

Supporting Information

Carboxy Derivatised Ir(III) Complexes: Synthesis, Electrochemistry, Photophysical Properties and Photocatalytic Hydrogen Generation

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(C) [Ir(ppy-COOEt) ₂ (dpb)](PF ₆);	
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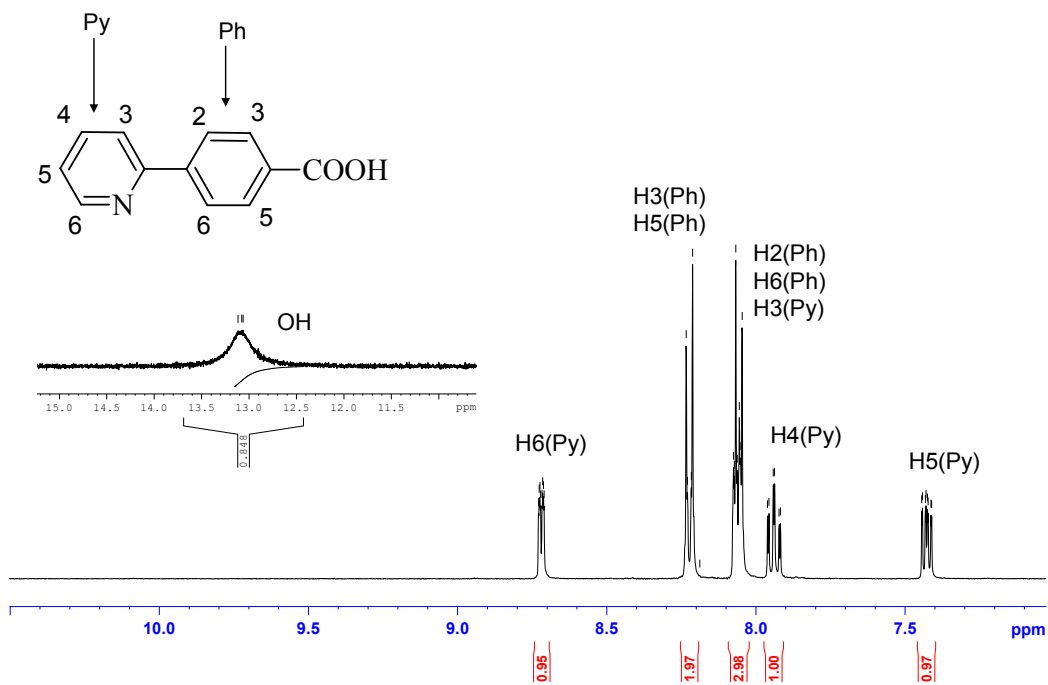


Figure S1: ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) of ppy-COOH.

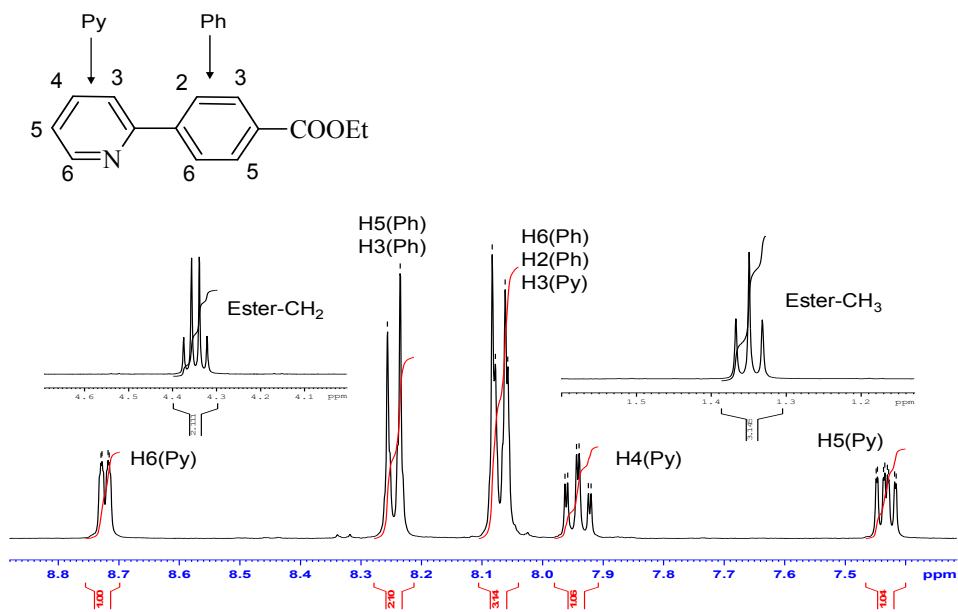


Figure S2: ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) of ppy-COOEt.

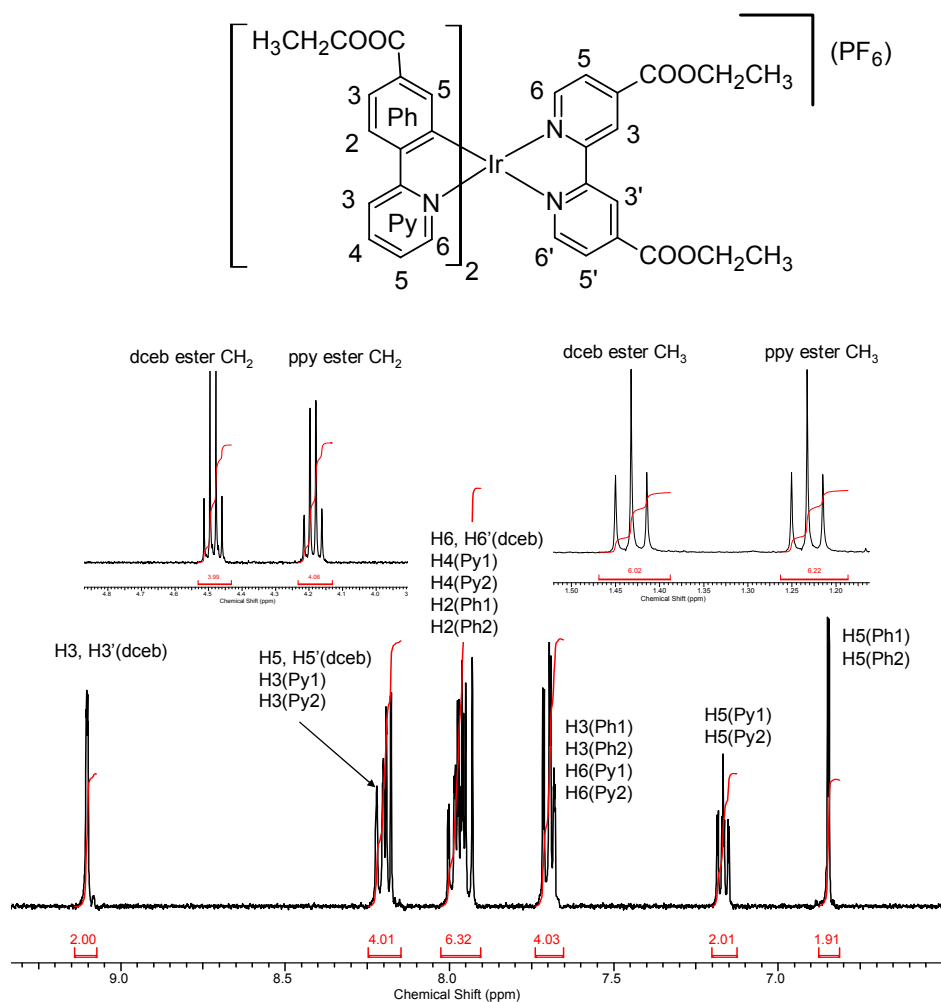


Figure S3: 1H NMR (Acetonitrile- d_6 , 400 MHz) of $[Ir(ppy-COOEt)_2(dceb)](PF_6)$

