

**Electronic Supporting Information (ESI) for:**

**Light-harvesting, 3<sup>rd</sup> generation MOF with large, tubular channel aperture**

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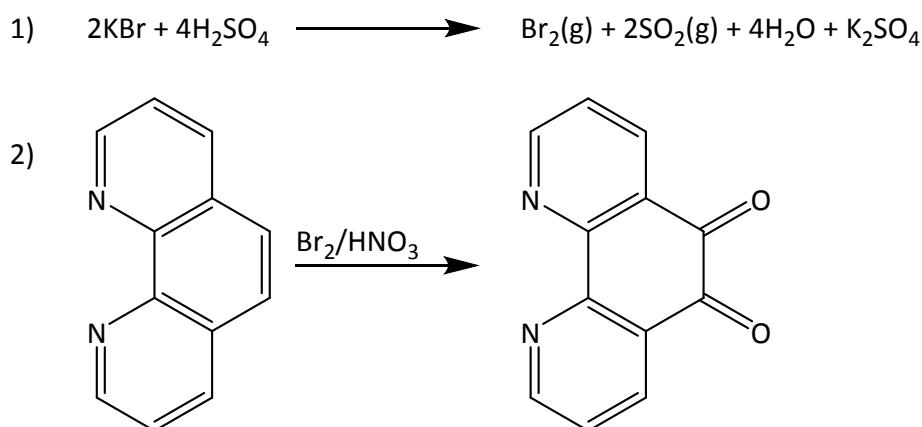
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## S1. Experimental Methods

### General Methods

Unless otherwise specified, all reagents and starting materials were purchased from standard commercial sources and without further purification.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX 400 machine operating at 400 and 600 MHz. Sample preparation was done in deuterated solvents. Standard abbreviations for spectra: s, singlet; d, doublet; t, triplet; m, multiplet;  $J$ , coupling constant were used. Infrared spectra were recorded on PerkinElmer Spectrum One FT-IR spectrometer using a universal ATR sampling accessory. Data was collected and processed using Spectrum v5.0.1 (2002 PerkinElmer Instrument LLC) software. Spectrometer in the range 4000-500  $\text{cm}^{-1}$ , with samples mounted on a diamond anvil. Thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer Pyris-1 TGA/DSC 1 thermal analysis instrument. Data were collected in the temperature range of 20 to 500  $^{\circ}\text{C}$  under a  $\text{N}_2$  flow rate of 20  $\text{mL min}^{-1}$ . Data were analysed using the Pyris evaluation program. X-ray data were collected at 100(2) K using a Bruker Apex Duo instrument equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Gas sorption isotherms for pressures in the range of 0 – 1.0 bar were measured by the volumetric method using a Quantachrome Autosorb iQ instrument. Temperatures were maintained at 293 ( $\pm 0.1$ ) and 77 K using a circulating Dewar and a refrigerated/heated bath circulator (ISOTEMP 4100 R20, Fischer Scientific), and at 77 K using a liquid nitrogen bath. The software used for data processing and NLDFT fitting was ASiQwin version 2.  $\text{N}_2$ , He and  $\text{CO}_2$  gases were obtained in CP grade from BOC Gases Ireland. Samples were activated at 150  $^{\circ}\text{C}$  under dynamic vacuum at 10 – 6 Torr for 12 hours to remove residual solvent molecules.

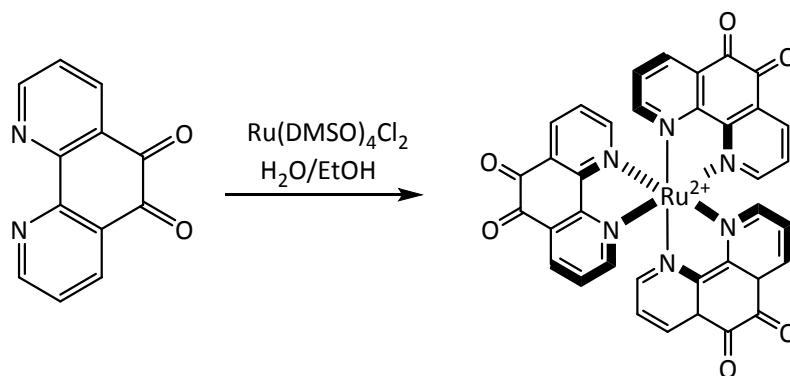
Preparation of 1,10-phenanthroline-5,6-dione



**Scheme S1.** Synthesis of 1,10-phenanthroline-5,6-dione.

1,10-Phenanthroline-5,6-dione was synthesized using an adapted literature procedure.<sup>1</sup> 1,10-Phenanthroline (7.50 g, 41.62 mmol) and potassium bromide (36.65 g, 307.98 mmol) were placed in a 3-neck round bottom flask in an ice bath. Sulfuric acid (97 %, 150 mL, at 0 °C) and nitric acid (66%, 60 mL) were added to the flask sequentially through dropwise addition. The reaction was heated to 80 °C for 1.5 hrs and to 100 °C for a further 3.5 hours. The solution was cooled to room temperature and poured onto ice, accompanied by a colour change from orange to green. The pH of the solution was raised to *ca.* 6 using an aqueous solution of sodium carbonate and the residual sodium salt precipitate was removed *via* filtration and washed with dichloromethane until the precipitate was colourless. The aqueous layer was subsequently extracted with dichloromethane, the organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent removed under reduced pressure. The resulting compound was recrystallised from hot methanol to yield needle-shaped yellow crystals. Yield of 1,10-phenanthroline-5,6-dione: 5.69 g (27.05 mmol, 65%). <sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>): δ = 9.00 (2H, d, *J*<sub>1</sub> = 3.06), 8.40 (2H, d, *J*<sub>1</sub> = 7.39), 7.68 (2H, dd, *J*<sub>1</sub> = 7.82 *J*<sub>2</sub> = 7.46); <sup>13</sup>C NMR (400 MHz, DMSO-D<sub>6</sub>): δ = 177.8, 154.3, 152.3, 135.7, 129.1, 125.2.

