Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

Efficient Near-Infrared Luminescence from Bis-Cyclometalated Iridium(III) Complexes with Rigid Quinoline-Derived Ancillary Ligands

Po-Ni Lai, Sungwon Yoon, and Thomas S. Teets*

University of Houston, Department of Chemistry, 3585 Cullen Blvd. Room 112, Houston, TX USA, 77204-5003. E-mail: tteets@uh.edu

Experimental

Materials. All reactions were executed in a nitrogen-filled glovebox operating at <1 ppm of O_2 and H_2O or on dual vacuum/nitrogen manifold using standard Schlenk techniques. All starting materials and reagents were obtained from commercial sources except for the protonated ancillary ligands, 8-(1*H*-pyrrol-2-yl)quinoline (8PyQH) and *N*-phenyl-8-quinolinecarboxamide (8CONPhQH), were synthesized by known procedures.[1,2] Solvents for reactions and optical measurements were dried by the method of Grubbs, passing through dual alumina columns on a commercial solvent purification system (SPS), and stored over 3 Å molecular sieves. The cyclometalating ligand 6-(benzo[*b*]thien-2-yl)phenanthridine (btphH) was synthesized according to literature procedures.[3] The cyclometalated iridium dimer $[Ir(btph)_2(\mu\text{-}Cl)]_2$ was prepared by the method of Nonoyama,[4] refluxing $IrCl_3{\cdot}nH_2O$ with 2.1 equiv. of the cyclometalating ligand in a 3:1 mixture of 2-ethoxyethanol and water. The resulting dimer was used without further purification. The potassium salt of 8CONPhQ was prepared *via* deprotonation of the protonated ligand precursor with benzyl potassium, as described previously by our lab.[5,6] Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized from hot ethanol and ferrocene was sublimed at ambient pressure before use in electrochemical experiments.

Physical Methods. ^1H spectra (shown in Fig. S7–S11) were recorded at room temperature using a JEOL ECA-500, or ECA-600 NMR spectrometer. The static nanoESI-MS experiments were carried out using a Thermo Exactive mass spectrometer and operated in positive ionization mode, with a spray voltage at 1.5 kV. UV−vis absorption spectra were recorded in THF solutions in screw-capped quartz cuvettes using an Agilent Carey 8454 UV−vis spectrophotometer. Luminescence lifetimes were measured with a Horiba DeltaFlex Lifetime System, using 430 nm pulsed diode excitation. Steady-state emission spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer with appropriate long-pass filters to exclude stray excitation light from detection. In order to exclude air, samples for emission spectra were prepared in a nitrogen-filled glovebox using anhydrous solvents. Samples for room-temperature emission were housed in 1 cm quartz cuvettes with septum-sealed screw caps, and samples for low-temperature emission were contained in a custom quartz EPR tube with high-vacuum valve and immersed in liquid nitrogen using a finger dewar. Solution quantum yields were determined relative to a standard of tetraphenylporphyrin in toluene, which has a reported fluorescence quantum yield (Φ_F) of 0.11.[7] Cyclic voltammetry (CV) measurements were performed with a CH Instruments 602E potentiostat interfaced with a nitrogen glovebox via wire feedthroughs. Samples were dissolved in THF with 0.1 M $TBAPF_6$ as a supporting electrolyte. A 3 mm diameter glassy-carbon working electrode, a platinum wire counter electrode, and a silver wire pseudo-reference electrode were used. Potentials were referenced to an internal standard of ferrocene.

X-ray Crystallography Details. Single crystals were grown by vapor diffusion of hexane vapor into concentrated dichloromethane solution. Crystals were mounted on a Bruker Apex II three-circle diffractometer using MoKα radiation (λ = 0.71073 Å). The data was collected at 123(2) K and was processed and refined within the APEXII software. Structures were solved by direct methods in SHELXS and refined by standard difference Fourier techniques in the program SHELXL.[8] Hydrogen atoms were placed in calculated positions using the standard riding model and refined isotropically; all non-hydrogen atoms were refined anisotropically. Crystallographic details are summarized in Table S1.

Synthesis

General procedure for preparation of complexes 1–3. 2 mL of dichloromethane, 2 mL of ethanol, and 1 mL of triethylamine were deoxygenated for 30 mins by bubbling with nitrogen. $[Ir(btph)_2(\mu\text{-}Cl)]_2$ and the respective quinoline-based ancillary ligand were added. The reaction was bought to reflux at 80 °C for 16 h. The reaction was cooled to room temperature and the solution was concentrated to dryness. 2 mL of methanol was added to form the precipitate. The mixture was filtered, and the solids were washed with methanol, hexane, and pentane to yield the desired products.

