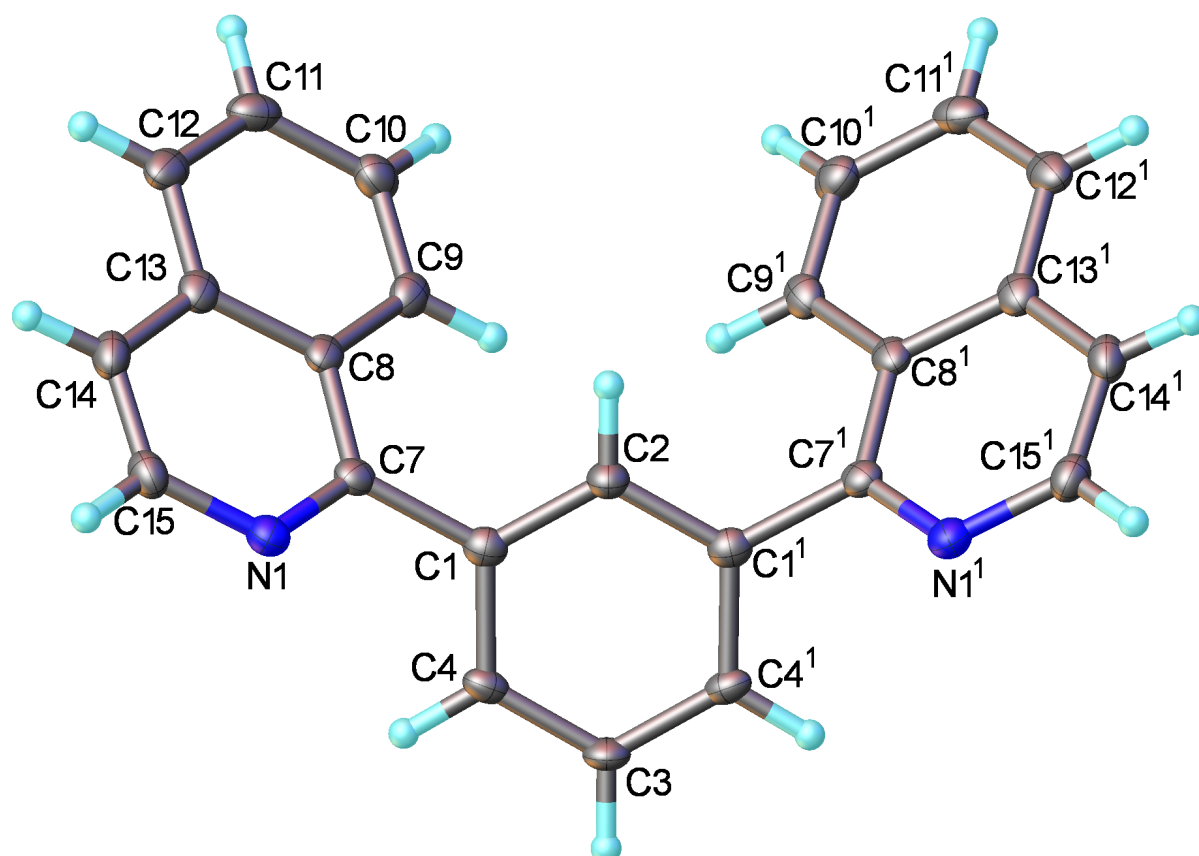


## Bright orange/red-emitting rhodium(III) and iridium(III) complexes: tridentate N<sup>^</sup>C<sup>^</sup>N-cyclometallating ligands lead to high luminescence efficiencies

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**Figure S1** X-ray molecular structure of biqbH, showing thermal ellipsoids at 50% probability level. The molecule has a crystallographic mirror plane passing through the C(2) and C(3) atoms. Atoms generated by this plane are primed. The quinoline moieties form interplanar angles of 48.7° with the central benzene ring and 48.8° with one another

