

## Supporting Information for

### **A robust and efficient cobalt molecular catalyst for CO<sub>2</sub> reduction**

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## Experimental Section

### Synthesis and Characterization

All chemical reagents were analytical grade and used as received without any further purification. Tris(2-pyridylmethyl)amine (TPA) was synthesized according to literature method with 48 % yield.<sup>1</sup> [Co(TPA)Cl]Cl (**1**) was prepared by mixing methanolic solution containing TPA (0.48 mmol) with CoCl<sub>2</sub>·6H<sub>2</sub>O (0.48 mmol) for an 1 h with 70 % yield.<sup>2</sup> Single crystal was obtained by diffusion of diethyl ether into dichloromethane solution of **1**. Ir(ppy)<sub>3</sub> was prepared according to literature method.<sup>3</sup> <sup>1</sup>H NMR spectrum (400 MHz) of **1** was measured at room temperature with a Bruker DPX400 NMR Spectrometer. UV-vis spectrum was measure using Hewlett Packard 8453 Photo-diode Array UV-Visible spectrometer. Electro-spray ionization was recorded with The Finnigan LCQ Advantage. FT-IR spectrum on KBr was performed with Nicolet Avatar 380 Fourier-transform Infrared Spectrometers. Room temperature magnetic data was collected on a Guoy Balance (Sherwood Scientific, Cambridge, UK). Diamagnetic contribution was estimated based on the equation  $\chi_D = (-MW/2) \cdot 10^{-6} \text{ emu mol}^{-1}$ .<sup>4</sup> The diamagnetic contribution estimated from this equation is only within 1–2 % difference compared with that of using Pascal's constants.<sup>4</sup>

X-Ray diffraction data of the single crystal was collected on Bruker X8 Proteum diffractometer. The crystal was kept at 100 K during data collection. The diffraction images were interpreted and the diffraction intensities were integrated by using the SAINT program. Multiscan SADABS was applied for absorption correction. By using Olex2,<sup>5</sup> the structure was solved with the ShelXS<sup>6</sup> structure solution program using direct methods and refined with the XL<sup>5</sup> refinement package using least-squares minimization. The positions of the hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and these positions participated in the calculation of the final Rindices. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. CCDC-1044164 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

<sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>CN) of **1**:  $\delta$ 132.8 (H <sub>$\alpha$</sub> ), 106.9 (NCH<sub>2</sub>), 60.0 (H <sub>$\beta$</sub> ), 46.0 (H <sub>$\beta'$</sub> ), -3.3 (H <sub>$\gamma$</sub> ). UV/Vis (CH<sub>3</sub>CN):  $\lambda_{\text{max}}/ \text{nm} (\epsilon/\text{M}^{-1}\text{cm}^{-1}) = 273 (3000) (\pi \rightarrow \pi^*$  of TPA ligand), 486 (170) (d-d transition) 616 (130), 634(sh) (110) (d-d transition). FT-

IR (KBr pellet):  $\nu/\text{cm}^{-1} = 3061(\text{w}), 2916(\text{w}), 1609(\text{s}), 1569(\text{m}), 1483(\text{s}), 1440(\text{s}), 1369(\text{m}), 1311(\text{s}), 1295(\text{m}), 1265(\text{s}), 1159(\text{m}), 1103(\text{m}), 1054(\text{m}), 1025(\text{s})$ . ESI-MS (MeOH):  $m/z$  (%) = 384 (M – Cl)<sup>+</sup> (100).  $\mu_{\text{eff}}$  (298K) = 4.09  $\mu_{\text{B}}$

### Electrochemistry of **1**

Cyclic voltammetry was performed using a potentiostat CHI electrochemical analyzer 1030A or BAS 100 W (Bioanalytical Systems). A conventional three electrode system was employed. A glassy carbon electrode (surface area = 0.2 cm<sup>2</sup>) was used as the working electrode, a Pt wire as the auxiliary electrode, and an Ag/AgNO<sub>3</sub> (0.1 M) electrode was used as reference electrode. Tetrabutylammonium hexafluorophosphate, the supporting electrolyte, was crystallized three times and dried in vacuum oven before used. The electrolyte solution, 0.1 M [(n-Bu)<sub>4</sub>N][PF<sub>6</sub>] in CH<sub>3</sub>CN, was saturated with Ar or CO<sub>2</sub> by purging with Ar or CO<sub>2</sub> (purity  $\geq 99.8\%$ , Hong Kong Oxygen and Acetylene Co., Ltd.) for 15 min prior to each experiment.