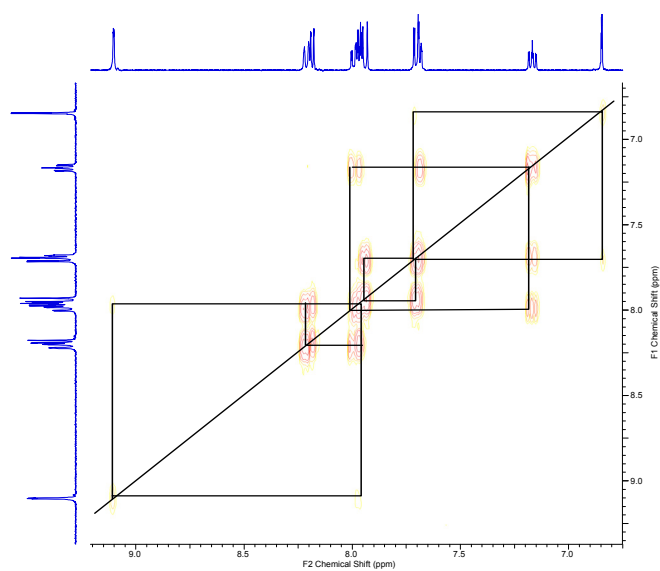


Figure S4: COSY NMR (Acetonitrile- d_3 , 400 MHz) of $[Ir(ppy-COOEt)_2(dceb)](PF_6)$

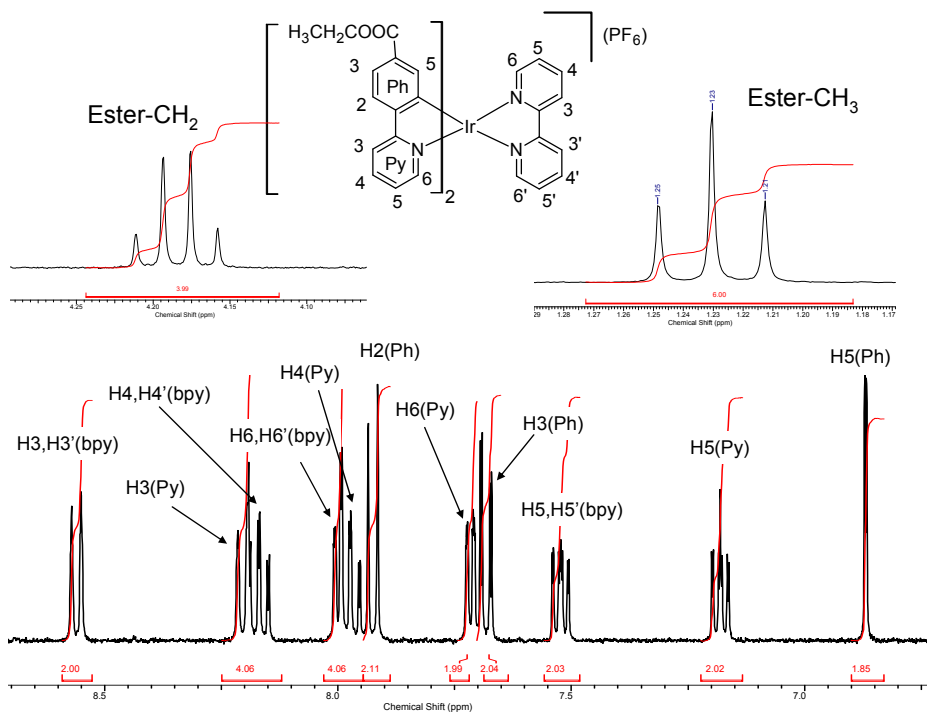


Figure S5: ^1H NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpy})](\text{PF}_6)$

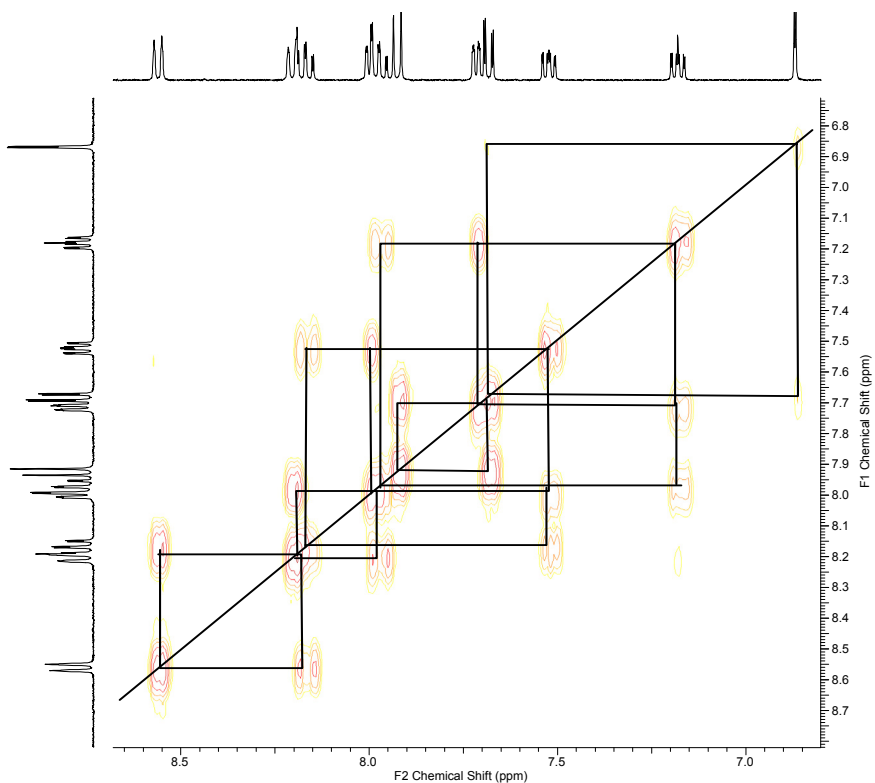


Figure S6: 2D COSY NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpy})](\text{PF}_6)$

