

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

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

aCite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

Benjamin J. Deibert and Jing Li\*

DOI: 10.1039/x0xx00000x

www.rsc.org/

**A water stable zirconium-porphyrin MOF (PCN-222) was synthesized according to the reported method and found to produce a distinct reversible colorimetric and fluorescent "turn-off-turn-on" pH response. The colorimetric response is achieved under acidic conditions starting at pH = ~3 and persists under concentrated acidic conditions. To the best of our knowledge, this is the first report of a colorimetric MOF pH sensor.**

Metal-organic frameworks (MOFs) have been under intense investigation since their popularization around the turn of the millennium for a wide variety of potential applications.<sup>1</sup> The immobilization of organic linker ligands to metal ions or metal clusters not only gives rise to a vast number of fundamentally interesting porous crystalline structures, but also opens up the possibility of converting homogenous systems into heterogeneous analogues capable of emulating or surpassing the original properties of the parent molecule(s).<sup>2</sup> The rational design of MOF chemical sensors build on this premise; the systematic ordering and immobilization of fluorescent organic ligands into MOF structures often enhances and optimizes the original optical properties of the ligand, as well as providing a stable and porous manifold to function within.<sup>1b, 1k, 1m</sup> As such, it is no surprise that MOFs are being so widely investigated for chemical sensing. An idealized MOF sensor will demonstrate at minimum the following attributes: selective interaction with the analyte, a distinct fluorescent or colorimetric response, a high degree of stability in the analyte media, and a high degree of recyclability.

The fluorescent and colorimetric properties of tetrapyrrolic macrocycles (porphyrin derivatives) is a vast and rich field containing innumerable entries.<sup>3</sup> However, their appearance as linkers in MOF structures is relatively new, and while there are a number of porphyrin MOFs reported, their properties have been investigated to a much lesser extent.<sup>4</sup> Recently, Hong-Cai Zhou's group reported a zirconium-porphyrin MOF (PCN-225) capable of fluorescent pH sensing through luminescent emission enhancement in basic solution, demonstrating the feasibility of pH fluorescent sensing with these materials. The material was found to have the most sensitive response in the range of pH 7 - 10.<sup>4c</sup>

Herein we report an idealized case of MOF chemical sensing through the reversible colorimetric and fluorescent pH response of the reported zirconium-porphyrin MOF, PCN-222, in the range of pH 3 - 0.<sup>4d</sup> This MOF contains a  $Zr_6(\mu_3-OH)_8(OH)_8(CO_2)_8$  secondary building unit (SBU), where  $(CO_2)_8$  correspond to the carboxylate groups from eight meso-tetra(4-carboxyphenyl)porphyrin (H<sub>4</sub>tcpp) ligands. The MOF also contains one dimensional open channels of 3.7 and 1.3 nm diameter lined by the porphyrin moieties that allow for easy passage of analyte or substrate molecules as well as direct interaction with the porphyrin subunits (Fig. S1). It is worth noting that PCN-222 can be constructed using metallated tcpp (Mtcpp), however for this study the metal free ligand was chosen.

Single-phase crystalline product was obtained and activated using the reported hydrothermal method and confirmed by powder X-ray diffraction (PXRD) (Fig. S2, Supporting

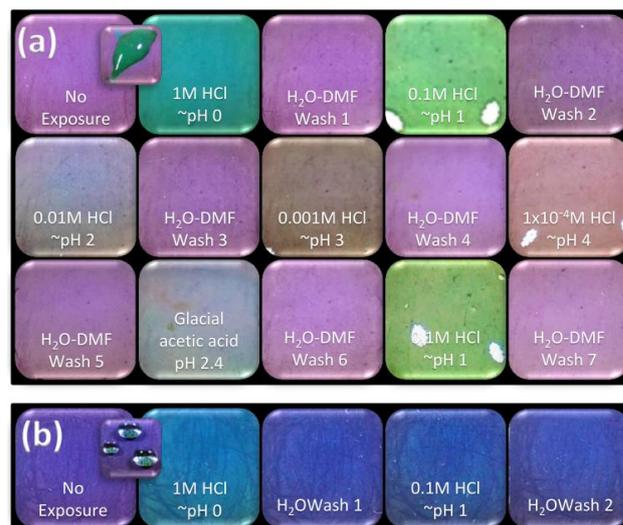


Fig. 1. Photographs of PCN-222 samples (a) and ligand H<sub>4</sub>tcpp (b) under ambient light. These samples are exposed to acidic solutions at various concentrations, followed by reversal washes in between each exposure; exposures were made in the order in which they appear from top left to bottom right. Caption photos are intended demonstrate responsiveness.

