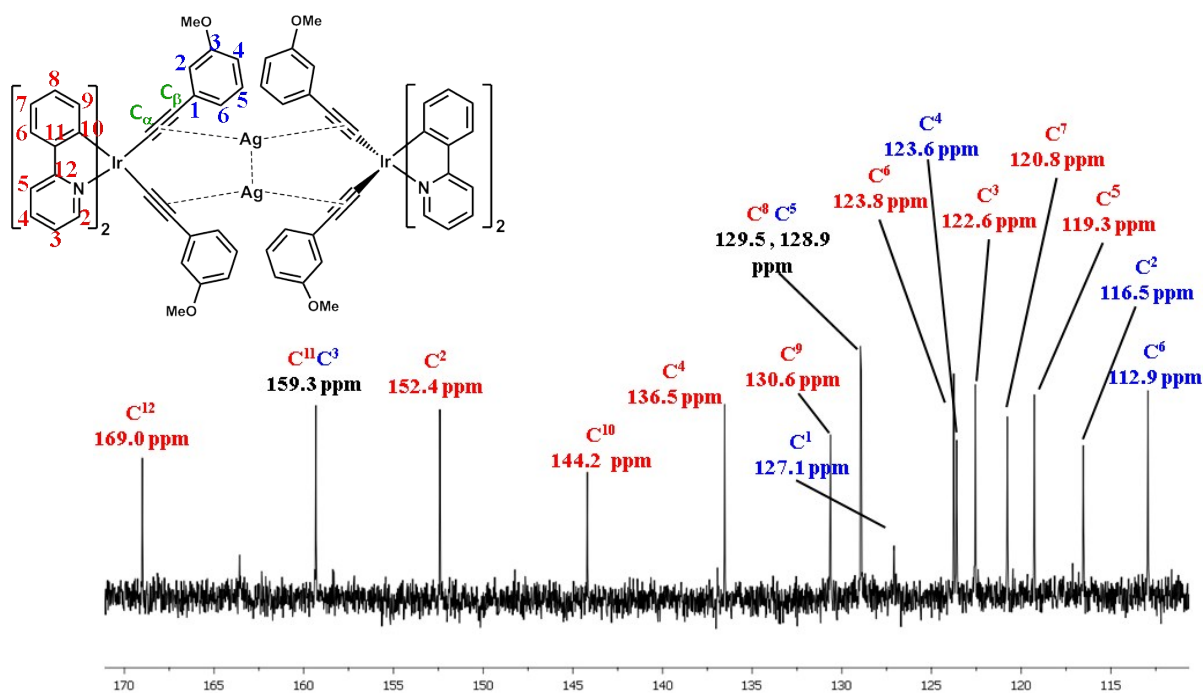
**Fig. S5** Selected region of HMBC the in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}(\text{ppy})_2(\mu\text{-}\kappa\text{C}^\alpha:\eta^2\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})]_2$  (1)



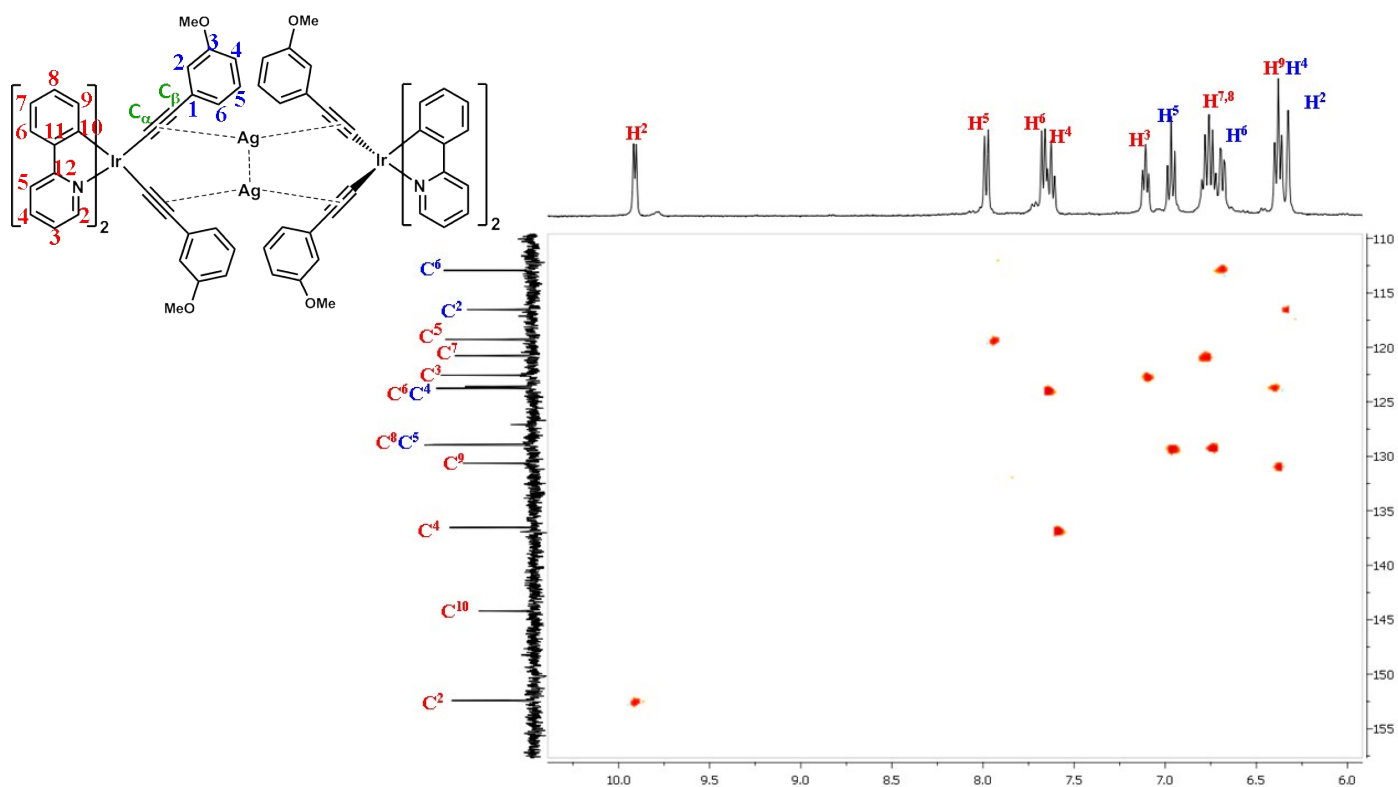
**Fig. S6** Selected region of the <sup>1</sup>H NMR in CD<sub>3</sub>COCD<sub>3</sub> of complex [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>( $\mu$ -C $\equiv$ CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>4</sub>] (**2**)



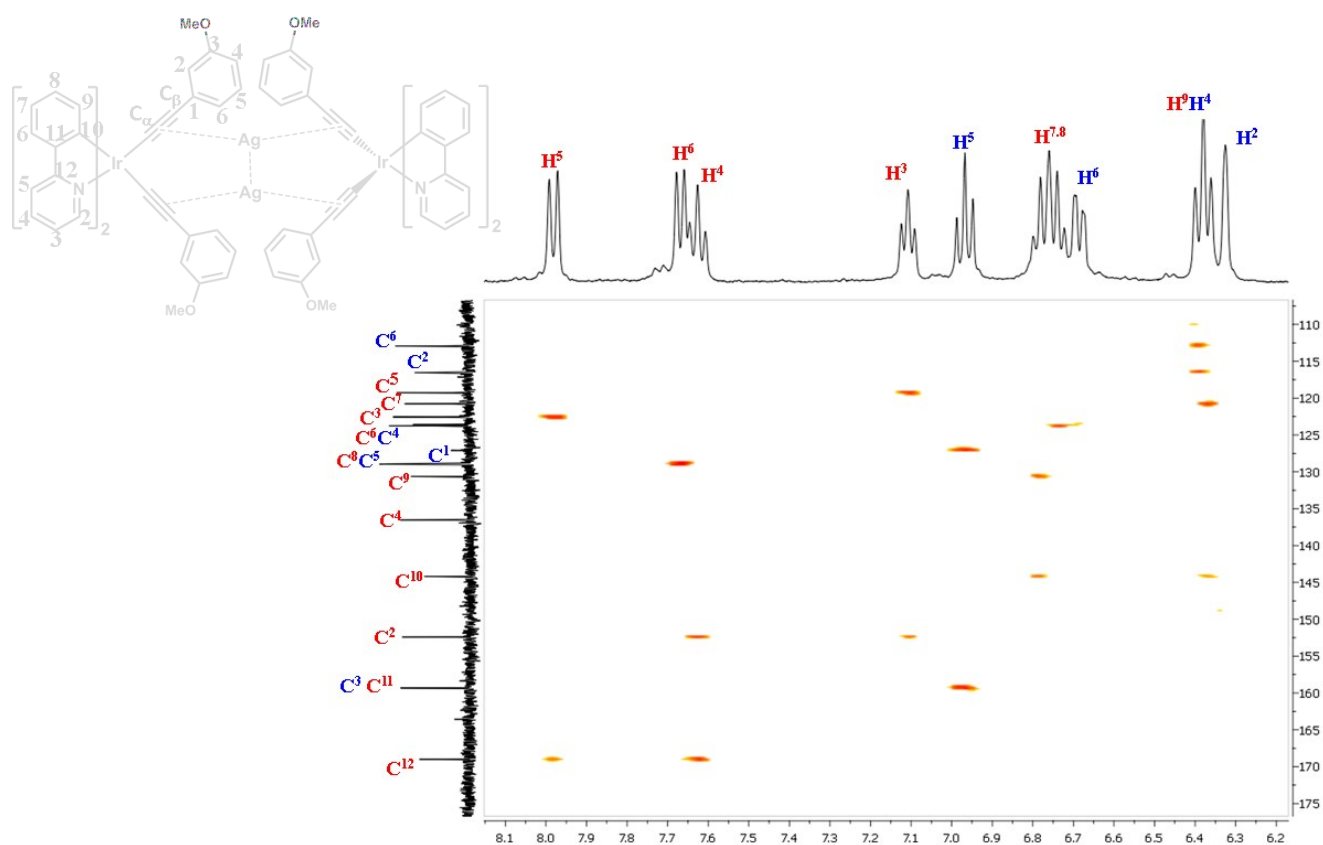
**Fig. S7** Selected region of the <sup>1</sup>H-<sup>1</sup>H COSY in CD<sub>3</sub>COCD<sub>3</sub> of complex [Ir<sub>2</sub>Ag<sub>2</sub>(ppy)<sub>4</sub>( $\mu$ -C $\equiv$ CC<sub>6</sub>H<sub>4</sub>OMe-3)<sub>4</sub>] (**2**)



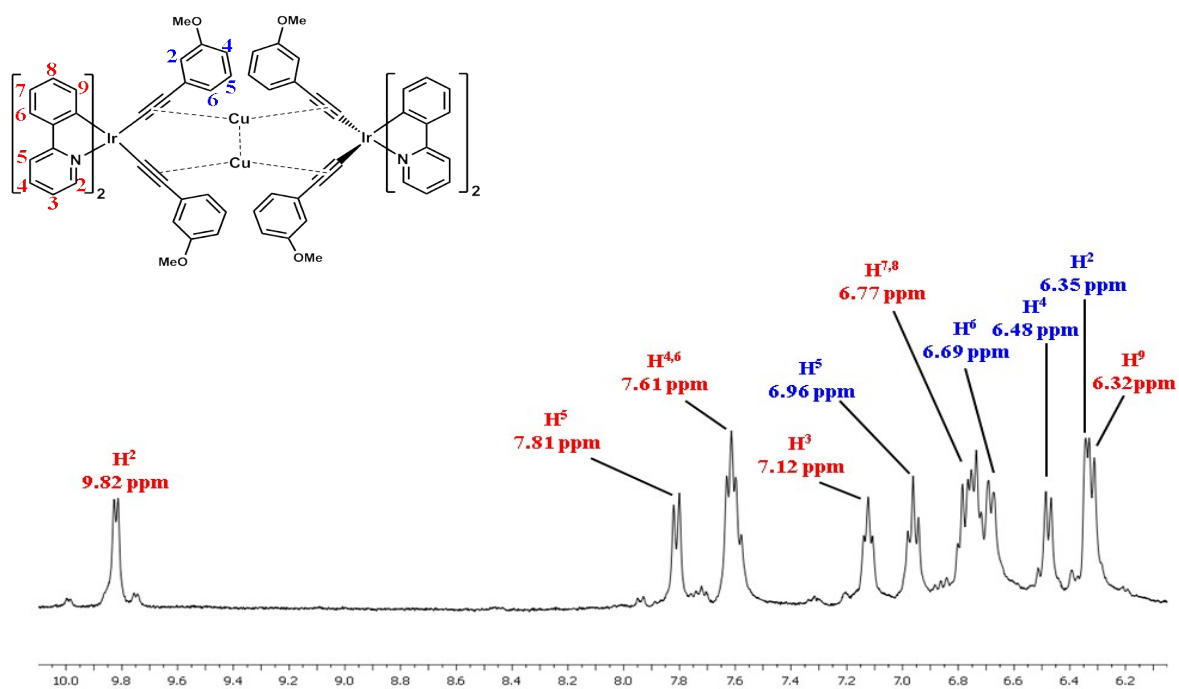
**Fig. S8** Selected region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Ag}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (2)