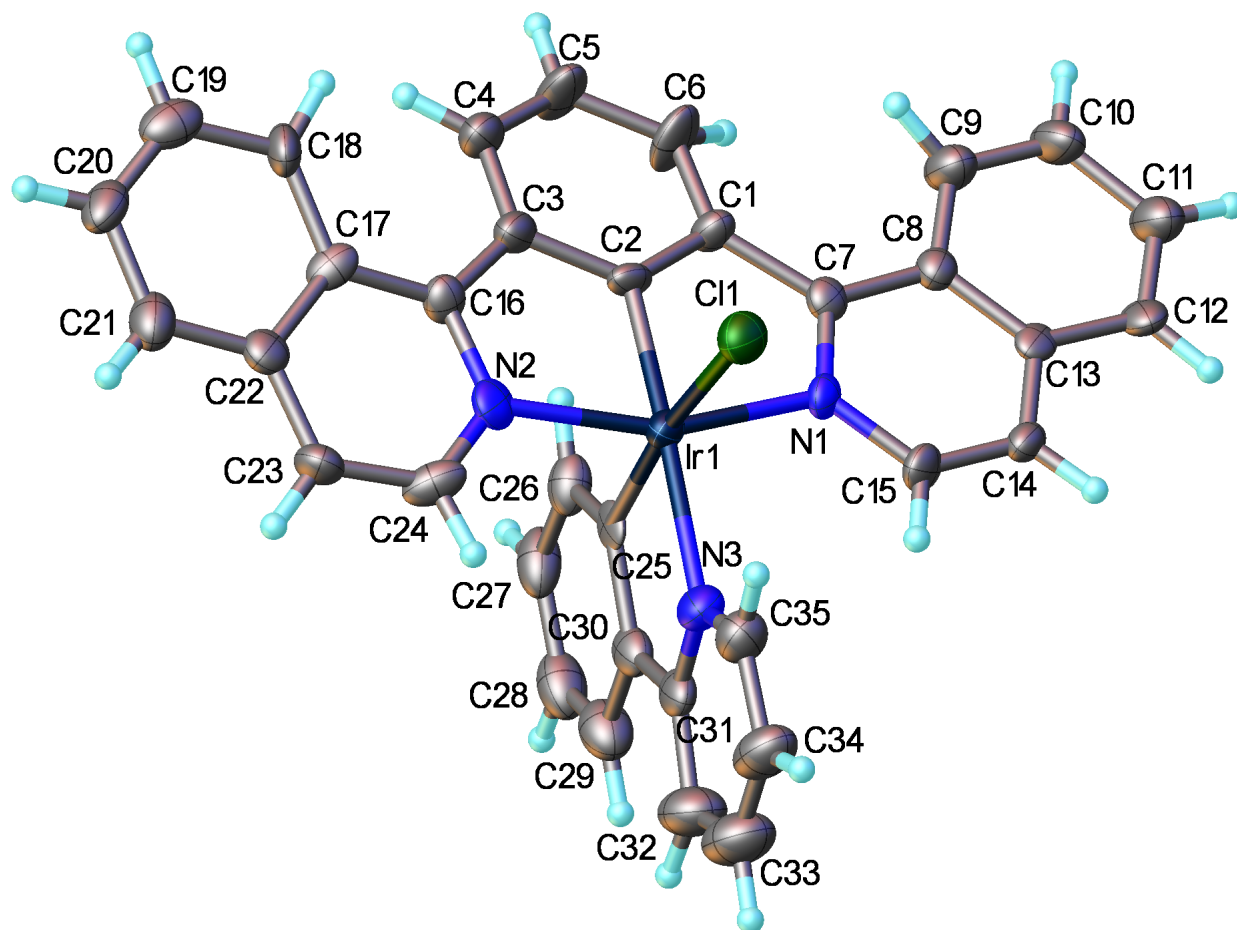


Figure S2 Independent molecule A of **2b**

### Details of instrumentation used

#### Electrochemistry

Cyclic voltammetry was carried out using a  $\mu$ -Autolab Type III potentiostat with computer control and data storage *via* GPES Manager software. Solutions of concentration 1 mM in  $\text{CH}_2\text{Cl}_2$  at  $298 \pm 3$  K were used, containing  $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$  as the supporting electrolyte. A three-electrode assembly was employed, consisting of a glassy carbon working electrode, and platinum wire counter and reference electrodes. Solutions were purged for at least 5 minutes with solvent-saturated nitrogen gas with stirring, prior to measurements being taken under a nitrogen atmosphere without stirring. The voltammograms were referenced to the ferrocene-ferrocenium couple measured under the same conditions.