Preparation of Ir(btph)$_2$(8OQ) (1). Prepared by the general procedure using 30 mg of $[Ir(C\text{^}N)_2(\mu\text{-}Cl)]_2$ (0.018 mmol) and 11 mg of 8-hydroxyquinoline (0.076 mmol, 3.8 equiv.). Yield: 4 mg, 12%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.46−9.44 (m, 1H, Ar*H*), 9.38−9.36 (m, 1H, Ar*H*), 8.71 (d, *J* = 8.6 Hz, 1H, Ar*H*), 8.58−8.56 (m, 2H, Ar*H*) , 8.25−8.19 (m, 3H, Ar*H*), 7.92−7.83 (m, 5H, Ar*H*), 7.72−7.67 (m, 2H, Ar*H*), 7.35−7.28 (m, 2H, Ar*H*), 7.12−7.04 (m, 3H, Ar*H*), 7.00−6.94 (m, 2H, Ar*H*), 6.84 (d, *J* = 8.1 Hz, 1H, Ar*H*), 6.63−6.52 (m, 4H, Ar*H*), 6.46 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.35−6.29 (m, 2H, Ar*H*). UV−vis (THF): λ/nm (ε/$M^{-1}cm^{-1}$) 293 (86000), 326 (sh) (57000), 367 (54000), 413 (sh) (40000), 520 (25000), 551 (sh) (21000). HRMS-ESI (*m*/*z*): $[M+H]^+$ cald for $C_{51}H_{31}IrN_3OS_2$, 958.15323; found, 958.15350.

Preparation of Ir(btph)$_2$(8COOQ) (2). Prepared by the general procedure using 33 mg of $[Ir(C\text{^}N)_2(\mu\text{-}Cl)]_2$ (0.019 mmol) and 9 mg of 8-quinolinecarboxylic acid (0.052 mmol, 2.7 equiv.). Yield: 23 mg, 61%. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 9.52−9.51 (m, 1H, Ar*H*), 9.38−9.36 (m, 1H, Ar*H*), 8.99−8.95 (m, 2H, Ar*H*), 8.74−8.72 (m, 1H, Ar*H*), 8.65−8.63 (m, 1H, Ar*H*), 8.42−8.41 (m, 1H, Ar*H*), 8.21−8.14 (m, 2H, Ar*H*), 8.05–7.95 (m, 4H, Ar*H*), 7.81−7.74 (m, 2H, Ar*H*), 7.51−7.32 (m, 4H, Ar*H*), 7.19−7.17 (m, 2H, Ar*H*), 7.04−6.97 (m, 3H, Ar*H*), 6.69−6.68 (m, 1H, Ar*H*), 6.53−6.49 (m, 3H, Ar*H*), 6.40−6.38 (m, 1H, Ar*H*), 6.21−6.18 (m, 1H, Ar*H*). UV−vis (THF): λ/nm (ε/$M^{-1}cm^{-1}$) 293 (38000), 307 (36000), 360 (26000). 385 (26000), 407 (22000), 527 (11000), 557 (sh) (10000). HRMS-ESI (*m*/*z*): $[M+H]^+$ cald for $C_{52}H_{31}IrN_3O_2S_2$, 986.14814; found, 986.14856.

Preparation of Ir(btph)$_2$(10OBQ) (3). Prepared by the general procedure using 30 mg of $[Ir(C\text{^}N)_2(\mu\text{-}Cl)]_2$ (0.018 mmol) and 8 mg of 10-hydroxybenzo[*h*]quinoline (0.041 mmol, 2.3 equiv.). Yield: 13 mg, 36%. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.54−9.52 (m, 1H, Ar*H*), 9.45−9.43 (m, 1H, Ar*H*), 9.21−9.19 (m, 1H, Ar*H*), 9.05−9.03 (m, 1H, Ar*H*), 8.70−8.68 (m, 1H, Ar*H*), 8.61−8.58 (m, 2H, Ar*H*), 8.17 (m, 3H, Ar*H*), 8.01–7.96 (m, 3H, Ar*H*), 7.88−7.82 (m, 2H, Ar*H*), 7.44−7.36 (m, 3H, Ar*H*), 7.22−7.21 (m, 2H, Ar*H*), 7.15−7.13 (m, 1H, Ar*H*), 7.03−7.00 (m, 2H, Ar*H*), 6.88 (m, 1H, Ar*H*), 6.58−6.42 (m, 5H, Ar*H*), 6.31−7.29 (m, 1H, Ar*H*), 6.14−6.10 (m, 2H, Ar*H*). UV−vis (THF): λ/nm (ε/$M^{-1}cm^{-1}$) 294 (38000), 377 (27000), 401 (sh) (26000), 541 (9000), 576 (sh) (8000). HRMS-ESI (*m*/*z*): $[M+H]^+$ cald for $C_{55}H_{33}IrN_3OS_2$, 1008.16888; found, 1008.16901.