Information).<sup>4d</sup> To evaluate the potential of the material to serve as a reversible and stable material for pH sensing, the MOF was exposed to HCl and NaOH solutions varying in concentration to span the pH range of -1 (concentrated HCl) to ~12 (0.01 M NaOH). In regards to the materials' aqueous stability, it is worth pointing out that a sample of PCN-222 was immersed in water for a period of nine months, after which time a PXRD measurement was made showing that the structure is largely intact compared to the simulated pattern; the subtle differences in the patterns are due to a very small amount of impurities that were present in the original sample. After this time the material took on a charcoal grey color, which is likely a result of replacing residual N,N-dimethylformamide (DMF) solvent molecules with water. While the material proves to be exceedingly stable in aqueous acidic conditions, a feature quite rare for MOFs, it was found that dissolution occurs somewhere between pH 11 - 12, which is consistent with the original report. In addition, we noted that when exposed to pH 2 solutions and lower, a very distinct color change from purple to green occurs (Fig. 1a). While there is still a color change that occurs at pH 3 and upwards, it is less noticeable to the naked eye. Further study reveals that not only is the color change from purple to green instant and reproducible, but that it is also completely reversible. Below pH 0, no additional change occurs besides the intensifying of the green color. As seen in Fig. 1a, in the case of PCN-222, the response is instant and pronounced. When PCN-222 was exposed to glacial acetic acid, which has a known pH of 2.4, the colorimetric response mimics that of the 0.01 M HCl (~pH 2) solution, showing that this sensing effect is indeed due to pH and is both reversible and reproducible.

When the same set of experiments was performed using just the H<sub>6</sub>tcpp ligand there was little initial response. This is likely due to the insolubility of H<sub>6</sub>tcpp in aqueous acidic solution paired with its comparatively low available surface area, thereby limiting the protons' access to the majority of the nitrogen Lewis basic sites (LBSs) on the tetrapyrrolic macrocycle.<sup>3a</sup> Eventually, after thoroughly rubbing the acid solution into the sample, some minor color change occurred in the case of 1.0 M HCl. Based upon previous studies of tetraphenylporphyrin (TPP) and its ability to act as a pH sensing molecule, we also believe that this effect is due to protonation of the nitrogen LBS present on the H<sub>2</sub>tcpp linker.<sup>3a, 3f, 4e</sup> Upon photoexcitation, the porphyrin macrocycle can undergo both S<sub>2</sub> and S<sub>1</sub> transitions from a doubly-degenerate set of HOMOs and LUMOs resulting in the UV-Vis absorption Soret band, which occurs at ~450 nm for H<sub>6</sub>tcpp, and the Q bands, which are the four smaller bands ranging ~520-660 nm (Fig. S3).<sup>3b</sup> It stands to reason that if this conjugated  $\pi$  system is perturbed, the molecule's UV-Vis spectrum will change accordingly. In order to verify that perturbation of the macrocyclic  $\pi$  system is responsible for the visible response, solid-state UV-Vis reflectance measurements were taken on both the ligand (Fig. S3) and the MOF before (Fig. 2b) and after (Fig. 2a) acid exposure. In between each different pH exposure, PCN-222 was washed once with water and DMF in order to reverse the effect of the acid, resulting in a full return of the original purple color. In the event that the MOF is washed with just water alone, the material maintains a grey/brown color, the same color witnessed from pH 4 - 11, however DMF washing was omitted for the ligand due to its solubility in the solvent. As the results in Fig. 2a demonstrate, as the