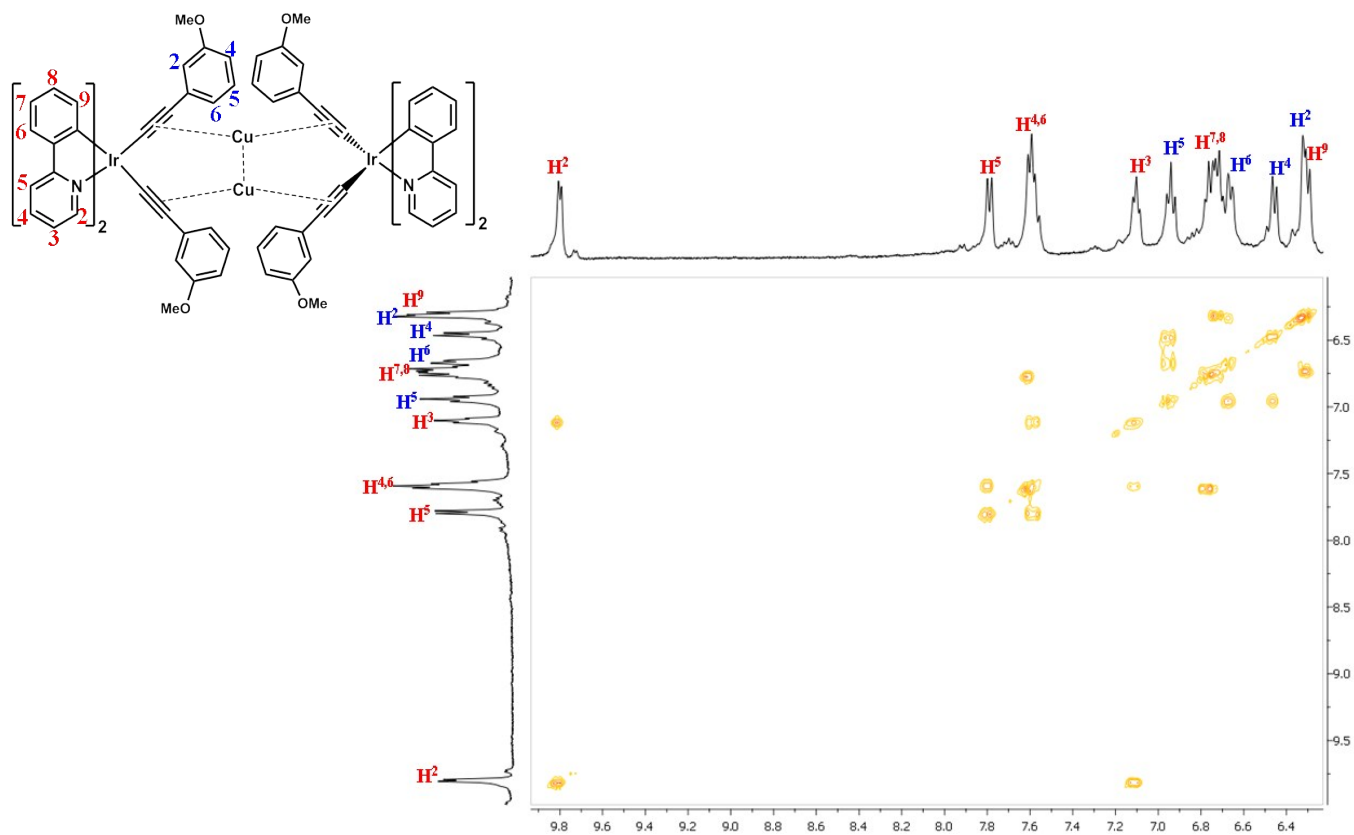
**Fig. S9** Selected region of the HSQC in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Ag}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (2)



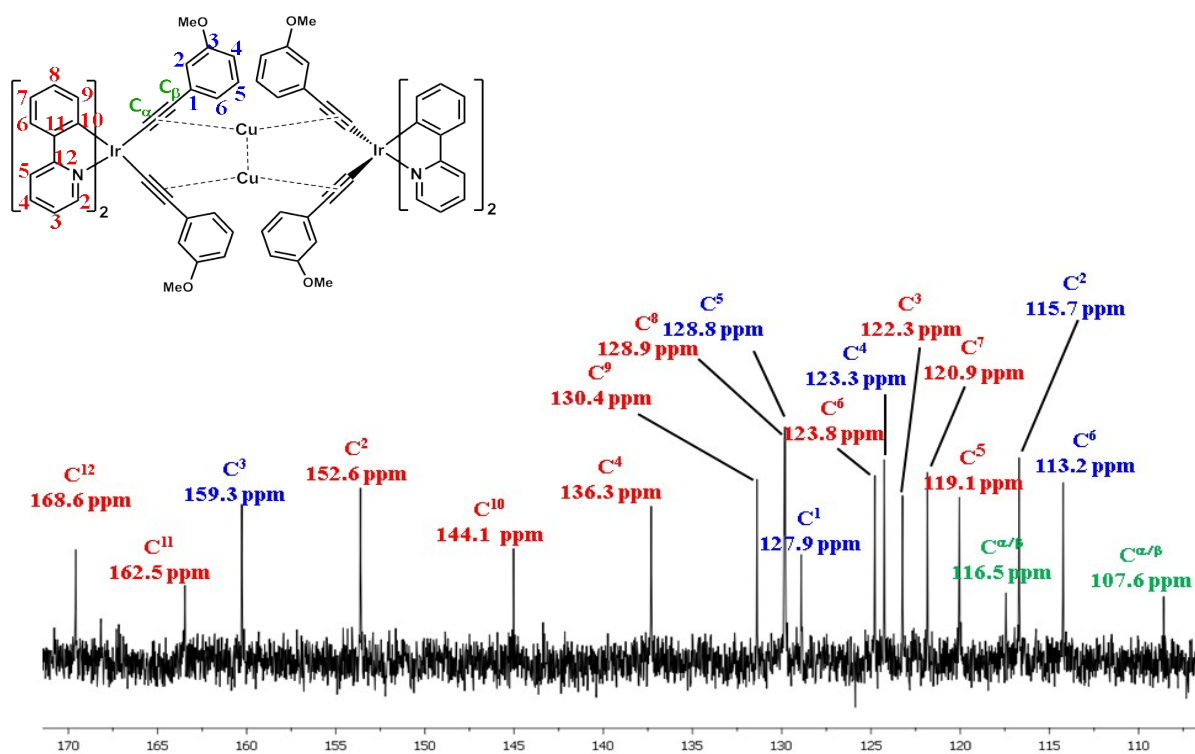
**Fig. S10** Selected region of HMBC the in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Ag}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (**2**)



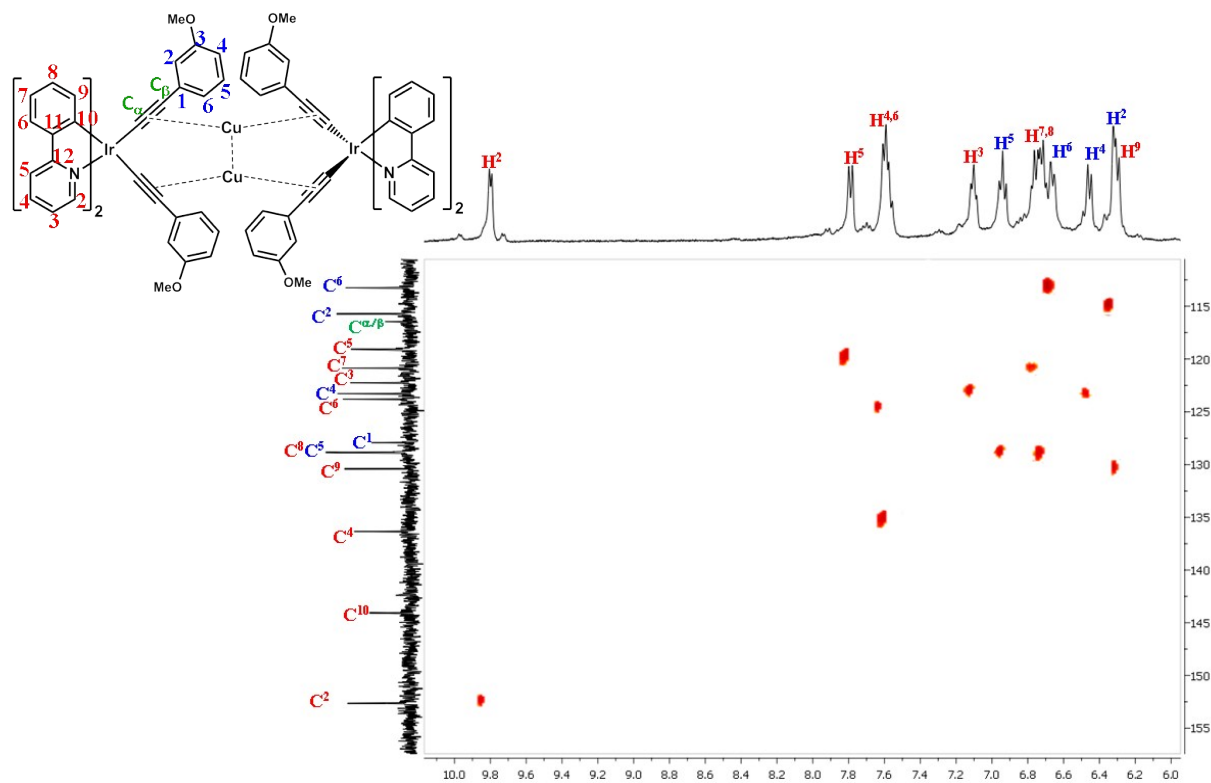
**Fig. S11** Selected region of the  $^1\text{H}$  NMR in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (**3**)



**Fig. S12** Selected region of the  $^1\text{H}$ - $^1\text{H}$  COSY in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (**3**)