Procedure for preparation of complex 4. $[Ir(btph)_2(\mu\text{-}Cl)]_2$ (30 mg, 0.018 mmol), 8-(1*H*-pyrrol-2-yl)quinoline (8PyQ) (10 mg, 0.051 mmol), and NaH (7 mg, 0.18 mmol) were added into the flask and the mixture was purged with nitrogen for 30 mins. 3 mL of dry THF was added. The reaction was bought to reflux at 70 °C and allowed to stir for 16 h. After the reaction was cooled, the solution was passed through a plug of Celite. The remaining solvent was evaporated to leave a dark residue. 2 mL of methanol was added to form a red precipite. The mixture was filtered, and the solids were washed with 1 mL of methanol, 2 mL of hexane, and 2 mL of pentane. The recovered solid was dissolved in 1 mL of dichloromethane. 3 mL of hexane was added while it was stirring to precipitate the product. The mixture was then filtered to yield the desired products. Yield: 20 mg, 55%. ^{1}H NMR (500 MHz, C_6D_6): δ = 9.60 (d, *J* = 8.0 Hz, 1H, Ar*H*), 8.81−8.77 (m, 2H, Ar*H*), 8.20−8.17 (m, 2H, Ar*H*), 7.93−7.91 (m, 2H, Ar*H*), 7.80 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.69 (d, *J* = 8.1 Hz, 1H, Ar*H*), 7.43−7.24 (m, 7H, Ar*H*), 7.07−7.04 (m, 3H, Ar*H*), 6.93–6.89 (m, 3H, Ar*H*), 6.82 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.73−6.56 (m, 5H, Ar*H*), 6.43−6.30 (m, 3H, Ar*H*), 6.20 (t, *J* = 7.7 Hz, 1H, Ar*H*), 5.70−5.65 (m, 1H, Ar*H*). UV−vis (THF): λ/nm (ε/$M^{-1}cm^{-1}$) 294 (28000), 363 (16000), 376 (16000),

423 (13000), 532 (sh) (6000). HRMS-ESI (*m*/*z*): $[M+H]^+$ cald for $C_{55}H_{34}IrN_4S_2$, 1007.18486; found, 1007.18518.

Preparation of Ir(btph)$_2$(8CONPhQ) (5). In the glovebox, $[Ir(btph)_2(\mu\text{-}Cl)]_2$ (50 mg, 0.029 mmol) was suspended in 2 mL of THF. A solution of the potassium salt of *N*-phenyl-8-quinolinecarboxamide, 8CONPhQK (0.069 mmol, 2.4 equiv.), dissolved in 5 mL of THF, was added to the stirred mixture. The resulting mixture was stirred overnight at room temperature, during which time the solids were drawn into solution and a purple solution resulted. The resulting residue was extracted with 5 mL of toluene and filtered through Celite. The toluene was removed *in vacuo*, and the residue was triturated with 2 mL of room-temperature diethyl ether before filtering off the red product. The solid was collected from the filter by dissolving in dichloromethane, and the resulting solution was concentrated to dryness. Finally, the product was redissolved in minimum amount of THF, and pentane was slowly added in to precipitate out the crude product. The solids were again dissolved in minimum amount of dichloromethane, and hexane was added while it was stirring to precipitate the desired product. The product was filtered and dried under vacuum. Yield: 10 mg, 16%. ^{1}H NMR (500 MHz, C_6D_6): δ = 9.36 (d, *J* = 7.4 Hz, 1H, Ar*H*), 9.24 (d, *J* = 8.2 Hz, 1H, Ar*H*), 9.04–8.96 (m, 2H, Ar*H*), 8.20−8.07 (m, 4H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.43 (t, *J* = 7.4 Hz, 2H, Ar*H*), 7.36–7.24 (m, 5H, Ar*H*), 7.17–7.15 (m, 2H, Ar*H*), 7.08–7.07 (m, 2H, Ar*H*), 7.01–6.91 (m, 4H, Ar*H*), 6.80 (d, *J* = 8.4 Hz, 1H, Ar*H*), 6.66−6.51 (m, 4H, Ar*H*), 6.38−6.20 (m, 6H, Ar*H*). UV−vis (THF): λ/nm (ε/$M^{-1}cm^{-1}$) 293 (31000), 370 (16000), 408(sh) (12000), 568 (6400). $[M+H]^+$ cald for $C_{58}H_{36}IrN_4S_2$, 1061.19598; found, 1061.19617.

Table S1. Crystallographic summary for complexes **1** and **2**.

	1·CH_2Cl_2	**2**
CCDC	1995456	1995457
Crystal data		
Chemical formula	$C_{52}H_{32}Cl_2IrN_3OS_2$	$C_{52}H_{30}IrN_3O_2S_2$
M_r	1042.02	985.11
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
a, b, c (Å)	10.9146 (16), 12.9032 (19), 14.947 (2)	11.6553 (5), 17.7049 (7), 21.3456 (9)
α, β, γ (°)	91.818 (1), 106.550 (1), 94.174 (1)	90, 98.312 (1), 90
V (Å^3)	2009.4 (5)	4358.5 (3)
Z	2	4
μ (mm^{-1})	3.61	3.20
Crystal size (mm)	0.27 × 0.20 × 0.11	0.28 × 0.16 × 0.15
Data collection		
T_{min}, T_{max}	0.591, 0.746	0.584, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42541, 9341, 7865	26503, 9757, 8238
R_{int}	0.063	0.026
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.653	0.645
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.092, 1.06	0.029, 0.076, 1.03
No. of reflections	9341	9757
No. of parameters	578	542
No. of restraints	68	107
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3}))	2.60, −1.49	1.60, −1.20