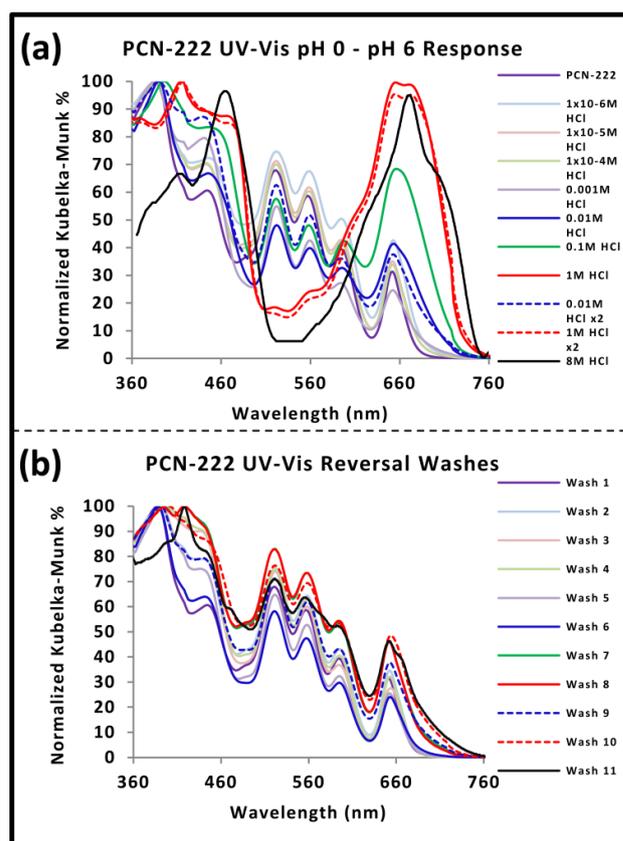


Fig. 2. UV-Vis spectra for PCN-222 after exposure to varying concentrations of HCl solution (a) and after reversing the effect by washing with H<sub>2</sub>O and DMF (b). Measurements were made in the order in which they appear in the legend from top to bottom, where Wash 1 corresponds to washing PCN-222 with no acid exposure.

acidity of the test solution increases, absorption corresponding to the high energy Soret band (~460 nm) and the lowest energy Q band (~660 nm) dramatically increase and are red shifted relative to the other three Q bands. These shifts correlate to the band-gap of PCN-222 decreasing from ~1.85 to ~1.7 eV. The net effect is that the material absorbs more red and blue light over a wider range resulting in a combination of orange and teal reflectance, which produces a greenish color when combined. Starting at 1.0 M HCl the three higher energy Q bands associated with the H<sub>2</sub>tcpp are all but invisible from the absorption spectrum. Because these Q bands are a product of the different S<sub>1</sub> transitions of the porphyrin unit, protonation of the macrocycle results in a disturbance of the conjugated  $\pi$  electron system. This finding supports the reasoning that the color change effect arises from the degree of protonation and subsequent deprotonation of the H<sub>2</sub>tcpp macrocycle within the structure. After exposure to 8.0 M HCl solution, there is a broadening of the low energy band from 690 nm to ~715 nm that persists even through washing. This effect is likely due to incomplete washing of the highly concentrated acid resulting in residual protonation.

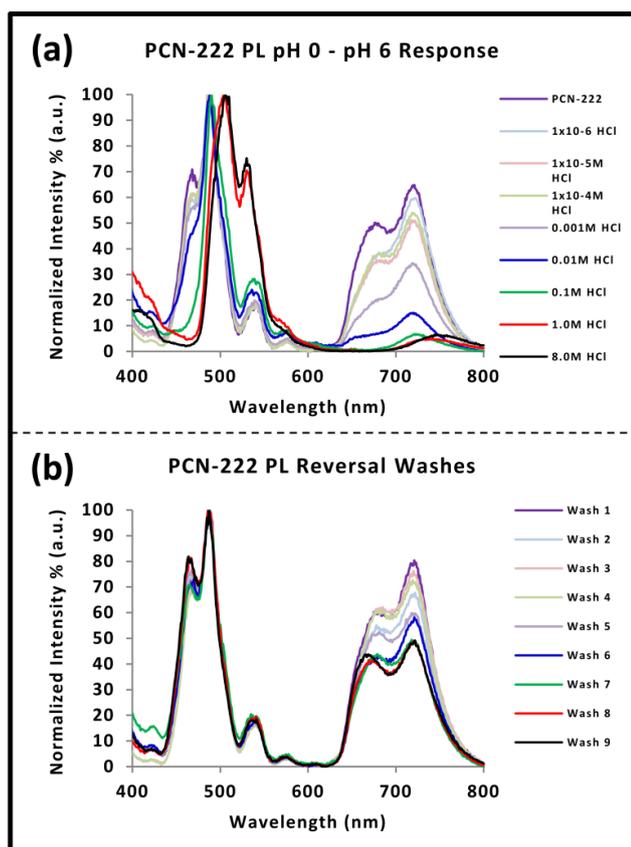


Fig. 3. Photoluminescence data for PCN-222 after exposure to varying concentrations of HCl solution (a) and after reversing the effect by washing with H<sub>2</sub>O and DMF (b). Measurements were made in the order in which they appear in the legend from top to bottom, where Wash 1 corresponds to washing PCN-222 with no acid exposure.