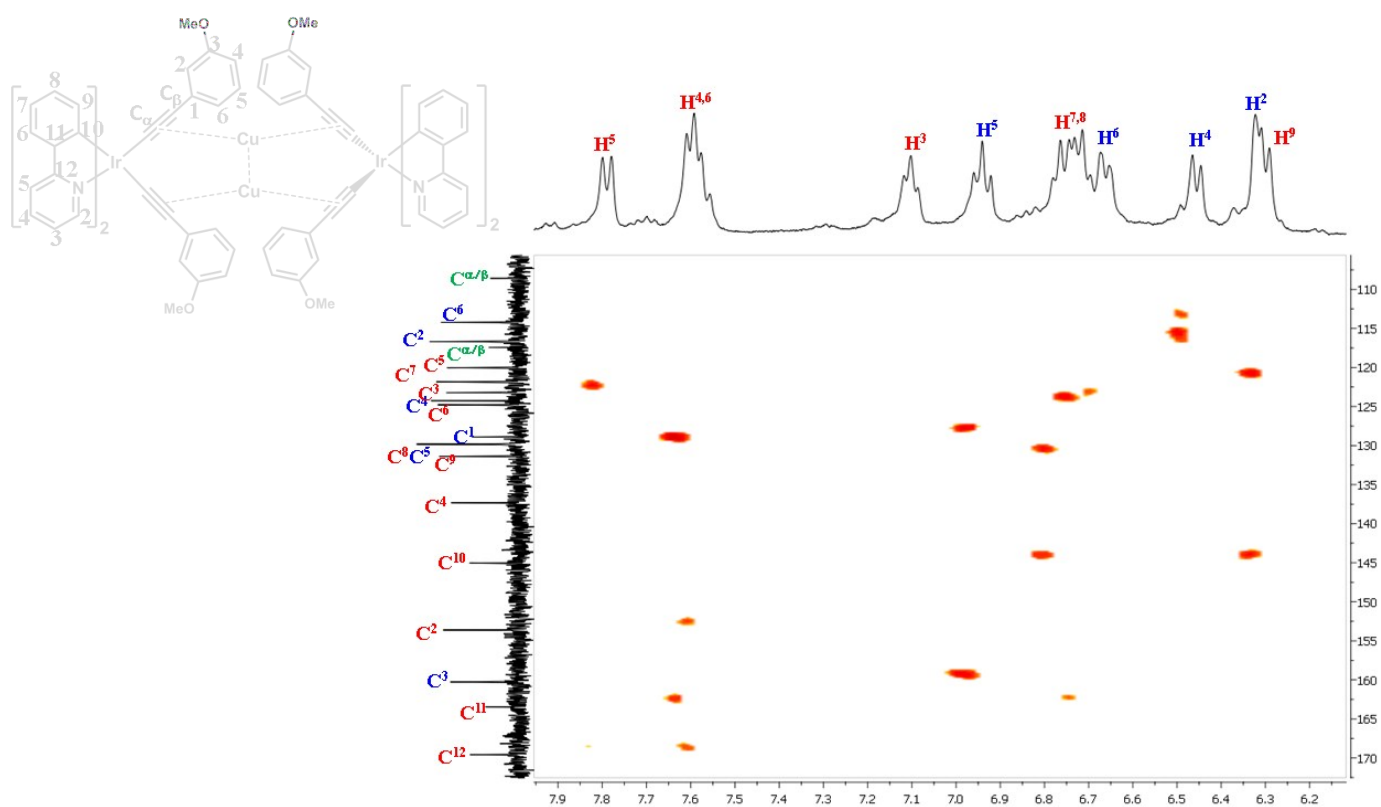


**Fig. S13** Selected region of the  $^{13}\text{C}\{^1\text{H}\}$  NMR in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (3)



**Fig. S14** Selected region of the HSQC in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (3)



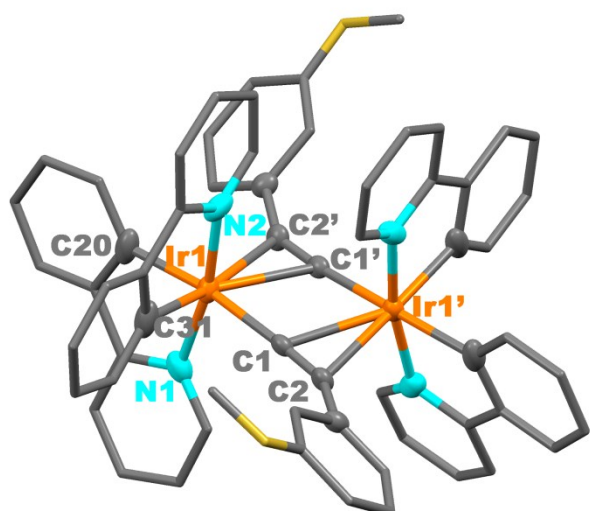


**Fig. S15** Selected region of HMBC the in  $\text{CD}_3\text{COCD}_3$  of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{OMe-3})_4]$  (**3**)

**Table S1.** X-ray Crystallographic Data for **1**·2CH<sub>3</sub>COCH<sub>3</sub>, **2**·2CH<sub>2</sub>Cl<sub>2</sub> and **3**

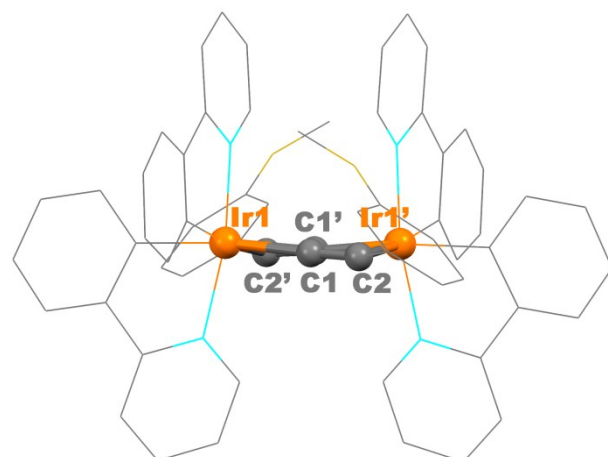
|   | <b>1</b> ·2CH <sub>3</sub> COCH <sub>3</sub>                                  | <b>2</b> ·2CH <sub>2</sub> Cl <sub>2</sub>  | <b>3</b>  |
|---|---|---|---|
| Empirical formula                                   | C <sub>68</sub> H <sub>58</sub> Ir <sub>2</sub> N <sub>4</sub> O <sub>4</sub> | C <sub>82</sub> H <sub>64</sub> Ag <sub>2</sub> Cl <sub>4</sub> Ir <sub>2</sub> N <sub>4</sub> O <sub>4</sub> | C <sub>80</sub> H <sub>60</sub> Cu <sub>2</sub> Ir <sub>2</sub> N <sub>4</sub> O <sub>4</sub> |
| $F_w$   | 1379.58   | 1826.38   | 1652.80   |
| T (K)   | 220(2)  | 173(1)  | 173(1)  |
| crystal system, space group                         | Orthorhombic, Fd2d  | Triclinic, <i>P</i> -1  | Tetragonal, <i>I</i> -4   |
| a(Å)  | 14.8430(4)  | 15.1965(6)  | 17.5940(4)  |
| b(Å)  | 26.4860(7)  | 15.8191(7)  | 17.5940(4)  |
| c(Å)  | 27.9730(8)  | 17.1188(4)  | 21.0590(7)  |
| $\alpha$ (deg)                                      | 90  | 68.885(2)   | 90  |
| $\beta$ (deg)                                       | 90  | 77.294(2)   | 90  |
| $\gamma$ (deg)                                      | 90  | 71.2650(10)   | 90  |
| volume (Å <sup>3</sup> )                            | 10997.1(5)  | 3610.2(2)   | 6518.8(4)   |
| Z   | 8   | 2   | 4   |
| $D_{\text{calcd}}$ (Mg/m <sup>3</sup> )             | 1.667   | 1.680   | 1.684   |
| absorption coefficient (mm <sup>-1</sup> )          | 4.891   | 4.259   | 4.769   |
| F(000)  | 5440  | 1780  | 3248  |
| $\theta$ range for data collection (deg)            | 3.107 to 27.477   | 2.469 to 27.342   | 3.606 to 27.425   |
| no of data / restraints / params                    | 6268 / 1 / 353  | 16153 / 0 / 860   | 7402 / 422 / 436  |
| goodness-of-fit on $F^2$ <sup>[a]</sup>             | 1.029   | 1.031   | 1.041   |
| final R indices [ $I > 2\sigma(I)$ ] <sup>[a]</sup> | R1 = 0.0243, wR2 = 0.0483   | R1 = 0.0446, wR2 = 0.1054   | R1 = 0.0389, wR2 = 0.0784   |
| R indices (all data) <sup>[a]</sup>                 | R1 = 0.0311, wR2 = 0.0503   | R1 = 0.0684, wR2 = 0.1134   | R1 = 0.0552, wR2 = 0.0839   |
| largest diff peak and hole (e.Å <sup>-3</sup> )     | 0.812 and -0.745  | 1.863 and -1.972  | 2.535 and -0.921  |

<sup>a]</sup>  $R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ ;  $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^2]^{1/2}$ ; goodness of fit =  $\{\Sigma[w(F_o^2 - F_c^2)^2] / (N_{\text{obs}} - N_{\text{param}})\}^{1/2}$ ;  $w = [\sigma^2(F_o) + (g_1 P)^2 + g_2 P]^{-1}$ ;  $P = [\max(F_o^2; 0 + 2F_c^2)]/3$ .



**1**·2CH<sub>3</sub>COCH<sub>3</sub> (only shown the ΔΔ form)

**Fig. S16**  
Two different views of the X-ray crystal structure of

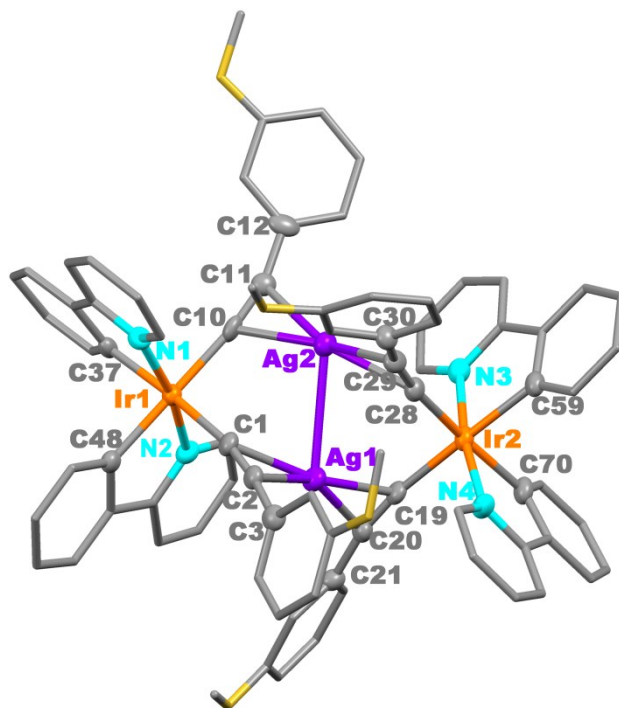


The structural features of **1** are comparable to those reported for the related tolyl acetylide derivative <sup>1</sup>-Fig. S16 and Table S2-. Thus, the Ir-C(ppy) bond lengths and Ir-C<sub>α</sub> and Ir-C<sub>β</sub> distances within the central dimetallacycle Ir<sub>2</sub>(C≡C)<sub>2</sub> are almost identical to those of [Ir<sub>2</sub>(ppy)<sub>4</sub>(μ-C≡CTol)<sub>2</sub>].<sup>1</sup> The observed slightly larger Ir···Ir separation (3.6896(6) **1** vs. 3.669(1) Å in [Ir<sub>2</sub>(ppy)<sub>4</sub>(μ-C≡CTol)<sub>2</sub>]) and the smaller puckering at the central Ir<sub>2</sub>(C≡C)<sub>2</sub> core [dihedral angle at the C<sub>α</sub>···C<sub>α'</sub> line 169.06° in **1** vs. 169.2° in [Ir<sub>2</sub>(ppy)<sub>4</sub>(μ-C≡CTol)<sub>2</sub>]] can be attributed to the more steric bulkiness of the methoxy units at the *meta* position.