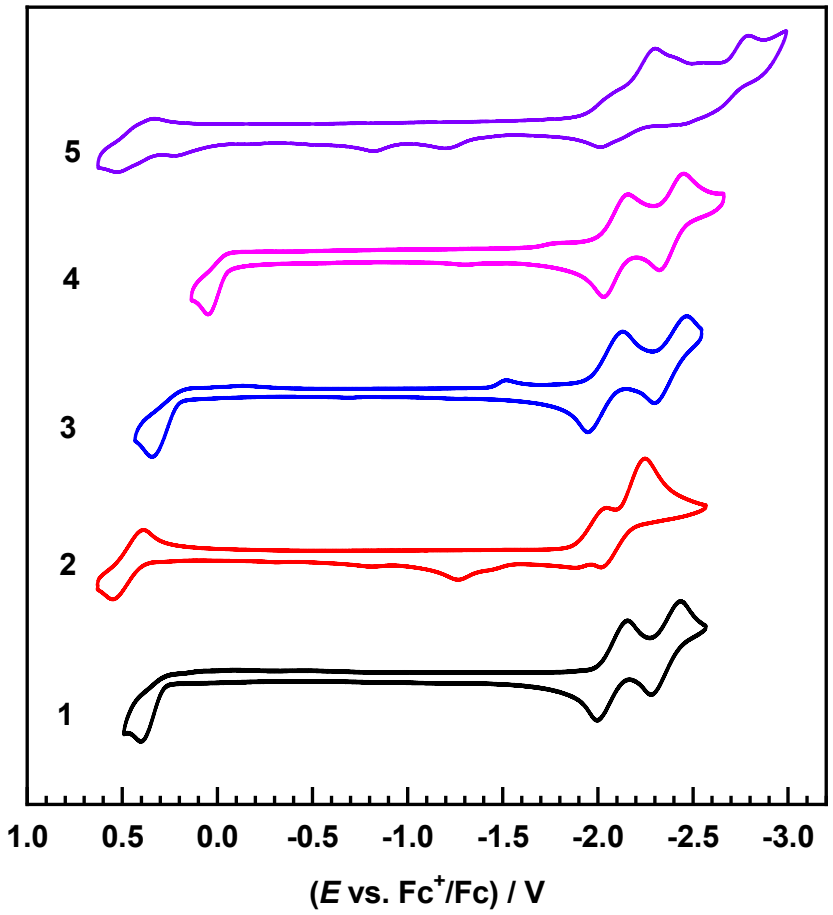

Fig. S1. Cyclic voltammograms of $Ir(btph)_2(L\text{^}X)$ complexes. Potentials are referenced to an internal standard of ferrocene, and currents are normalized to bring all the traces onto the same scale.

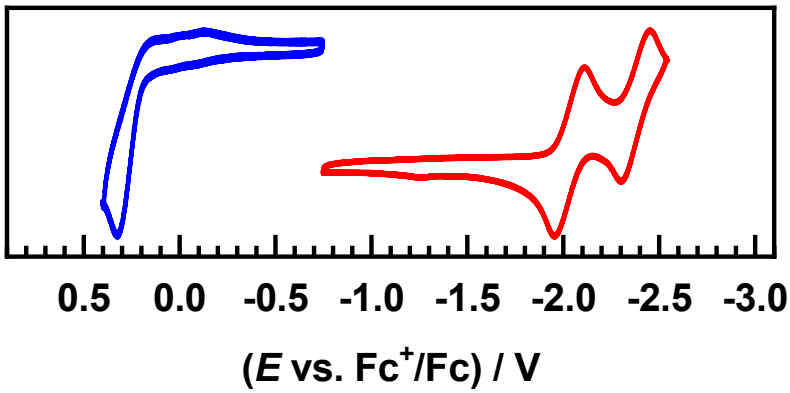

Fig. S2. Cyclic voltammograms of Ir(btph)$_2$(10OBq) (**3**), showing separate anodic (blue) and cathodic (red) scans. Potentials are referenced to an internal standard of ferrocene. The small cathodic wave, appearing at ca. −1.5 V in Fig S1, is absent when performing separate anodic and cathodic scans and thus is a return wave coupled to the irreversible oxidation.

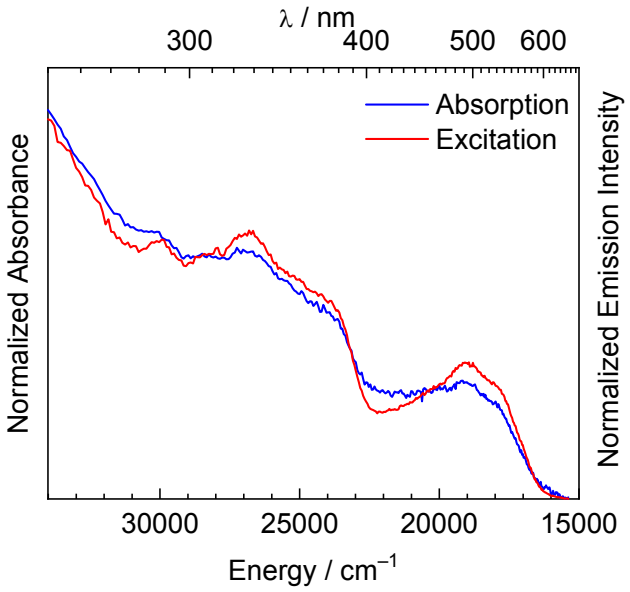

Fig. S3. Excitation spectrum of Ir(btph)$_2$(8OQ) (**1**), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with λ_{em} = 711 nm for the excitation spectrum.

