A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
GDCh
International Edition
www.angewandte.org

Title: Functionalization of Zr-based Metal-Organic Layers with Tailored Pore-Environments for Heterogeneous Catalysis

Authors: Junsheng Qin, Guan-Yu Qiao, Shuai Yuan, Jiandong Pang, Heng Rao, Christina T. Lollar, Dongbin Dang, Hong-Cai Zhou, and Jihong Yu

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202007781

Link to VoR: https://doi.org/10.1002/anie.202007781

WILEY-VCH

Functionalization of Zr-based Metal-Organic Layers with Tailored Pore-Environments for Heterogeneous Catalysis

Guan-Yu Qiao,[a] Shuai Yuan,[b] Jiandong Pang,[b] Heng Rao,[a,c] Christina T. Lollar,[b] Dongbin Dang,[b] Jun-Sheng Qin,*[a,c] Hong-Cai Zhou,*[b,d] and Jihong Yu*[a,c]

Dedication ((optional))

---

[a] G.-Y. Qiao, Dr. H. Rao, Prof. Dr. J.-S. Qin, Prof. Dr. J. Yu
State Key Laboratory of Inorganic Synthesis and Preparative Chemistry
College of Chemistry
Jilin University
Changchun 130012 (China)
E-mail: qin@jlu.edu.cn, jihong@jlu.edu.cn
[b] Dr. S. Yuan, Dr. J. Pang, C. T. Lollar, Prof. Dr. D. Dang, Prof. Dr. H.-C. Zhou
Department of Chemistry
Texas A&M University
College Station, Texas 77843-3255 (USA)
E-mail: zhou@chem.tamu.edu
[c] Dr. H. Rao, Prof. Dr. J.-S. Qin, Prof. Dr. J. Yu
International Center of Future Science
Jilin University
Changchun 130012 (China)
[d] Prof. Dr. H.-C. Zhou
Department of Materials Science and Engineering
Texas A&M University
College Station, Texas 77843-3003 (USA)

Supporting information for this article is given via a link at the end of the document.

Abstract: Intriguing properties and functions are expected to implant into metal-organic layers (MOLs) to achieve tailored pore environments and multiple functionalities owing to the synergies among multiple components. Herein, we demonstrated a facile one-pot synthetic strategy to incorporate multi-functionalities into stable zirconium MOLs via secondary ligand pillaring. Through the combination of Zr_6–BTB (BTB = benzene-1,3,5-tribenzoate) layers and diverse secondary ligands (including ditopic and tetratopic linkers), 31 MOFs with multi-functionalities were systematically prepared. Notably, a metal-phthalocyanine fragment was successfully incorporated into this Zr-MOL system, giving rise to an ideal platform for the selective oxidation of anthracene. We demonstrate that the organic functionalization of two-dimensional MOLs can generate tunable porous structures and environments, which may facilitate the excellent catalytic performance of as-synthesized materials.

As most industrial catalysts are heterogeneous, it is highly desired to anchor molecular catalysts onto porous solid supports that are suitable for industrial processes. Metal–organic frameworks (MOFs),[1] also known as porous coordination polymers (PCPs), possess tunable porosities and designable functionalities that make them promising candidates for a variety of applications such as gas adsorption and separation, sensing, and catalysis.[2] Metal–organic layers (MOLs),[3] monolayer versions of two-dimensional (2D) MOFs, intrinsically boast similar advantages to MOFs and represent an emerging class of tunable and functionalizable 2D materials.[4] According to the functional requirement, the secondary ligand can be introduced into MOLs, which not only tune the hydrophobic properties of the of MOL surface to create special in-layer microenvironments,[5] but also alter the photophysical properties of parent materials.[6] In this sense, intriguing properties and functions are expected to implant into MOLs to achieve tailored pore environments and multiple functionalities via introducing desired secondary pillaring ligands.

Phthalocyanine derivatives that have a similar structure to porphyrins are widely used as pigments and dyes owing to the presence of a large aromatic ring system consisting of 18 π-electrons.[7] Due to the substantially delocalized electronic structure, phthalocyanines possess unique optical, physical, and chemical features, making them prospects in many fields including catalysis and solar cells.[8] However, phthalocyanine derivatives suffer from poor solubility in most solvents,[9] and thus the preparation of phthalocyanine-based materials is severely restricted. Although water-soluble phthalocyanine derivatives were explored as homogeneous catalysts over the last few years, the synthesis of phthalocyanine-based heterogeneous catalysts is still rarely reported. Therefore, it remains a difficult challenge to introduce phthalocyanine fragments into porous supports for the preparation of heterogeneous catalysts in synthetic chemistry and materials science.

