

## Supporting Information

### **Distinct reversible colorimetric and fluorescent low pH response on a water-stable zirconium-porphyrin metal-organic framework**

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## Section 1: Experimental Details

All chemicals used for this study were purchased from commercial sources and used without further purification. Zirconium chloride (99+%), benzoic acid (99%), N,N-diethylformamide (DEF, 99%), acetic acid (99%), hydrochloric acid (36.5-38%, for concentrated solutions only) were purchased from Alfa Aesar, hydrochloric acid (0.1N) from Electron Microscopy Sciences, sodium hydroxide (0.1000N) from VWR, N,N-dimethylformamide (DMF, 99+%) from Oakwood Products Inc, and H<sub>6</sub>tcpp (>97%) from Tokyo Chemical Industries (TCI).

### *PCN-222 synthesis:*

Crystalline product was obtained using the reported synthesis method.<sup>1</sup> H<sub>6</sub>tcpp (50 mg) was added to a 30 mL glass vial containing benzoic acid (2.7 g) as a modulating agent. Zirconium chloride (75 mg) was added to the vial last followed by the immediate addition of N,N-diethylformamide (8 mL). The reaction vial was capped, sonicated for ~3 mins (Branson 2510) and heated at 120°C for 48 hours. Product was collected by vacuum filtration and washed with DMF and acetone. The product was then soaked in DMF for three days, replacing with fresh DMF daily to remove residual modulating agents and unreacted ligand. Product yield was 79.2% (0.1014 g) based on zirconium chloride.

### *Sample preparation:*

The as synthesized sample was further prepared for study by soaking in DMF (40 mL) and 8 M HCl (1.5 mL) at 120°C for 24 hours. At the end of this time, the DMF/HCl mixture was carefully decanted off and replaced with 40 mL of acetone. Fresh acetone was replaced daily for three days. The product was again vacuum filtered and washed once with DMF and acetone and dried in a vacuum oven at ~100°C under vacuum overnight. At this point the first PXRD measurement was taken ("activated PCN-222").

### *Film preparation for visible response testing, UV-Vis measurements, and PL studies:*

Double sided tape was applied to a quartz slide and a background measurement was taken. A thin coating of sample (~0.01 g) was applied to the tape and spread evenly with excess sample being removed by friction using both standard weighing paper and lens tissue. At this time measurements were taken on the film.

### *Acid solution exposures and washes:*

Three to four drops of HCl solution were applied to the surface of the film and allowed to equilibrate with the sample, at which time the excess solution was blotted off with lens tissue and corresponding UV-Vis and PL measurements were taken. In order to reverse the effect of the acid, the film was washed thoroughly with water by immersion, followed by a drop-wise application of DMF to a kimwipe while covering the surface of the film.