### Measurement of Photolysis Products

Gas chromatographic analysis was conducted using Agilent 7890B gas chromatography equipped with a thermal conductivity detector (TCD) and a HP-Plot 5Å column with Ar as the carrier gas. The oven temperature was held at 40 °C. Inlet and detector temperature were set at 80 °C and 150 °C respectively. A multi-point calibration curves were established separately for CO ( $R^2 = 0.9995$ ), H<sub>2</sub> ( $R^2 = 0.9997$ ) and CH<sub>4</sub> ( $R^2 = 1.000$ ).

The production of formic acid from the reaction mixtures was analysed by ion chromatography (Metrohm 761 SD Compact IC with conductivity detection after chemical suppression). Anions were separated using Metrosep A Supp 5 (diameter: 100x4.0 mm) with NaHCO<sub>3</sub> (1.0 mmol/L) and Na<sub>2</sub>CO<sub>3</sub> (3.2 mmol/L) as eluent at a flow rate of 0.7 mL/min. Regarding the analyte preparation, all organic solvents were removed and then reconstituted with 2 mL MilliQ water (18.2 mΩ). The solution was then filtered through 0.45  $\mu\text{m}$  Millipore Filter before injection. 20  $\mu\text{L}$  of sample was used in each analysis. According to ion chromatographic analysis, no formic acid was produced in the reaction mixture (detection limit: 0.1  $\mu\text{mol}$ ).

### Photocatalytic Performance of CO<sub>2</sub> reduction

In a 4 mL mixture of CH<sub>3</sub>CN/TEA (4:1, v/v; TEA = triethylamine), **1** (5  $\mu\text{M}$ ) and Ir(ppy)<sub>3</sub> (0.4 mM) was purged with CO<sub>2</sub> (purity  $\geq 99.8\%$ ) for 10 min, and 250  $\mu\text{L}$  CH<sub>4</sub> was injected to the reaction prior to the irradiation using blue LEDs (centered at 460 nm).

All reactions and LEDs were cooled by aluminium blocks cooled using PC cooling fan and compressed air. Gas sample (200  $\mu\text{L}$ ) was drawn from the headspace of the tube and injected to GC-TCD for measurement.

### **Emission Quenching of Ir(ppy)<sub>3</sub> by **1** and TEA**

Emission and lifetime measurements: Steady-state emission spectra were recorded using a SPEX 1681 Fluorolog-3 spectrophotometer. Solutions in a two-compartment cell for photophysical studies were degassed by using a high vacuum line with five freeze–pump–thaw cycles. The emission lifetime measurements were performed using a LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd, Livingston, UK). The excitation source was 355 nm output from a Nd:YAG laser. For the quenching experiments, the concentration of Ir(ppy)<sub>3</sub> was  $2 \times 10^{-5}$  M for each cells, and the concentration of **1** varied from  $2 \times 10^{-5}$  M to  $6 \times 10^{-4}$  M, while that of TEA ranged from 0.72 M to 3.59 M.