Traditional zirconium phosphates as a subset of layered materials represent a kind of versatile substrate for functionalization with a variety of organic substituents.[10] As an extension of this type of material, $Zr_6O_4(OH)_4(COO)_{12}$ (Zr_6) units have been chosen as the ideal metal clusters for the preparation of MOL platform because of their exceptional stability and the tendency to form stable coordination bonds with carboxylates from 6 to 12 connectivities.[11] In a previous work, the Zr_6–BTB (benzene-1,3,5-tribenzoate) layer with a (3,6)-connected **kgd**

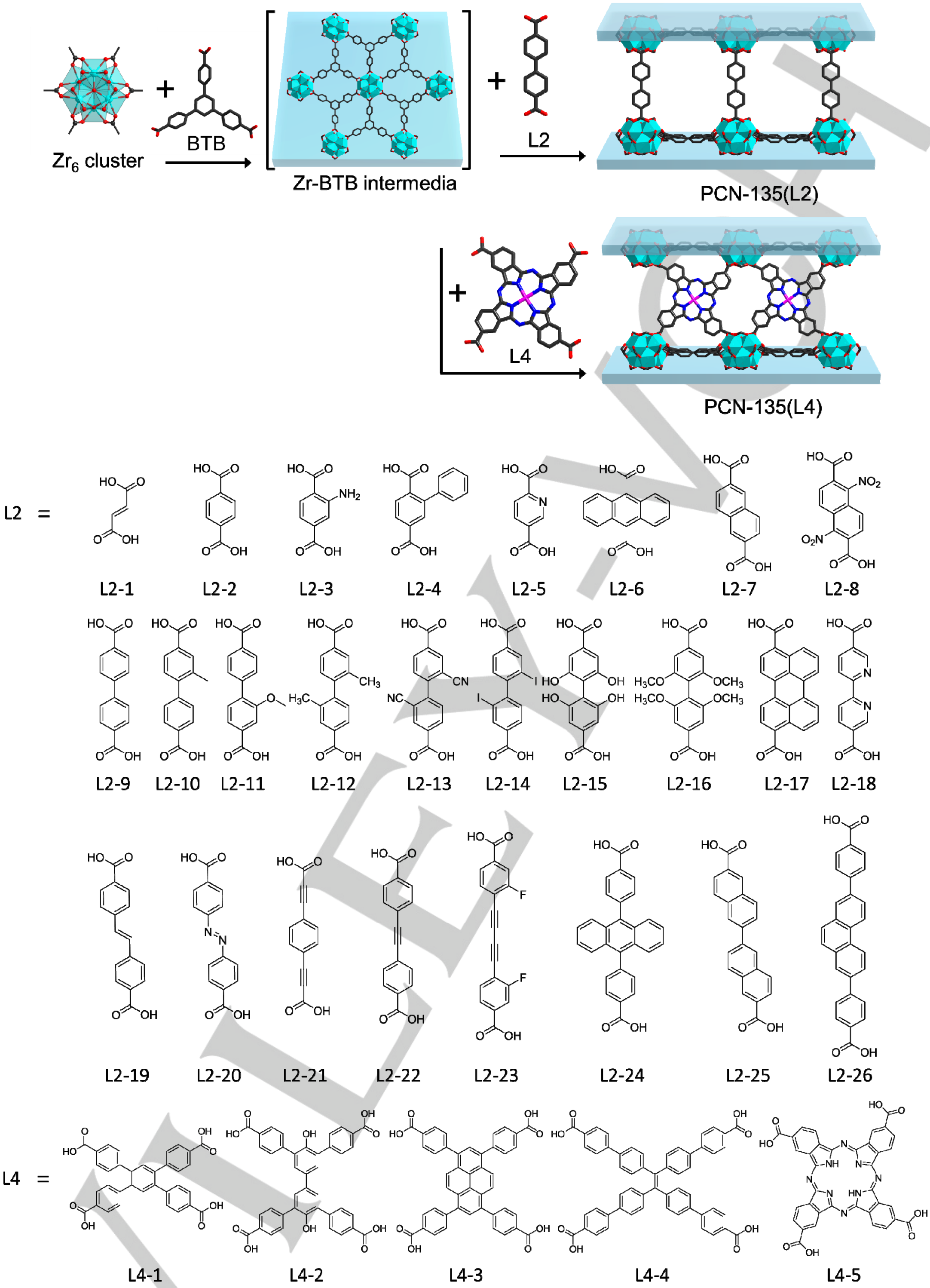


Figure 1. The schematic synthesis procedure of the **PCN-135** family: Zr_6–BTB layer as the precursor and a series of ligands (including linear linkers (with or without functional groups) and tetratopic ligands (with square geometries)) as the secondary pillaring ligands.

topology was constructed,[12] in which six pairs of terminal $-OH^-/H_2O$ ligands on the Zr_6 cluster were left above and below the layer, poised for carboxylate linkers. Furthermore, the Zr_6−BTB layer can be extended into a 3D network using bent ditopic or tetratopic linkers, which act as pillars to support the layers.[13] Besides this, Zr_6−BTB layers boast the following advantages compared with inorganic zirconium phosphate layers: (i) They are easily and reliably prepared with a high degree of crystallinity. (ii) They are insoluble in water and common organic solvents, demonstrate strong tolerances toward acidity and certain alkalinity, possess high thermal stability and mechanical strength, and benefit from high chemical stability. Layered structures can be maintained after secondary linkers are introduced into the layer. (iii) They have large specific surface areas and, can act as strong solid acids with large surface charge densities. The terminal $-OH^-/H_2O$ ligands capped on the coordinatively unsaturated sites of the Zr_6 clusters can be substituted by diverse carboxylate ligands with different functional groups via an acid−base reaction.[14] In this context, these features make MOLs promising candidates to implement our strategy of incorporating multi-functionalities into stable MOFs.