## Section 2: Structural Drawings of PCN-222 and H<sub>2</sub>tcpp Protonation

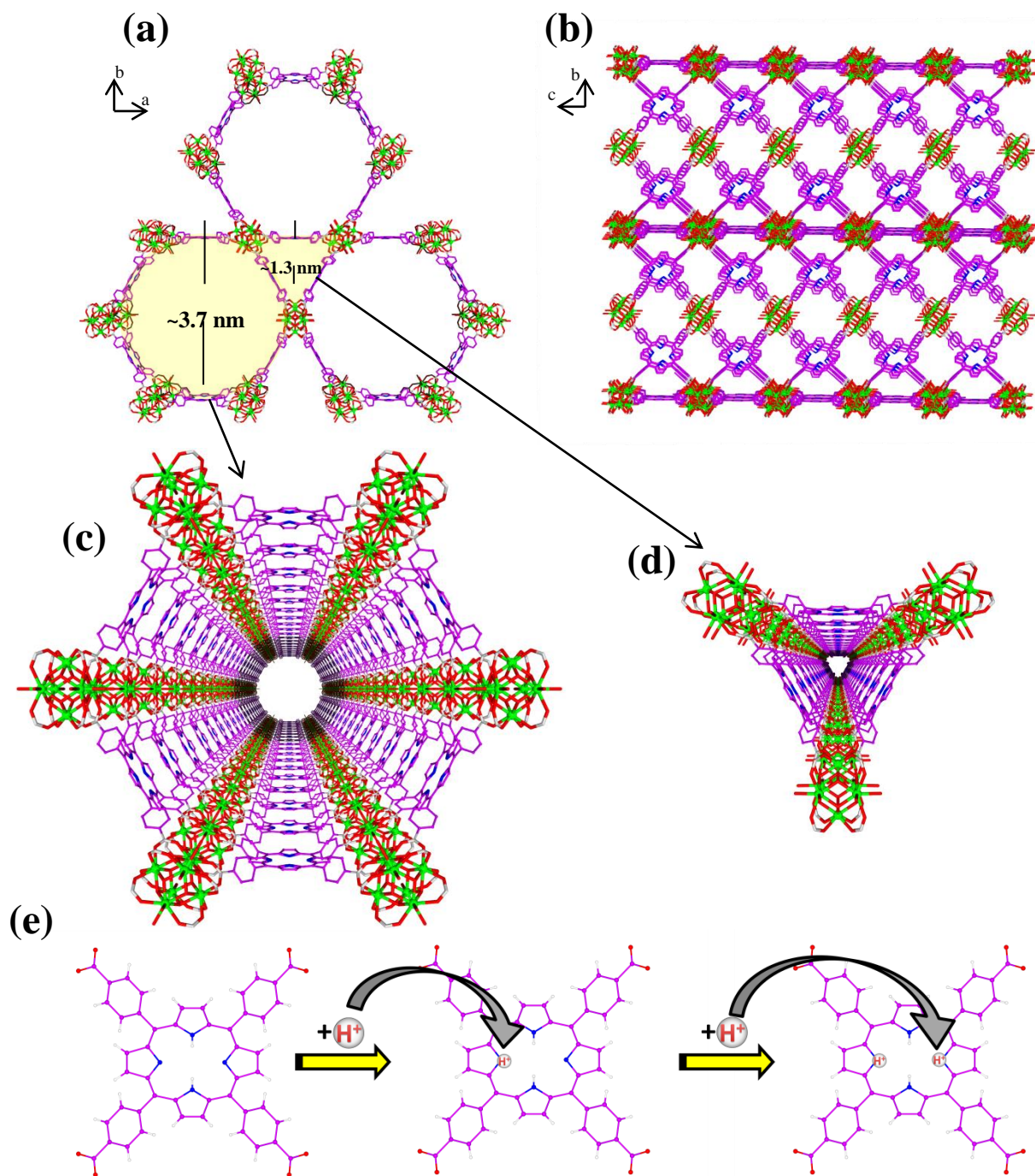


Fig. S1. Structural drawings of PCN-222 along the crystallographic c axis (a), and a axis (b); images showing the accessibility of the porphyrin linker from inside the ~3.7 (c) and ~1.3 (d) nm diameter pores; protonation of the H<sub>2</sub>tcpp linker (e).

### Section 3: Powder X-ray Diffraction Data

All powder X-ray diffraction data were collected using a Rigaku Ultima-IV diffractometer. The patterns were collected between  $3^\circ$  and  $40^\circ$  of the  $2\theta$  at a scan speed of 1.5 deg/min.