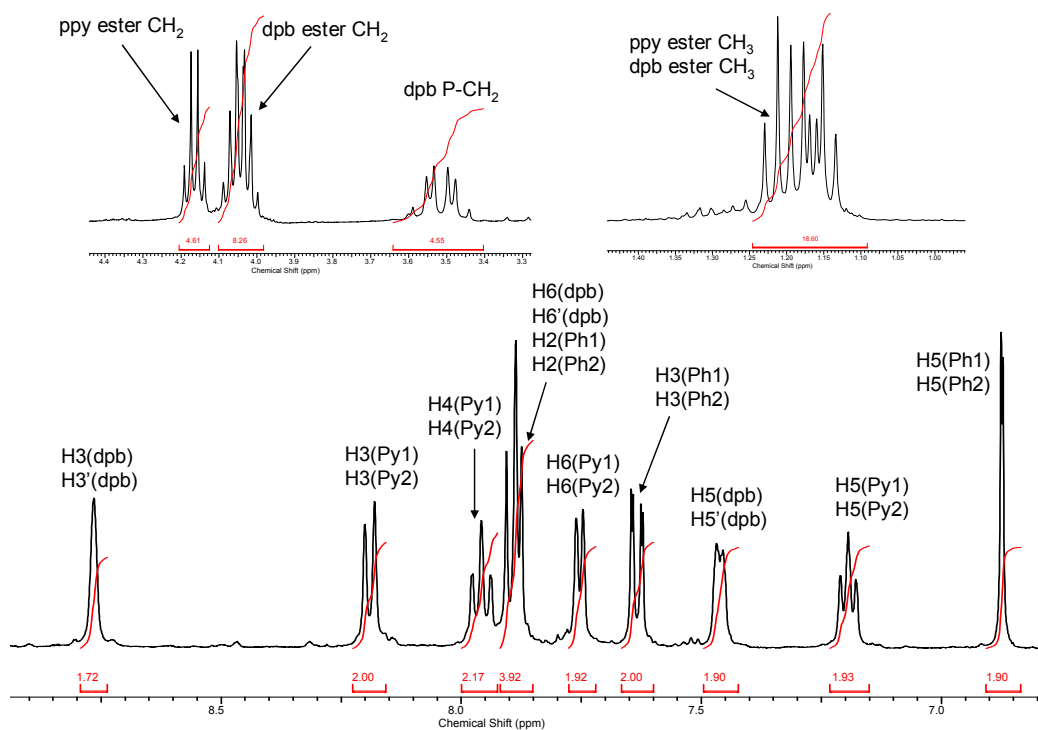


Figure S7: ^1H NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{dpb})](\text{PF}_6)$

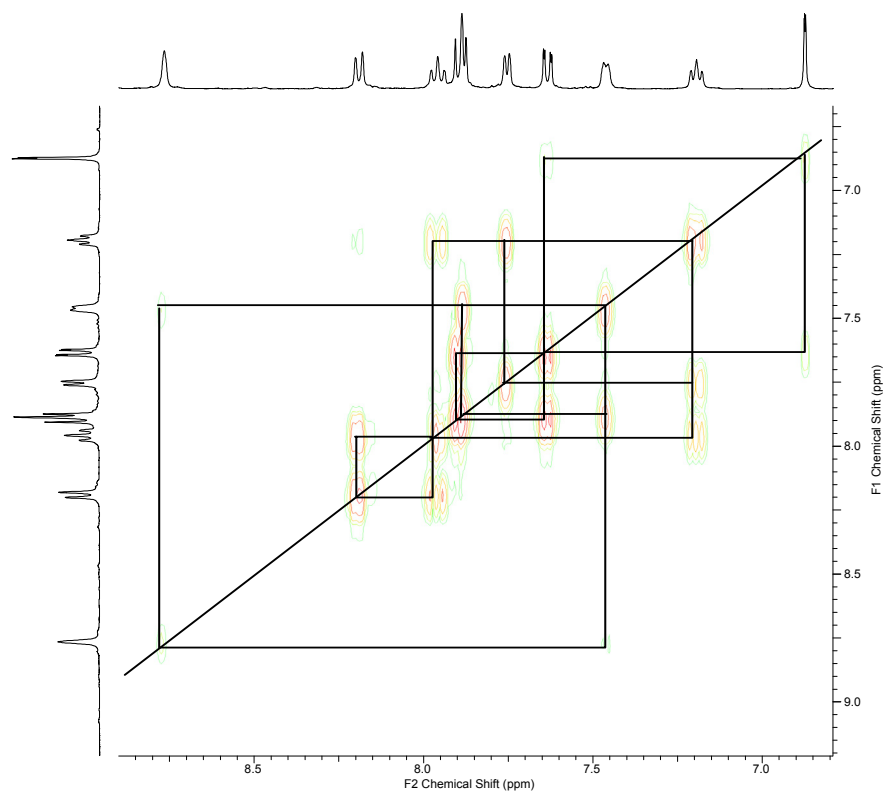


Figure S8: COSY NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{dpb})](\text{PF}_6)$

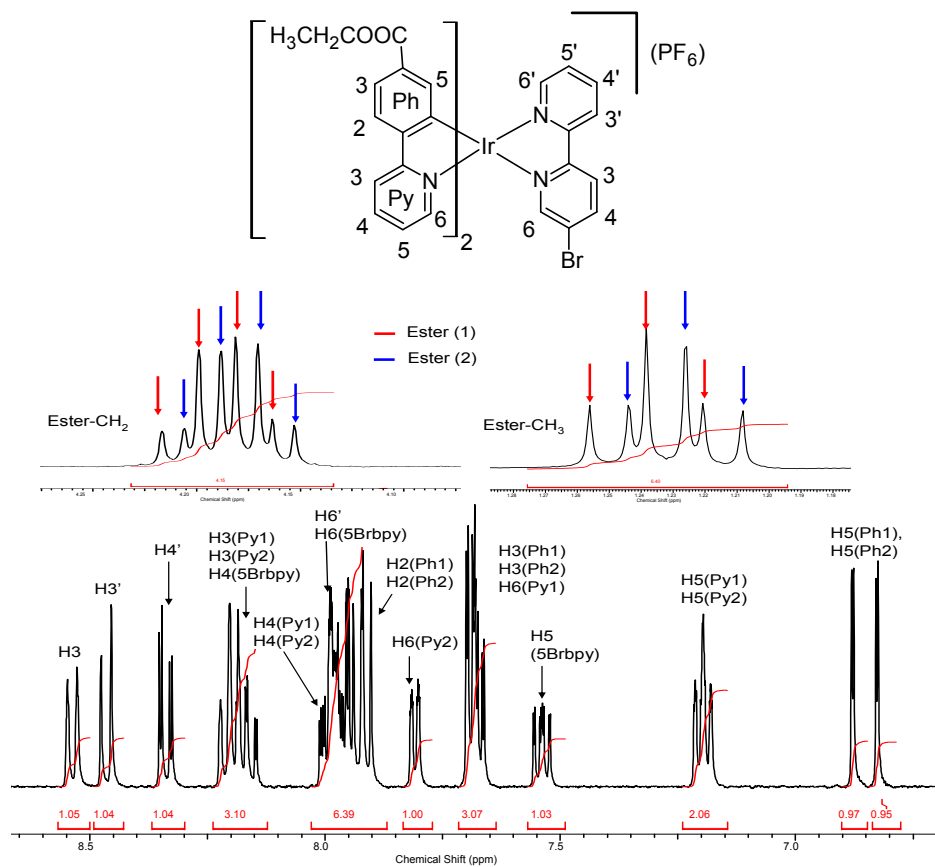


Figure S9: ^1H NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(5\text{Brbpy})](\text{PF}_6)$