In this work, 31 MOFs (PCN-135 series, Figure 1) with multiple functionalities were constructed through the combinations of Zr_6−BTB layers and various carboxylate ligands (including ditopic and tetratopic linkers). This approach utilized 2D MOLs with coordinatively unsaturated Zr_6 clusters as precursors followed by pillaring with linear linkers (with or without functional groups) or tetratopic ligands (with square geometries) onto the Zr_6 clusters by replacing the terminal $-OH/H_2O$ with carboxylate groups. Experimentally, solvothermal reactions of $ZrCl_4$, H_3BTB, the secondary ligands, and benzoic acid (BA) in *N*,*N*'-dimethylformamide (DMF) yielded crystalline powders of the PCN-135 series (Supporting Information, Section S2). The secondary ligands include ditopic and tetratopic carboxylate linkers, noted as Lm-n (m = 2 and 4, corresponding to the number of carboxylate ends, and n = index number to identify each linker). Figure 1 describes the typical synthesis procedure of the PCN-135 family, in which Zr_6−BTB layers are utilized as the precursor and a series of ligands (including linear linkers (with or without functional groups) and tetratopic ligands (with square geometries)) are used as the pillars. Zr-BTB layers are preferred as the MOL to be functionalized because of their high stability and unique structure.[12b] Furthermore, PCN-135(Co-TCPc) (TCPc = 2,9,16,23-tetracarboxyphthalocyanine, also noted as L4-5 in this work) was used as a highly active and reusable solid heterogeneous catalyst for the selective oxidation of anthracene under visible light owing to its excellent optical properties and stability. In particular, the inclusion of cobalt-containing phthalocyanine fragments in MOFs would be greatly benefitted from the MOFs' ability to prevent aggregation and leaching. Our findings are expected to open a new avenue for achieving high efficiency catalysis through the successful introduction of phthalocyanine fragments.