#### Photophysical measurements

Absorption spectra were measured on a Biotek Instruments XS spectrometer, using quartz cuvettes of 1 cm path length. Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928

photomultiplier tube; the spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Samples for emission measurements were contained within quartz cuvettes of 1 cm path length modified with appropriate glassware to allow connection to a high-vacuum line. Degassing was achieved *via* a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was  $< 5 \times 10^{-2}$  mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in degassed aqueous solution as the standard ( $\Phi = 0.042^1$ ); estimated uncertainty in  $\Phi$  is  $\pm 20\%$  or better. Luminescence lifetimes of the complexes  $< 10 \mu\text{s}$  were measured by time-correlated single-photon counting, following excitation at 374.0 nm with an EPL-375 pulsed-diode laser. The emitted light was detected at  $90^\circ$  using a Peltier-cooled R928 PMT after passage through a monochromator. The estimated uncertainty in the quoted lifetimes is  $\pm 10\%$  or better. Lifetimes at 77 K in excess of  $10 \mu\text{s}$  were measured by multichannel scaling following excitation with a  $\mu\text{s}$ -pulsed xenon lamp; a suitable excitation wavelength was selected with a monochromator.

### Density functional theory calculations

Density functional theory calculations were performed using the Gaussian 09 software package.<sup>2</sup> The B3LYP functional<sup>3</sup> with “Double- $\zeta$ ” quality basis sets were employed for the ligands (6-31G and 6-311G) and the transition metal centres (LanL2DZ).<sup>4</sup> The inner core electrons were replaced with a relativistic effective core potential (ECP) so calculations were run considering the outer core electrons and the valence electrons:  $[(4s)^2(4p)^6]$  and  $[(4d)^6]$ , respectively, for rhodium and  $[(5s)^2(5p)^6]$  and  $[(5d)^6]$ , respectively, for iridium. Geometries were fully optimised without symmetry constraints. Time-dependent DFT (TD-DFT) calculations were performed at the optimised ground-state geometries using the B3-LYP functional.

### Details of instrumentation for X-ray diffraction analysis

Single-crystal diffraction experiments were carried out at 120 K on Bruker 3-circle diffractometers with CCD area detectors SMART 6000 (biqbH and **2a**) or SMART 1000 (**2b**), using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ) and Cryostream (Oxford Cryosystems) open-flow  $\text{N}_2$  cryostats. Data of **2a** and **2b** were corrected for absorption by semi-empirical method based on Laue equivalents, using SADABS 2009/1 program (G. M. Sheldrick, University of Göttingen, Germany). The structures were solved by direct methods and refined by full-matrix least squares against  $F^2$  of all data, using SHELXTL-2013/2 software.<sup>5</sup> Further analysis made use of Olex2 software.<sup>6</sup> Crystals of **2a** grow as non-merohedral twins with partial

overlap of reflections, for which no satisfactory model was found, hence limited precision of this structure.

BiqbH crystallises in space group *Cm*, the molecule lying astride a mirror plane which passes through C(2) and C(3); the absolute polarity of the biqbH crystal was undeterminable. The asymmetric unit of **2a** comprises one molecule of the complex and three molecules of chloroform, two of them librationaly disordered and hydrogen-bonded to the Cl(1) atom of molecule **2a**, the third one hydrogen-bonded to the  $\pi$ -electron cloud of the cyclometallating phenyl ring of the ppy ligand. The asymmetric unit of **2b** comprises one molecule of the complex in a general position and half of another molecule, which lies on a crystallographic mirror plane. Besides, it includes one molecule of water and 2.5 molecules of methanol of crystallisation, one methanol molecule being disordered between two positions related by a mirror plane.

### Synthesis and characterisation

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at the frequencies indicated and referenced relative to residual protio solvent resonances. In the NMR assignments, primed numbers refer to atoms in the phenyl rings, whilst non-primed numbers refer to those in the quinolyl or pyridyl rings, as indicated;  $\text{C}^q$  indicates quaternary carbon atoms.

