Electronic Supplementary Information for:

# Dioxygen Binding at a Four-Coordinate Cobaltous Porphyrin Site in a Metal-Organic Framework: Structural, EPR, and O<sub>2</sub> Adsorption Analysis

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### **Table of Contents**

| Experimental Section  | <b>S2</b>  |
|---|------------|
| Figure S1: Diffuse-reflectance UV/Visible spectra for PCN-224 and 1                             | <b>S4</b>  |
| <b>Figure S2:</b> N <sub>2</sub> adsorption data for <b>1</b>                                   | <b>S5</b>  |
| Figure S3: BET consistency check for 1  | <b>S6</b>  |
| Figure S4: Determination of BET surface area for 1  | <b>S7</b>  |
| Figure S5: Thermal ellipsoid plot for 1 and 2   | <b>S8</b>  |
| Table S1: Crystallographic table for 1  | <b>S9</b>  |
| Table S2: Crystallographic table for 2  | <b>S10</b> |
| Figure S6: Comparison of O <sub>2</sub> adsorption data for PCN-224 and 1                       | <b>S11</b> |
| <b>Description of Isotherm Fitting/Table S3:</b> Langmuir fit parameters for 1 + O <sub>2</sub> | S12        |
| References  | <b>S13</b> |

### **Experimental Section**

**General Considerations.** Unless otherwise noted, all materials and chemicals were purchased from commercial suppliers and used without further purification. Additionally, unless otherwise noted, all manipulations were carried out under an atmosphere of  $N_2$  using either standard Schlenk techniques or in a Vacuum Atmospheres Nexus II glovebox. All glassware was dried at 150 °C and allowed to cool under vacuum prior to use. All solvents were dried on a solvent purification system from Pure Process Technology and stored under  $N_2$  over 4 Å molecular sieves. Effective removal of  $O_2$  and  $H_2O$  from solvents was verified using a standard solution of Na benzophenone ketyl radical anion. The material PCN-224 was prepared according to a slightly modified literature procedure.<sup>1,2</sup>

**PCN-224Co** (1). A 20 mL vial was charged with PCN-224 (0.100 g, 0.0245 mmol),  $CoCl_2$  (0.0954 g, 0.735 mmol), DMF (5 mL), and 2,6-lutidine (1 g). This vial was then sealed and heated for 12 h at 150 °C. The supernatant was then decanted and the remaining solid was washed with DMF (6 × 5 mL) by iteratively soaking the material for 30 min at 150 °C and then decanting the supernatant. The solid was then iteratively washed with THF (3 × 5 mL) by soaking the material for 1 h and then decanting the supernatant. The remaining solid was then dried for 12 hours at 150 °C under reduced pressure to yield 1 as a dark red crystalline solid (0.0932 g, 89%). ICP-AES for Zr:Co mass ratio: Expected 6.1:1; Found 5.1:1. FT-IR (KBr pellet, cm<sup>-1</sup>): 1654 (s), 1601 (s), 1548 (s), 1409 (s), 1254 (w), 1205 (w), 1176 (w), 1142 (w), 1099 (m), 999 (m), 870 (w), 830 (w), 797 (m), 779 (m), 720 (m), 660 (m), 579 (w), 495 (m), 463 (w).

**PCN-224CoO<sub>2</sub>** (2). Compound 2 for analysis was generated by exposing PCN-224Co to ca. 1 atm of dry  $O_2$  at ambient temperature followed by cooling. Samples for gas adsorption measurements were activated on a Micromeritics ASAP 2020 at 150 °C until an outgas rate of less than 1 mTorr/minute was observed prior to  $O_2$  uptake measurements. Samples for single-crystal X-ray diffraction were prepared by adding one crystal to a 0.3 mm boron rich X-ray capillary (Charles-Supper Company), which was then evacuated at 150 °C for 12 h on a Schlenk line. The capillary was then dosed with 1 atm  $O_2$  at ambient temperature and then flame sealed under reduced pressure at 77 K.