To the best of our knowledge, one major advantage of MOFs is the synthetic versatility derived from the rational design of diverse ligands compared with other conventional porous materials. With this in mind, we intend to incorporate a broad scope of functionalities into the MOF through judicious selection of linkers with BPDC moieties (BPDC = 4,4'-biphenyldicarboxylate, see Figure 1, from L2-9 to L2-18). BPDC modified with methyl groups, methoxyl groups, cyano groups, hydroxy groups and iodine substituents were selected, as well as relevant fragments like perylene and 2,2'-bipyridine. MOFs with these functional groups can be easily modified with further functionalization. In addition, PCN-135 series with BDC fragment (BDC = benzene dicarboxylate, from L2-2 to L2-6), and NDC (NDC = naphthalene dicarboxylate, L2-7 and L2-8) were also constructed. These results offer a convenient mean to modulate the pore microenvironments and pore volume of MOFs. These results suggest that our approach is promising to introduce desired functionality into stable MOFs by one-pot synthesis, which can in turn extensively promote the potential applications of MOFs.

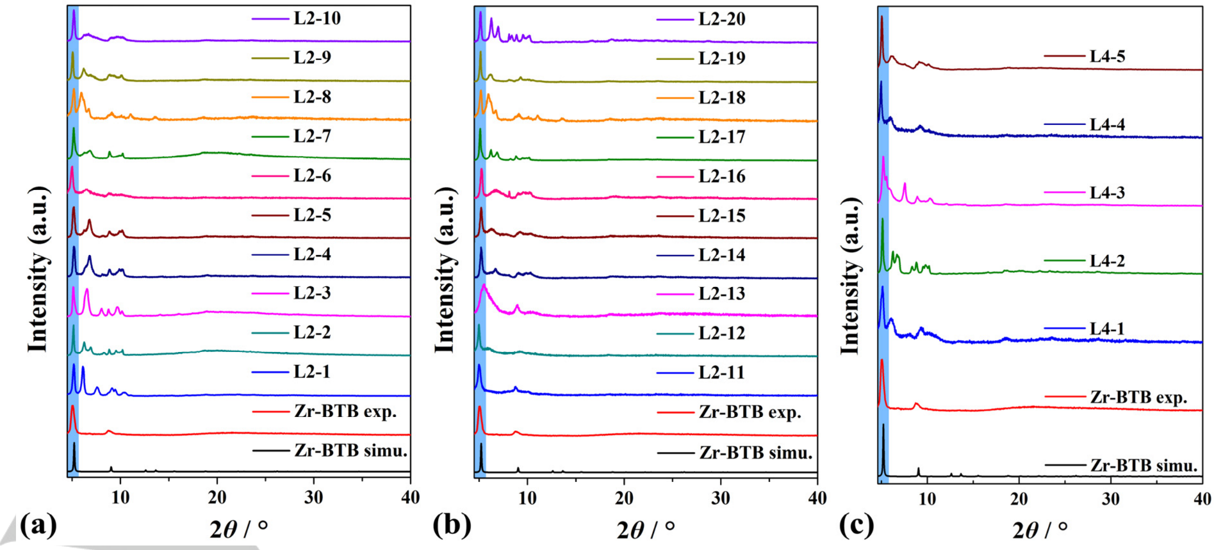


Figure 2. The PXRD patterns of the **PCN-135** family compared with the experimental and simulated XRD patterns of Zr-BTB. The characteristic peaks of Zr-BTB layer structure and **PCN-135** series are highlighted in blue.

The powder X-ray diffraction (PXRD) patterns of the PCN-135 series all possess the characteristic peak of Zr_6-BTB layer structure at 2θ = ~5° (Figure 2 and S1). The crystallinity of as-synthesized MOFs is well maintained after the organic functionalization, taking advantage of the acid stability of high valence metal-based MOLs and their strong tolerance towards defects.[13] Small shifts in the PXRD patterns can be observed, which could be assigned to a change in the interlayer distance. In addition, their crystalline structures were also confirmed by scanning electron microscopy (SEM). As shown in Figure S2, PCN-135(Co-TCPc) exhibits a similar lamellar structure with Zr-BTB after the introduction of phthalocyanine fragments. The corresponding elemental mapping analysis obtained from energy dispersive X-ray spectroscopy (EDS) provides a homogeneous distribution of all the elements (especially Zr and N) over the entire structure of PCN-135(Co-TCPc) (Figure S3), implying the integration of phthalocyanine into the framework. These results suggested that the phases of the as-synthesized Zr-MOF materials are uniform. Furthermore, ^1H NMR analyses were carried out to quantify the amounts of the secondary ligands in the as-synthesized materials (Supporting Information, Section S5). ^1H NMR spectra of the digested products clearly show the resonance signals of the secondary ligands (Figures S4 – S34). The linkers ratios of BTB:Lm-n are listed in Table S1.