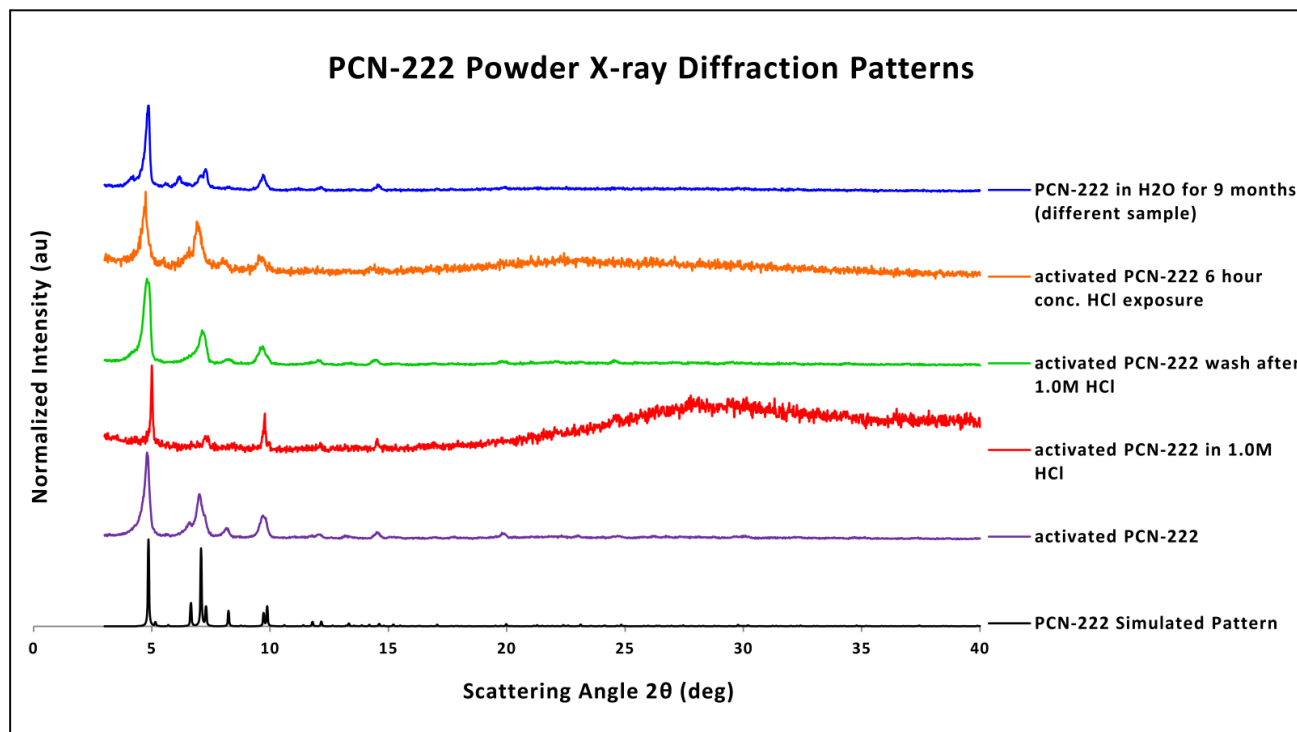


Fig. S2. PXRD patterns: simulated pattern for PCN-222(Fe) (black); activated PCN-222 sample (purple); activated PCN-222 sample while immersed in 1.0M HCl (red); recovered 1.0M HCl sample washed with H<sub>2</sub>O/DMF/acetone (green); recovered sample soaking in conc. HCl for 6 hours then washed with H<sub>2</sub>O/DMF/acetone (orange); older/different sample of PCN-222 soaked in H<sub>2</sub>O for 9 months (blue).

#### Section 4: UV-Vis Details and Data for PCN-222 and H<sub>6</sub>tcpp

The optical absorption spectra of solid samples were collected on a Shimadzu UV-3600 spectrophotometer at room temperature. The baseline was taken on a BaSO<sub>4</sub> standard with a quartz slide with double-sided tape applied. Diffuse reflectance measurements were then taken (see Experimental Details, Section 1), converted to the Kubelka-Munk Function and normalized.

