

Supporting Information

Oxygen sensing via phosphorescence quenching of doped metal-organic frameworks

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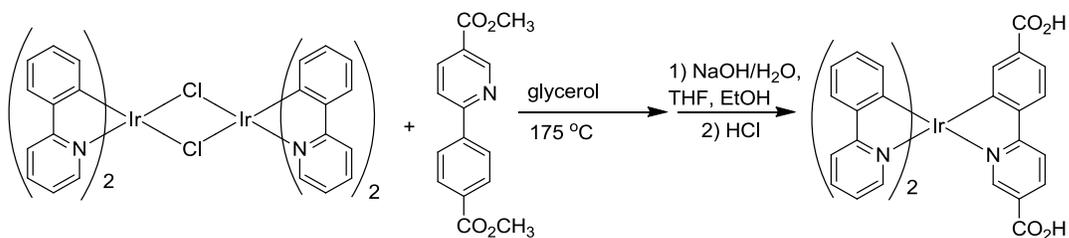
1. General Experimental.

¹H-NMR spectra were recorded on a Bruker NMR 400 DRX Spectrometer at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of deuterated chloroform (δ 7.26). Mass spectrometric analyses were conducted using positive-ion electrospray ionization on a Bruker BioTOF Mass Spectrometer. The MOFs were characterized by Powder X-ray diffraction (PXRD) using a Bruker SMART APEX II Diffractometer using Cu radiation. The PXRD patterns were processed with the APEX II package using PILOT plug-in. The Brunauer-Emmett-Teller (BET) surface areas were measured on a Quantachrome Autosorb-1C. BET plots and HK method pore size distributions were also obtained from a Quantachrome Autosorb-1C. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 equipped with a platinum pan, and all samples were heated at a rate of 5 °C per minute under air. Emission spectra and luminescence quenching experiments were performed on a Shimadzu Rf-5301PC Spectrofluorophotometer. Scanning electron microscopy (SEM) images were obtained on a Hitachi 4700 Field Emission Scanning Microscope. A Cressington 108 Auto Sputter Coater equipped with a Au/Pd (80/20) target and an MTM-10 thickness monitor was used to coat the samples with a conductive layer before taking SEM images. Each SEM sample was prepared by first suspending the material in ethanol, then a drop of the suspension was placed on a glass slide and the solvent was allowed to evaporate. Metal contents were determined using a Varian 820-MS Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). Diffuse reflectance UV-Vis spectra were obtained using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer.

2. Procedures for Complex Syntheses.

2.1 Synthesis of fac-bis((2-phenyl)pyridinato,_{N,C₂})(5-carboxyl-2-(5-

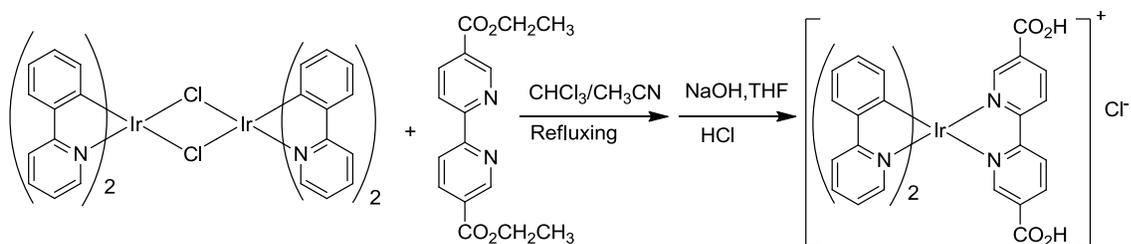
carboxyl)phenyl)pyridinato,N,C_{2'}) Iridium (III) (L₁-H₂)



$[\text{Ir}(\text{ppy})_2\text{Cl}_2]_2$ (ppy = 2-phenylpyridinato,N,C_{2'}) was synthesized by following the published procedure.^[1] A solution of $[\text{Ir}(\text{ppy})_2\text{Cl}_2]_2$ (400 mg, 0.37 mmol), methyl 6-(4-(methoxycarbonyl)phenyl)nicotinate (300 mg, 1.1 mmol), and K_2CO_3 (300 mg, 2.2 mmol) in 20 mL of glycerol was heated to 175 °C under argon protection for 24 hours. After cooling to room temperature, 100 mL of water was added into the mixture, and the precipitates were collected by filtration. The crude product was then purified by silica gel column chromatography with hexanes/ethyl acetate (2:1 v/v) as the eluent to afford the fac-bis((2-phenyl)pyridinato,N,C_{2'})((5-methoxycarbonyl)-2-(5-carboxyl)phenyl)pyridinato,N,C_{2'})iridium(III). ¹H-NMR in CDCl_3 : δ 8.125 (s, 1H), 7.930 (d, 1H), 7.889-7.823 (m, 4H), 7.702-7.478 (m, 9H), 7.411 (s, 1H), 6.924-6.665 (m, 5H), 6.657 (d, 1H).