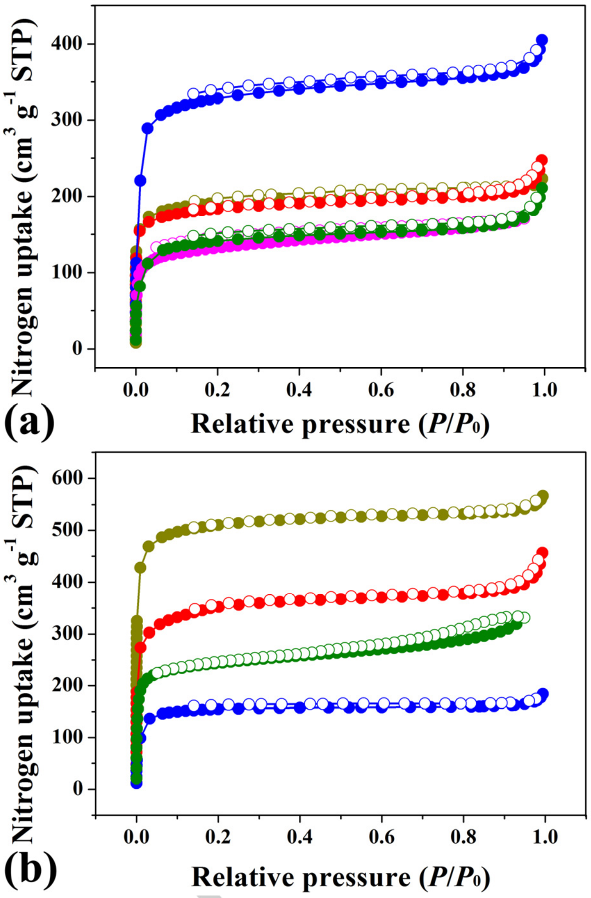
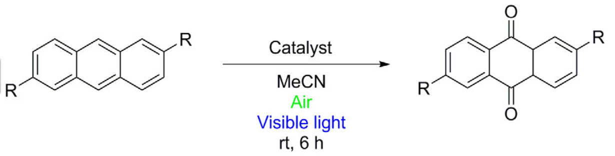


Figure 3. (a) The nitrogen isotherms of select **PCN-135(L2-n)**-type MOFs (dark yellow, L2-1; red, L2-2; blue, L2-9; magenta, L2-17; and olive, L2-22). (b) The nitrogen isotherms of select **PCN-135(L4-n)**-type MOFs (dark yellow, L4-2; red, L4-3; blue, L4-4; and olive, L4-5). Solid circle, adsorption; and open circle, desorption.

In order to evaluate the porosity and the architectural stability of the PCN-135 series, nitrogen gas adsorption measurements at 77 K were carried out. Before gas sorption experiment, the as-synthesized samples were washed with DMF and immersed in acetone for 3 d, during which the solvent was decanted and freshly replenished three times. The solvent was removed under vacuum at 100 °C, yielding the porous material. Nitrogen adsorption isotherms were recorded on the activated samples of PCN-135(L2-n, n = 1, 2, 9, 17 and 22 (Figure 3a) and L4-n, n = 2, 3, 4 and 5 (Figure 3b)). All the profiles of these isotherms reveal reversible type I behavior ($P/P_0 < 0.9$) that is typical for microporous materials.[15] The plateau occurs at relatively low pressure and shows no significantly accompanied hysteresis. In addition, a prompt capillary condensation resulted from meso- or macropores at relative high pressure ($P/P_0 > 0.9$) is observed, which can be ascribed to dense packing of surface-bound MOF crystals.[16]

In general, the UV–Vis signals of metal phthalocyanines mainly derive from π → π* transitions of the strong Q-band (600 – 750 nm) and the broad B-band (300 – 450 nm) with weaker transitions near those bands.[17] Correspondingly, PCN-135(Co-TCPc) exhibits specific Q-band absorption at λ_{max} = 687 nm and B-band absorption at λ_{max} = 293 nm (Figure S35), which is similar to the absorption behavior of the central phthalocyanine aromatic ring of TCPc. On the basis of the above characterizations and analyses, the stable Zr-MOL functionalized by phthalocyanine fragments has been successfully obtained, while maintaining the crystalline structure, morphology, and chemical stability of the Zr-BTB layer, as well as the photoresponsivity of the phthalocyanine moiety. Our work highlights new opportunity in utilizing MOLs as highly tunable 2D materials for the synthesis of stable multi-functional MOFs.