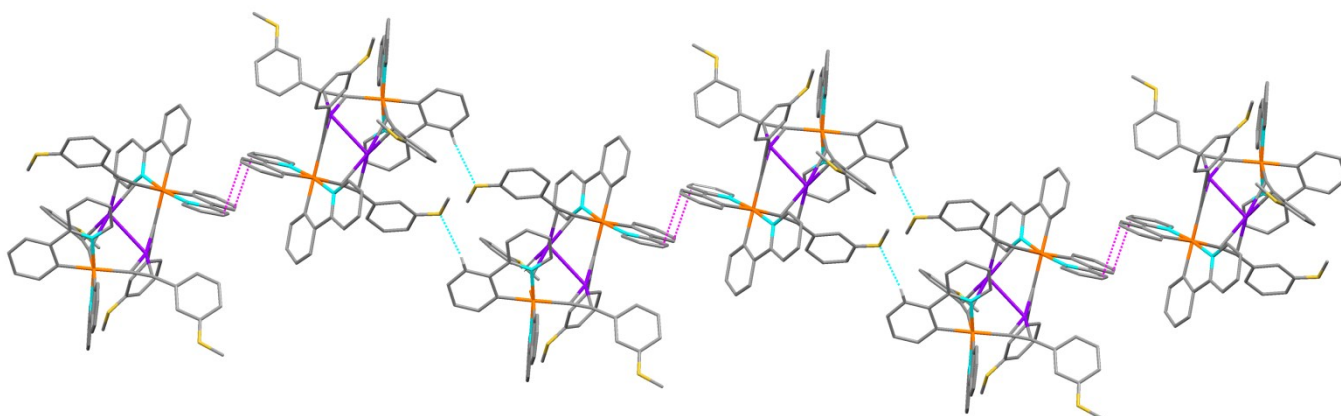
<sup>1</sup> J. Fernández-Cestau, N. Giménez, E. Lalinde, P. Montaño, M. T. Moreno and S. Sánchez, *Organometallics*, 2015, **34**, 1766

**Table S2.** Selected Bond Lengths (Å) and Angles (°) of **1**·2CH<sub>3</sub>COCH<sub>3</sub>

| Distances [Å] |          |             |           |
|---------------|----------|-------------|-----------|
| Ir1-C1        | 2.061(6) | Ir1-N1      | 2.051(6)  |
| C1-C2         | 1.227(8) | Ir1-N2      | 2.069(7)  |
| C2-C3         | 1.458(8) | Ir1-C20     | 2.045(6)  |
| Ir1-C1'       | 2.414(5) | Ir1-C31     | 2.033(6)  |
| Ir1-C2'       | 2.387(5) | Ir1-Ir1'    | 3.6891(6) |
| Angles [°]    |          |             |           |
| Ir1-C1-C2     | 174.6(5) | C2'-Ir1-C31 | 171.5(3)  |
| C1-C2-C3      | 148.5(6) | C2'-Ir1-N2  | 91.8(2)   |
| C1-Ir1-C2'    | 97.8(2)  | N1-Ir1-C20  | 79.4(5)   |
| C1-Ir1-N1     | 93.7(3)  | N1-Ir1-C31  | 93.6(3)   |
| C1-Ir1-C20    | 171.7(4) | N1-Ir1-N2   | 169.6(3)  |
| C1-Ir1-C31    | 86.2(2)  | N2-Ir1-C31  | 80.3(3)   |
| C1-Ir1-N2     | 94.3(3)  | N2-Ir1-C20  | 92.1(5)   |
| C2'-Ir1-N1    | 93.6(2)  | C20-Ir1-C31 | 89.7(3)   |
| C2'-Ir1-C20   | 87.3(2)  |             |           |



**Fig. S17** X-ray crystal structure of  $2 \cdot 2\text{CH}_2\text{Cl}_2$



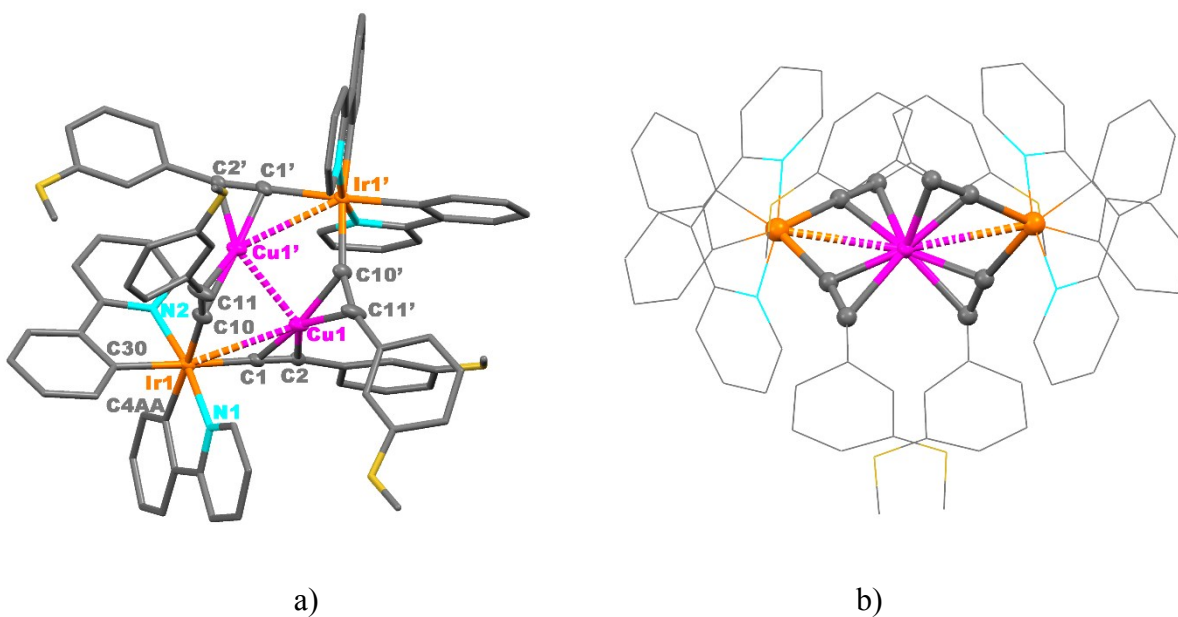
**Fig. S18** Crystal packing of complex  $[\text{Ir}_2\text{Ag}_2(\text{ppy})_4(\text{C}\equiv\text{C}(\text{C}_6\text{H}_4\text{OMe-3})_4)] (2 \cdot 2\text{CH}_2\text{Cl}_2)$  (minimum  $\pi \dots \pi$  interactions  $3.370 \text{ \AA}$  forming dimers, pink). The dimers are packing through secondary weak interactions (blue)  $[\text{O}_{\text{OMe}} \dots \text{H}_{\text{ppy}} 2.670 \text{ \AA}]$ .

**Table S3.** Selected Bond Lengths (Å) and Angles (°) of 2·2CH<sub>2</sub>Cl<sub>2</sub>

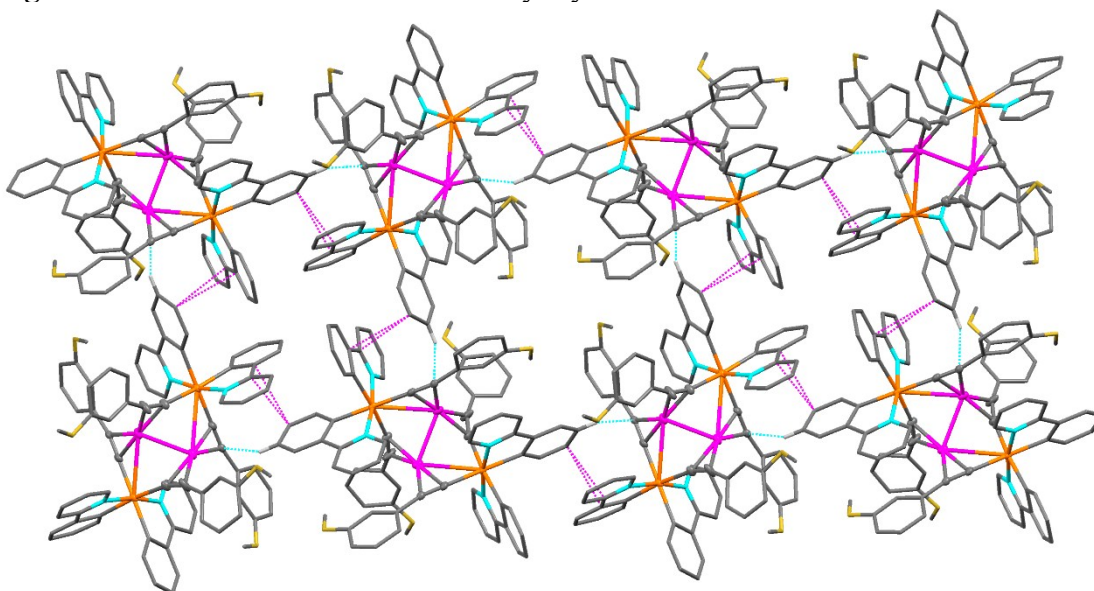
| Distances [Å] |          |         |           |
|---------------|----------|---------|-----------|
| Ir1-C1        | 2.082(6) | Ir2-C28 | 2.065(6)  |
| C1-C2         | 1.213(8) | C28-C29 | 1.234(8)  |
| C2-C3         | 1.467(8) | C29-C30 | 1.456(8)  |
| Ir1-C10       | 2.051(6) | Ir2-N3  | 2.058(5)  |
| C10-C11       | 1.241(8) | Ir2-N4  | 2.073(5)  |
| C11-C12       | 1.449(8) | Ir2-C59 | 2.068(6)  |
| Ir1-N1        | 2.062(4) | Ir2-C70 | 2.065(6)  |
| Ir1-N2        | 2.055(4) | Ag2-C10 | 2.288(5)  |
| Ir1-C37       | 2.041(5) | Ag2-C28 | 2.305(6)  |
| Ir1-C48       | 2.037(6) | Ag2-C11 | 2.292(6)  |
| Ag1-C1        | 2.302(6) | Ag2-C29 | 2.287(6)  |
| Ag1-C2        | 2.283(5) | Ir1-Ag1 | 3.6603(6) |
| Ag1-C19       | 2.233(5) | Ir1-Ag2 | 3.5937(7) |
| Ag1-C20       | 2.324(6) | Ir2-Ag1 | 3.4654(7) |
| Ir2-C19       | 2.075(6) | Ir2-Ag2 | 3.7806(6) |
| C19-C20       | 1.216(8) | Ag1-Ag2 | 2.9985(7) |
| C20-C21       | 1.448(8) | Ir1-Ir2 | 6.5373(6) |

| Angles [°]  |            |             |            |
|-------------|------------|-------------|------------|
| Ir1-C1-C2   | 169.2(5)   | Ir2-C19-C20 | 171.6(5)   |
| C1-C2-C3    | 171.4(6)   | C19-C20-C21 | 168.5(6)   |
| C1-Ir1-N1   | 95.1(2)    | C19-Ir2-N3  | 96.7(2)    |
| C1-Ir1-N2   | 92.5(2)    | C19-Ir2-N4  | 89.2(2)    |
| C1-Ir1-C48  | 84.4(2)    | C19-Ir2-C70 | 85.9(2)    |
| C1-Ir1-C10  | 97.5(2)    | C19-Ir2-C28 | 99.7(2)    |
| Ir1-C10-C11 | 172.6(5)   | Ir2-C28-C29 | 166.4(5)   |
| C10-C11-C12 | 164.4(6)   | C28-C29-C30 | 163.5(6)   |
| C10-Ir1-N1  | 88.6(2)    | C28-Ir2-N3  | 92.5(2)    |
| C10-Ir1-N2  | 97.7(2)    | C28-Ir2-N4  | 92.9(2)    |
| C10-Ir1-C37 | 87.4(2)    | C28-Ir2-C59 | 84.7(2)    |
| N1-Ir1-C37  | 79.7(2)    | N3-Ir2-C59  | 79.6(2)    |
| N2-Ir1-C48  | 79.4(2)    | N4-Ir2-C70  | 79.3(2)    |
| N1-Ir1-C48  | 94.0(2)    | N3-Ir2-C70  | 94.6(2)    |
| N2-Ir1-C37  | 92.1(2)    | N4-Ir2-C59  | 94.0(2)    |
| C37-Ir1-C48 | 91.0(2)    | C59-Ir2-C70 | 90.2(2)    |
| N1-Ir1-N2   | 169.46(19) | N3-Ir2-N4   | 171.21(19) |
| C1-Ag1-C2   | 30.67(19)  | C10-Ag2-C11 | 31.4(2)    |
| C19-Ag1-C20 | 30.9(2)    | C28-Ag2-C29 | 31.2(2)    |
| C1-Ag1-C19  | 166.7(2)   | C10-Ag2-C28 | 161.7(2)   |
| C2-Ag1-C20  | 151.5(2)   | C11-Ag2-C29 | 154.2(2)   |



**Fig. S19** Two different views of the X-ray crystal structure of **3**

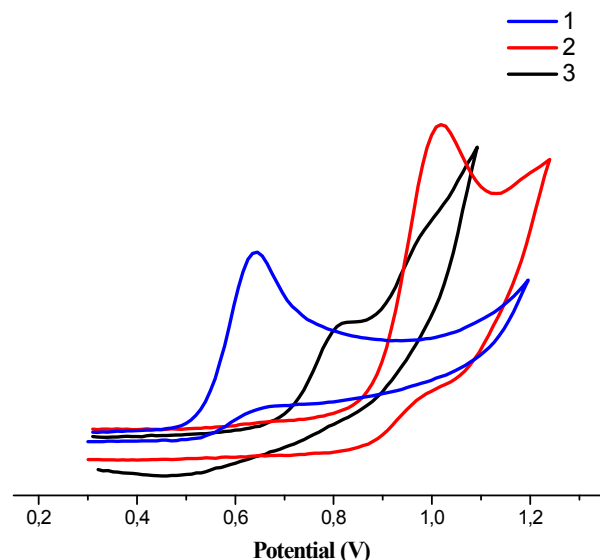


**Fig. S20** Crystal packing of complex  $[\text{Ir}_2\text{Cu}_2(\text{ppy})_4(\text{C}\equiv\text{C}(\text{C}_6\text{H}_4\text{OMe-3})_4)]$  (**3**) [minimum  $\pi\cdots\pi$  interactions (pink) 3.299 Å and secondary weak interactions (blue)  $\text{H}_{\text{ppy}}\cdots\text{C}_\beta$  2.672 Å].