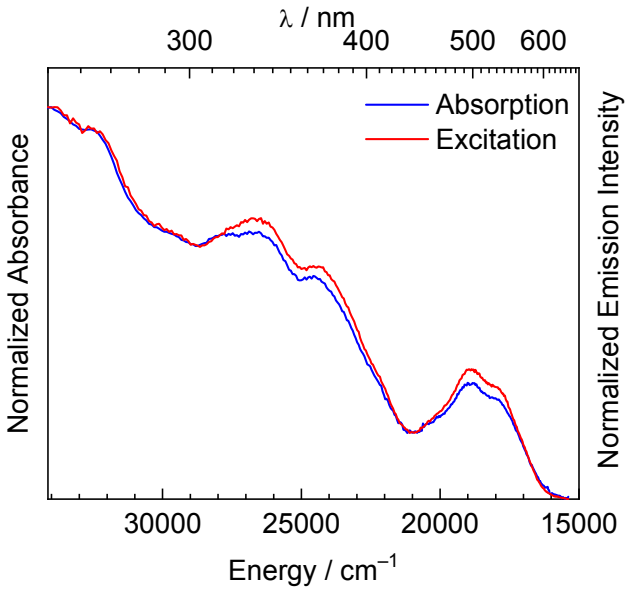

Fig. S4. Excitation spectrum of Ir(btph)$_2$(8COOQ) (**2**), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with λ_{em} = 724 nm for the excitation spectrum.

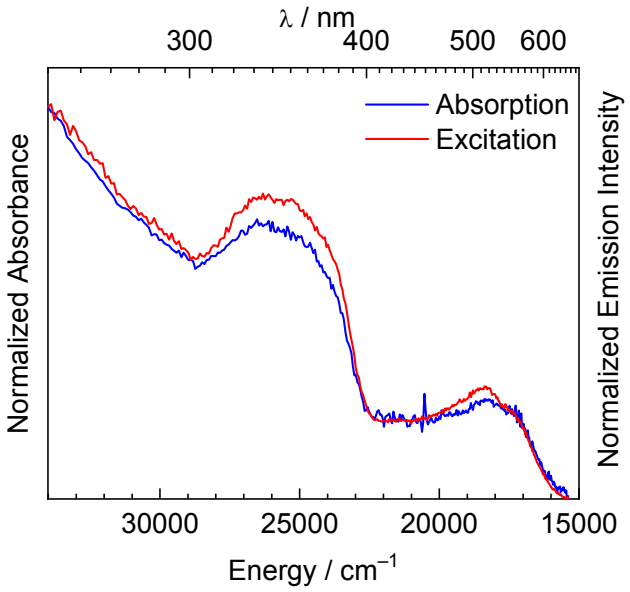

Fig. S5. Excitation spectrum of Ir(btph)$_2$(10OQ) (**3**), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with λ_{em} = 723 nm for the excitation spectrum.

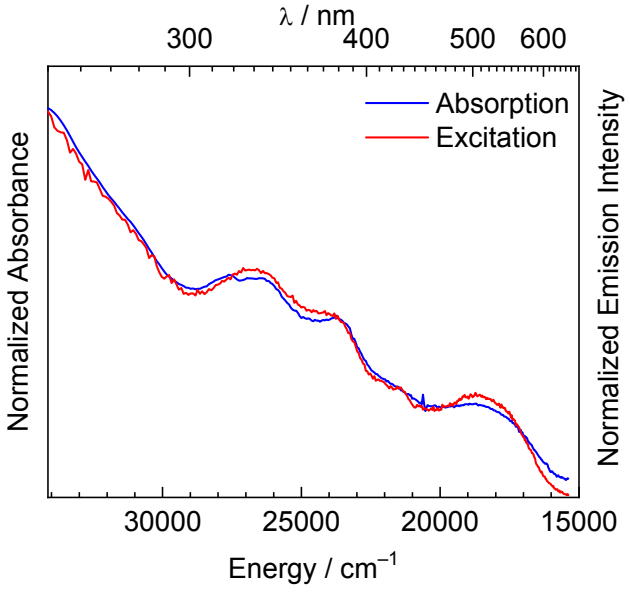

Fig. S6. Excitation spectrum of Ir(btph)$_2$(8PyQ) (**4**), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with λ_{em} = 729 nm for the excitation spectrum.