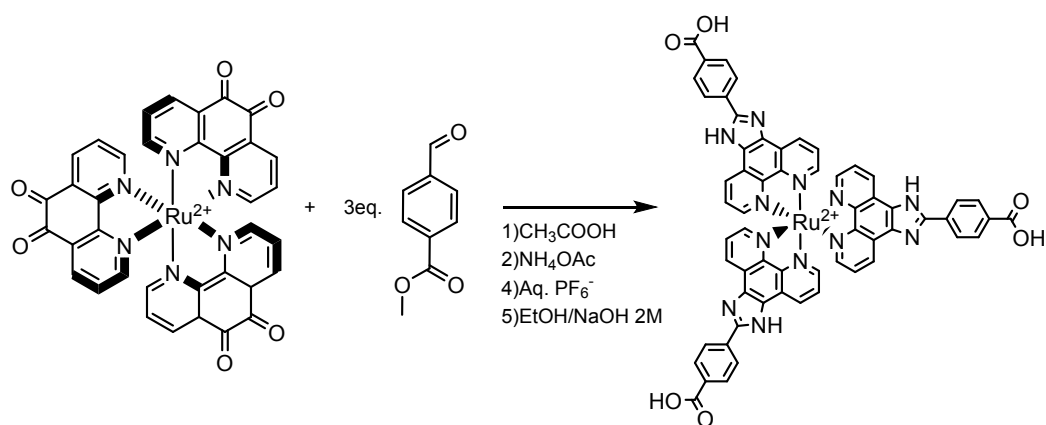
## Preparation of $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$



**Scheme S2.** Synthesis of  $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$  (phendione = 1,10-phenanthroline-5,6-dione).

The Ru(II) complex of 1,10-phenanthroline-5,6-dione,  $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$ , was prepared according to a literature procedure.<sup>2</sup> For this purpose,  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$  (305 mg, 0.63 mmol) and 1,10-phenanthroline-5,6-dione (453 mg, 2.16 mmol) were dissolved in 10 mL of  $\text{H}_2\text{O}/\text{EtOH}$  (1:1, v/v). The reaction mixture was then refluxed for 6 hours after which the product was isolated by centrifugation. Residual solvent was removed through evaporation, resulting in a dark compound,  $[\text{Ru}(\text{phendione})_3]\text{Cl}_2$ . Yield: 425.4 mg (0.530 mmol, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = 7.73 (dd  $J_1 = J_2 = 5.5$  Hz, 6H,  $\text{H}^{2,5}$ ), 8.18 (d, 6H,  $\text{H}^{1,6}$ ), 8.61 (d,  $J_1 = 8.0$  Hz, 4H,  $\text{H}^{3,4}$ ).

## Preparation of $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$



**Scheme S3.** Synthesis of  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$ .

$[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  was prepared according to an adapted literature procedure.<sup>3</sup>  $[\text{Ru}(\text{phenanthroline})_3]\text{Cl}_2$  (83 mg, 0.104 mmol), methyl 4-formylbenzoate (51.00 mg, 0.312 mmol) and  $\text{NH}_4\text{OAc}$  (160 mg, 2.08 mmol) were dissolved in 10 mL of glacial acetic acid. The reaction mixture was then heated at 80 °C for 8 hours under  $\text{N}_2$  atmosphere followed by solvent evaporation. The resulting product was dissolved in methanol. The addition of saturated aqueous solution of ammonium hexafluorophosphate led to the precipitation of the product. The obtained compound was then deprotected *via* basic hydrolysis by dissolving it in ethanol (30 mL) and aqueous  $\text{NaOH}$  (2 M, 5 mL) and heating the reaction mixture at reflux for 3 hours. The volatiles were then removed by evaporation under reduced pressure. The residue was dissolved in 100 mL of water and acidified to *ca.* pH 3 using 2 M  $\text{HCl}$  until precipitation of the product which was followed by vacuum filtration. Yield: 70.02 mg (0.062 mmol, 60%). Analysis calculated for  $\text{C}_{60}\text{H}_{36}\text{N}_{12}\text{O}_6\text{RuP}_2\text{F}_{12}$ : C, 51.04; H, 2.57; N, 11.90 Found: C 51.75, H 3.00, N 10.72. IR(ATR):  $\tilde{\nu} = 1698$  (s) ( $\text{CO}_{2\text{asymm}}$ ), 1690 (s) ( $\text{CO}_{2\text{symm}}$ ), 1574 (w), 1526 (w), 1514 (w), 1482 (w), 1451 (w), 1426(w), 1365 (m) (CN), 1316 (m), 1272 (m), 1244 (m), 1194 (w), 1117 (w), 1012 (w), 957 (w), 868 (w), 831 (w), 809 (s), 719 (s) ( $\text{PF}_6$ ), 682 (m, 666 (s), 651 (w), 556 (w), 527 (w)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 14.98$  (m, 3H,  $\text{H}^4$ ), 9.31 (m, 3H,  $\text{H}^7$ ), 9.12 (m, 6H,  $\text{H}^1$ ), 8.53 (d,  $J_1 = 8.5$  Hz, 6H;  $\text{H}^6$ ), 8.19 (d,  $J_1 = 6.8$  Hz, 6H;  $\text{H}^5$ ), 8.08 (m, 6H,  $\text{H}^2$ ) 7.82 (m, 6H;  $\text{H}^3$ ).  $^{13}\text{C NMR}$  (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta = 167.9, 152.1, 151.0, 146.1, 133.7, 132.4, 131.2, 130.6, 130.0, 128.1, 127.2, 126.8$ .

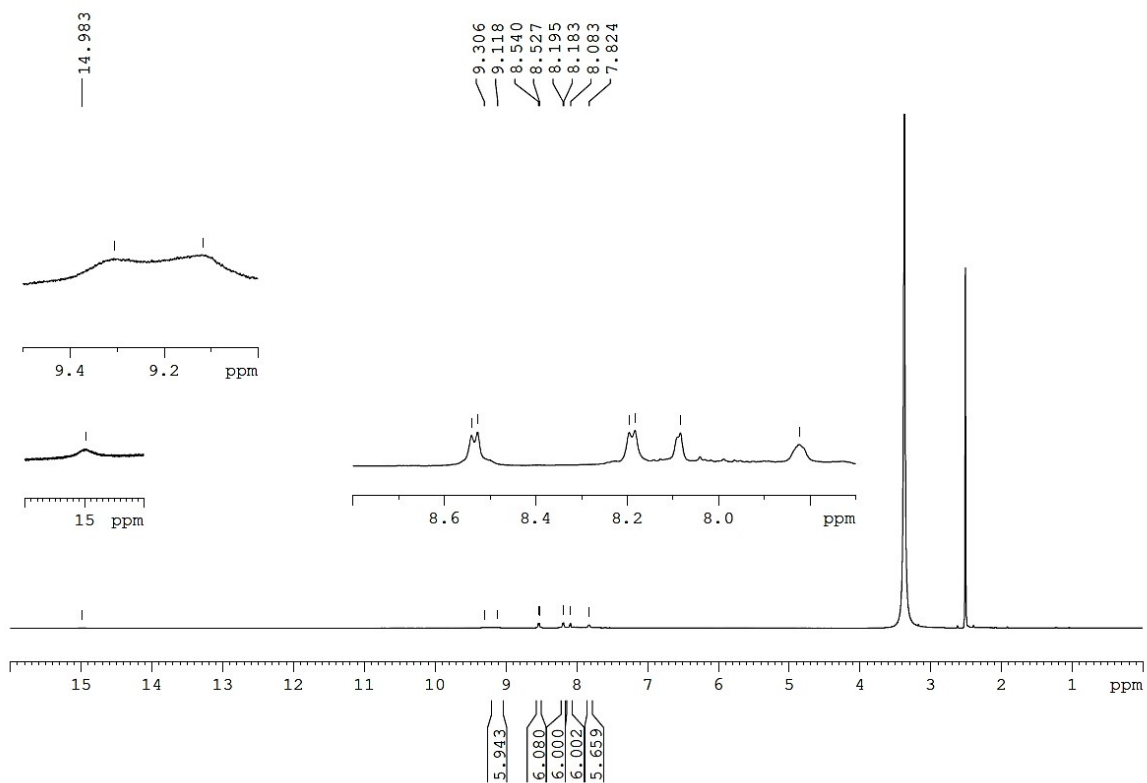


Figure S1.  $^1\text{H}$ -NMR spectrum (400 MHz) of  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  in  $\text{DMSO-D}_6$ .