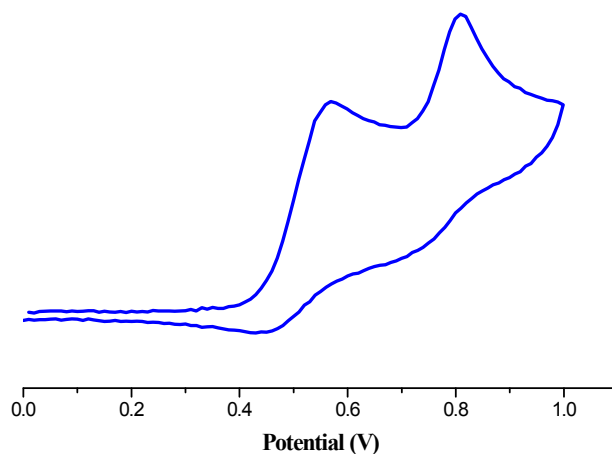
**Table S4.** Selected Bond Lengths (Å) and Angles (°) of **3**

| <b>Distances [Å]</b>      |           |              |           |
|---------------------------|-----------|--------------|-----------|
| Ir1-C1                    | 2.080(10) | Ir1-C30      | 2.077(9)  |
| C1-C2                     | 1.220(13) | Cu1-C1       | 1.991(10) |
| C2-C3                     | 1.445(15) | Cu1-C2       | 2.102(10) |
| Ir1-C10                   | 2.086(10) | Cu1'-C10     | 2.032(9)  |
| C10-C11                   | 1.212(15) | Cu1'-C11     | 2.062(12) |
| C11-C12A <sup>a</sup>     | 1.487(15) | Cu1-Cu1'     | 2.732(2)  |
| Ir1-N1                    | 2.066(8)  | Ir1-Cu1      | 3.154(1)  |
| Ir1-N2                    | 2.047(8)  | Ir1-Cu1'     | 3.529(1)  |
| Ir1-C4AA                  | 2.063(9)  | Ir1-Ir1'     | 6.0202(5) |
| <b>Angles [°]</b>         |           |              |           |
| Ir1-C1-C2                 | 178.1(9)  | N1-Ir1-C4AA  | 79.7(3)   |
| C1-C2-C3                  | 167.2(10) | N2-Ir1-C30   | 80.0(3)   |
| C1-Ir1-N1                 | 91.8(3)   | N1-Ir1-C30   | 93.2(3)   |
| C1-Ir1-N2                 | 94.5(3)   | N2-Ir1-C4AA  | 93.2(3)   |
| C1-Ir1-C4AA               | 88.0(3)   | C4AA-Ir1-C30 | 88.2(3)   |
| C1-Ir1-C10                | 99.5(4)   | N1-Ir1-N2    | 170.4(3)  |
| Ir1-C10-C11               | 166.1(10) | C1-Cu1-C2    | 34.6(4)   |
| C10-C11-C12A <sup>a</sup> | 158.4(13) | C10-Cu1'-C11 | 34.4(4)   |
| C10-Ir1-N1                | 92.9(4)   | C1-Cu1-C10'  | 163.2(4)  |
| C10-Ir1-N2                | 93.2(4)   | C2-Cu1-C11'  | 136.8(5)  |
| C10-Ir1-C30               | 85.0(4)   | Cu1-Ir1-Cu1' | 47.86(3)  |

<sup>a</sup> Relative to the majority component of the disordered methoxyphenyl ring (See Experimental)



**Fig. S21a** Cyclic voltammogram of **1-3** in 0.1 M NBu<sub>4</sub>PF<sub>6</sub>/THF at a scan rate of 100 mVs<sup>-1</sup>.



**Fig. S21b** Cyclic voltammogram of **1** in 0.1 M NBu<sub>4</sub>PF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mVs<sup>-1</sup>.

**Table S5.** Absorption data (solid state and solution 10<sup>-4</sup> M, 298 K) and Electrochemical Data<sup>a</sup> (THF 10<sup>-4</sup> M)

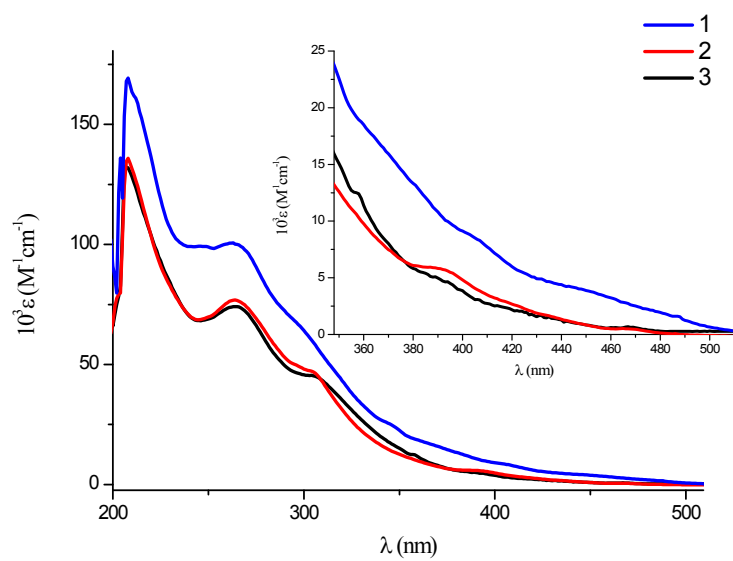
|          | $\lambda$ (nm)(10 <sup>3</sup> $\epsilon$ M <sup>-1</sup> cm <sup>-1</sup> )  | $E_{(ox)}^b$ (V)                |
|----------|---|---------------------------------|
| <b>1</b> | 208(169), 246(99.3), 262(100.6), 296(67.5), 345(25.2), 367(16.7), 406(8.4), 452(3.7), 487(1.6) <b>THF</b>   | 0.65<br>0.57, 0.81 <sup>c</sup> |
| <b>2</b> | 216, 260, 322, 355, 370, 400, 415, 467 <b>solid</b><br>208(136), 264(77.1), 304(47.5), 392(6.0), 433(2.0), 468(0.8) <b>THF</b><br>221(180), 267(145.8), 304(92.0), 394(13.4), 433(6.1), 464(2.9) <b>CH<sub>2</sub>Cl<sub>2</sub></b>                      | 0.94                            |
| <b>3</b> | 226, 271, 294, 314, 368, 400, 436, 469 <b>solid</b><br>207 (132), 264(74.1), 305(45.3), 358(12.4), 392(4.7), 427(1.7), 469(0.7) <b>THF</b><br>221(131), 266(112), 304(71.6), 354(20.8), 392(13.5), 433(6.1), 464(3.7) <b>CH<sub>2</sub>Cl<sub>2</sub></b> | 0.82, 0.98                      |

<sup>a</sup> Using 0.1M NBu<sub>4</sub>PF<sub>6</sub> as electrolyte, scan rate 100 mVs<sup>-1</sup> and vs Ag/AgCl reference electrode.

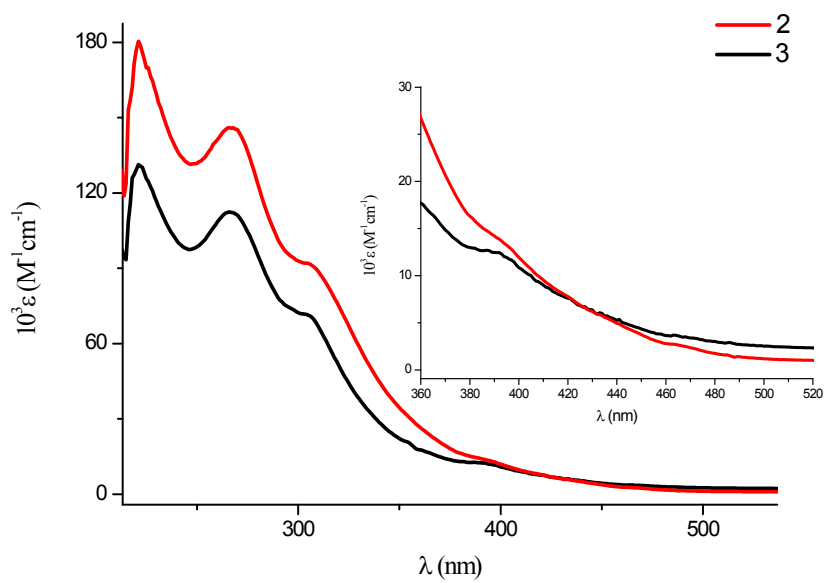
<sup>b</sup> Peak potentials,  $E_{pa}$ , for irreversible processes.

<sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub>





a)



b)

**Fig. S22** UV-visible absorption spectra at 298 K of a) **1-3** in THF ( $10^{-4}$  M) b) **2, 3** in  $\text{CH}_2\text{Cl}_2$  ( $10^{-4}$  M).

**Table S6.** Photophysical data for complexes in solid state, in THF ( $1 \times 10^{-4}$  M) and in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-4}$  M) at 298 and 77 K.

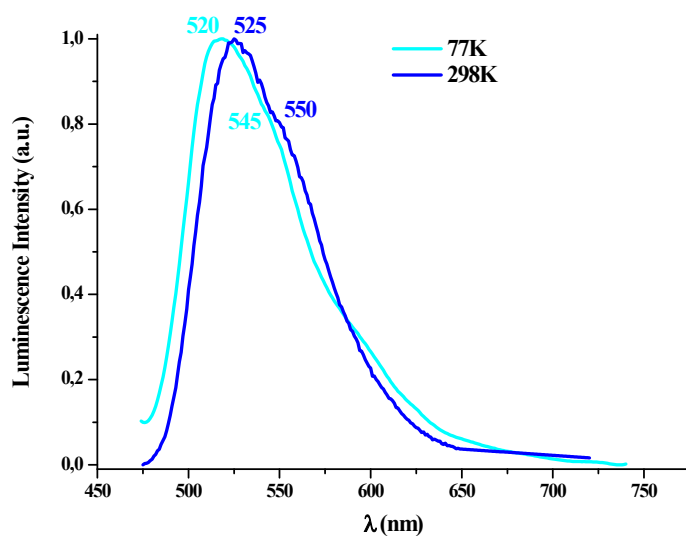
|                                     |                                     | <i>T</i> /K        | $\lambda_{\text{em}}(\lambda_{\text{ex}})/\text{nm}$ | $\tau/\mu\text{s}^a$ | $\phi^b$ | $K_r(\text{s}^{-1})^c$ | $K_{nr}(\text{s}^{-1})^d$ |
|-------------------------------------|-------------------------------------|--------------------|--|----------------------|----------|------------------------|---------------------------|
| <b>1</b>                            | <b>THF</b>                          | 298                | 525,550 (410-470)                                    | 0.7                  | 0.006    | $8.5 \times 10^3$      | $3.1 \times 10^6$         |
|                                     |                                     | 77                 | 520,545 (365-470)                                    | 15.9                 |          |                        |                           |
|                                     | <b>10% in PMMA</b>                  | 298                | 530 (365-430)  | 0.4                  | 0.009    | $2.3 \times 10^4$      | $2.5 \times 10^6$         |
| <b>2</b>                            | <b>Solid state</b>                  | 298                | 515, 540 (400-430)                                   | 0.3                  | 0.07     | $2.3 \times 10^5$      | $3.1 \times 10^6$         |
|                                     |                                     | 77                 | 505,530 (365-430)                                    | 14.6(88%),60.7(12%)  |          |                        |                           |
|                                     | <b>THF</b>                          | 298                | 511,540 (365-430)                                    | 1.1                  | 0.018    | $1.6 \times 10^4$      | $8.9 \times 10^5$         |
|                                     |                                     | 77                 | 475, 505, 535 (365-430)                              | 9.6                  |          |                        |                           |
|                                     | <b>CH<sub>2</sub>Cl<sub>2</sub></b> | 298                | 480, 505 (365-430)                                   | 0.02                 | 0.01     | $5 \times 10^5$        | $4.9 \times 10^7$         |
|                                     |                                     | 77                 | 475,505,545 (390-430)                                | 9.4                  |          |                        |                           |
|                                     | <b>10% in PMMA</b>                  | 298                | 487, 507 (365-430)                                   | 1.3                  | 0.23     | $1.8 \times 10^5$      | $5.9 \times 10^5$         |
|                                     | <b>3</b>                            | <b>Solid state</b> | 298  | 615 (420-500)        | 6.1      | 0.18                   | $2.9 \times 10^4$         |
| 77                                  |                                     |                    | 605 (390-480)  | 24.4(61%),6.5(39%)   |          |                        |                           |
| <b>THF</b>                          |                                     | 298                | 625 (390-430)  | 1.0                  | 0.018    | $1.8 \times 10^4$      | $9.8 \times 10^5$         |
|                                     |                                     | 77                 | 520, 550 (365-450)                                   | 42.3                 |          |                        |                           |
| <b>CH<sub>2</sub>Cl<sub>2</sub></b> |                                     | 298                | 620 (390-480)  | 0.9                  | 0.01     | $1.1 \times 10^4$      | $1.1 \times 10^6$         |
|                                     |                                     | 77                 | 595 (420-480)  | 32.7                 |          |                        |                           |
| <b>10% in PMMA</b>                  |                                     | 298                | 600 (365-490)  | 22.1                 | 0.07     | $3.2 \times 10^3$      | $4.2 \times 10^4$         |