**X-ray Structure Determination.** A single crystal of **1** suitable for X-ray analysis was coated in Paratone-N oil and mounted on a Micro Mounts<sup>TM</sup> rod attached to a goniometer head. A single crystal of **2** sealed in a capillary under dry  $O_2$  was inserted into a goniometer head and held in place with clay. The crystallographic data were collected at 100 and 85 K for **1** and **2**, respectively, on a Bruker APEX II diffractometer equipped with CuK $\alpha$  microsource. Raw data were integrated and corrected for Lorentz and polarization effects using Bruker APEX2 v. 2009.1.4 Absorption corrections were applied using SADABS.<sup>3</sup> Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. Structures were solved and refined with SHELXL<sup>4</sup> operated with the Olex2 interface with the aid of standard restraints.<sup>5,6</sup> Disorder in the structure was modeled, and residual electron density found in the difference Fourier map was removed using the solvent mask protocol included in Olex2. This residual electron density likely arises from either residual solvent, or partial occupation of a separate morphology of the previously reported and closely related

compound MOF-525.<sup>7</sup> The Co ellipsoids are consistent with complete occupation of the site by Co. The elongation of the ellipsoids is consistent with disorder in and out of the plane, which is reflected throughout the porphyrin scaffold. Note that due to disorder about the four-fold axis of the porphyrin, both the O-O distance and C-O-O angle should be regarded with caution.

**Gas Adsorption Measurements.** Crystalline material was transferred into a pre-weighed analysis tube which was then sealed with a Transeal. Activation and analysis were then performed on a Micromeritics ASAP 2020 instrument. The samples were activated at 150 °C until an outgas rate of less than 1 mTorr/minute was observed. After activation, the samples were weighed to determine the final mass of analyte. The sample was checked to ensure the outgas rate remained below 1 mTorr/minute. Oxygen uptake was measured using volumetric methods and the free space of all samples was determined with UHP He prior to analysis. Temperature control was provided with a variety of cold baths: liquid nitrogen/isopentane for 113 K, liquid nitrogen/pentane for 141 K, liquid nitrogen/ethanol for 156 K, and dry ice/isopropanol for 195 K. Measurements at 113, 141, and 156 K were collected only to 0.072, 0.20, and 0.40 bar, respectively, corresponding to the maximum amount of time during which a constant temperature of the bath could be ensured. The experimental BET surface area of 3070(70) m<sup>2</sup> g<sup>-1</sup> is close to the accessible surface area of 3402 m<sup>2</sup> g<sup>-1</sup> that is calculated from the crystal structure of **1**.

**Electron Paramagnetic Resonance (EPR) Spectroscopy.** Continuous-wave EPR spectra were collected on samples of **1** in the absence and presence of  $O_2$ . A crystalline sample of **1** was loaded into a quartz tube under a dinitrogen atmosphere. The tube was then evacuated and dosed with 1 atm  $O_2$  at ambient temperature and then flame sealed under reduced pressure at 77 K. Measurements were performed at the University of Chicago EPR facility using a Bruker Elexsys 500 X-band EPR spectrometer. The temperature of the samples was held at 15 K using an Oxford Systems continuous-flow He Cryostat coupled with a 10 K He stinger from Bruker. Spectra were acquired with the Bruker Win-EPR software suite. The spectrometer was equipped with a dual mode cavity, operating in parallel mode. Data were collected using the following instrumental parameters: radiation frequency = 9.632 GHz; microwave power = 6.31 mW; modulation amplitude = 5 G; modulation frequency = 100 kHz.

**Other Physical Measurements.** UV/Vis/NIR spectra were recorded on a Cary 5000 spectrometer equipped with an integrating sphere for diffuse reflectance measurements. Samples were prepared by a 10 fold dilution of the compound in KBr followed by mulling of the mixture with mineral oil. The collected data were treated with background and baseline subtractions. Inductively coupled plasma atomic emission (ICP-AE) spectra were collected with a Thermo iCAP 7600 ICP-OES instrument. Infrared spectra were recorded on a Bruker Alpha FTIR spectrometer with the samples prepared as KBr pellets.



Figure S1 | Diffuse-reflectance UV/Visible spectra of PCN-224 (blue) and 1 (red).