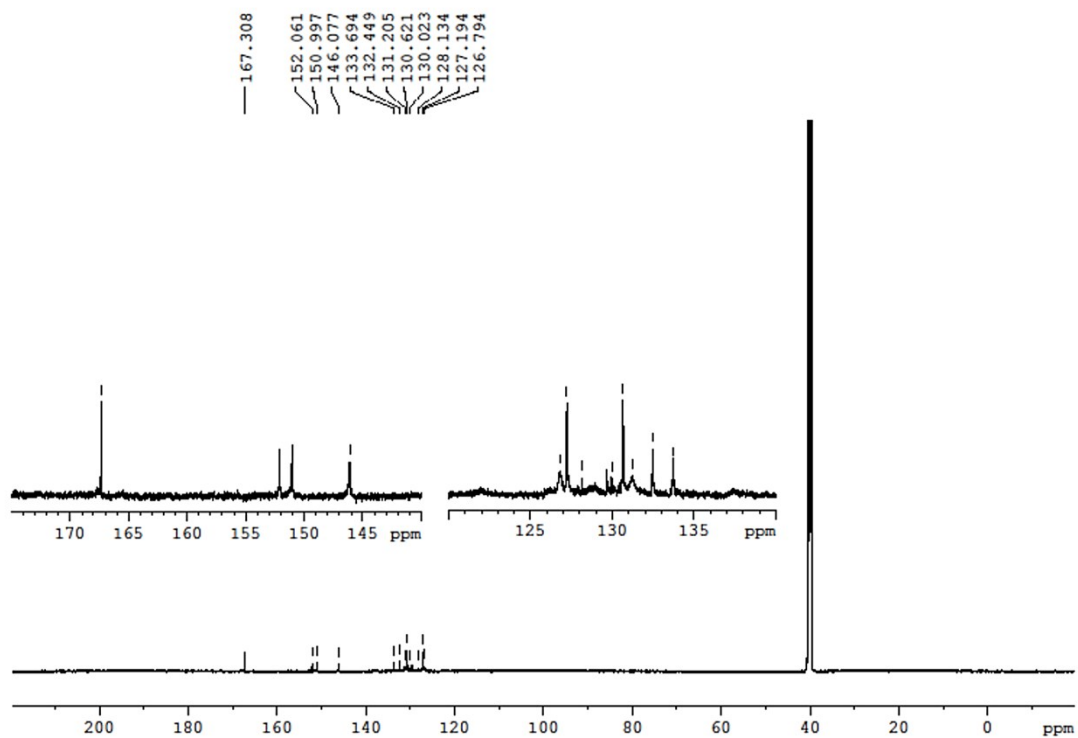
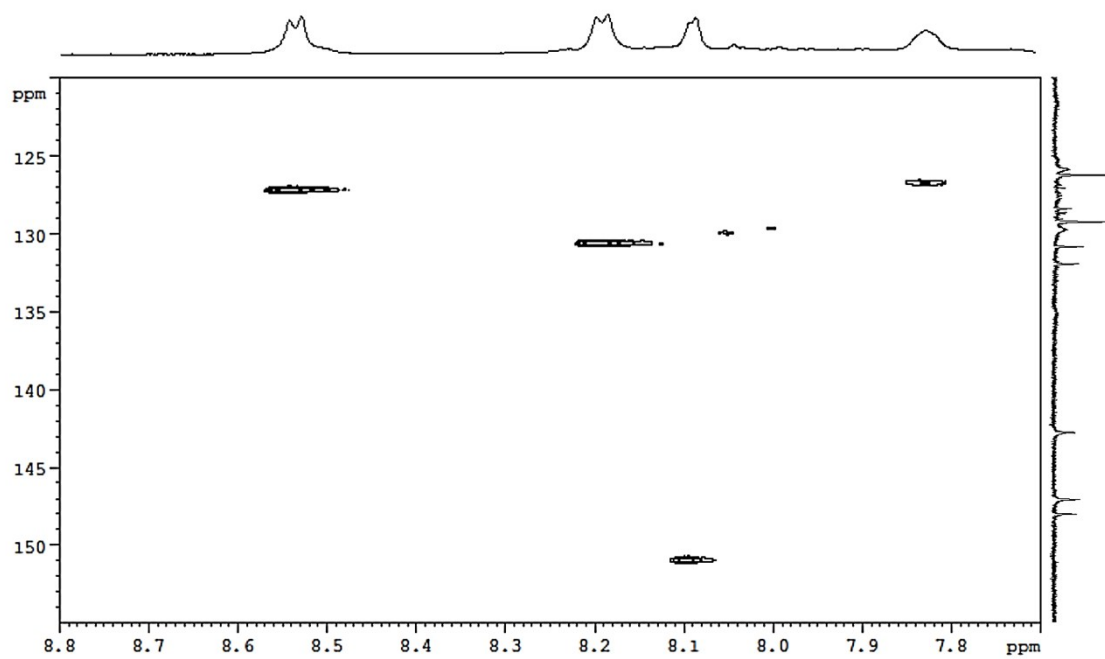


Figure S2.  $^{13}\text{C}$ -NMR spectrum of  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  in  $\text{DMSO-D}_6$ .