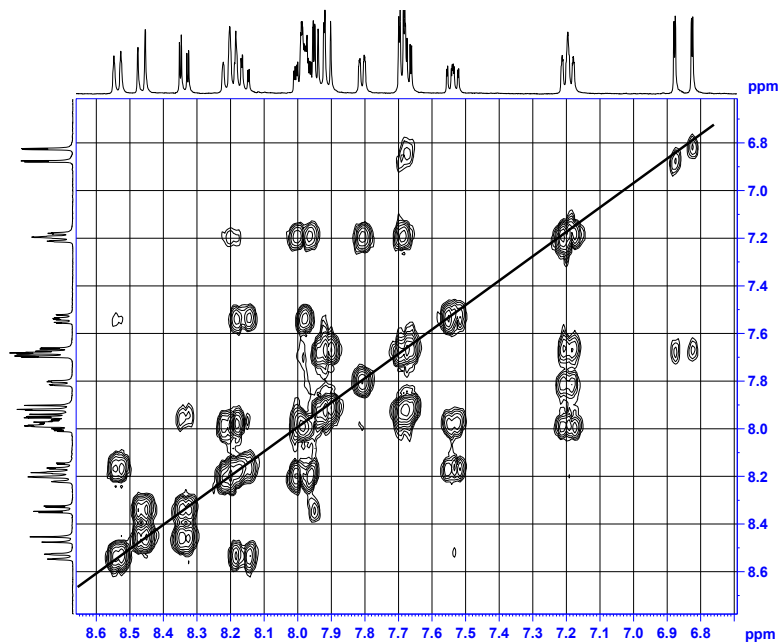


Figure S10: COSY NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(5\text{Brbpy})](\text{PF}_6)$

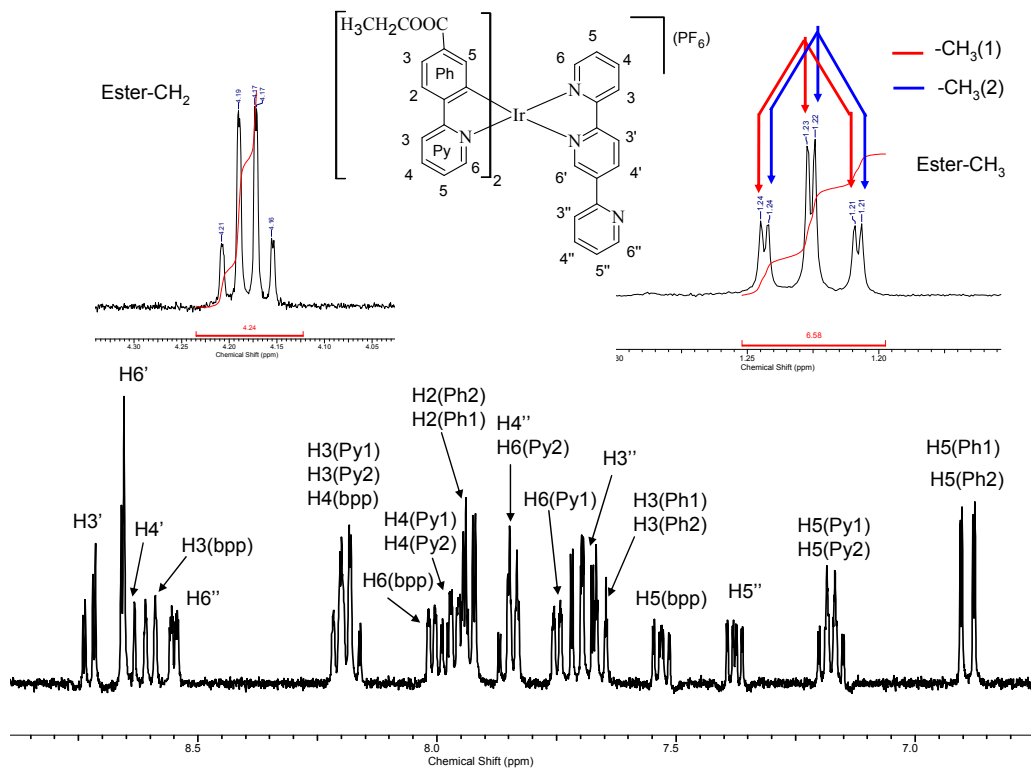


Figure S11: ^1H NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpp})](\text{PF}_6)$

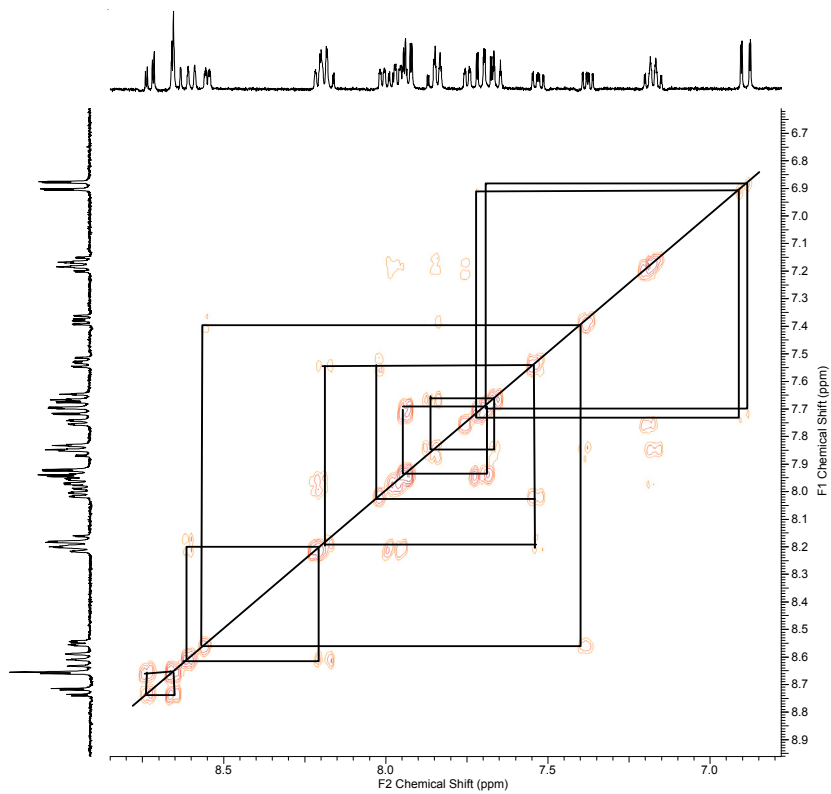


Figure S12: COSY NMR (Acetonitrile- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpp})](\text{PF}_6)$