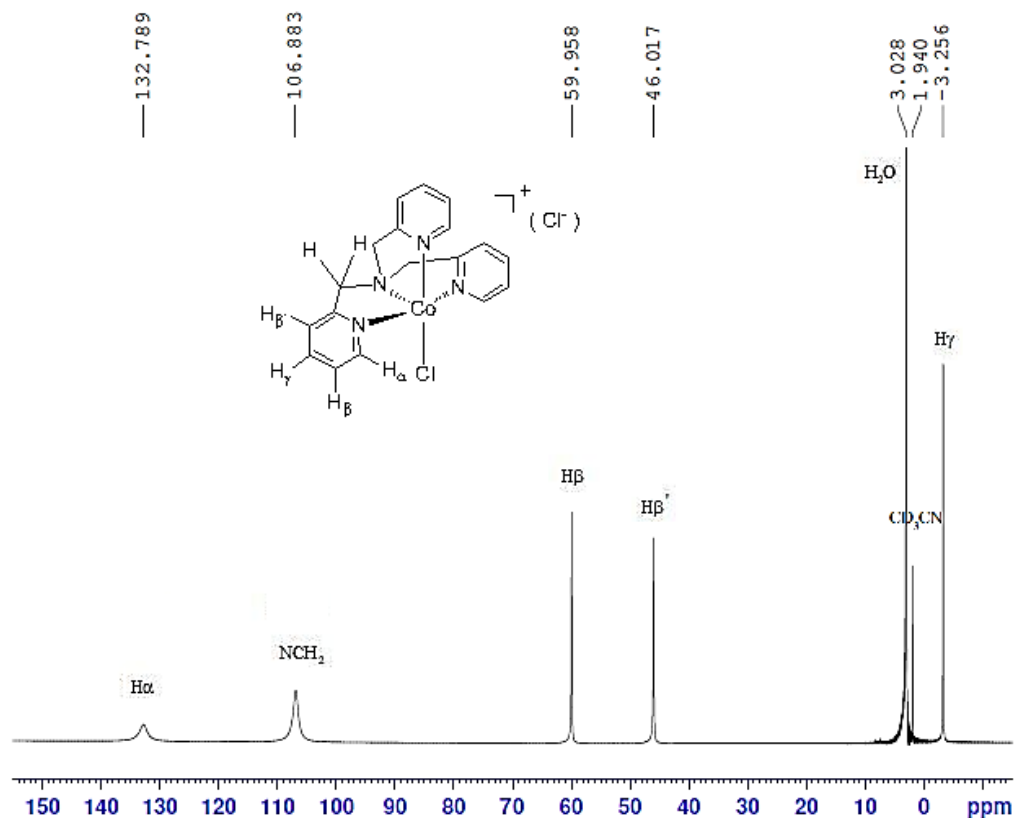


Fig S1.  $^1\text{H}$  NMR spectrum (400 MHz) of **1** recorded in  $\text{CD}_3\text{CN}$  at room temperature and is assigned according to literature.<sup>7,8</sup> The  $^1\text{H}$  NMR of **1** is consistent with the  $^1\text{H}$  NMR of the trigonal bipyramidal structures  $[\text{Co}(\text{TPA})\text{Cl}]_2[\text{CoCl}_4]$  and  $[\text{Co}(\text{TPA})\text{Cl}][\text{PF}_6]$  (in  $\text{CD}_3\text{CN}$ ) reported by Gal and co-workers.<sup>8</sup> In addition,  $[\text{Co}(\text{TPA})\text{Cl}]^+$  is substitutionally inert against  $\text{CH}_3\text{CN}$  at room temperature as revealed from the  $^1\text{H}$  NMR. The proton signals of **1** remained unchanged over a period of a week in  $\text{CD}_3\text{CN}$  solution, and is notably different from the chemical shift in  $[\text{Co}(\text{TPA})(\text{CH}_3\text{CN})][\text{ClO}_4]_2$  reported by Karlin and co-workers.<sup>9</sup> Therefore, it is reasonable to assume that the integrity of  $[\text{Co}(\text{TPA})(\text{Cl})]^+$  retains in solution state at room temperature.