#### 1,3-Bis(1-isoquinolyl)benzene – biqbH

Benzene-1,3-diboronic acid (0.152 g, 0.917 mmol), 1-chloroisoquinoline (0.297 g, 1.82 mmol) and sodium carbonate (0.645 g, 2M aq.) were combined in toluene (6 mL), ethanol (6 mL) and water (3 mL). The solution was degassed *via* four freeze-pump-thaw cycles and  $\text{Pd}(\text{PPh}_3)_4$  (0.030 g, 0.026 mmol) was added under positive pressure of nitrogen. The apparatus was evacuated briefly, charged with nitrogen and heated at reflux under nitrogen for 3 d. After cooling to room temperature, water (5 mL) was added and the product was extracted into  $\text{CH}_2\text{Cl}_2$  (3 x 35 mL). The combined extracts were dried over  $\text{K}_2\text{CO}_3$ , filtered and the solvent removed under reduced pressure to yield a yellow solid, which was recrystallised from acetonitrile to give the desired product as a pale yellow solid (0.250 g, 82 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  = 8.63 (2H, d,  $^3J$  = 5.6,  $\text{H}^3$ ), 8.20 (2H, d,  $^3J$  = 8.4,  $\text{H}^8$ ), 8.04 (1H, s,  $\text{H}^{2'}$ ), 7.89 (2H, d,  $^3J$  = 8.0,  $\text{H}^5$ ), 7.86 (2H, dd,  $^3J$  = 7.4,  $^4J$  = 1.2,  $\text{H}^{4'}$ ), 7.65-7.76 (5H, m,  $\text{H}^4$ ,  $\text{H}^{5'}$  and  $\text{H}^6$ ), 7.55 (2H, t,  $^3J$  = 8.0,  $\text{H}^7$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 126 MHz)  $\delta$  = 160.6 ( $\text{C}^q$ ), 142.5 ( $\text{C}^3$ ), 140.0 ( $\text{C}^q$ ), 137.1 ( $\text{C}^q$ ), 131.7 ( $\text{C}^{2'}$ ), 130.4 ( $\text{C}^{4'}$ ), 130.3 ( $\text{C}^{5'}$ ), 128.8 ( $\text{C}^4$ ), 127.9 ( $\text{C}^8$ ), 127.6 ( $\text{C}^7$ ), 127.2 ( $\text{C}^5$ ), 127.0 ( $\text{C}^q$ ), 120.3 ( $\text{C}^6$ ). MS ( $\text{ES}^+$ )  $m/z$  332.1 [ $\text{M}$ ] $^+$ . HRMS ( $\text{ES}^+$ ) Calcd for  $\text{C}_{24}\text{H}_{16}\text{N}_2$ :  $m/z$  333.1392. Found:  $m/z$  333.1409

$[M + H]^+$ . Elem. anal. calcd for  $C_{24}H_{16}N_2$ : C, 86.72; H, 4.95; N, 8.43 %. Found: C, 86.61; H, 4.90; N, 8.43 %. Mp = 132–134 °C.

### **[Ir(biqb)( $\mu$ -Cl)Cl]<sub>2</sub>**

A suspension of 1,3-bis(1-isoquinoly)l-benzene (0.050 g, 0.150 mmol) and iridium trichloride trihydrate (0.053 g, 0.150 mmol) in 2-ethoxyethanol (7 mL) and water (3 mL) was heated to 80 °C for 24 h. After cooling to room temperature, the precipitate was collected *via* centrifugation and washed with water (3 x 5 mL), ethanol (3 x 5 mL) and diethyl ether (3 x 5 mL). Upon drying *in vacuo*, the crude product was obtained as a dark orange solid; further product was obtained by repeating the procedure using the reaction solution removed after centrifugation (0.077 g, 86 %). Low solubility in all common solvents hindered further purification, and the crude product was therefore used for subsequent reaction.

### **[Rh(biqb)( $\mu$ -Cl)Cl]<sub>2</sub>**

A suspension of 1,3-bis(1-isoquinoly)l-benzene (0.050 g, 0.150 mmol) and rhodium trichloride trihydrate (0.053 g, 0.150 mmol) in 2-ethoxyethanol (7 mL) and water (3 mL) was heated to 80 °C for 24 h. After cooling to room temperature, the precipitate was collected *via* centrifugation and washed with water (3 x 5 mL), ethanol (3 x 5 mL) and diethyl ether (3 x 5 mL). Upon drying *in vacuo*, the crude product was obtained as a yellow solid; further product was obtained by repeating the procedure with the remaining solutions (0.059 g, 66 %). The crude product was used directly for subsequent reaction.