Figure S2 |  $N_2$  adsorption data for 1 at 77 K.



**Figure S3.** Plot of  $n \cdot (1-p/p_0)$  vs.  $p/p_0$  for **1** to determine the maximum  $p/p_0$  used in the BET linear fit according to the first BET consistency criterion.<sup>8</sup>



**Figure S4.** Plot of  $p/p_0/(n \cdot (1-p/p_0))$  vs.  $p/p_0$  to determine the BET surface area. The slope of the best fit line for  $p/p_0 < 0.084$  is 0.032, and the y-intercept is 7.8 x 10<sup>-5</sup>, which satisfies the second BET consistency criterion.<sup>8</sup> This results in a saturation capacity of 31.5 mmol/g and a BET surface area of  $3070\pm70 \text{ m}^2/\text{g}$ .



**Figure S5** | Reaction of PCN-224Co (1) with  $O_2$  at 85 K to form PCN-224CoO<sub>2</sub> (2). Ellipsoids shown at the 30% level. Green octahedra represent Zr atoms, and teal, red, blue, and gray ellipsoids represent Co, O, N, and C atoms, respectively; hydrogen atoms are omitted for clarity.

## Table S1 Crystallographic data for 1.

| Identification Code                         | PCN-224Co <sup>II</sup>                                       |
|---|---|
| Empirical Formula                           | $C_{144}H_{72}Co_3N_{12}O_{64}Zr_{12}$                        |
| Formula weight                              | 4265.58   |
| Temperature/K                               | 100   |
| Crystal System                              | Cubic   |
| Space group                                 | Im-3m   |
| a/Å   | 38.5873(13)   |
| b/Å   | 38.5873(13)   |
| c/Å   | 38.5873(13)   |
| α/°   | 90  |
| β/°   | 90  |
| $\gamma/^{\circ}$                           | 90  |
| Volume/Å <sup>3</sup>                       | 57456(6)  |
| Z   | 24  |
| $\rho_{calc}g/cm^3$                         | 0.493   |
| $\mu/\text{mm}^{-1}$                        | 2.592   |
| F(000)                                      | 8372.0  |
| Crystal Size/mm <sup>3</sup>                | $0.249 \times 0.283 \times 0.318 \text{ mm}$                  |
| Radiation                                   | $CuK\alpha \ (\lambda = 1.54178)$                             |
| $2\theta$ range for data collection/°       | 2.805-66.589  |
| Index ranges                                | $-45 \le h \le 44, -42 \le k \le 44, -39 \le l \le 43$        |
| Reflections collected                       | 132590  |
| Independent reflections                     | 4730 [ $R_{\text{int}} = 0.0799, R_{\text{sigma}} = 0.0236$ ] |
| Data/Restraints/Parameters                  | 4730/0/104  |
| Goodness-of-fit on $F^2$                    | 1.117   |
| Final R indexes $[I \ge 2\sigma(I)]$        | $R_1 = 0.0861, wR_2 = 0.2598$                                 |
| Final R indexes [all data]                  | $R_1 = 0.0974, wR_2 = 0.2743$                                 |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 1.812/-0.714  |