<sup>a</sup> Measured in the  $\lambda_{\text{max}}$

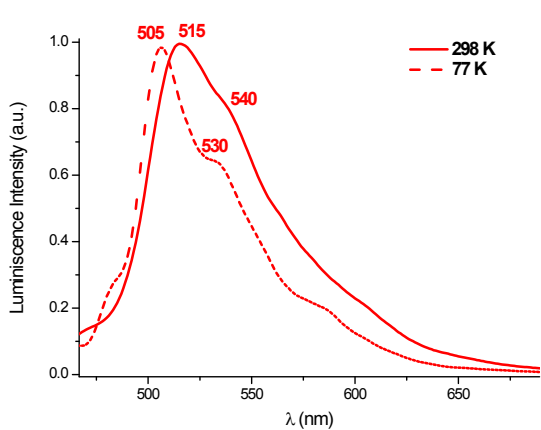
<sup>b</sup> Absolute quantum yields determined by the absolute method using an integrated sphere

<sup>c</sup> Radiative rate constant  $K_r = \phi/\tau$

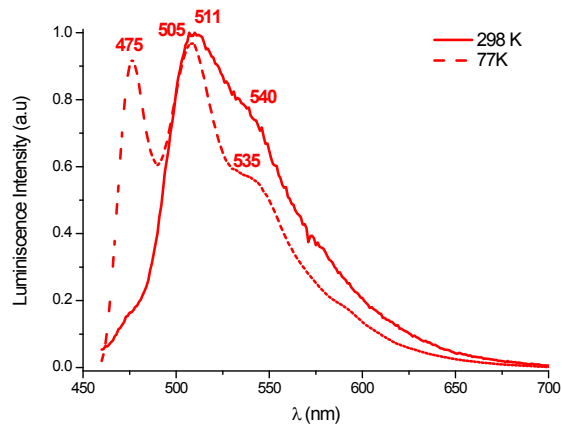
<sup>d</sup> Nonradiative rate constant  $K_{nr} = (1-\phi)/\tau$



**Fig. S23** Normalized emission spectra in THF ( $10^{-4}$  M) at 298 and 77 K of **1**

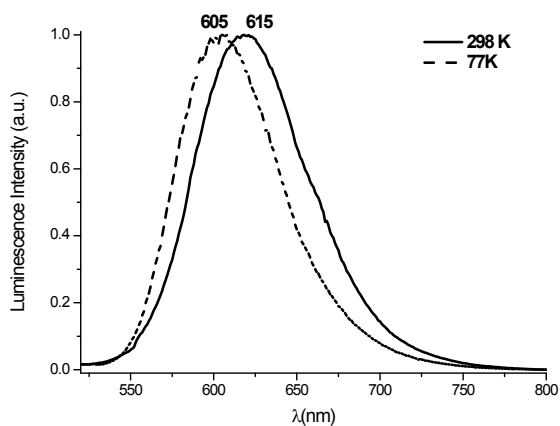


a)

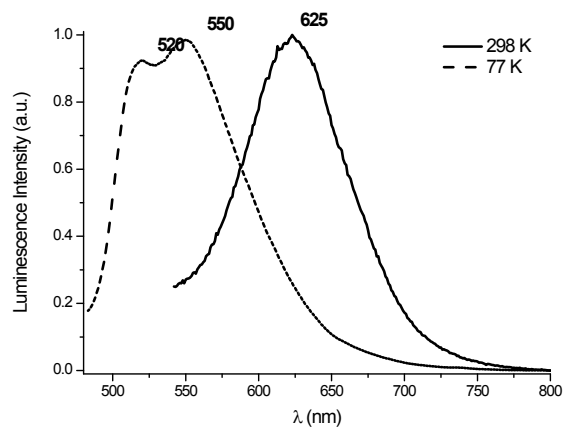


b)

**Fig. S24** Normalized emission spectra of **2** a) in solid state b) in THF ( $10^{-4}$  M) at 298K and 77 K

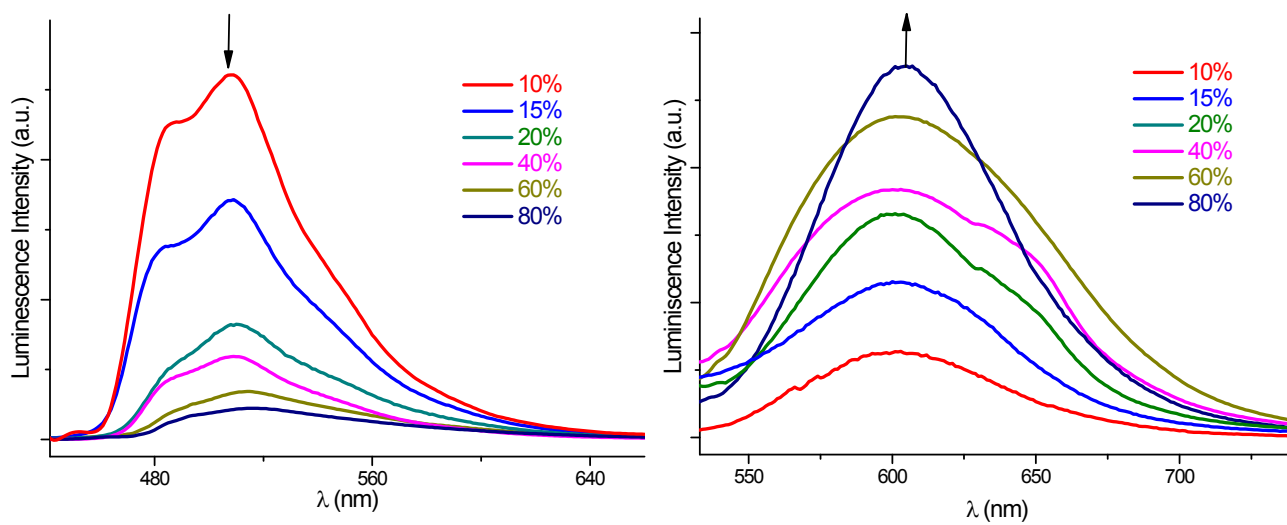


a)



b)

**Fig. S25** Normalized emission spectra of **3** a) in solid state b) in THF ( $10^{-4}$  M) at 298K and 77 K



**Fig. S26** Emission spectra of **2** ( $\phi = 0.23-0.01$ ) and **3** ( $\phi = 0.07-0.14$ ) in PMMA thin films at variable concentrations (wt%) at 298 K.

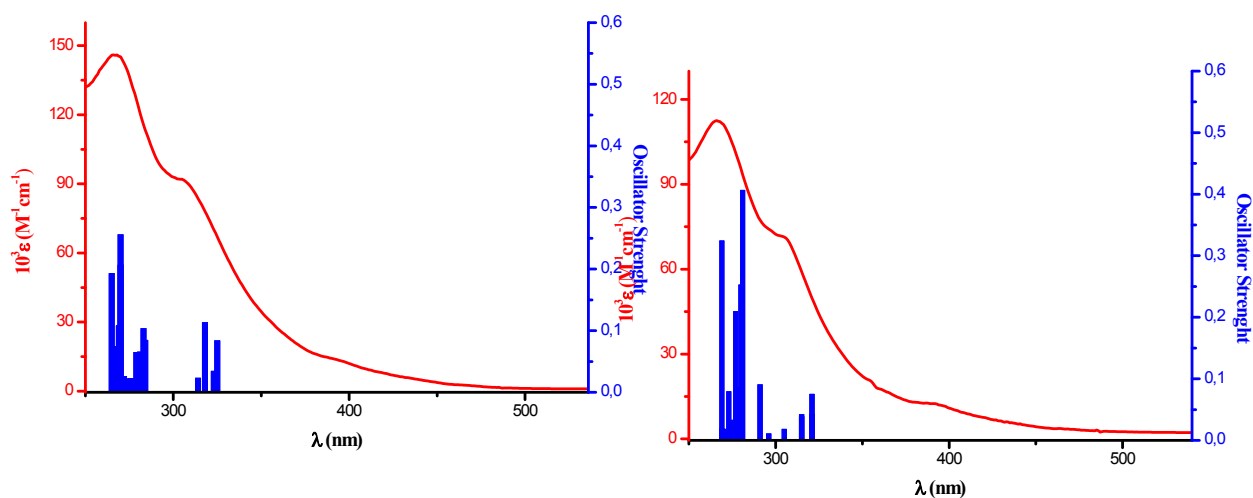
**Table S7.** DFT optimized geometries for ground state and triplet state of complex **2**.

|                      | X-ray     | S <sub>0</sub> | T <sub>1</sub> |
|----------------------|-----------|----------------|----------------|
| <b>Distances [Å]</b> |           |                |                |
| Ir1-Ag2              | 3.5937(7) | 3.742          | 3.752          |
| Ir1-Ag1              | 3.6603(6) | 3.782          | 3.767          |
| Ir2-Ag1              | 3.4654(7) | 3.366          | 3.363          |
| Ir2-Ag2              | 3.7806(6) | 3.838          | 3.846          |
| Ir1-C1               | 2.082(6)  | 2.048          | 2.073          |
| Ir1-C10              | 2.051(6)  | 2.063          | 2.062          |
| Ir2-C19              | 2.075(6)  | 2.077          | 2.082          |
| Ir2-C28              | 2.065(6)  | 2.081          | 2.077          |
| C1-C2                | 1.213(8)  | 1.241          | 1.241          |
| C10-C11              | 1.241(8)  | 1.250          | 1.248          |
| C19-C20              | 1.216(8)  | 1.246          | 1.239          |
| C28-C29              | 1.234(8)  | 1.240          | 1.246          |
| Ag1-C1               | 2.302(6)  | 2.398          | 2.397          |
| Ag2-C10              | 2.288(5)  | 2.309          | 2.308          |
| Ag1-C19              | 2.233(5)  | 2.364          | 2.355          |
| Ag2-C28              | 2.305(6)  | 2.400          | 2.401          |
| Ag1-C2               | 2.283(5)  | 2.364          | 2.368          |
| Ag2-C11              | 2.292(6)  | 2.434          | 2.434          |
| Ag1-C20              | 2.324(6)  | 2.268          | 2.282          |
| Ag2-C29              | 2.287(6)  | 2.311          | 2.311          |
| Ag1-Ag2              | 2.9985(7) | 3.103          | 3.095          |
| Ir1-Ir2              | 6.5373(6) | 6.527          | 6.536          |
| <b>Angles[Å]</b>     |           |                |                |
| Ir1-C1-C2            | 169.2(5)  | 172.33         | 171.75         |
| Ir2-C19-C20          | 171.6(5)  | 171.84         | 171.42         |
| Ir1-C10-C11          | 172.6(5)  | 169.41         | 168.99         |
| Ir2-C28-C29          | 166.4(5)  | 177.31         | 177.10         |
| C1-C2-C3             | 168.5(6)  | 171.88         | 172.28         |
| C19-C20-C21          | 168.2(7)  | 158.13         | 159.81         |
| C10-C11-C12          | 164.4(6)  | 166.51         | 166.72         |
| C28-C29-C30          | 163.5(6)  | 176.65         | 176.13         |