### **Ir(biqb)(ppy)Cl (2b)**

Bis( $\mu$ -chloro)bis(1,3-bis(1-isoquinoly)lbenzene- $N,C^{2'},N$ )-iridium chloride (0.065 g, 0.055 mmol), silver triflate (0.078 g, 0.300 mmol) and 2-phenylpyridine (200  $\mu$ L, 1.780 mmol) were placed in a Schlenk tube, which was degassed three times *via* evacuating and backfilling with nitrogen. The mixture was heated at 110 °C under nitrogen for 20 h then cooled to room temperature and  $CH_2Cl_2$  (35 mL) added. Solid residue was removed by filtrations and the filtrate washed with HCl (1M, 3 x 35 mL), dried over  $MgSO_4$  and the solvent removed under reduced pressure to give a dark red solid. Purification was carried out by column chromatography (silica,  $CH_2Cl_2$ /methanol, gradient elution from 100:0 to 99.75:0.25) to give the product as a red solid (0.018 g, 46 %).  $^1H$  NMR ( $CDCl_3$ , 700 MHz)  $\delta$  = 10.24 (1H, d,  $^3J$  = 4.8,  $H^6$ -ppy), 9.16 (2H, d,  $^3J$  = 9.1,  $H^3$ -NCN), 8.65 (2H, d,  $^3J$  = 8.4,  $H^4$ -NCN), 8.13 (1H, d,  $^3J$  = 4.2,  $H^3$ -ppy), 8.03 (1H, t,  $^3J$  = 3.8,  $H^4$ -ppy), 7.99 (2H, d,  $^3J$  = 7.7,  $H^4$ -NCN), 7.72-7.80 (4H, m,  $H^5$ -NCN or  $H^8$ -NCN, and  $H^6$ -NCN or  $H^7$ -NCN), 7.60-7.68 (3H, m,  $H^5$ -ppy, and  $H^6$ -NCN or  $H^7$ -NCN), 7.59 (1H, d,  $^3J$  =

8.4, H<sup>31</sup>-ppy), 7.54 (1H, t, <sup>3</sup>J = 7.7, H<sup>51</sup>-NCN), 7.40-7.50 (1H, m, H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 7.18 (1H, d, <sup>3</sup>J = 6.3, H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 6.65 (1H, t, <sup>3</sup>J = 6.3, H<sup>41</sup>-ppy), 6.44 (1H, t, <sup>3</sup>J = 6.3, H<sup>51</sup>-ppy), 5.71 (1H, d, <sup>3</sup>J = H<sup>61</sup>-ppy). MS (ES<sup>+</sup>) *m/z* 713.2 [M]<sup>+</sup>. HRMS (ASAP<sup>+</sup>) Calcd for C<sub>35</sub>H<sub>23</sub><sup>35</sup>Cl<sup>191</sup>IrN<sub>3</sub>: *m/z* 711.1187. Found: *m/z* 711.1153. Mp > 250 °C.