The resultant methyl ester was then hydrolyzed by refluxing in a solution mixture of 6M NaOH aqueous solution, ethanol, THF (volume ratio 2:1:1) overnight. After acidified by concentrated HCl, the product was extracted by ethyl acetate and then dried over MgSO_4 . After removing solvents under vacuum, dark red powders were obtained in approximately 40% yield. ¹H-NMR in MeOD: δ 8.192 (s, 1H), 8.088 (d, 1H), 7.927 (dd, 2H), 7.792-7.753 (m, 3H), 7.595-7.448 (m, 6H), 7.450 (d, 1H), 7.064 (m, 2H), 6.899 (m, 2H), 6.777 (m, 2H), 6.676 (dd, 2H). ESI-MS ($[\text{M}]^+ = [\text{IrC}_{35}\text{H}_{24}\text{N}_3\text{O}_4]^+$): 743.09 ($[\text{M}]^+$ cal 743.14), 766.09 ($[\text{M}+\text{Na}]^+$ cal 766.13), 782.14 ($[\text{M}+\text{K}]^+$ cal 782.10).

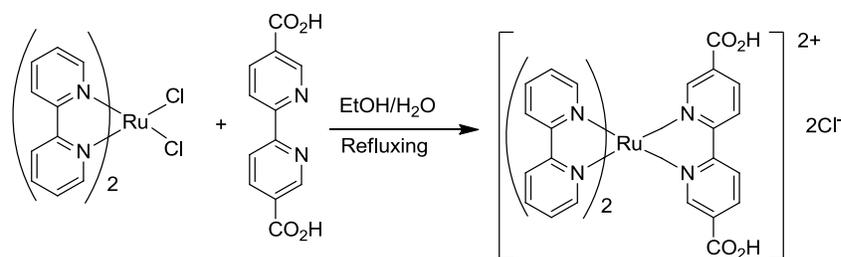
2.2 Synthesis of [fac-bis(2-phenylpyridinato,N,C_{2'})((2,2'-bipyridine)-5,5'-dicarboxyl,N₁,N_{1'}) Iridium (III)] chloride (L₂-H₂)



$[\text{Ir}(\text{ppy})_2\text{Cl}_2]_2$ (200 mg, 0.19 mmol) and [2,2']bipyridinyl-5,5'-dicarboxylic acid diethyl ester (112 mg, 0.37 mmol) were suspended in 15 mL of $\text{MeCN}/\text{CHCl}_3$ (1:1 v/v) under argon. After refluxing overnight, evaporation of the solvent under reduced pressure yielded a red solid. The precipitates were dissolved in a small amount of CHCl_3 and filtered through a short silica column. A redish-orange band was eluted by 1:1 $\text{MeCN}/0.4\text{N KNO}_3$. Afterward, the organic solvent was removed under vacuum, and the precipitate was collected by filtration and redissolved in CHCl_3 . The solution was dried over MgSO_4 , and the solvent was removed under vacuum. Yield: 200 mg (67%) $^1\text{H NMR}$ (CDCl_3): 9.29 (d, 2H), 8.63 (d, 2H), 8.41 (s, 2H), 7.87 (d, 2H), 7.71(t, 2H), 7.65 (d, 2H), 7.44 (d, 2H), 6.95 (m, 4H), 6.88 (t, 2H), 6.25 (d, 2H), 4.20 (q, 4H), 1.18 (t, 6H).

$[\text{Ir}(\text{ppy})_2\text{bpy}]\text{Cl}$ ethyl ester (200 mg, 0.25 mmol) in tetrahydrofuran (THF) (10 mL), ethanol (10 mL), and 3 M aqueous NaOH (10 mL) was stirred at 70°C overnight. The solution was cooled to room temperature and acidified to a pH of 1 and extracted with ethyl acetate/ H_2O . The organic layer was dried over MgSO_4 and the solvent was evaporated under reduced pressure to give the pure product. Yield: 170 mg (88%). $^1\text{H NMR}$ (DMSO): 9.02 (d, 2H), 8.61 (d, 2H), 8.35 (s, 2H), 8.24 (d, 2H), 7.90 (m, 4H), 7.72 (s, 2H), 7.10 (d, 2H), 7.02 (d, 2H), 6.91 (d, 2H), 6.16 (d, 2H). MS (ESI): 745.02 m/Z, expected 745.14 m/Z for $[\text{C}_{34}\text{H}_{24}\text{O}_4 \text{N}_4\text{Ir}]^+$.