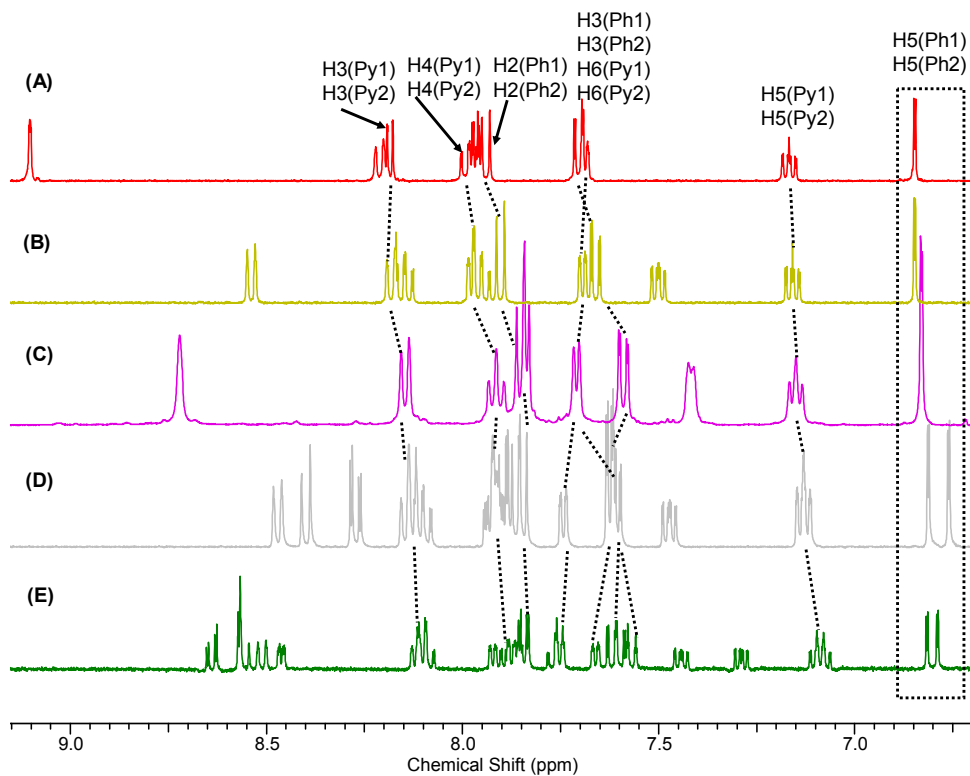


Figure S13: Chemical shifts of protons (*ppy*-COOEt) in different iridium complexes. ^1H NMR(Acetonitrile- d_3 , 400 MHz); **(A)** $[\text{Ir}(\text{ppy}\text{-COOEt})_2(\text{dceb})](\text{PF}_6)$; **(B)** $[\text{Ir}(\text{ppy}\text{-COOEt})_2(\text{bpy})](\text{PF}_6)$; **(C)** $[\text{Ir}(\text{ppy}\text{-COOEt})_2(\text{dpb})](\text{PF}_6)$; **(D)** $[\text{Ir}(\text{ppy}\text{-COOEt})_2(5\text{Brbpy})](\text{PF}_6)$; **(E)** $[\text{Ir}(\text{ppy}\text{-COOEt})_2(\text{bpp})](\text{PF}_6)$.

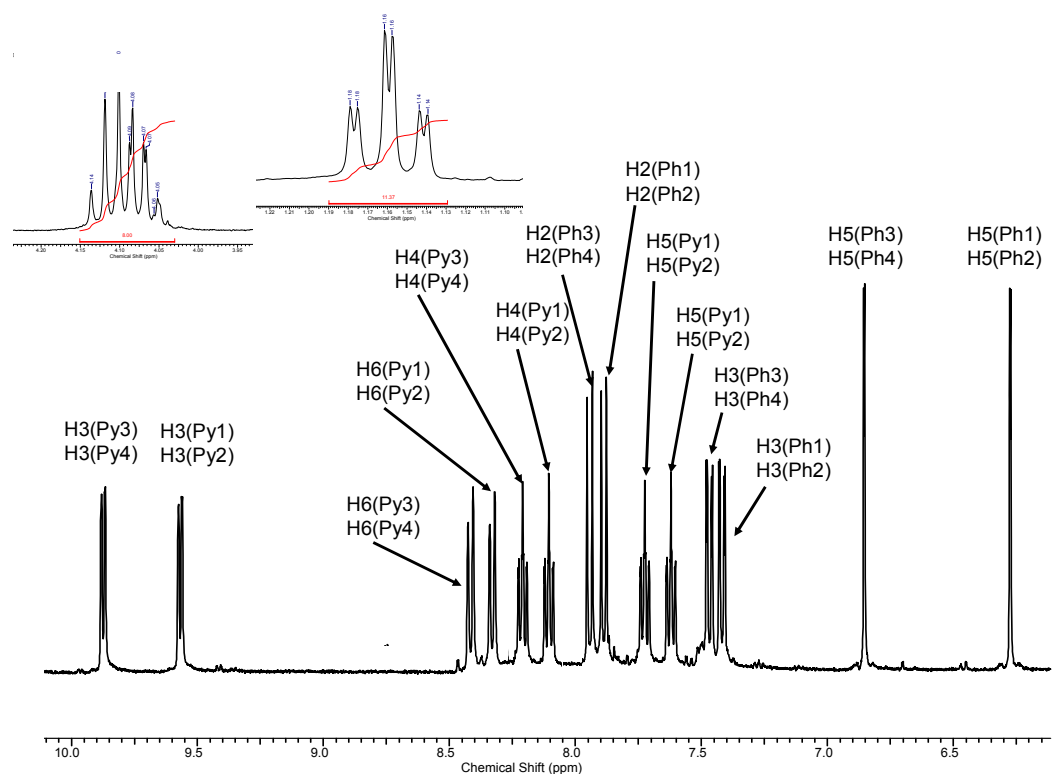


Figure S14: ^1H NMR (DMSO- d_6 , 400 MHz) of $[\text{Ir}(\text{ppy-COOEt})_2\text{Cl}]_2$