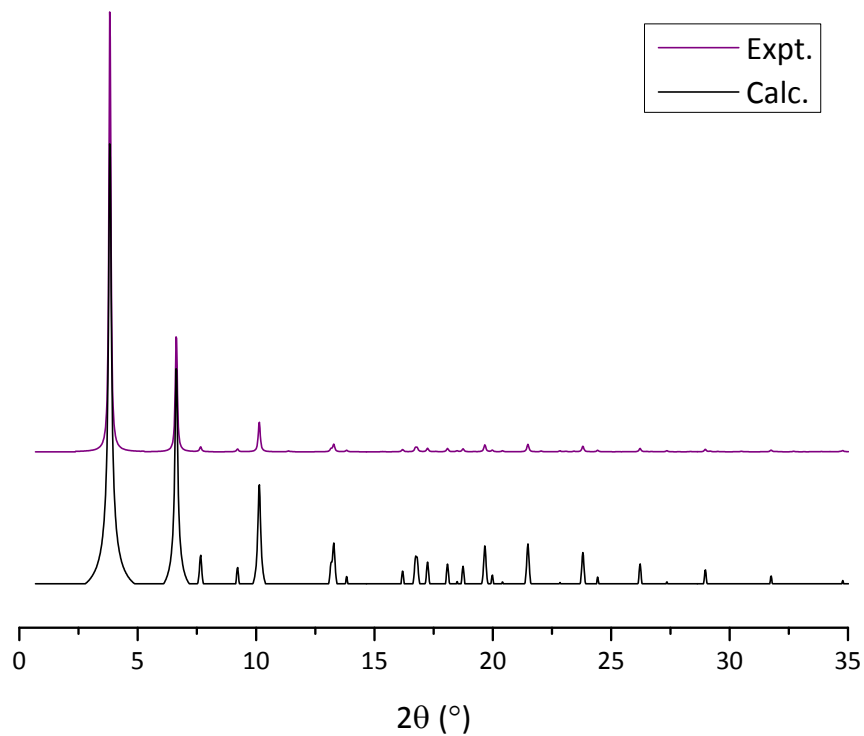


**Figure S3.**  $^{13}\text{C}$  $^1\text{H}$ -COSY spectrum (600 MHz) of  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  in  $\text{DMSO-D}_6$ .

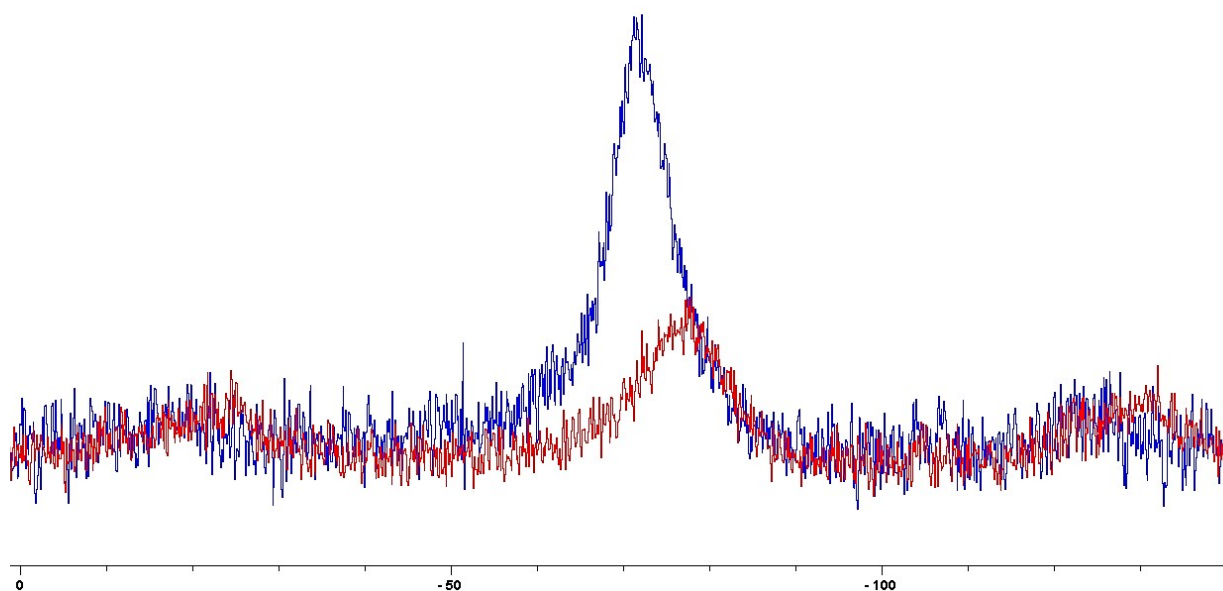
## Preparation of Photo-MOF

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29.00 mg, 0.1 mmol) and [H<sub>3</sub>L<sup>Ru</sup>](PF<sub>6</sub>)<sub>2</sub> (11 mg, 0.01 mmol) were added to a 2 mL vial with a silicon cap and dissolved in 1.5 mL of DMF/TFA (50:1, v/v) solution. The reaction mixture was sonicated at room temperature for 10 minutes, during which both reactants dissolved resulting in a deep, red solution. The vial was placed in a 20 mL Teflon-lined autoclave and put in an oven and heated at 120 °C. Upon heating for 72 hours, orange needles were observed. Analysis calculated for C<sub>72</sub>CoF<sub>18</sub>H<sub>62</sub>N<sub>12</sub>O<sub>30</sub>Ru (as synthesized including 1 CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>, 5 CF<sub>3</sub>CO<sub>2</sub>H and 12 H<sub>2</sub>O guest molecules): C 41.63, H 3.01, N 8.09 Found: C 41.14, H 2.60, N 8.35. Yield: 10.46 mg (0.005 mmol, 50 %). <sup>19</sup>F NMR: δ = 72.3 ; IR(ATR):  $\tilde{\nu}$  = 1599 (s-broad) (CO<sub>2</sub><sub>asymm</sub>), 1536 (s-broad) (CO<sub>2</sub><sub>symm</sub>), 1477 (w), 1453 (w), 1428 (w), 1365 (s-broad) (CN), 1316 (m), 1282 (w), 1248 (w), 1192 (m), 1144 (w), 1029 (w), 948 (w), 870 (w), 798 (s), 717 (s), 690 (m), 653 (w), 624 (w), 604 (w), 590 (w), 578 (w), 566 (w) cm<sup>-1</sup>.