### Rh(biqb)(ppy)Cl (2a)

Bis(μ-chloro)bis(1,3-bis(1-quinolinyl)benzene-N,C<sup>2'</sup>,N) rhodium chloride (0.050 g, 0.049 mmol), silver triflate (0.056 g, 0.22 mmol) and 2-phenylpyridine (200 μL, 1.78 mmol) were placed in a Schlenk tube, which was degassed three times *via* evacuating and backfilling with nitrogen. The mixture was heated at 110 °C under nitrogen for 20 h then cooled to room temperature and CH<sub>2</sub>Cl<sub>2</sub> (35 mL) was added. Solid residue was removed by filtration and the filtrate washed with HCl (1M, 3 x 35 mL), dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure. Purification was carried out by column chromatography (silica, CH<sub>2</sub>Cl<sub>2</sub>/methanol, gradient elution from 100:0 to 99:1) to give the product as a yellow solid (0.065 g, 35 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz) δ = 10.27 (1H, d, <sup>3</sup>J = 5.0, H<sup>6</sup>-ppy), 9.12 (2H, d, <sup>3</sup>J = 7.7, H<sup>3</sup>-NCN), 8.62 (2H, d, <sup>3</sup>J = 7.7, H<sup>41</sup>-NCN), 8.14 (1H, d, <sup>3</sup>J = 11.2, H<sup>3</sup>-ppy), 8.10 (1H, td, <sup>3</sup>J = 8.4, <sup>3</sup>J = 1.4, H<sup>4</sup>-ppy), 7.63-7.70 (8H, m, H<sup>4</sup>-NCN and H<sup>5</sup>-ppy and H<sup>31</sup>-ppy and H<sup>5</sup>-NCN and H<sup>8</sup>-NCN, and H<sup>6</sup>-NCN or H<sup>7</sup>-NCN), 7.53-7.56 (3H, m, H<sup>51</sup>-ppy, and H<sup>6</sup>-NCN or H<sup>7</sup>-NCN), 7.22 (2H, d, <sup>3</sup>J = 4.5, H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 6.74 (1H, td, <sup>3</sup>J = 6.0, <sup>4</sup>J = 1.0, H<sup>41</sup>-ppy), 6.51 (1H, td, <sup>3</sup>J = 5.5, <sup>4</sup>J = 1.0, H<sup>51</sup>-ppy), 5.91 (1H, d, <sup>3</sup>J = 8.4, H<sup>61</sup>-ppy). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz) δ = 188.5, 167.9, 165.7, 157.9, 150.7, 143.8, 143.8, 142.7, 138.0, 136.8, 130.7, 129.8, 128.2, 127.7, 127.6, 125.9, 123.0, 122.6, 122.3, 121.9, 120.9, 119.0, 113.6, 110.2, 92.3, 92.1. MS (ASAP<sup>+</sup>) *m/z* 623.0 [M]<sup>+</sup>. HRMS (ASAP<sup>+</sup>) Calcd for C<sub>35</sub>H<sub>23</sub><sup>35</sup>ClN<sub>3</sub><sup>108</sup>Rh: *m/z* 623.0636. Found: *m/z* 623.0643. Mp > 250 °C.

### Ir(biqb)(ppy)C≡C-tfp (3b)

A Schlenk tube containing 1-ethynyl-3,5-bis(trifluoromethyl)benzene (100 μL) and KOH (0.030 g, 0.535 mmol) in methanol (2 mL) was briefly evacuated then a rapid stream of nitrogen bubbled through the solution. The solution was stirred under nitrogen for 1 h whilst a separate solution of Ir(biqb)(ppy)Cl (0.025 g, 0.035 mmol) and copper(I) iodide (0.004 g) in methanol (2 mL) was degassed using the same method. The complex was transferred *via* syringe under nitrogen to the initial Schlenk tube and a further degassing step performed, as before. The mixture was stirred under nitrogen at room temperature for 18 h and the red precipitate collected by centrifugation then washed with methanol (3 x 3 mL). Upon drying *in vacuo*, the product was isolated as a dark red solid (0.008 g, 25 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz) δ = 10.30 (1H, t,