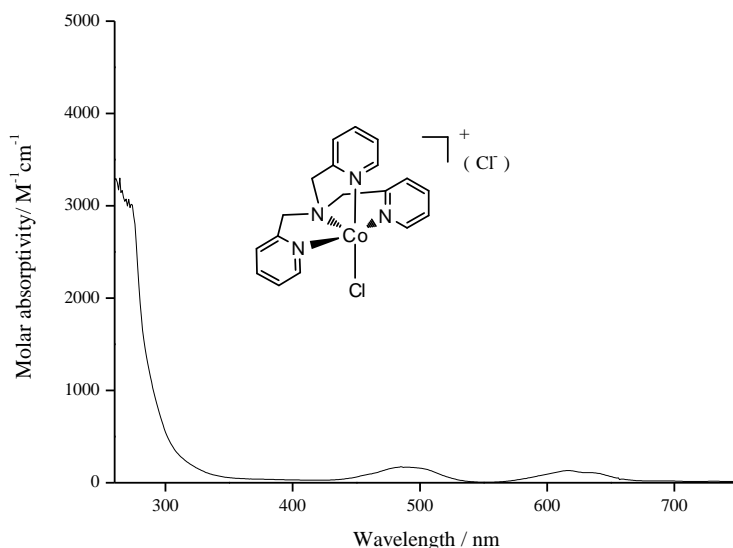


Fig S2. UV-vis absorption spectrum of **1** measured in CH<sub>3</sub>CN at  $1 \times 10^{-3}$  M at room temperature. UV/Vis (CH<sub>3</sub>CN):  $\lambda_{\max}/\text{nm}$  ( $\epsilon / \text{M}^{-1}\text{cm}^{-1}$ ) = 273 (3000) ( $\pi \rightarrow \pi^*$  of TPA ligand), 486 (170) (d-d transition) 616 (130), 634(sh)(110) (d-d transition) which is assigned according to literature.<sup>10-14</sup> The absorption spectrum is consistent with that reported by Wang and Thapper,<sup>13</sup> and is similar to [Co(TPA)Cl][ClO<sub>4</sub>] reported by Massoud and Bernal.<sup>14</sup>

The UV-vis spectrum of **1** is significantly different from the UV-vis spectrum of [Co(TPA)(CH<sub>3</sub>CN)]<sup>2+</sup> reported by Kaline and co-workers (no absorption peak after 600 nm, and two absorption peaks at 472 nm ( $85 \text{ M}^{-1}\text{cm}^{-1}$ ) and 552 nm ( $72 \text{ M}^{-1}\text{cm}^{-1}$ ) in [Co(TPA)(CH<sub>3</sub>CN)]<sup>2+</sup>).<sup>9</sup> Therefore, we exclude the possibility of the replacement of Cl<sup>-</sup> by CH<sub>3</sub>CN.

We also exclude the possibility of the formation of a six-coordinated [Co(TPA)(CH<sub>3</sub>CN)Cl][Cl] in solution according to UV-vis spectrum. For a six-coordinated Co<sup>II</sup> complex, the extinction coefficient ( $\epsilon$ ) of d-d transitions is  $< 50 \text{ M}^{-1}\text{cm}^{-1}$  whereas the  $\epsilon$  of d-d transitions of five-coordinated Co<sup>II</sup> complexes ranges from 50 – 300  $\text{M}^{-1}\text{cm}^{-1}$ .<sup>15</sup> The  $\epsilon$  of d-d transitions of **1** are 110–170  $\text{M}^{-1}\text{cm}^{-1}$ . Thus, **1** should preserve as five-coordinated in solution. Indeed, Paine and co-workers reported that the  $\epsilon$  of d-d transitions for a six-coordinated [Co<sup>II</sup>(6Me<sub>3</sub>TPA)(HSA)][BPh<sub>4</sub>] (6Me<sub>3</sub>TPA = tris(6-methyl-2-pyridylmethyl)amine, H<sub>2</sub>SA = salicylic acid) in CH<sub>3</sub>CN is 476 nm ( $50 \text{ M}^{-1}\text{cm}^{-1}$ ), 515 nm ( $40 \text{ M}^{-1}\text{cm}^{-1}$ ) and 557 nm ( $50 \text{ M}^{-1}\text{cm}^{-1}$ ) whereas that of a five-coordinated [Co<sup>II</sup>(TPA)(HSA)][ClO<sub>4</sub>] in CH<sub>3</sub>CN is 465 nm ( $200 \text{ M}^{-1}\text{cm}^{-1}$ ), 605 nm ( $160 \text{ M}^{-1}\text{cm}^{-1}$ ) and 622 nm ( $140 \text{ M}^{-1}\text{cm}^{-1}$ ).<sup>11</sup>

Therefore, both NMR and UV-vis spectroscopies suggested that **1** should retain its structure in both solid and solution states.