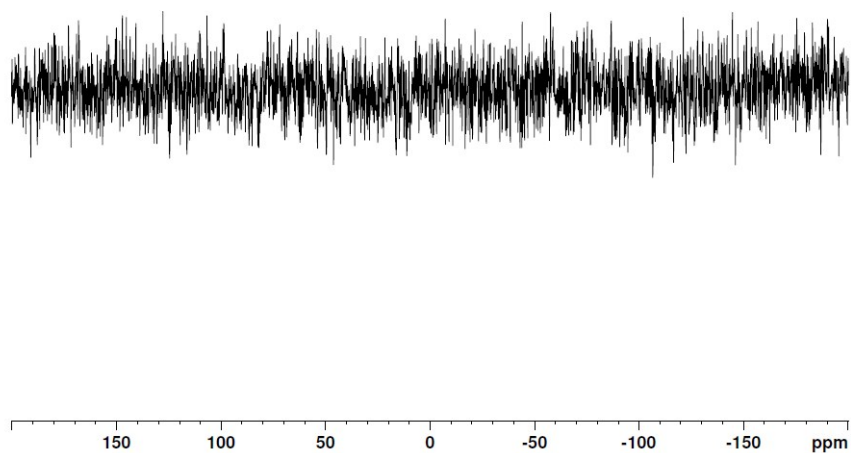




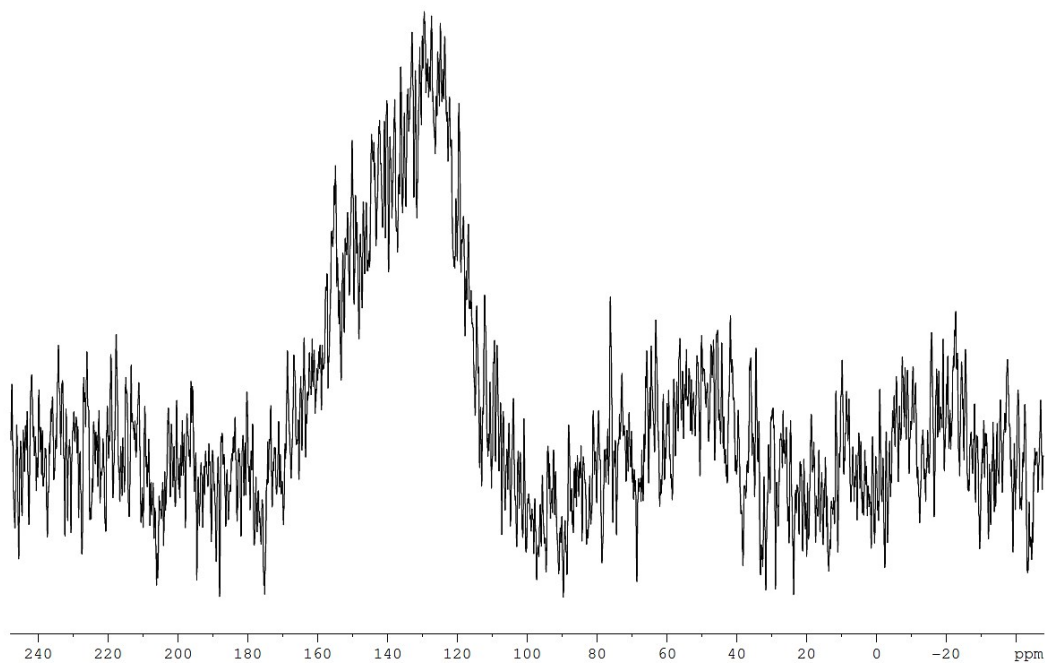
**Figure S4.** Powder X-ray diffraction (PXRD) pattern for **Photo-MOF** and calculated pattern (based on the single crystal X-ray diffraction data).



**Figure S5.** Solid-state  $^{19}\text{F}$ -NMR (400 MHz) spectrum of **Photo-MOF** as synthesized (blue) and **Photo-MOF** activated (red). The activated sample was heated in under vacuum to 150 °C for 24 hrs.



**Figure S6.** Solid-state  $^{31}\text{P}$ -NMR (400 MHz) spectrum of **Photo-MOF** confirming the absence of possible  $\text{PF}_6^-$  counterions in the structure.



**Figure S7.** Solid state 60 kHz broad-band  $^{13}\text{C}$ -NMR spectrum of activated **Photo-MOF** showing aromatic and aliphatic regions.

## S2. Single Crystal X-Ray Diffraction of Photo-MOF

X-ray crystallographic analysis was performed on a single crystal of suitable quality of **Photo-MOF** with dimensions *ca.* 0.05 mm x 0.08 mm x 0.12 mm. The X-ray intensity data were measured at 100(2)K on a Bruker Apex Duo diffractometer equipped with an Oxford Cobra low temperature device. The crystal was mounted using a MiTeGen micromount. The Bruker APEX software<sup>4</sup> was used to correct for Lorentz and polarization effects.

A total of 1589 frames were collected. The total exposure time was 18.54 hours. The integration of the data using a trigonal unit cell yielded a total of 54055 reflections to a maximum  $\theta$  angle of 52.844°, of which 2508 were independent (average redundancy 21.827, completeness = 99.8%,  $R_{\text{int}} = 19.39\%$ ,  $R_{\text{sig}} = 7.10\%$ ) and 1416 were greater than  $2\sigma(F^2)$ . The final cell constants of  $a = 26.645(4)$  Å,  $b = 26.645(4)$  Å,  $c = 10.542(2)$  Å, volume = 6482(2) Å<sup>3</sup>. Data were corrected for absorption effects using the Multi-Scan method (SADABS).<sup>5</sup> The ratio of minimum to maximum apparent transmission was 0.5395 and 0.7504.

The structure was solved using the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.<sup>6</sup> The final anisotropic full-matrix least-squares refinement on  $F^2$  with 124 variables converged at  $R1 = 10.10\%$ , for the observed data and  $wR2 = 28.00\%$  for all data. The goodness-of-fit was 1.056. The largest peak in the final difference electron density synthesis was  $1.239 \text{ e}^-/\text{Å}^3$  and the largest hole was  $-0.460 \text{ e}^-/\text{Å}^3$  with an RMS deviation of  $0.082 \text{ e}^-/\text{Å}^3$ . On the basis of the final model, the calculated density was  $0.661 \text{ mg/m}^3$  and  $F(000)$ , 1302 e<sup>-</sup>. The size and shape of the thermal ellipsoids of the disordered atoms were consistent with the observed disorder pattern.

**Refinement Note:** Data only collected to a  $d_{(\text{min})}$  of 0.97 Å due to poor diffraction. The structure was refined with restraints (DFIX, DELU). The electron density in exceptionally large voids (*ca.* 21 Å diameter channels) was removed from the diffraction data using the Platon SQUEEZE routine.<sup>7</sup> This yielded a solvent accessible volume (SAV) of 4393 Å<sup>3</sup> with 1549 electrons in this volume. As there are two formula units located within the unit cell, the removed electron contribution corresponds to  $1549/2 = 774$  electrons. This may include the counter anion, 5 CF<sub>3</sub>CO<sub>2</sub>H, 12 H<sub>2</sub>O (455 electrons) and other solvent molecules (DMF/H<sub>2</sub>O), which were lost by the drying process at room temperature, prior to elemental analysis (samples were sent to an analytical service).