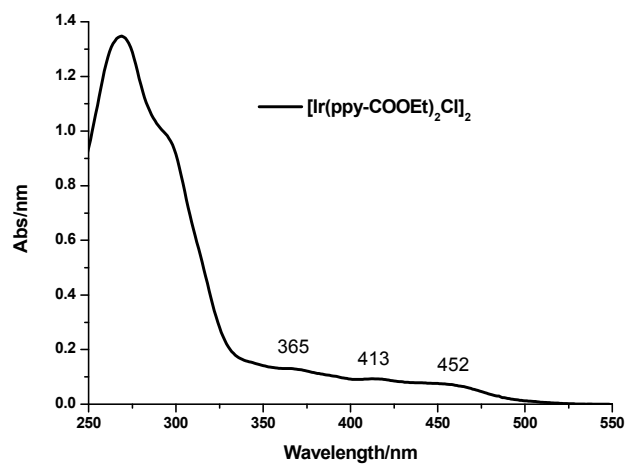


Figure S15a: UV-Vis spectra of $[\text{Ir}(\text{ppy-COOEt})_2\text{Cl}]_2$ was recorded in acetonitrile at room temperature. Concentration of the solution is $\sim 10^{-5}$ M.

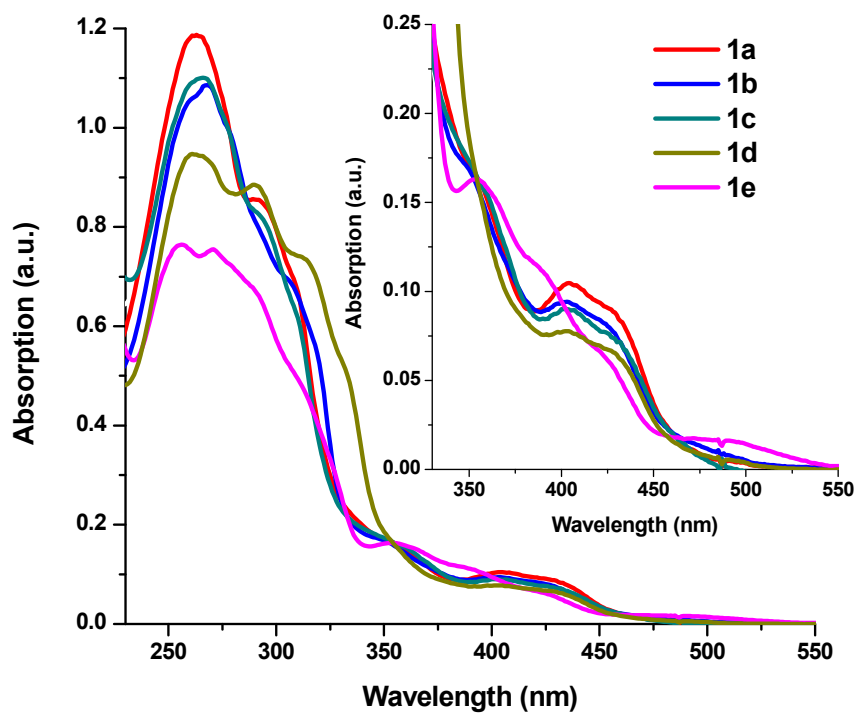


Figure S15b: UV-Vis spectra of Iridium complexes, recorded in acetonitrile at room temperature. Concentration of the solution is $\sim 10^{-5}$ M.

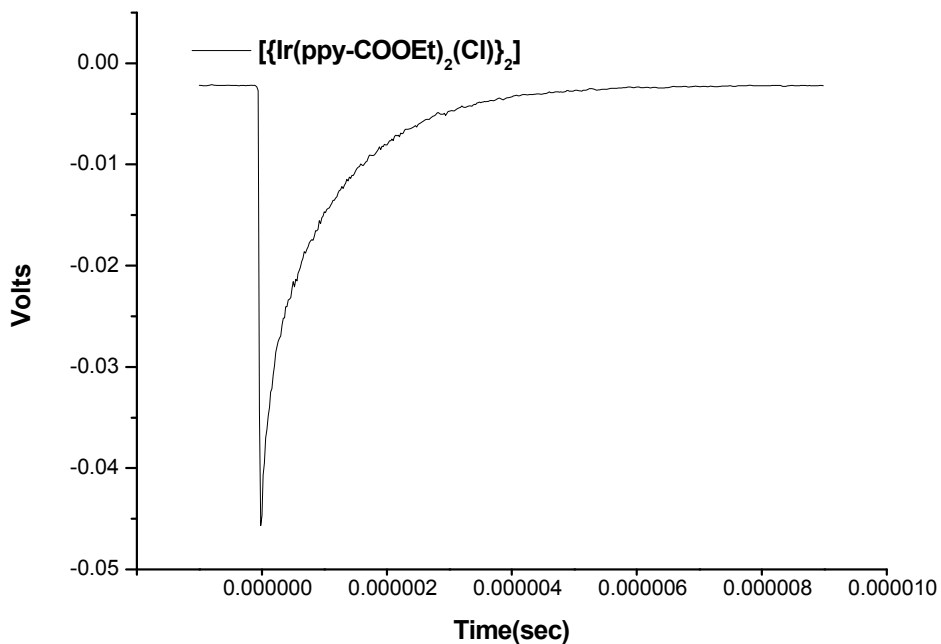


Figure S16: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(\mu\text{-Cl})]_2$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

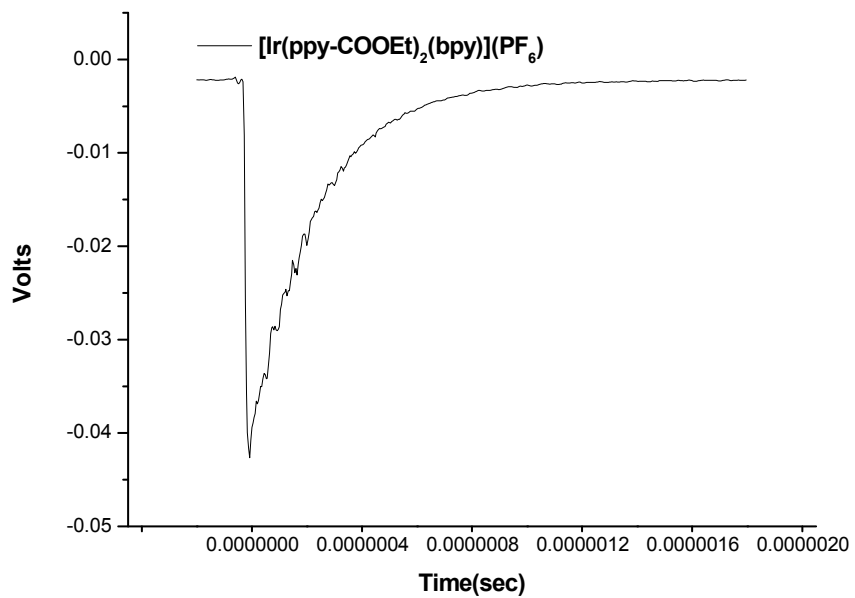


Figure S17: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpy})](\text{PF}_6)$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