**Table S8.** DFT optimized geometries for ground state and triplet state of complex **3**.

|                              | X-ray     | S <sub>0</sub> | T <sub>1</sub> |
|------------------------------|-----------|----------------|----------------|
| Distances [Å]                |           |                |                |
| Ir1-Cu1                      | 3.154(1)  | 2.928          | 3.078          |
| Ir1-Cu1'                     | 3.529(1)  | 3.653          | 3.707          |
| Ir1'-Cu1                     | 3.529(1)  | 3.651          | 3.575          |
| Ir1'-Cu1'                    | 3.154(1)  | 2.928          | 2.725          |
| Ir1-C1                       | 2.080(10) | 2.083          | 2.079          |
| Ir1-C10                      | 2.086(10) | 2.085          | 2.069          |
| Ir1'-C1'                     | 2.08(1)   | 2.083          | 2.083          |
| Ir1'-C10'                    | 2.09(1)   | 2.088          | 2.081          |
| C1-C2                        | 1.220(13) | 1.240          | 1.241          |
| C10-C11                      | 1.212(15) | 1.245          | 1.244          |
| C1'-C2'                      | 1.220(13) | 1.240          | 1.239          |
| C10'-C11'                    | 1.212(15) | 1.245          | 1.304          |
| Cu1-C1                       | 1.991(10) | 2.004          | 2.008          |
| Cu1-C10'                     | 2.032(9)  | 2.134          | 1.996          |
| Cu1'-C10                     | 2.032(9)  | 2.134          | 2.211          |
| Cu1'-C1'                     | 1.991(10) | 2.004          | 2.069          |
| Cu1-C2                       | 2.102(10) | 2.227          | 2.182          |
| Cu1-C11'                     | 2.062(12) | 2.127          | 2.423          |
| Cu1'-C11                     | 2.062(12) | 2.127          | 2.188          |
| Cu1'-C2'                     | 2.102(10) | 2.226          | 2.315          |
| Cu1-Cu1'                     | 2.732(2)  | 2.692          | 2.520          |
| Ir1-Ir1'                     | 6.0202(5) | 5.943          | 6.025          |
| Angles[Å]                    |           |                |                |
| Ir1-C1-C2                    | 178.1(9)  | 173.55         | 176.26         |
| Ir1-C10-C11                  | 166.1(10) | 162.20         | 166.96         |
| Ir1'-C1'-C2'                 | 178.1(9)  | 173.35         | 166.83         |
| Ir1'-C10'-C11'               | 166.1(10) | 162.14         | 143.11         |
| C1-C2-C3                     | 167.2(10) | 177.3          | 177.11         |
| C10-C11-C12A <sup>a</sup>    | 158.4(13) | 162.47         | 169.18         |
| C1'-C2'-C3'                  | 167.2(10) | 176.98         | 174.82         |
| C10'-C11'-C12A' <sup>a</sup> | 158.4(13) | 162.66         | 171.64         |

<sup>a</sup> Relative to the majority component of the disordered methoxyphenyl ring (See Experimental)

**Fig. S27** Calculated absorptions bars in CH<sub>2</sub>Cl<sub>2</sub> and the low energy section of experimental UV-vis in CH<sub>2</sub>Cl<sub>2</sub> (1 x 10<sup>-4</sup> M) at 298 K for **2** (left) and **3** (right).

**Table S9.** Composition of Frontier Molecular Orbitals (%) in Terms of Ligands and Metals in the Ground-State for **2** and **3**.

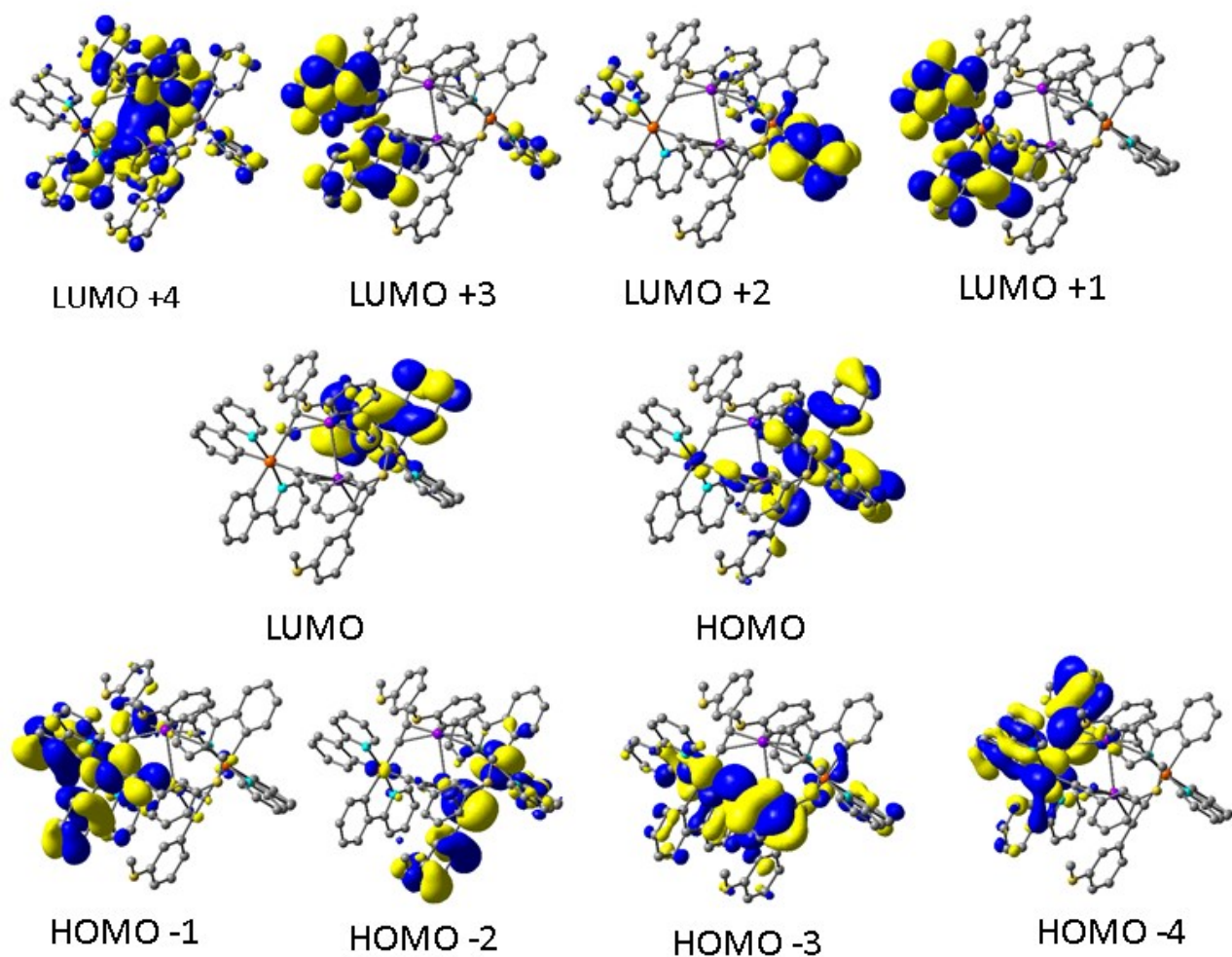
| <b>2</b> | eV    | Ag(1) | Ag(2) | Ir(1) | C≡C(C <sub>6</sub> H <sub>4</sub> OMe-3)(Ir1) | ppy(Ir1) | Ir(2) | C≡C(C <sub>6</sub> H <sub>4</sub> OMe-3)(Ir2) | ppy(Ir2) |
|----------|-------|-------|-------|-------|---|----------|-------|---|----------|
| L+8      | 1.22  | 3     | 1     | 1     | 26  | 2        | 0     | 6   | 61       |
| L+7      | 1.18  | 1     | 2     | 2     | 20  | 59       | 0     | 4   | 12       |
| L+6      | 1.09  | 3     | 4     | 1     | 14  | 15       | 2     | 2   | 58       |
| L+5      | 0.96  | 2     | 4     | 0     | 4   | 12       | 3     | 56  | 18       |
| L+4      | 0.74  | 10    | 8     | 0     | 17  | 17       | 0     | 23  | 25       |
| L+3      | 0.68  | 1     | 0     | 2     | 1   | 88       | 0     | 2   | 6        |
| L+2      | 0.65  | 1     | 0     | 0     | 1   | 4        | 2     | 2   | 89       |
| L+1      | 0.6   | 0     | 1     | 2     | 3   | 92       | 0     | 1   | 1        |
| LUMO     | 0.51  | 0     | 1     | 0     | 1   | 1        | 2     | 4   | 91       |
| HOMO     | -6.82 | 2     | 0     | 1     | 3   | 0        | 40    | 14  | 40       |
| H-1      | -6.91 | 1     | 1     | 38    | 11  | 46       | 1     | 2   | 0        |
| H-2      | -7.17 | 2     | 0     | 1     | 2   | 2        | 25    | 61  | 8        |
| H-3      | -7.25 | 4     | 0     | 30    | 42  | 11       | 2     | 5   | 6        |
| H-4      | -7.3  | 0     | 2     | 34    | 43  | 19       | 0     | 0   | 1        |
| H-5      | -7.5  | 1     | 1     | 1     | 2   | 5        | 8     | 10  | 73       |
| H-6      | -7.53 | 0     | 0     | 4     | 9   | 79       | 1     | 3   | 5        |
| H-7      | -7.58 | 0     | 3     | 0     | 1   | 1        | 36    | 26  | 33       |
| H-8      | -7.77 | 1     | 1     | 4     | 8   | 36       | 5     | 32  | 13       |

| <b>3</b> | eV    | Cu(1) | Cu(2) | Ir(1) | C≡C(C <sub>6</sub> H <sub>4</sub> OMe-3)(Ir1) | ppy(Ir1) | Ir(2) | C≡C(C <sub>6</sub> H <sub>4</sub> OMe-3)(Ir2) | ppy(Ir2) |
|----------|-------|-------|-------|-------|---|----------|-------|---|----------|
| L+8      | 1.21  | 1     | 1     | 1     | 20  | 30       | 1     | 18  | 28       |
| L+7      | 1.17  | 2     | 2     | 1     | 42  | 3        | 1     | 45  | 4        |
| L+6      | 1.06  | 1     | 3     | 1     | 21  | 6        | 2     | 26  | 39       |
| L+5      | 1.06  | 3     | 1     | 1     | 11  | 55       | 1     | 5   | 22       |
| L+4      | 0.84  | 9     | 9     | 0     | 7   | 34       | 0     | 7   | 33       |
| L+3      | 0.62  | 0     | 0     | 1     | 1   | 34       | 1     | 1   | 62       |
| L+2      | 0.61  | 0     | 0     | 1     | 1   | 62       | 1     | 1   | 34       |
| L+1      | 0.58  | 0     | 0     | 1     | 1   | 50       | 1     | 1   | 46       |
| LUMO     | 0.56  | 0     | 0     | 1     | 1   | 46       | 1     | 1   | 50       |
| HOMO     | -6.72 | 4     | 4     | 17    | 18  | 11       | 17    | 18  | 11       |
| H-1      | -6.8  | 4     | 4     | 20    | 12  | 14       | 20    | 12  | 14       |
| H-2      | -7.16 | 3     | 3     | 10    | 34  | 5        | 9     | 31  | 5        |
| H-3      | -7.24 | 1     | 1     | 13    | 26  | 8        | 13    | 28  | 9        |
| H-4      | -7.27 | 3     | 4     | 9     | 27  | 9        | 10    | 29  | 9        |
| H-5      | -7.39 | 2     | 2     | 11    | 18  | 20       | 11    | 17  | 19       |
| H-6      | -7.55 | 1     | 0     | 0     | 4   | 50       | 1     | 4   | 41       |
| H-7      | -7.57 | 3     | 3     | 0     | 10  | 31       | 0     | 10  | 43       |
| H-8      | -7.61 | 2     | 2     | 6     | 11  | 31       | 7     | 10  | 31       |