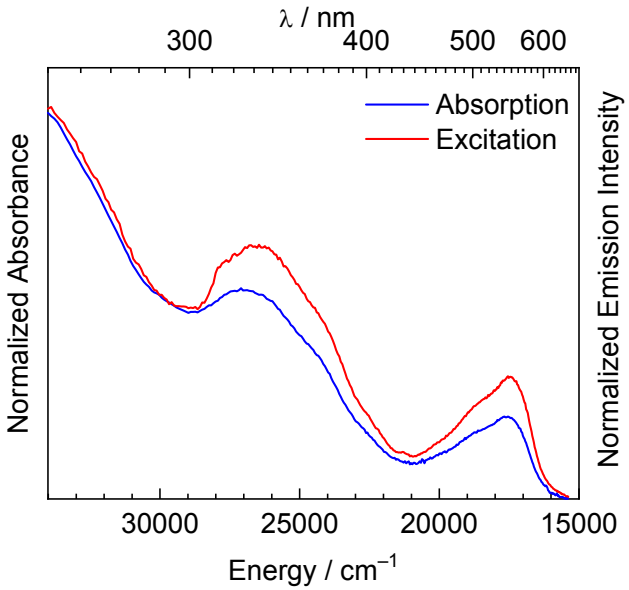

Fig. S7. Excitation spectrum of Ir(btph)$_2$(8CONPhQ) (**5**), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with λ_{em} = 716 nm for the excitation spectrum.

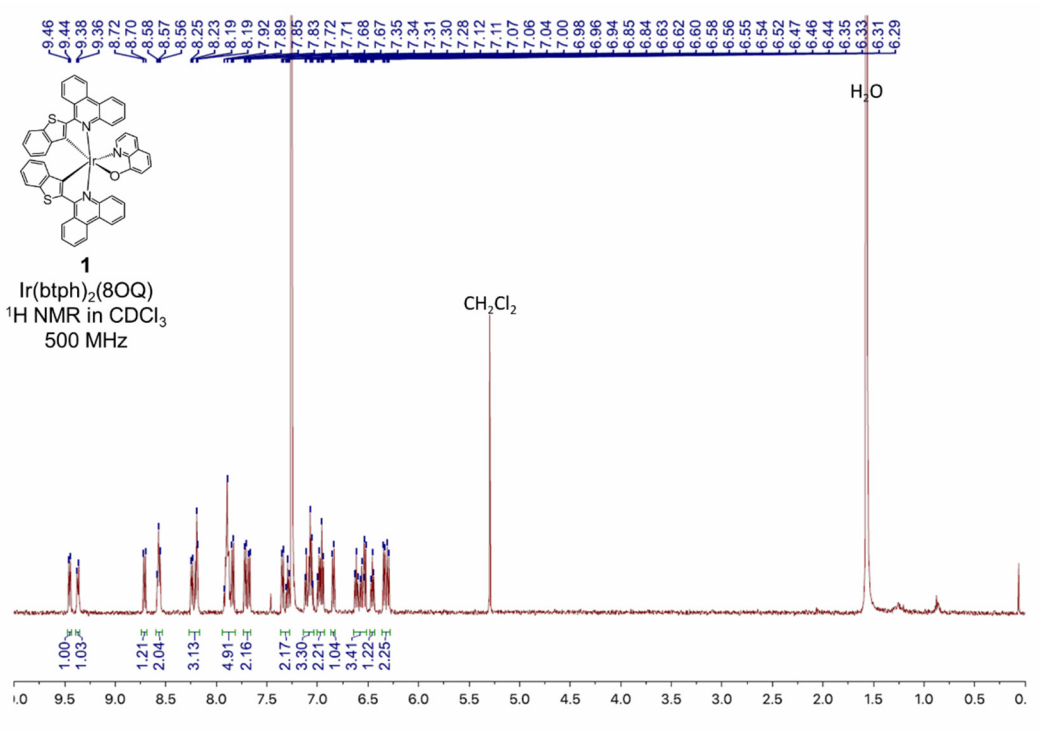

Fig. S8. ^{1}H NMR spectrum of Ir(btph)$_2$(8OQ) (**1**), recorded at 500 MHz in $CDCl_3$.