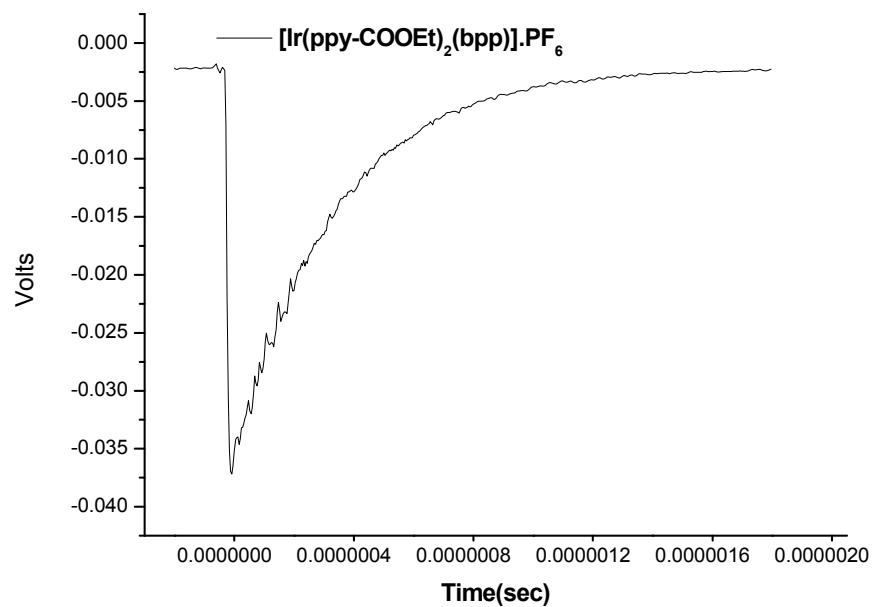


Figure S18: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(\text{bpp})](\text{PF}_6)$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

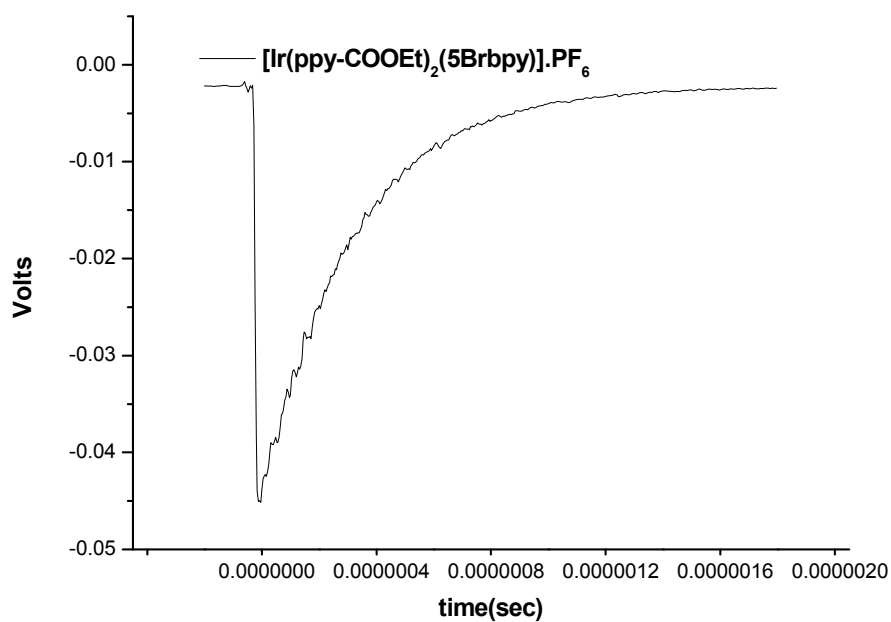


Figure S19: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(5\text{Brbpy})](\text{PF}_6)$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

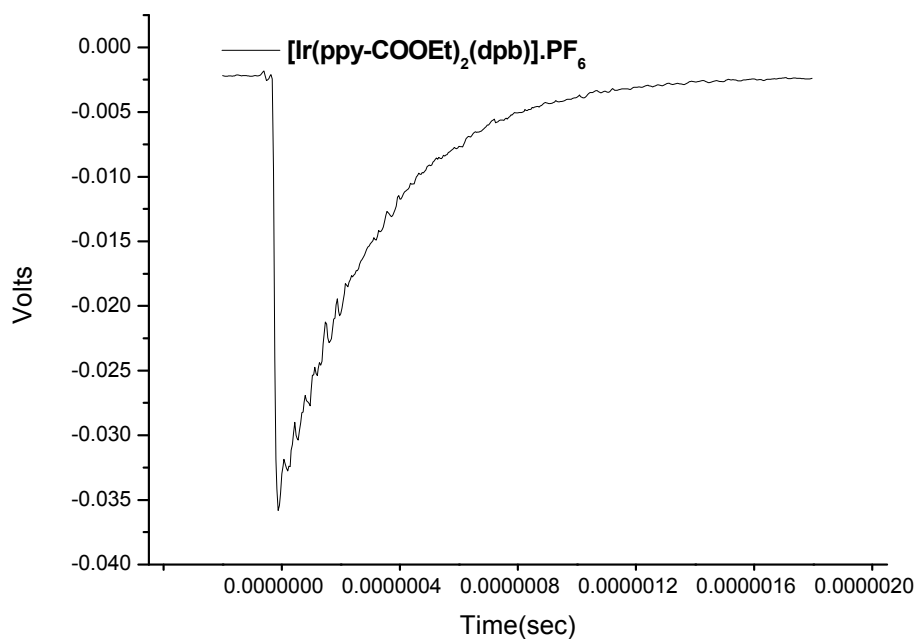


Figure S20: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(\text{dpb})](\text{PF}_6)$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