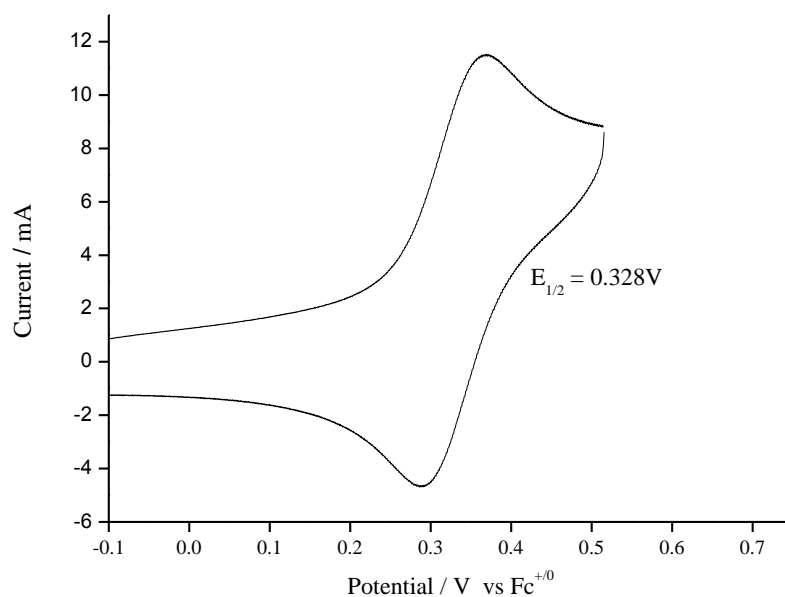


Fig S3. Cyclic voltammogram of *fac*-[Ir(ppy)<sub>3</sub>] in 0.1 M [(n-Bu)<sub>4</sub>N][PF<sub>6</sub>] /CH<sub>3</sub>CN, scan rate = 100 mVs<sup>-1</sup>.

Table S1. Excited state potential of *fac*-[Ir(ppy)<sub>3</sub>] from SCE and Fc<sup>+0</sup>.

	Ir <sup>IV/III</sup> (V)	Ir <sup>III/II</sup> (V)	E <sub>0-0</sub> (V)	Ir <sup>*-/</sup> (V)	Ir <sup>+/*</sup> (V)
<i>fac</i> -[Ir(ppy) <sub>3</sub> ] <sup>a</sup> (vs SCE)	0.77	-2.19	2.50	0.31	-1.73
<i>fac</i> -[Ir(ppy) <sub>3</sub> ] <sup>b</sup> (vs Fc <sup>+0</sup> )	0.328	-	-	-	-2.17

a. From reference 16.

b. Experimental data determined in this work

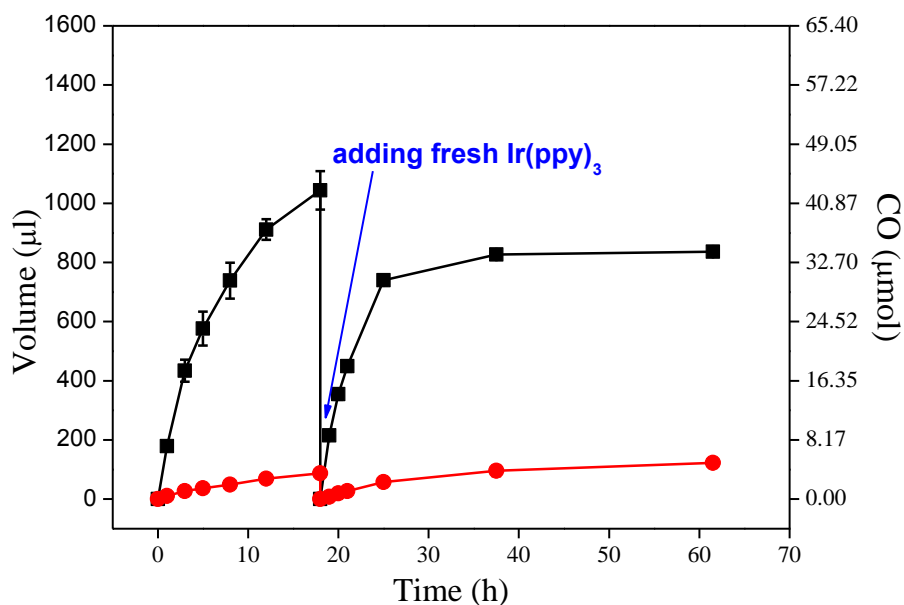


Fig S4. Resumption of CO (black) and H<sub>2</sub> (red) production rate after injection of fresh Ir(ppy)<sub>3</sub> into the CH<sub>3</sub>CN/TEA (4:1, v/v) solution containing 50 μM **1**, 0.4 mM Ir(ppy)<sub>3</sub> and re-bubbled with CO<sub>2</sub> after 18 h.

Table S2. CO production with different concentration of **1** with 0.4 mM Ir(ppy)<sub>3</sub> in a CO<sub>2</sub>-saturated CH<sub>3</sub>CN/TEA (4:1, v/v) solution for 24h.

<b>1</b> (mM)	H <sub>2</sub> (μmol)	CO (μmol)
0.005	0.6	10.4
0.01	0.7	16.1
0.025	1.4	20.8
0.05	2.9	41.5



Table S3. CO production with different concentration of Ir(ppy)<sub>3</sub> with 50 μM **1** in a CO<sub>2</sub>-saturated CH<sub>3</sub>CN/TEA (4:1, v/v) solution for 24h.