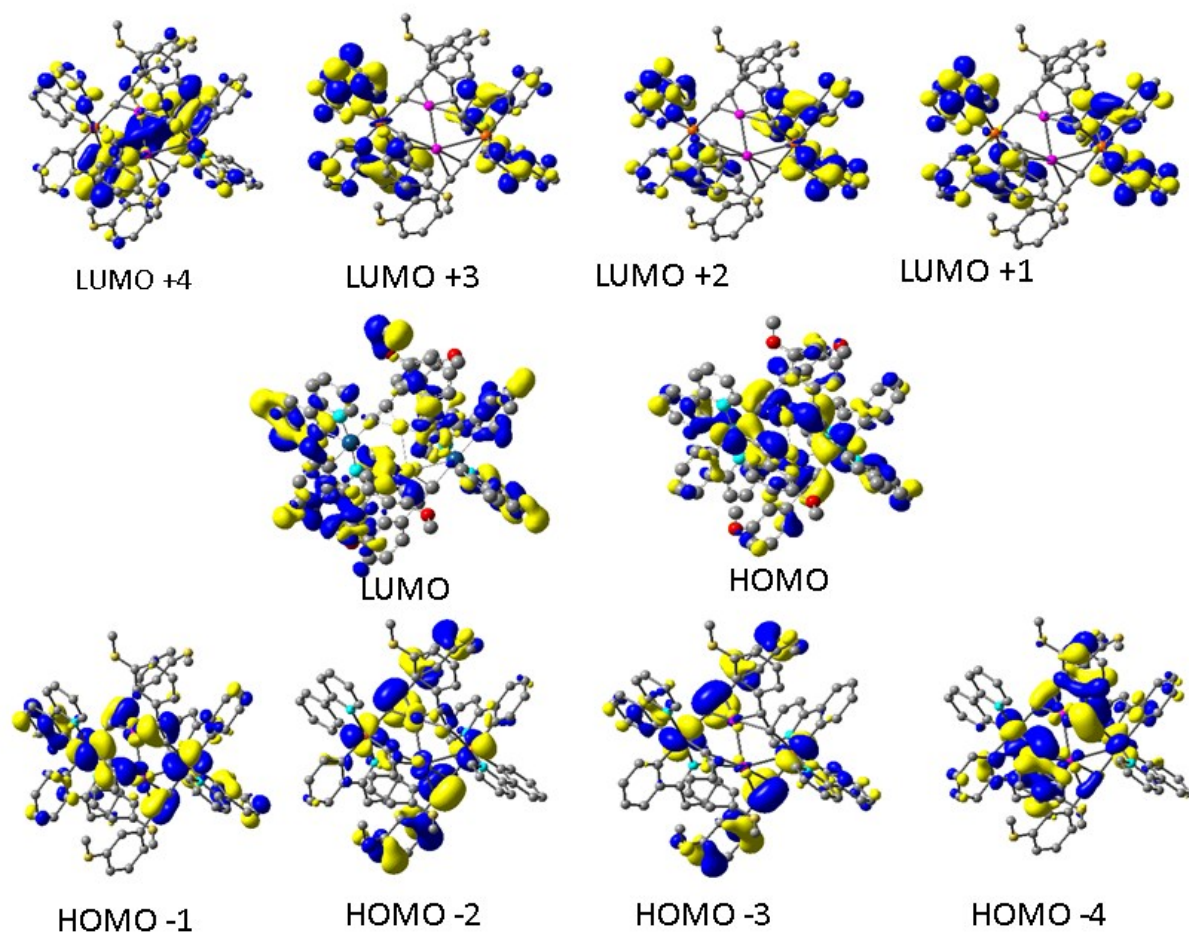
**Table S10.** Selected vertical excitation energies computed by TD-DFT in CH<sub>2</sub>Cl<sub>2</sub> with the orbitals involved for complexes **2** and **3**.

| <b>2</b>        |                |        |   |
|-----------------|----------------|--------|---|
|                 | $\lambda$ (nm) | $f^a$  | Transition  |
| S <sub>1</sub>  | 325            | 0.0835 | HOMO->LUMO (32%), HOMO->L+2 (46%)                 |
| S <sub>2</sub>  | 323            | 0.034  | HOMO->LUMO (45%), HOMO->L+2 (31%)                 |
| S <sub>3</sub>  | 318            | 0.113  | H-1->L+1 (78%)                                    |
| S <sub>4</sub>  | 314            | 0.0227 | H-6->L+1 (10%), H-1->L+3 (75%)                    |
| S <sub>5</sub>  | 284            | 0.0843 | H-4->L+3 (10%), H-3->L+1 (28%)                    |
| S <sub>6</sub>  | 283            | 0.1032 | H-4->L+1 (46%), H-4->L+3 (14%)                    |
| S <sub>7</sub>  | 281            | 0.0654 | H-2->L+2 (48%)                                    |
| S <sub>8</sub>  | 279            | 0.0647 | H-5->LUMO (18%), H-2->LUMO (21%), HOMO->L+4 (13%) |
| S <sub>9</sub>  | 278            | 0.0068 | H-4->L+3 (34%), H-3->L+1 (19%)                    |
| S <sub>10</sub> | 276            | 0.0221 | H-3->L+3 (42%)                                    |
| S <sub>11</sub> | 274            | 0.0219 | H-1->L+4 (30%)                                    |
| S <sub>12</sub> | 272            | 0.0257 | HOMO->L+6 (25%)                                   |
| S <sub>13</sub> | 271            | 0.0159 | H-9->L+2 (12%), H-5->L+2 (50%)                    |
| S <sub>14</sub> | 270            | 0.2064 | HOMO->L+6 (23%)                                   |
| S <sub>15</sub> | 270            | 0.2555 | HOMO->L+5 (13%)                                   |
| S <sub>16</sub> | 269            | 0.1081 |   |
| S <sub>17</sub> | 267            | 0.0741 | HOMO->L+8 (12%)                                   |
| S <sub>18</sub> | 265            | 0.1929 | H-9->L+2 (14%), H-7->L+2 (16%)                    |
| <b>3</b>        |                |        |   |
|                 | $\lambda$ (nm) | $f^a$  | Transition  |
| S <sub>1</sub>  | 321            | 0.0748 | H-1->LUMO (30%), HOMO->L+1 (27%)                  |
| S <sub>2</sub>  | 321            | 0.0424 | H-1->L+1 (33%), HOMO->LUMO (26%)                  |
| S <sub>3</sub>  | 315            | 0.0417 | H-1->L+2 (11%), H-1->L+3 (22%), HOMO->L+2 (24%)   |
| S <sub>4</sub>  | 315            | 0.0384 | H-1->L+2 (21%), H-1->L+3 (11%), HOMO->L+3 (26%)   |
| S <sub>5</sub>  | 305            | 0.0179 | HOMO->L+4 (47%), HOMO->L+12 (14%)                 |
| S <sub>6</sub>  | 296            | 0.0104 | H-1->L+4 (51%), H-1->L+12 (10%)                   |
| S <sub>7</sub>  | 291            | 0.0901 | H-3->L+4 (15%), H-2->L+4 (12%)                    |
| S <sub>8</sub>  | 281            | 0.4061 | H-1->L+5 (22%), HOMO->L+7 (21%)                   |
| S <sub>9</sub>  | 280            | 0.0348 | H-5->L+3 (10%)                                    |
| S <sub>10</sub> | 280            | 0.2523 | H-1->L+7 (14%), HOMO->L+5 (18%)                   |
| S <sub>11</sub> | 279            | 0.0856 | H-4->L+2 (13%), H-2->L+3 (14%)                    |
| S <sub>12</sub> | 278            | 0.0345 | H-4->L+1 (16%), H-2->LUMO (11%), H-2->L+2 (10%)   |
| S <sub>13</sub> | 277            | 0.2094 | H-4->LUMO (10%), H-2->L+1 (11%)                   |
| S <sub>14</sub> | 274            | 0.0328 | H-8->LUMO (11%)                                   |
| S <sub>15</sub> | 273            | 0.0791 | H-8->L+3 (12%), H-3->L+3 (12%)                    |
| S <sub>16</sub> | 271            | 0.018  | H-5->LUMO (10%), HOMO->L+6 (21%)                  |
| S <sub>17</sub> | 269            | 0.3241 | H-7->LUMO (16%)                                   |
| S <sub>18</sub> | 269            | 0.0194 | H-1->L+6 (21%), HOMO->L+8 (14%)                   |





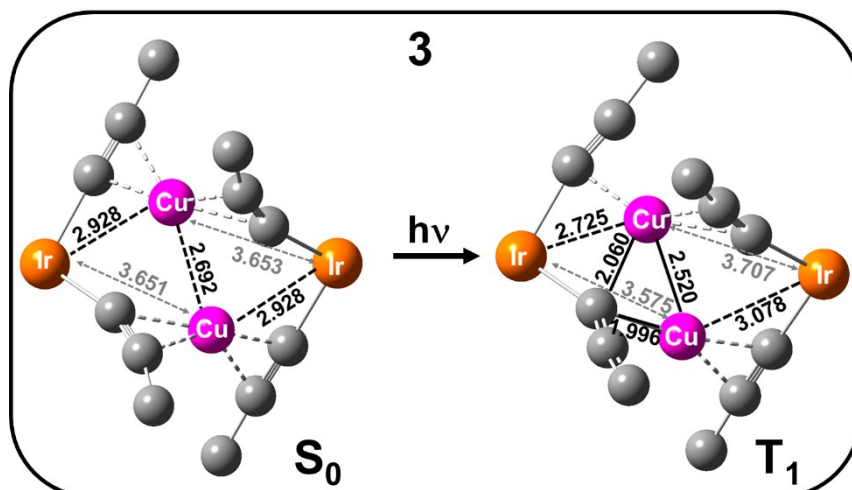
**Fig. S28** Frontier MOs of **2** optimized in the ground state.



**Fig. S29** Frontier MOs of **3** optimized in the ground state.

**Table S11.** Composition of Frontier Molecular Orbitals in the Triplet state for **2** and **3**

| <b>2</b> | <b>Ag(1)</b> | <b>Ag(2)</b> | <b>Ir(1)</b> | <b>C≡C(C<sub>6</sub>H<sub>4</sub>OMe-3)<br/>(Ir1)</b> | <b>ppy<br/>(Ir1)</b> | <b>Ir(2)</b> | <b>C≡C(C<sub>6</sub>H<sub>4</sub>OMe-3)<br/>(Ir2)</b> | <b>ppy<br/>(Ir2)</b> |
|----------|--------------|--------------|--------------|---|----------------------|--------------|---|----------------------|
| SOMO     | 0            | 0            | 3            | 1   | 95                   | 0            | 1   | 0                    |
| SOMO-1   | 0            | 0            | 9            | 1   | 89                   | 0            | 1   | 0                    |
| <b>3</b> | <b>Cu(1)</b> | <b>Cu(2)</b> | <b>Ir(1)</b> | <b>C≡C(C<sub>6</sub>H<sub>4</sub>OMe-3)<br/>(Ir1)</b> | <b>ppy<br/>(Ir1)</b> | <b>Ir(2)</b> | <b>C≡C(C<sub>6</sub>H<sub>4</sub>OMe-3)<br/>(Ir2)</b> | <b>ppy<br/>(Ir2)</b> |
| SOMO     | 7            | 6            | 0            | 3   | 1                    | 4            | 73  | 6                    |
| SOMO-1   | 3            | 13           | 0            | 4   | 0                    | 24           | 49  | 7                    |



**Fig. S30** Optimized structures ( $S_0$  and  $T_1$  state) in **3**. Distances are in Å