2.3 Synthesis of [bis(2,2'-bipyridine, N_1,N_1')(2,2'-bipyridine-5,5'-dicarboxyl, N_1,N_1') Ruthenium(II)] dichloride ($\text{L}_3\text{-H}_2$)



L_3-H_2 was synthesized by following the published procedure.^[2] The compound cis-[Ru(bpy)₂Cl₂] (160mg, 0.33 mmol) was mixed with 2,2'-bipyridine 5,5'-dicarboxylated acid (101mg, 0.42 mmol) in 20 mL of EtOH/H₂O, refluxed for 12 hours under Ar protection and then concentrated. The solid was recrystallized from a MeOH/diethyl ether mixture. Yield: 200 mg (80%) 1H NMR (DMSO-*d*₆): 8.99 (d, 2H), 8.89 (m, 4H), 8.53 (d, 2H), 8.20 (m, 4H), 7.99 (s, 2H), 7.84 (d, 2H), 7.78 (d, 2H), 7.59 (t, 2H), 7.49 (t, 2H).

3. Procedures for MOF Synthesis

3.1 General procedure for synthesis of MOFs 1-3. MOFs **1-3** were typically synthesized by reacting ZrCl₄ (Acros, 98%, anhydrous), 4,4'-biphenyldicarboxylic acid (H₂bpdc, Aldrich, 97%), and one of the metal dicarboxylic acid complexes (H₂L₁-H₂L₃) in N,N'-dimethylformamide (DMF, Fisher, 99.9%, water content 0.02%) under solvothermal conditions. Glacial acetic acid was added to enhance the crystallinity of the samples. DMF was used as received. A stoichiometric amount of water is required for MOF formation (Equation 1). This amount of water was introduced from the DMF.



3.2. Synthesis of MOF-1. ZrCl₄ (10.7 mg, 0.046 mmol), H₂bpdc (9.5 mg, 0.039 mmol), and H₂L₁ (1.1 mg, 0.0015 mmol) were dispersed in glacial acetic acid (50 μL) and DMF (300 μL), sealed in a 2 mL Teflon-lined autoclave and placed in an oven. The temperature was kept at 100 °C for 7 days. After cooling down to room temperature, the resulting solid was isolated via centrifuge, and was washed with DMF and methanol repeatedly before drying under vacuum. The Ir-complex (**L1**) content in MOF-1 was determined by ICP-MS to be 1.0 wt%.

3.3. Synthesis of MOF-2. ZrCl₄ (9.2 mg, 0.039 mmol), H₂bpdc (9.4 mg, 0.039 mmol), and H₂L₂ (1.1 mg, 0.0015 mmol) were dispersed in glacial acetic acid (50 μL) and DMF (300 μL), sealed in a 2 mL Teflon-lined autoclave and placed in an oven. The temperature was kept at 100 °C for 7 days. After cooling down to room temperature, the resulting solid was isolated via centrifuge, and was washed with DMF and methanol repeatedly before drying under vacuum. The Ir-complex (**L2**) content in MOF-2 was determined by ICP-MS to be 2.1 wt%.

3.4. Synthesis of MOF-3. ZrCl₄ (10.7 mg, 0.046 mmol), H₂bpdc (10.2 mg, 0.042 mmol), and H₂L₃ (1.1 mg, 0.0017 mmol) were dispersed in glacial acetic acid (50 μL) and DMF (300 μL), sealed in a 2 mL Teflon-lined autoclave and placed in an oven. The temperature was kept at 100 °C for 7 days. After cooling down to room temperature, the resulting solid was isolated via centrifuge, and was washed with DMF and methanol repeatedly before drying under vacuum. The Ir-complex (**L3**) content in MOF-3 was determined by ICP-MS to be 5.9 wt%.

References:

- 1) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, 106, 6647-6653.
- 2) Xie, P. H.; Hou, Y. J.; Zhang, B. W.; Cao, Y.; Wu, F.; Tian, W. J.; Shen, J. C. *J. Chem. Soc., Dalton Trans.* **1999**, 4217-4221.