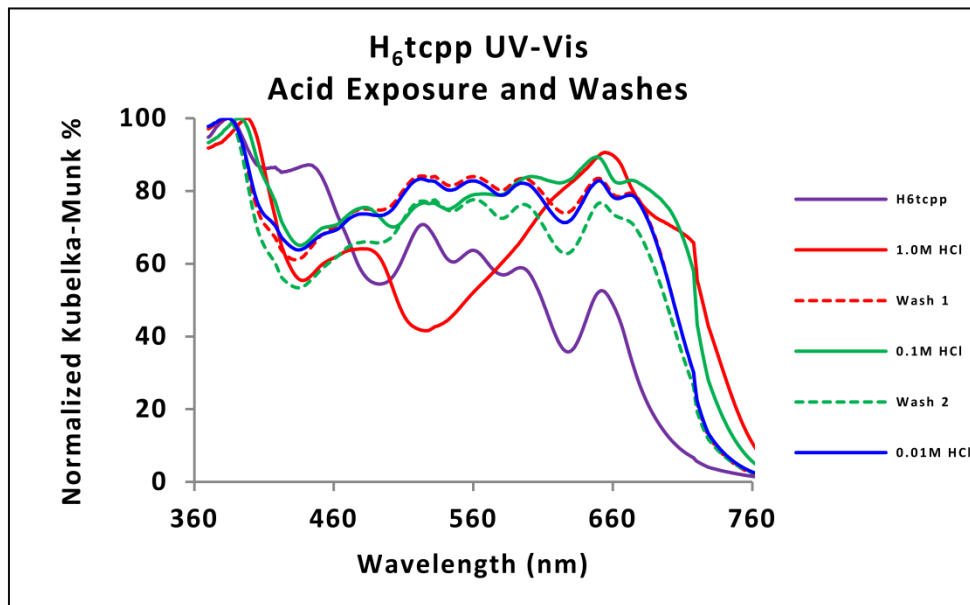


Fig. S3. Solid state UV-Vis data for H<sub>6</sub>tcpp collected after exposure to varying concentrations of HCl and reversal washes with H<sub>2</sub>O.

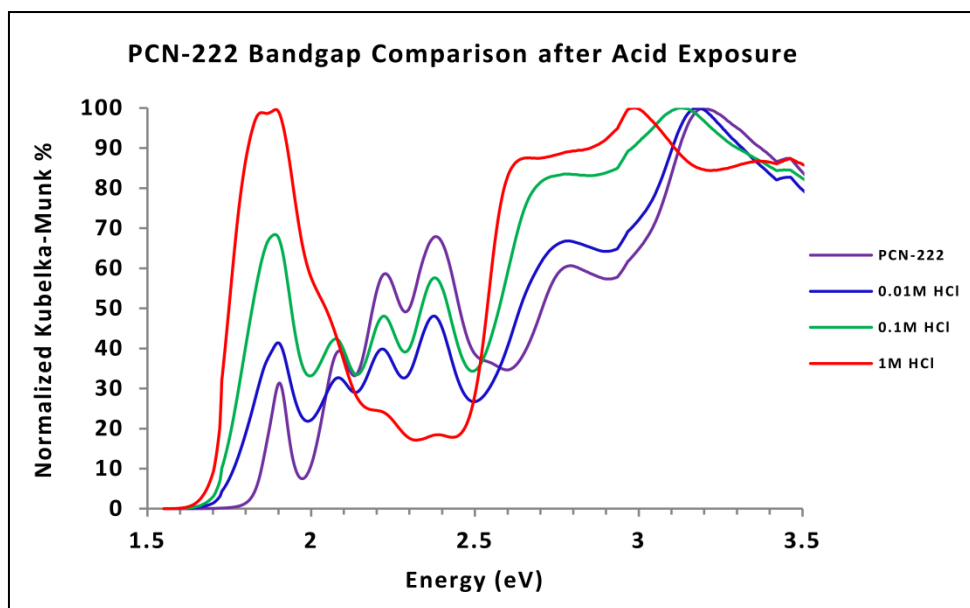


Fig. S4. Solid state UV-Vis data for PCN-222 comparing bandgap energies after exposure to varying concentrations of HCl.

## Section 5: Photoluminescence Details and Data for PCN-222 and H<sub>6</sub>tcpp

Photoluminescence measurements were carried out on a Varian Cary Eclipse spectrophotometer at room temperature on a quartz slide with double sided tape and sample evenly applied with excess sample removed by friction (see experimental details, Section 1). All data except for the excitation spectrum was normalized to emphasize the "turn-off-turn-on" response.