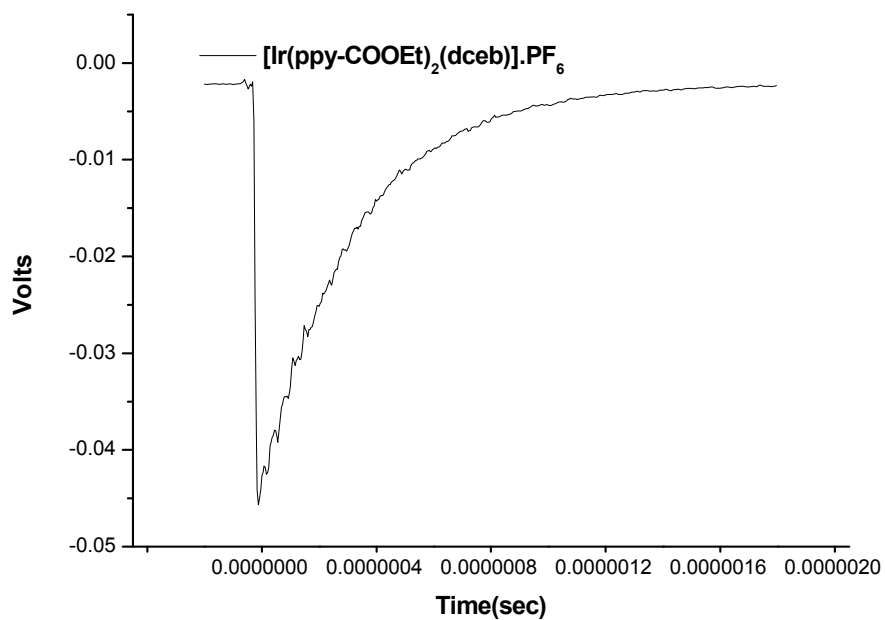


Figure S21: Life time experiment and kinetic fit graph of $[\text{Ir}(\text{ppy-COOEt})_2(\text{dceb})](\text{PF}_6)$. Life time experiment was recorded in nitrogen purged DCM solution at room temperature.

4,4'-Bis(diethylmethylphosphonato)-2,2'-bipyridine (dpb)¹

1.7 g (4.97 mmol) of 4,4'-dimethylbromo-2,2'-bipyridine in 11.3 cm³ chloroform was refluxed with 24.17 cm³ of triethylphosphite under a nitrogen atmosphere for 3 hours. Excess triethylphosphite and chloroform were removed under high vacuum. After the removal of solvent and excess triethylphosphite, an oily crude product was obtained which was further washed with pentane and collected as a white solid. Yield: 92% (2.08 g, 4.57 mmol). ¹H NMR (400 MHz, CDCl₃) δ ppm 1.21 (m, 12 H), 3.20 (d, 20 Hz, 4H), 3.96 - 4.06 (m, 8 H), 7.29 (d, J = 5.05, 2 H), 8.31 (s, 2 H), 8.55 (d, J = 5.05 Hz, 2 H). ³¹P NMR (400 MHz, CDCl₃) δ ppm 34.17 ppm.

5-bromo-2,2'-bipyridine (5Brbpy)²⁻⁶

0.299 g (0.258 mmol) of Pd(PPh₃)₄ and 2 g (8.44 mmol) of 2,5-dibromobipyridine were added to a dried two neck round bottom flask under nitrogen atmosphere. The temperature was kept low using ice bath during the addition of 19.35 ml (8.4 mmol) of 2-pyridylzinc bromide to the reaction mixture. The reaction mixture was then stirred for 12 hours at room temperature under nitrogen atmosphere. The reaction mixture was then poured into a saturated aqueous solution of EDTA/Na₂CO₃ until some yellow flakes appear. The aqueous mixture was extracted with dichloromethane and dried over MgSO₄. Dichloromethane was evaporated in air and the crude product was purified by alumina column using hexane/ethyl acetate (9:1) as eluent. Yield: 1.57 g (6.67 mmol, 79.5%). ¹H NMR (400 MHz, DMSO-d₆) δ ppm 7.49 (dd, J = 7.45, 4.80 Hz, 1 H), 7.97 (td, J = 7.71, 7.71 Hz, 1 H), 8.20 (dd, J = 8.46, 2.40 Hz, 1 H), 8.30 - 8.39 (m, 2 H), 8.67 - 8.73 (m, 1 H), 8.82 (d J = 2.40, 1 H)

2,2':5',2''-terpyridine (bpp)⁷

0.299 g (0.258 mmol) of [Pd(PPh₃)₄] and 2 g (8.44 mmol) of 2,5-dibromobipyridine were added to a two necked round bottom flask under a nitrogen atmosphere. 38.7 cm³ (16.8 mmol) of 2-pyridylzincbromide (in THF) was then added to the flask under a nitrogen atmosphere. The reaction mixture was then stirred for 15 hours in the dark at 20⁰C under nitrogen atmosphere. Subsequently the reaction mixture was poured into a saturated aqueous solution of EDTA/Na₂CO₃. The aqueous solution was extracted with dichloromethane and the organic layer was dried over MgSO₄. The solvent was evaporated in air and the crude product was purified on a neutral alumina column using hexane/ethyl acetate (9:1) as mobile phase. Yield: 1.57 g (6.75 mmol, 80%). ¹H NMR (400 MHz, DMSO-d₆) δ ppm 7.46 (dd, J =

7.58, 4.80 Hz, 1 H), 7.50 (dd, J = 6.69, 5.43, 1.01 Hz, 1 H), 7.98 (d, J = 7.58 Hz, 2H), 8.16 (d, J = 8.08 Hz, 1 H), 8.47 (d, J = 8.08 Hz, 1 H), 8.52 (d, J = 8.34 Hz, 1 H), 8.63 (d, J = 8.34 Hz, 1 H), 8.70 - 8.78 (m, 2 H), 9.40 (d, J = 2.27 Hz, 1 H). Elemental analysis for C₂₀H₁₄N₄: M.W. = 233.26; Calc. C 77.23, H 4.75, N 18.01, Found. C 77.07, H 4.77 and N 18.25%.

Quantum Yield Measurements:

Following equation was used to calculate the emission quantum yield for all the complexes both in aerated and deaerated acetonitrile.

$$\Phi_s = \Phi_r (I_s / I_r) \cdot (A_r / A_s)$$

Where Φ_s is the quantum yield of the sample. Φ_r is the quantum yield of the reference complex. I_s and I_r represent points of maximum intensity. A_r and A_s represent the absorbance value of the complex and reference at the excitation wavelength. [Ru(bpy)₂]Cl₂ is used as reference for both aerated ($\Phi = 0.02$) and deaerated samples in acetonitrile solvent ($\Phi = 0.06$).⁸

Experimental conditions for photocatalytic hydrogen:

Photocatalytic hydrogen production experiments were carried out using an air-cooling apparatus for maintaining the solutions at room temperature at 22°C, during irradiation using LEDs (355 and 470 nm). Acetonitrile used was dried over calcium hydride and the triethylamine dried over sodium before being freshly distilled under nitrogen. The samples were prepared in GC vials (4.9 ml volume, VWR) with a known headspace of 2.9 ml. Photosensitiser (Iridium complexes) and catalyst K₂[PtCl₄] were taken in 1:1 ratio and dissolved in 4:1 Acetonitrile/H₂O solution containing 1.2 x 10⁻⁴ M of PS. 1.91 ml of the Ir/Pt solution and 90 μL of 0.5 M triethylamine were added to the GC vials under argon atmosphere. Subsequently, the GC vials containing 2 ml samples were irradiated with 355 and 470 nm wavelength LED's for 18 hours. After irradiation, 100 μL samples were drawn from the headspace and injected into the GC apparatus. The experiments were repeated two times.

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