To further investigate the colorimetric response, photoluminescence (PL) measurements were also taken (Fig. 3) in a similar fashion to the UV-Vis measurements (370 nm excitation, Fig. S5, Supporting Information). These data show a very distinct "turn-off-turn-on" effect as a result of two separate phenomena. Significant quenching of the low energy emissions from about 645-760 nm result in a "turn-off" effect after exposure to < 0.01 M HCl solution. The UV-Vis absorption in this region (610-760 nm, Fig. 2) is also increased accordingly. The purple color can be thought of arising from a combination of the green/blue high energy emission and red low energy emission, and as the low energy emission is quenched upon exposure to acid, only the high energy emission from about 450-560 nm is observed, hence the greenish blue color arises when exposed to 0.01 M HCl solution or glacial acetic acid (Fig. 1a). At low pH, from pH 0 (1.0 M HCl) downwards, two additional "turn-on" peaks are observed. The maximum peak at 490 nm shifts to 500 nm, and the peak at 525 nm is significantly enhanced in conjunction with the disappearance of the shoulder peak at 465 nm; at this point the material appears to be entirely green to the naked eye. Similar to the UV-Vis measurements, the effect was completely reversed in between each different exposure (Fig. 3b). In order to further support the claim that the color change is an effect of protonation/deprotonation of the H<sub>2</sub>tcpp moiety, similar PL measurements were taken on a film comprised of just the H<sub>2</sub>tcpp molecule (Fig. S6, Supporting Information). While the PL spectra are different from one another as expected, the response of H<sub>2</sub>tcpp to acid exposure is similar in nature to PCN-222 (Fig. 3a), with red shifting peaks in the high energy region and quenching in the low

energy region. The PL data for the free ligand in the solid-state also suggests activation of a new emission peak at ~675 nm after washing once with H<sub>2</sub>O and DMF. It should be noted that while H<sub>2</sub>tcpp is hydrophobic to the aqueous acid solutions, it dissolves freely in DMF. Due to the nature of the way the sample was washed, minimal dissolution occurred, but it may have been enough to disrupt any long range order within the free ligand, as the PL spectrum looks more similar to that of H<sub>2</sub>tcpp when in solution. It should also be pointed out that when the H<sub>2</sub>tcpp<sup>2+</sup> diacid form of the ligand is dissolved in solution (through the use of co-solvents) it forms dimers and aggregates at low pH values.<sup>3a</sup> The immobilization of the porphyrin unit within PCN-222 prevents formation of such aggregates and thus provides unique UV-Vis and PL optical responses.

In summary, we have shown that by incorporating the H<sub>2</sub>tcpp moiety into the meso-porous crystalline framework, PCN-222, the sensitive optical response properties of the soluble porphyrin-derivative molecular species can be realized in an easily accessible and stable, solid-state single-phase bulk material and without the formation of aggregates.<sup>3a, 3f</sup> Additionally, we have shown that the material has the advantage of full reversibility and reusability that outperforms its molecular analogues and is highly suitable to act as both a luminescent as well as colorimetric solid-state sensor for the low pH values covering a relatively wide pH range.

## Notes and references

Special thanks to Dr. Debasis Banerjee, Dr. Sujing Wang, and Zhichao Hu for their comments and suggestions, and to William Lustig and Nathan Rudd for helping to prepare the materials used in this study. We are grateful for the financial support from the Department of Energy, Basic Energy Sciences, Division of Materials Sciences and Engineering (Grant No. DE-FG02-08ER46491).

Department of Chemistry and Chemical Biology, Rutgers University  
610 Taylor Road, Piscataway, New Jersey, 08854, USA.  
E-mail: Jingli@rutgers.edu; Fax: +1 732 445 5312

Electronic Supplementary Information (ESI) available: Experimental details, PCN-222 structural drawings, PXRD data, UV-Vis and PL data for H<sub>2</sub>tcpp are available in the supporting information. See DOI: 10.1039/c000000x/

1. || (a) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chemical Reviews*, 2012, **112**, 673-674. || (b) Z. Hu, B. J. Deibert and J. Li, *Chemical Society Reviews*, 2014. || (c) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angewandte Chemie International Edition*, 2009, **48**, 2334-2338. || (d) S. Pramanik, Z. Hu, X. Zhang, C. Zheng, S. Kelly and J. Li, *Chemistry – A European Journal*, 2013, **19**, 15964-15971. || (e) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chemical Reviews*, 2011, **112**, 724-781. || (f) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *Journal of the American Chemical Society*, 2011, **133**, 4153-4155. || (g) S. M. Cohen, *Chemical Reviews*, 2011, **112**, 970-1000. || (h) J. Liu, D. M. Strachan and P. K. Thallapally, *Chemical communications*, 2014, **50**, 466-468. || (i) Y. He, W. Zhou, R. Krishna and B. Chen, *Chemical communications*, 2012, **48**, 11813-11831. || (j) F. Jeremias, S. K. Henninger and C. Janiak, *Chemical communications*, 2012, **48**, 9708-9710. || (k) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chemical Reviews*, 2011, **112**, 1105-1125. || (l) J.-R. Li, J. Sculley and H.-C. Zhou, *Chemical Reviews*, 2011, **112**, 869-932. || (m) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chemical Society Reviews*, 2014.