**Table 1.** Crystal data and structure refinement for **Photo-MOF**.

Identification code	<b>Photo-MOF</b>	
Empirical formula	$C_{60}CoH_{33}N_{12}O_6Ru (C_2F_3O_2)^*$	
Formula weight	1291.00	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	$P\bar{3}1c$	
Unit cell dimensions	$a = 26.645(4)$ Å	$\alpha = 90^\circ$ .
	$b = 26.645(4)$ Å	$\beta = 90^\circ$ .
	$c = 10.542(2)$ Å	$\gamma = 120^\circ$ .
Volume	6482(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	0.661 mg/m <sup>3</sup>	
Absorption coefficient	2.237 mm <sup>-1</sup>	
F(000)	1302	
Crystal size	0.12 x 0.08 x 0.05 mm <sup>3</sup>	
Theta range for data collection	1.915 to 52.844°.	
Index ranges	-26 ≤ h ≤ 27, -27 ≤ k ≤ 27, -10 ≤ l ≤ 10	
Reflections collected	54055	
Independent reflections	2508 [R(int) = 0.1939]	
Completeness to theta = 52.844°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7504 and 0.5395	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2508 / 0 / 124	
Goodness-of-fit on F <sup>2</sup>	1.056	
Final R indices [I > 2σ(I)]	R1 = 0.1010, wR2 = 0.2370	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.239 and -0.461 e.Å <sup>-3</sup>	
<b>CCDC No.</b>	<b>1886201</b>	

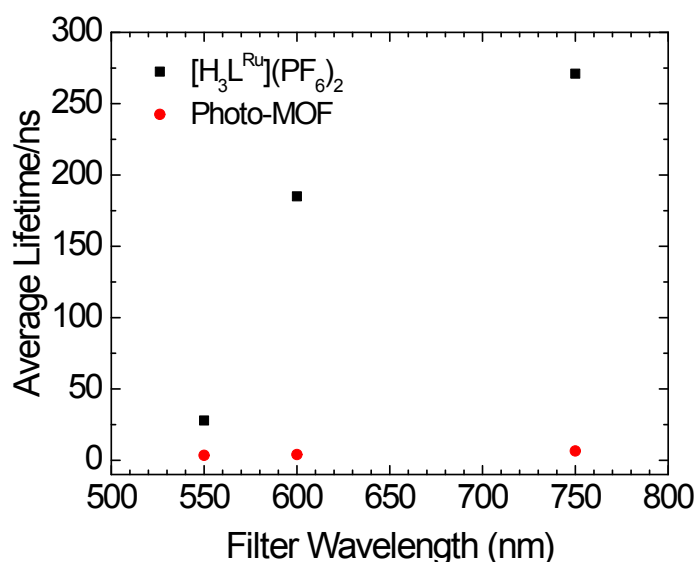
\* One trifluoroacetate (C<sub>2</sub>F<sub>3</sub>O<sub>2</sub>) has been added to the CIF formula for charge balance.

### S3. Photophysical Studies

The absorption spectra and PL spectra of **Photo-MOF** and  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  were measured using a Cary 50 UV-vis spectrophotometer. 3 mg of each sample was suspended in DMF in a quartz cuvette (1 cm  $\times$  1 cm). The photoluminescence spectra (PL) were recorded for an excitation wavelength of 405 nm.

Time-resolved photoluminescence (TRPL) measurements of the **Photo-MOF** and  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  in DMF were performed using a PicoQuant Microtime 200 time-resolved confocal microscope system using an excitation of 90 ps pulses at a wavelength of 405 nm with a repetition rate of 10 MHz and an integration time of 4 ms per pixel. The laser spot size was  $\sim$ 430 nm. The sample was excited through a 40x objective (NA = 0.65) and the photoluminescence (PL) was collected through the same objective. A 40 nm bandpass filter centre on 600 nm was used.

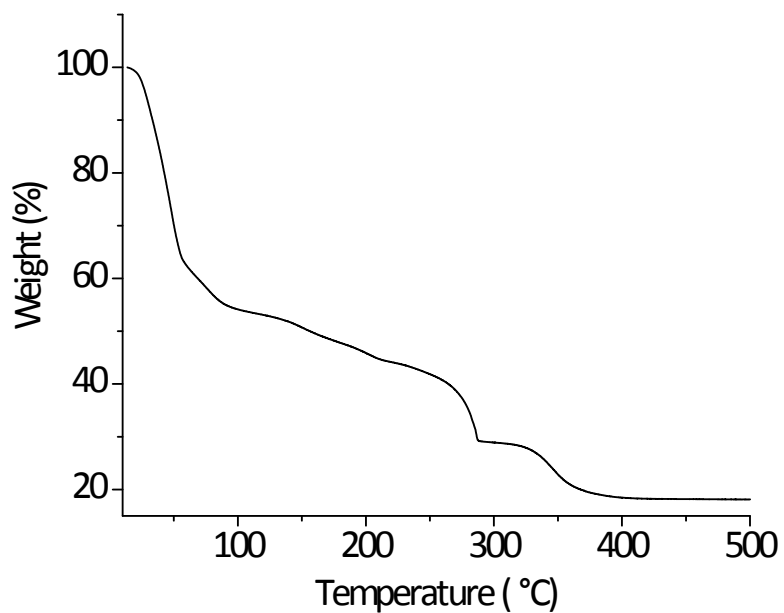
The FLIM scans on the solid-state samples were also performed using the PicoQuant Microtime 200 with the same conditions as for the PL decays. Solid state samples of **Photo-MOF** and  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  were used for the measurements.



**Figure S8.** Spectral-dependent photoluminescence lifetimes of  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  and **Photo-MOF** measured in DMF.

#### S4. Thermogravimetric Analysis of Photo-MOF

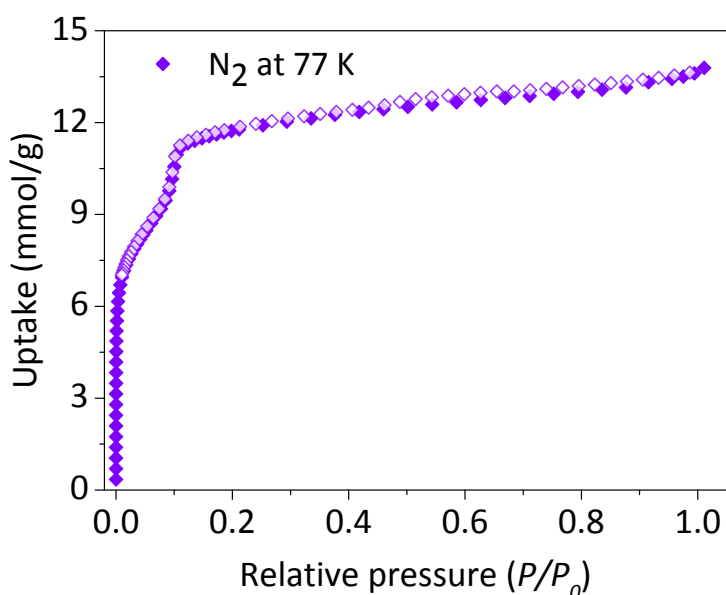
Prior to thermogravimetric analysis, **Photo-MOF** was stored in DMF. Heating rate: 3 °/min; N<sub>2</sub> flow rate: 20 mL min<sup>-1</sup>.