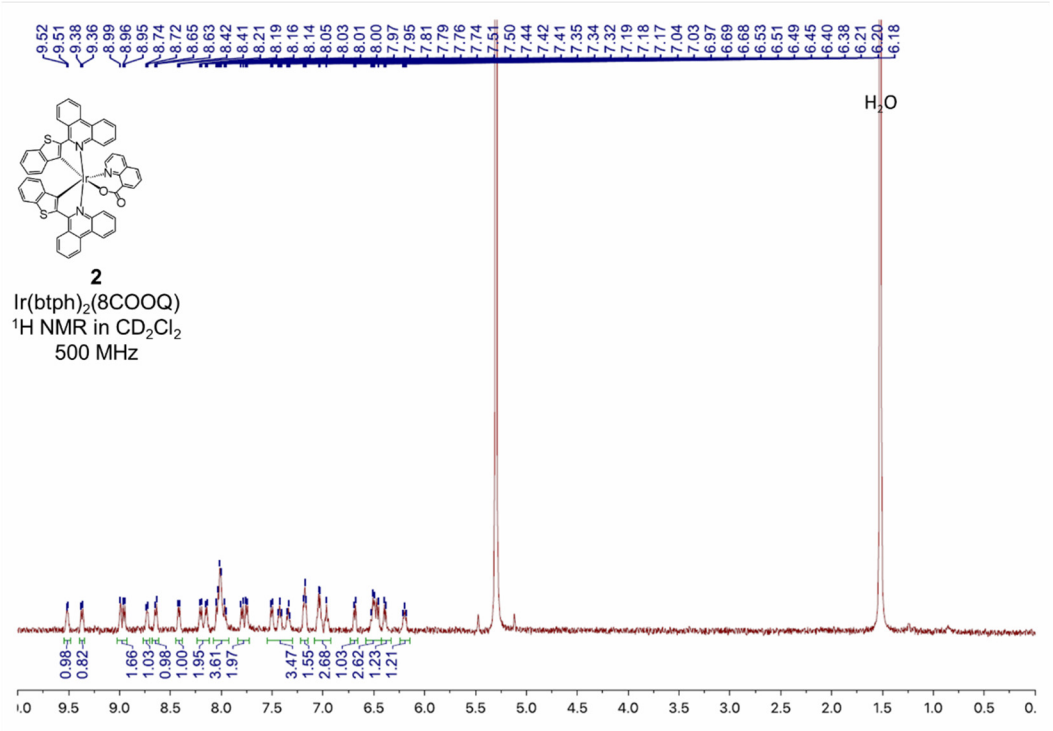

Fig. S9. ^{1}H NMR spectrum of Ir(btph)$_2$(8COOQ) (**2**), recorded at 500 MHz in CD_2Cl_2.

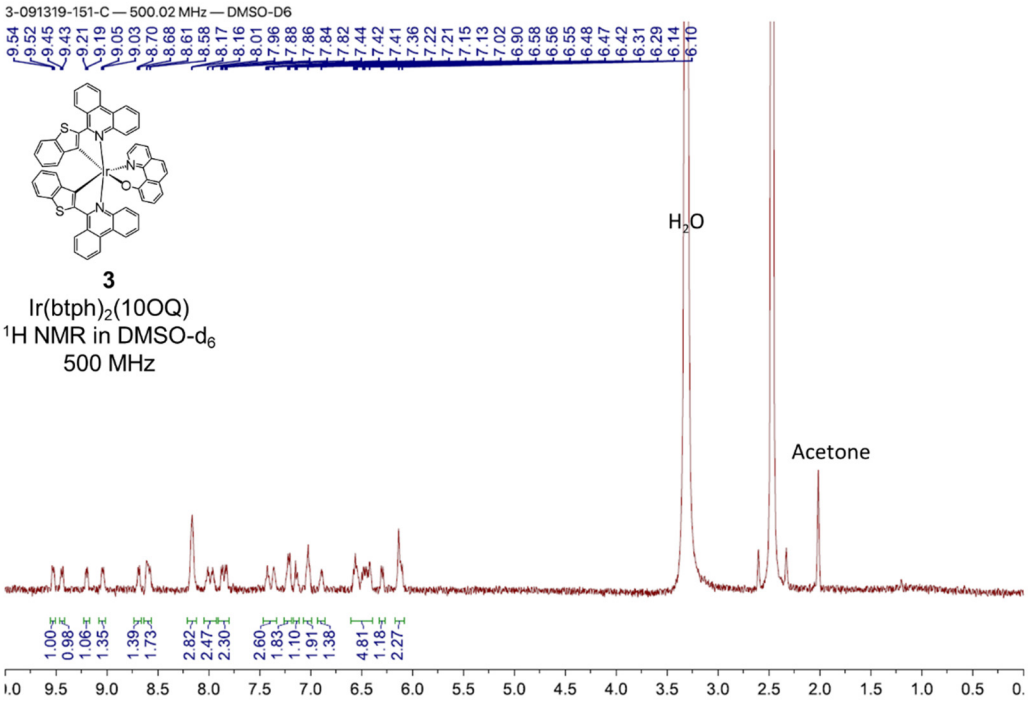

Fig. S10. ^{1}H NMR spectrum of Ir(btph)$_2$(10QQ) (**3**), recorded at 500 MHz in DMSO-d$_6$.