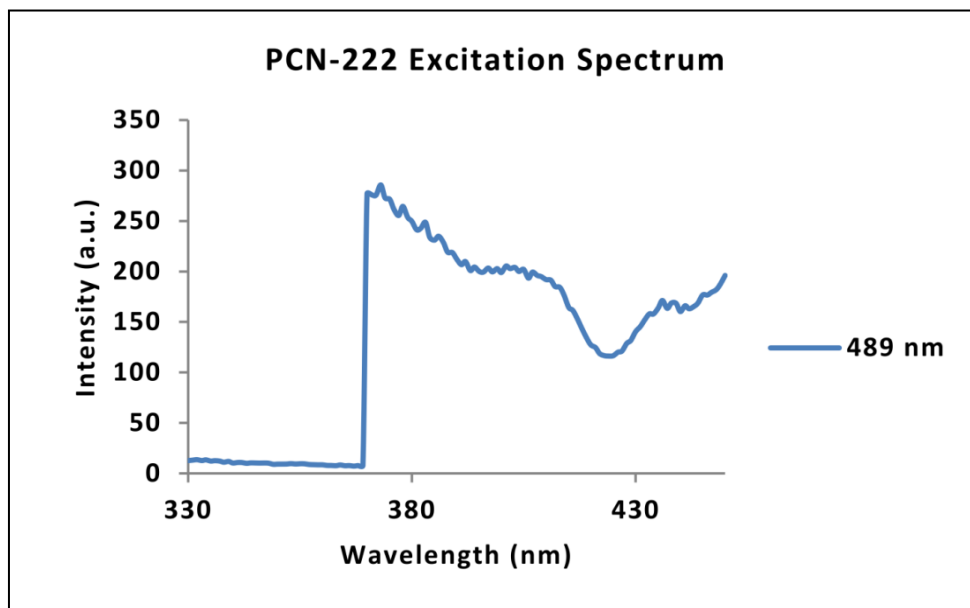


Fig. S5. PCN-222 fluorescence excitation spectrum; monitored at 489 nm emission.

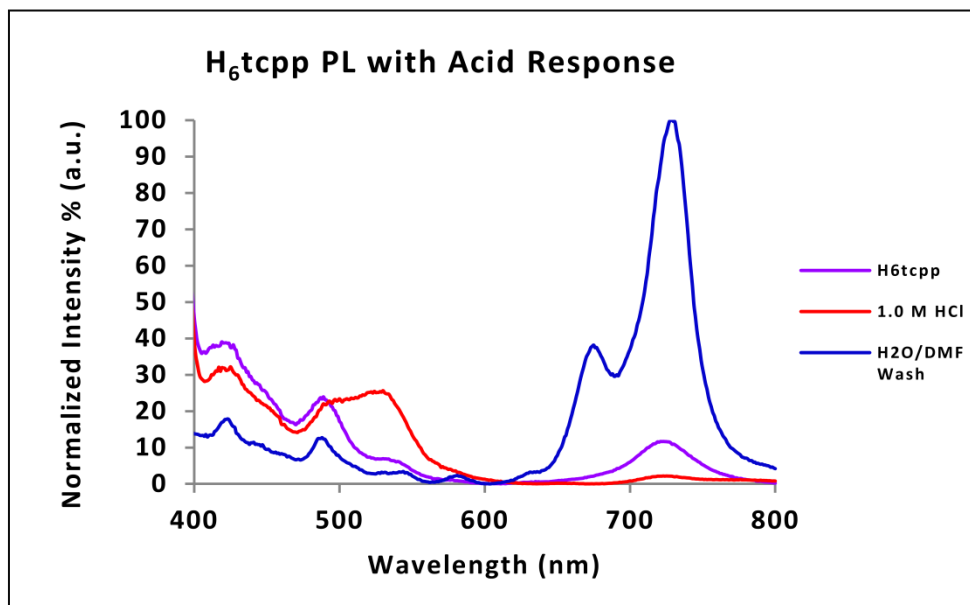


Fig. S6. H<sub>6</sub>tcpp solid state emission spectrum. Slide sample was prepared using the same method as for PCN-222.

## Section 6: References

1. D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angewandte Chemie*, 2012, **51**, 10307-10310.