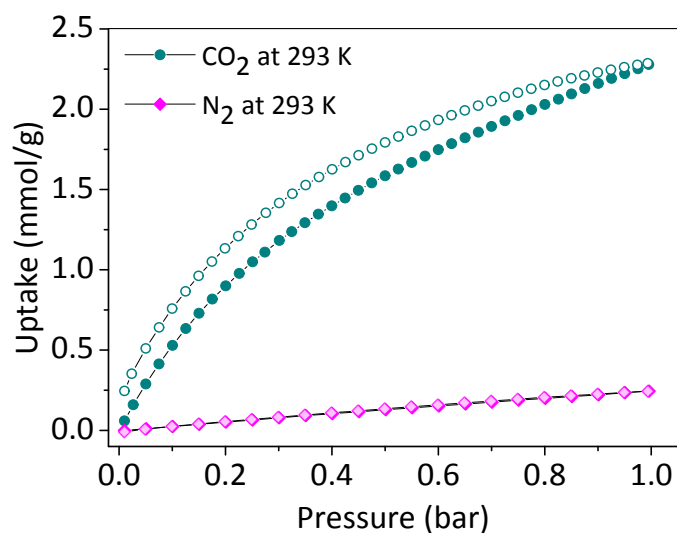
**Figure S9.** Thermogravimetric analysis of **Photo-MOF**.

## S5. Gas Adsorption Measurements of Photo-MOF

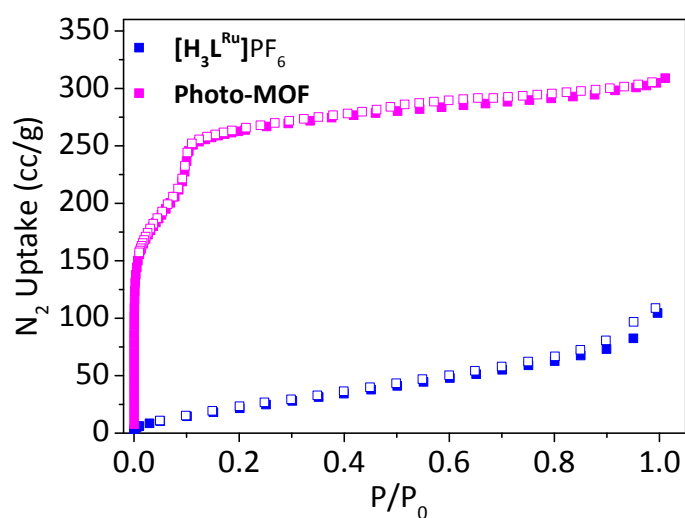
Gas adsorption isotherms of an activated sample of **Photo-MOF** were recorded in the 0 – 1 bar pressure range using a volumetric method using a Quantachrome Autosorb iQ instrument. For this purpose 65 mg of a dried CH<sub>3</sub>OH-exchanged sample was placed in a pre-dried and weighed glass cell. The sample was subjected to vacuum and activated at 150 °C under secondary vacuum for 12 hours to remove any constitutional solvent molecules. The accurate weight of the activated sample was measured prior to analysis. Gas adsorption measurements were performed using CP grade N<sub>2</sub> and CO<sub>2</sub> provided by BOC Ireland.



**Figure S10.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K using **Photo-MOF** as adsorbent.



**Figure S11.** CO<sub>2</sub> and N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms at 293 K and 293 K for **Photo-MOF**.



**Figure S12.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K using **Photo-MOF** (magenta) and **[H<sub>3</sub>L<sup>Ru</sup>](PF<sub>6</sub>)<sub>2</sub>** (blue) as adsorbent.



## S6. BET Surface Area

The BET surface area of **Photo-MOF** and  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  was determined considering the linear region of the  $\text{N}_2$  isotherm at 77 K prior to the pore filling step.

Summary:

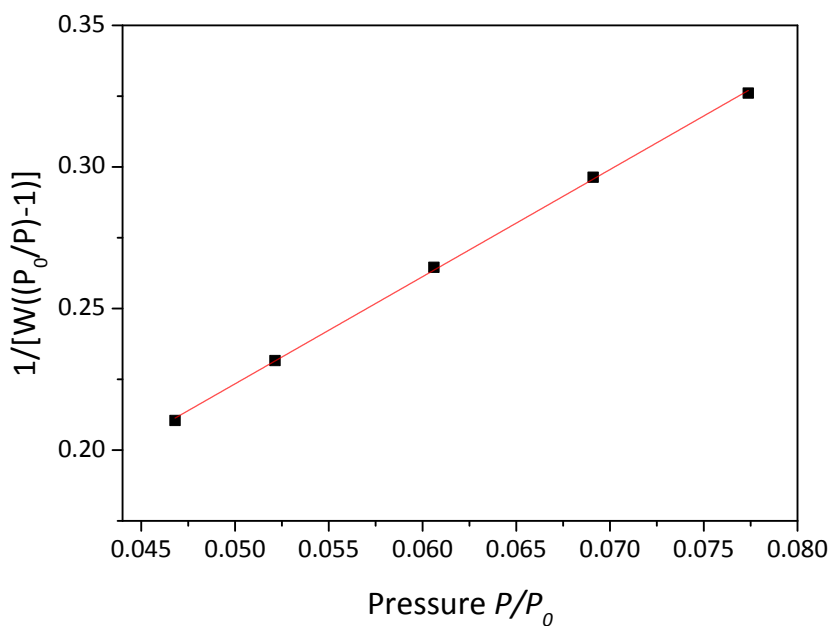
Slope = 3.784

Intercept =  $3.419 \times 10^{-2}$

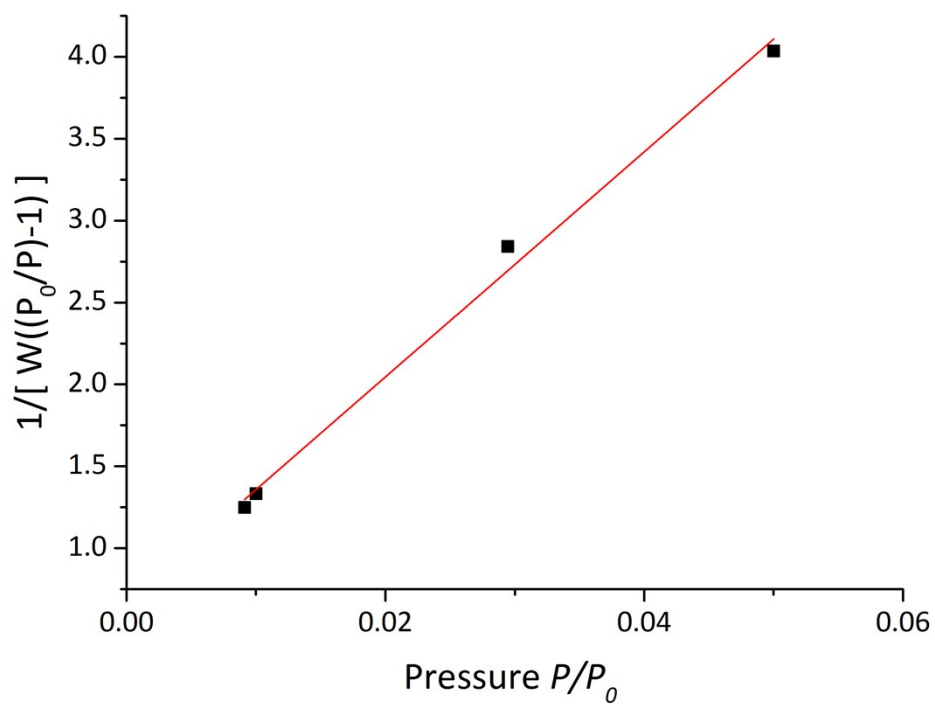
Correlation coefficient,  $r = 0.999827$