- || (n) J.-L. Wang, C. Wang and W. Lin, *ACS Catalysis*, 2012, **2**, 2630-2640. || (o) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chemical Reviews*, 2012, **112**, 836-868. || (p) H. Wang, K. Yao, Z. Zhang, J. Jagiello, Q. Gong, Y. Han and J. Li, *Chemical Science*, 2014, **5**, 620-624. || (q) C. M. Doherty, D. Buso, A. J. Hill, S. Furukawa, S. Kitagawa and P. Falcaro, *Accounts of Chemical Research*, 2013, **47**, 396-405. || (r) L. Pan, H. M. Liu, S. P. Kelly, X. Y. Huang, D. H. Olson and J. Li, *Chemical Communications*, 2003, 854-855. || (s) Y. Zhao, H. Wu, T. J. Emge, Q. Gong, N. Nijem, Y. J. Chabal, L. Kong, D. C. Langreth, H. Liu, H. Zeng and J. Li, *Chemistry-a European Journal*, 2011, **17**, 5101-5109.
2. || (a) C. Wang, Z. Xie, K. E. deKrafft and W. Lin, *Journal of the American Chemical Society*, 2011, **133**, 13445-13454. || (b) A. Corma, H. García and F. X. Llabrés i Xamena, *Chemical Reviews*, 2010, **110**, 4606-4655.
3. || (a) M. Y. Choi, J. A. Pollard, M. A. Webb and J. L. McHale, *Journal of the American Chemical Society*, 2002, **125**, 810-820. || (b) M. Gouterman, G. H. Wagnière and L. C. Snyder, *Journal of Molecular Spectroscopy*, 1963, **11**, 108-127. || (c) K. M. S. Karl M. Kadish, Roger Guillard, ed., *The Porphyrin Handbook: Inorganic, organic and coordination chemistry, Volume 3*, 1 edn., Elsevier, 2000. || (d) R. F. Khairutdinov and N. Serpone, *The Journal of Physical Chemistry B*, 1999, **103**, 761-769. || (e) M. K. Panda, K. Ladomenou and A. G. Coutsolelos, *Coordination Chemistry Reviews*, 2012, **256**, 2601-2627. || (f) S. Thyagarajan, T. Leiding, S. P. Årsköld, A. V. Cheprakov and S. A. Vinogradov, *Inorganic Chemistry*, 2010, **49**, 9909-9920. || (g) T. Vangberg and A. Ghosh, *Journal of the American Chemical Society*, 1998, **120**, 6227-6230. || (h) *The Porphyrin Handbook Volume 6, Applications: Past, Present, Future*, Academic Press, 2000. || (i) S. Y. Ma, Z. H. Li and R. Z. Liu, *Journal of Molecular Structure: THEOCHEM*, 2000, **528**, 121-131. || (j) P. Štěpánek, V. Andrushchenko, K. Ruud and P. Bouř, *The Journal of Physical Chemistry A*, 2011, **116**, 778-783.
4. || (a) O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *Journal of the American Chemical Society*, 2011, **133**, 5652-5655. || (b) A. Fateeva, P. A. Chater, C. P. Ireland, A. A. Tahir, Y. Z. Khimyak, P. V. Wiper, J. R. Darwent and M. J. Rosseinsky, *Angewandte Chemie*, 2012, **51**, 7440-7444. || (c) D. Feng, W. C. Chung, Z. Wei, Z. Y. Gu, H. L. Jiang, Y. P. Chen, D. J. Darensbourg and H. C. Zhou, *Journal of the American Chemical Society*, 2013, **135**, 17105-17110. || (d) D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angewandte Chemie*, 2012, **51**, 10307-10310. || (e) H. L. Jiang, D. Feng, K. Wang, Z. Y. Gu, Z. Wei, Y. P. Chen and H. C. Zhou, *Journal of the American Chemical Society*, 2013, **135**, 13934-13938. || (f) C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *Journal of the American Chemical Society*, 2011, **133**, 15858-15861. || (g) C. Zou, M.-H. Xie, G.-Q. Kong and C.-D. Wu, *CrystEngComm*, 2012, **14**, 4850.