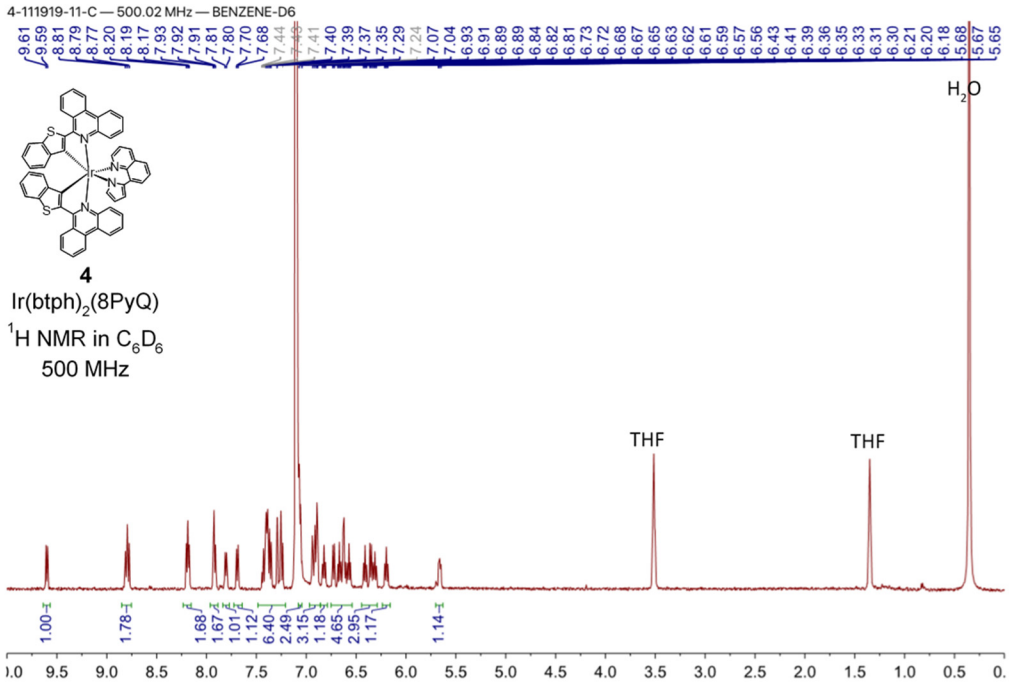

Fig. S11. ^{1}H NMR spectrum of Ir(btph)$_2$(8PyQ) (**4**), recorded at 500 MHz in C_6D_6.

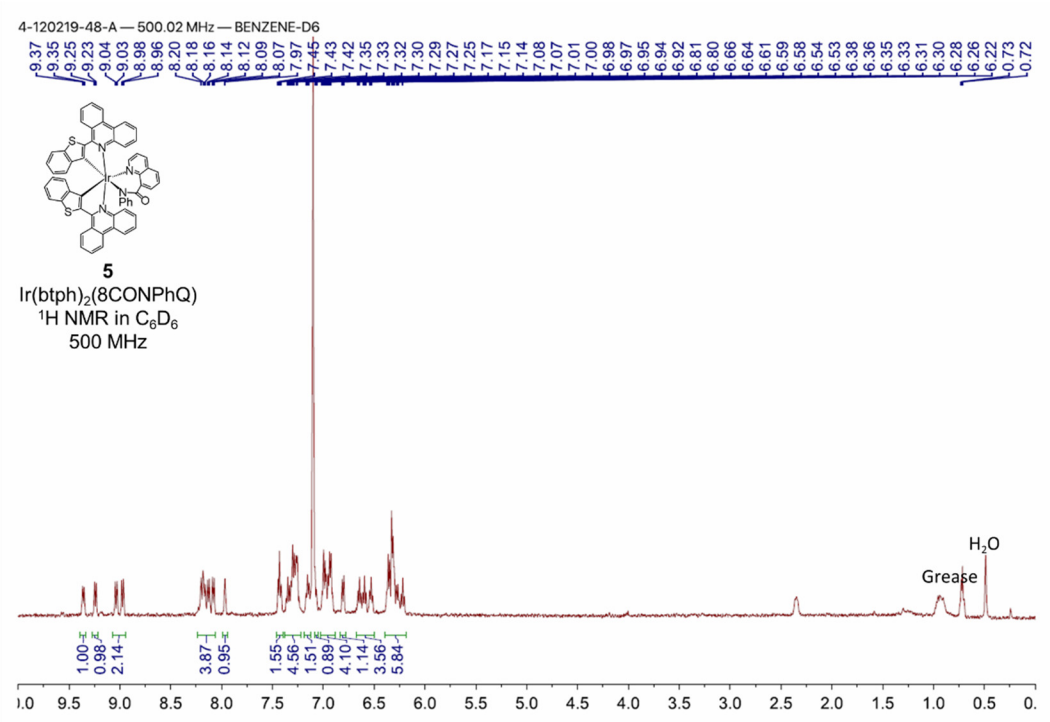

Fig. S12. ^{1}H NMR spectrum of $Ir(btph)_2(8ONPhQ)$ (**5**), recorded at 500 MHz in C_6D_6.

Supporting Information References

1 C. Papageorgiou, A. von Matt, J. Joergensen, E. Andersen, K. Wagner, C. Beerli, T. Than, X. Borer, A. Florineth, G. Rihs, M. H. Schreier, G. Weckbecker and C. Heusser, *J. Med. Chem.*, 2001, **44**, 1986–1992.

2 H. Brodnik, F. Požgan and B. Štefane, *Org. Biomol. Chem.*, 2016, **14**, 1969–1981.

3 T. Yoshihara, S. Murayama, T. Masuda, T. Kikuchi, K. Yoshida, M. Hosaka and S. Tobita, *J. Photochem. Photobiol. Chem.*, 2015, **299**, 172–182.

4 M. Nonoyama, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 767–768.

5 Y. K. Radwan, A. Maity and T. S. Teets, *Inorg. Chem.*, 2015, **54**, 7122–7131.

6 P.-N. Lai, C. H. Brysacz, M. K. Alam, N. A. Ayoub, T. G. Gray, J. Bao and T. S. Teets, *J. Am. Chem. Soc.*, 2018, **140**, 10198–10207.

7 P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, 1969, **31**, 1–13.

8 G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.