Constant,  $C = 111.68$

Surface Area =  $912.027 \text{ m}^2/\text{g}$



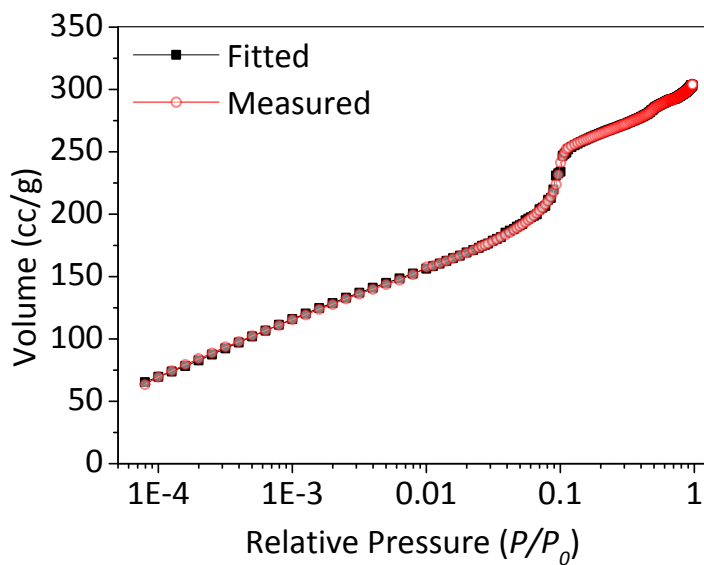
**Figure S13.** Multi-point BET fit for **Photo-MOF**.



**Figure S14.** Multi-point BET fit for  $[\text{H}_3\text{L}^{\text{Ru}}](\text{PF}_6)_2$  with calculated surface area of  $50.17 \text{ m}^2/\text{g}$ .

## S7. DFT Calculations

DFT calculations were performed using the Quantachrome ASiQwin software and the  $N_2$  isotherms were measured at 77 K in order to determine the pore size distribution of **Photo-MOF**. The model used for the calculations is the NLDFT equilibrium model for cylindrical pores in carbon. The fitting of the experimental data is presented in Figure S15.



**Figure S15.** DFT fitting for **Photo-MOF**.

## S8. Selectivity Calculations

In order to determine the CO<sub>2</sub>/N<sub>2</sub> selectivity of **Photo-MOF**, the experimental isotherms were simulated using Henry and Langmuir models. These models were selected in order to give the best fits while minimizing the number of parameters. Respectively, the pure CO<sub>2</sub> and N<sub>2</sub> isotherms were fitted using the following models:

$$q_{model,CO_2}(p_{CO_2}) = \frac{q_{s,CO_2} b_{CO_2} p_{CO_2}}{1 + b_{CO_2} p_{CO_2}} + K_{H,CO_2} p_{CO_2}$$

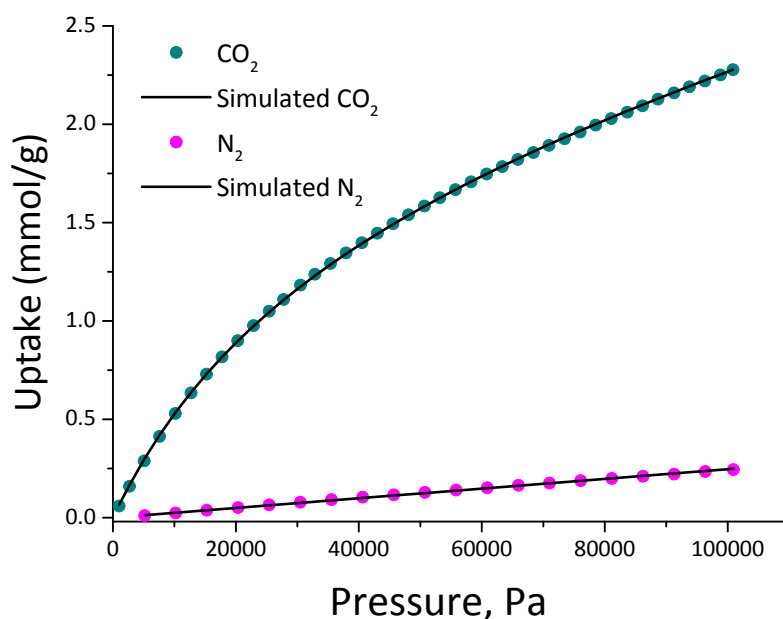
$$q_{model,N_2}(p_{N_2}) = K_{H,N_2} p_{N_2}$$

To quantify the quality of the fitting, the mean relative deviations were calculated for each isotherm using the following equations,

$$D(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|q_{exp}(i) - q_{model}(i)|}{q_{exp}(i)}$$

in which  $N$  represents the number of experimental values for the considered isotherm.

Figure S16 shows the experimental and simulated isotherms for CO<sub>2</sub> and N<sub>2</sub> (at 293 K) for **Photo-MOF**. Table S2 reports the associate parameters and the mean relative deviations.



**Figure S16.** Data fitted to experimental CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms (at 293 K).

**Table S2.** Parameters and deviation for fitted and experimental isotherms .

Compound	$K_H$ (mmol g <sup>-1</sup> Pa <sup>-1</sup> )	$q_s$ (mmol g <sup>-1</sup> )	$b$ (Pa <sup>-1</sup> )	D (%)
CO <sub>2</sub>	7.92 x 10 <sup>-6</sup>	1.9797	2.92 x 10 <sup>-5</sup>	3.12
N <sub>2</sub>	2.46 x 10 <sup>-6</sup>	-	-	0.75

The CO<sub>2</sub>/N<sub>2</sub> selectivity was calculated by dividing the slopes, of the simulated isotherms, in the Henry region:

$$S_{CO_2/N_2} = \frac{q_{s,CO_2} b_{CO_2} + K_{H,CO_2}}{K_{H,N_2}} = 26.72$$

## S9. References

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