[Ir(ppy) <sub>3</sub> ] (mM)	H <sub>2</sub> (μmol)	CO (μmol)
0.025	0.7	20.8
0.05	1.4	28.8
0.1	1.8	34.9
0.3	3.3	41.5
0.4	2.9	41.5

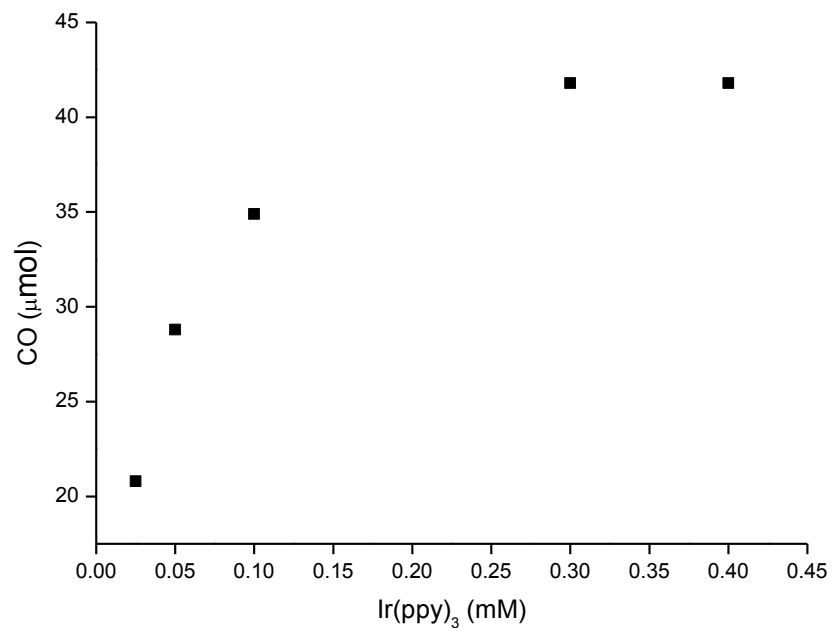


Fig S5. Plot of CO production versus different concentration of Ir(ppy)<sub>3</sub> in the presence of 50 μM **1** in a CO<sub>2</sub>-saturated CH<sub>3</sub>CN/TEA (4:1, v/v) solution for 24h.

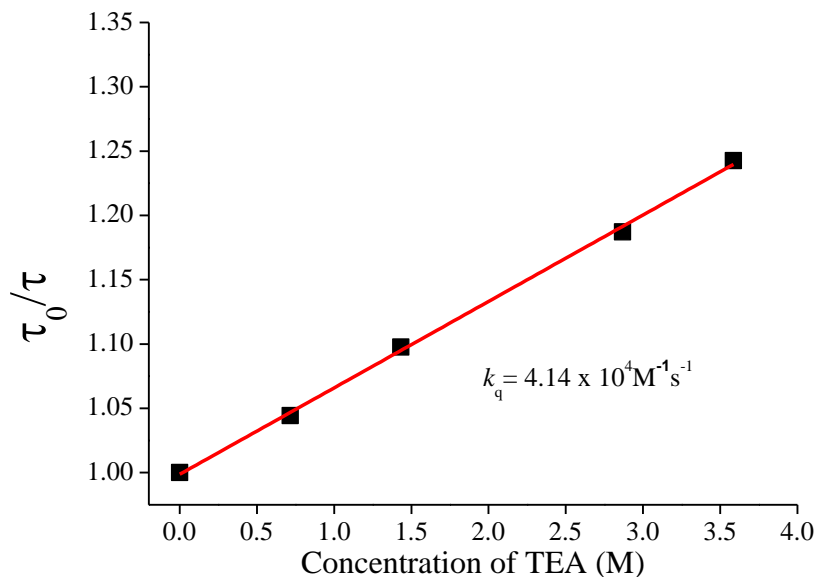


Fig S6. The linear plot ( $R^2=0.9999$ ) of ratio of Ir(ppy)<sub>3</sub> excited state lifetime at 524 nm versus TEA according to Stern-Volmer equation. Concentration of Ir(ppy)<sub>3</sub> =  $2 \times 10^{-5}$  M.

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