| Table SZ Crystanographic data to            | <u>ſ ∠.</u>   |
|---|---|
| Identification Code                         | PCN-224CoO <sub>2</sub>   |
| Empirical Formula                           | $C_{144}H_{72}Co_3N_{12}O_{70}Zr_{12}$  |
| Formula weight                              | 4361.56   |
| Temperature/K                               | 84.83   |
| Crystal System                              | Cubic   |
| Space group                                 | Im-3m   |
| a/Å   | 38.6198(10)   |
| b/Å   | 38.6198(10)   |
| c/Å   | 38.6198(10)   |
| a/°   | 90  |
| β/°   | 90  |
| γ/°   | 90  |
| Volume/Å <sup>3</sup>                       | 57601(4)  |
| Z   | 4   |
| $\rho_{calc}g/cm^3$                         | 0.503   |
| µ/mm <sup>-1</sup>                          | 2.598   |
| F(000)                                      | 8564.0  |
| Crystal Size/mm <sup>3</sup>                | $0.508 \times 0.417 \times 0.379 \text{ mm}$  |
| Radiation                                   | $CuK\alpha$ ( $\lambda = 1.54178$ )   |
| $2\theta$ range for data collection/°       | 11.684-131.232  |
| Index ranges                                | $\textbf{-44} \leq h \leq \textbf{33},  \textbf{-43} \leq k \leq \textbf{44},  \textbf{-45} \leq \textbf{l} \leq \textbf{44}$ |
| Reflections collected                       | 93162   |
| Independent reflections                     | 4619 [ $R_{\text{int}} = 0.1022, R_{\text{sigma}} = 0.0357$ ]   |
| Data/Restraints/Parameters                  | 4619/233/119  |
| Goodness-of-fit on $F^2$                    | 1.329   |
| Final R indexes $[I \ge 2\sigma(I)]$        | $R_1 = 0.0988, wR_2 = 0.2976$   |
| Final R indexes [all data]                  | $R_1 = 0.1102, wR_2 = 0.3131$   |
| Largest diff. peak/hole / e Å <sup>-3</sup> | 2.21/-1.07  |
|   |   |



**Figure S6** |  $O_2$  adsorption data for PCN-224 (triangles) and **1** (circles) at 113, 141, 156, and 195 K (blue to red gradient). Solid lines correspond to fits using a dual-site Langmuir-Freundlich model.

#### **Adsorption Isotherm Fitting**

The variable temperature  $O_2$  adsorption isotherms at 113, 141, 156, and 195 K were independently fit with a dual-site Langmuir-Freundlich model (Eqn 1), where *n* is the amount adsorbed in mmol/g, *P* is the pressure in bar,  $n_{\text{sat,i}}$  is the saturation capacity in mmol/g,  $v_i$  is the Freundlich parameter, and  $b_i$  is the Langmuir parameter in bar<sup>-v</sup> for two sites 1 and 2. Note that the Langmuir-Freundlich model was simply used to mathematically fit each adsorption isotherm in preparation for isosteric heat of adsorption calculations using the Clausius-Clapeyron equation, and we do not intend to attribute any physical meaning to the fit parameters. The fitted parameters for each adsorption isotherm can be found in Table S2.

$$n = \frac{n_{\text{sat},1} b_1 P^{\nu_1}}{1 + b_1 P^{\nu_1}} + \frac{n_{\text{sat},2} b_2 P^{\nu_2}}{1 + b_2 P^{\nu_2}} \tag{1}$$

The Clausius-Clapeyron equation (Eqn 2) was used to calculate the differential enthalpies of adsorption,  $-h_{ads}$ , for each compound using the dual-site Langmuir-Freundlich fits at each temperature.

$$\ln P = \frac{h_{ads}}{R} \left(\frac{1}{T}\right) + C \tag{2}$$

Here, *P* is the pressure, *n* is the amount adsorbed, *T* is the temperature, R is the universal gas constant, and C is a constant. The differential enthalpies of adsorption were obtained from the slope of plots of  $(\ln P)_n$  versus 1/T. An error in the enthalpy for a given loading can be calculated from the standard error in the slope of the best-fit line. Fundamentally, this error describes the quality of agreement between the fitted isotherms and the Clausius-Clapeyron relation.

**Table S3.** Dual-site Langmuir-Freundlich fit parameters for O<sub>2</sub> adsorption.

|                    | 113 K                 | 141 K             | 156 K | 195 K |
|--------------------|-----------------------|-------------------|-------|-------|
| n <sub>sat,1</sub> | 0.47                  | 0.12              | 0.16  | 0.41  |
| $b_1$              | $1.0 \mathrm{x} 10^7$ | $3.0 \times 10^4$ | 210   | 0.19  |
| $v_1$              | 1.8                   | 2.1               | 1.9   | 1     |
| $n_{\rm sat,2}$    | 36.8                  | 36.8              | 36.8  | 36.8  |
| $b_2$              | 0.83                  | 0.24              | 0.15  | 0.056 |
| $v_2$              | 0.60                  | 0.58              | 0.64  | 0.85  |

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