$^3J = 4.4$ , H<sup>6</sup>-ppy), 9.21 (2H, d,  $^3J = 8.7$ , H<sup>3</sup>-NCN), 8.72 (2H, d,  $^3J = 8.0$  H<sup>4'</sup>-NCN), 8.14 (1H, d,  $^3J = 8.2$ , H<sup>3</sup>-ppy), 8.05 (1H, td,  $^3J = 7.4$ ,  $^4J = 1.4$ , H<sup>4</sup>-ppy), 7.73-7.78 (6H, m, H<sup>4</sup>-NCN and H<sup>6</sup>-NCN and H<sup>7</sup>-NCN), 7.60-7.70 (4H, m, H<sup>3'</sup>-ppy and H<sup>5'</sup>-ppy, and H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 7.54-7.60 (2H, m, H<sup>5'</sup>-NCN and H<sup>4''</sup>-CCtfp), 7.33 (2H, d,  $^3J = 11.2$ , H<sup>2''</sup>-CCtfp), 7.17 (2H, d,  $^3J = 7.0$ , H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 6.70 (1H, td,  $^3J = 7.2$ ,  $^3J = 1.6$ , H<sup>4'</sup>-ppy), 6.48 (1H, td,  $^3J = 7.6$ ,  $^4J = 1.2$ , H<sup>5'</sup>-ppy), 5.58 (1H, d,  $^3J = 6.2$ , H<sup>6'</sup>-ppy). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta = -63.3$  (6F, s, CF<sub>3</sub>). MS (ASAP<sup>+</sup>)  $m/z$  916.2 [M + H]<sup>+</sup>. HRMS (ASAP<sup>+</sup>) Calcd for C<sub>45</sub>H<sub>26</sub>N<sub>3</sub>F<sub>6</sub><sup>191</sup>Ir:  $m/z$  913.1637. Found:  $m/z$  913.1648. Mp > 250 °C.

### Rh(biqb)(ppy)C≡C-tfp (3a)

A Schlenk tube containing 1-ethynyl-3,5-bis(trifluoromethyl)benzene (150  $\mu$ L) and KOH (0.030 g) in methanol (2 mL) was briefly evacuated then a rapid stream of nitrogen was bubbled through the solution. The solution was stirred under nitrogen for 1 h whilst a separate solution of Rh(biqb)(ppy)Cl (0.015 g, 0.024 mmol) and copper(I) iodide (0.004 g) in methanol (2 mL) was degassed using the same method. The complex was transferred *via* syringe under nitrogen to the initial Schlenk tube and a further degassing step performed. The reaction was stirred under nitrogen at room temperature for 18 h and the yellow precipitate collected by centrifugation then washed with methanol (3 x 3 mL). Upon drying *in vacuo*, the product was isolated as a yellow solid (0.010 g, 50 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz)  $\delta = 10.23$  (1H, d,  $^3J = 4.0$ , H<sup>6</sup>-ppy), 9.15 (2H, d,  $^3J = 8.5$ , H<sup>3</sup>-NCN), 8.68 (2H, d,  $^3J = 8.0$ , H<sup>4'</sup>-NCN), 8.15 (1H, d,  $^3J = 8.5$ , H<sup>3</sup>-ppy), 8.08 (1H, td,  $^3J = 8.5$ ,  $^4J = 1.0$ , H<sup>4</sup>-ppy), 7.61-7.76 (8H, m, H<sup>4</sup>-NCN and H<sup>5'</sup>-ppy and H<sup>3'</sup>-ppy, and H<sup>5</sup>-NCN or H<sup>8</sup>-NCN, and H<sup>6</sup>-NCN or H<sup>7</sup>-NCN), 7.56 (2H, t,  $^3J = 8.0$ , H<sup>6</sup>-NCN or H<sup>7</sup>-NCN), 7.33 (2H, m, H<sup>4''</sup>-CCtfp and H<sup>2''</sup>-CCtfp or H<sup>5</sup>-NCN), 7.30 (2H, d,  $^3J = 6.3$ , H<sup>4''</sup>-CCtfp and H<sup>2''</sup>-CCtfp or H<sup>5</sup>-NCN), 7.20 (2H, d,  $^3J = 6.5$ , H<sup>5</sup>-NCN or H<sup>8</sup>-NCN), 6.74 (1H, t,  $^3J = 7.5$ , H<sup>4'</sup>-ppy), 6.51 (1H, t,  $^3J = 6.0$ , H<sup>5'</sup>-ppy), 5.77 (1H, d,  $^3J = 7.0$ , H<sup>6'</sup>-ppy). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta = -63.6$  (6F, s, CF<sub>3</sub>). MS (ASAP<sup>+</sup>)  $m/z$  825.1 [M]<sup>+</sup>. HRMS (ASAP<sup>+</sup>) Calcd for C<sub>45</sub>H<sub>26</sub>N<sub>3</sub>F<sub>6</sub><sup>108</sup>Rh:  $m/z$  825.1086 [M]<sup>+</sup>. Found:  $m/z$  825.1069 [M]<sup>+</sup>. Mp > 250 °C.

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