Table 1: Heterogeneous catalytic oxidation of anthracene to anthraquinone.[a]



Entry	R	Catalyst	Yield [%][b]
1	H	PCN-135(Co-TCPc)	95
2	Me	PCN-135(Co-TCPc)	92
3	H	PCN-135(Co-TCPc)[c]	92
4	H	PCN-135(Co-TCPc)[d]	NR[e]
5	H	PCN-135(Co-TCPc)[f]	NR
6	H	Co-TCPc	60
7	H	Co-TCPc[g]	26
8	H	—[h]	NR

[a] Reaction conditions: anthracene (1 mmol), catalyst (0.001 mmol), MeCN (10 mL), room temperature, visible light (300 W xenon lamp), 6 h, air. [b] Yield was determined by ^1H NMR spectroscopy. [c] After three catalytic cycles. [d] Without visible light. [e] No reaction. [f] 100 °C without visible light. [g] After three catalytic cycles. [h] No catalyst.

As is known, metal phthalocyanine complexes are structurally related to metal porphyrin complexes, which are widely used by nature in the active sites of enzymes responsible for catalytic aerobic oxidation, reduction and transport of dioxygen and the destruction of peroxides. Although phthalocyanine is a completely synthetic compound, its properties in the chemical and biological fields are most similar to those of porphyrin. The structure of phthalocyanine has a strong π-π accumulation effect, so it is difficult to introduce metal phthalocyanine into MOFs by conventional means. In our work, we used Zr-BTB as the 2D MOL and Co-TCPc (Co-TCPc = tetracarboxyphthalocyaninato cobalt(II)) as an auxiliary linker to achieve a stable TCPc-based MOF material, namely PCN-135(Co-TCPc). With Zr-BTB layer as the support, the agglomeration and loss of Co-TCPc in the catalytic system would be minimized. In this context, to evaluate the catalytic performance of PCN-135(Co-TCPc), we selected anthracene as a model compound for anthraquinone conversion, in which only air was required as an oxidizing agent. The general strategy for the catalytic reaction is to use anthracene as the reaction substrate, air as the oxidant, and acetonitrile as the solvent at room temperature under visible light (Table 1). It was found that the PCN-135(Co-TCPc) exhibited a high anthraquinone yield of 95% (Table 1, Entry 1). When the reaction substrate was replaced with 2,6-dimethylanthracene, the methyl group was retained without being oxidized (Table 1, Entry 2), suggesting the highly selective catalytic oxidation activity. Additionally, a series of control experiments were also performed under the given conditions, for instance, without visible light at room temperature or at 100 ºC in the dark (Table 1, Entries 4 and 5). The results suggest that visible light illumination is a key factor for this catalytic system. Meanwhile, the control experiment without the addition of PCN-135(Co-TCPc) was also carried out, and the oxidation reaction of anthracene was not observed to occur (Table 1, Entry 8). By using Co-TCPc as the catalyst under similar conditions, only about 60% of anthraquinone yield was obtained after the first run, and the catalytic performance decreased significantly after three cycles (Table 1, Entries 6 and 7). When Co-TCPc is inserted into the layered Zr-MOL as an auxiliary linker, the ordering of the phthalocyanine ligand is likely enhanced and the packing effect is eliminated, meaning the light energy of the phthalocyanine structure can be fully utilized. Moreover, the structure becomes more stable and is less susceptible to damage during the catalytic process. Compared to the traditional synthesis of anthraquinone, highly toxic oxidants, high pressure oxygen, and high temperature are unnecessary, establishing a green and efficient synthesis strategy. Therefore, we have developed a truly heterogeneous high-efficiency catalytic oxidation system using PCN-135(Co-TCPc) as a catalyst. Our synthetic strategy provides a facile route to introduce desired functionality into stable MOFs with potential for a wide variety of applications.

Furthermore, the cycling performance of PCN-135(Co-TCPc) was investigated to examine its photocatalytic durability. After three continuous catalytic cycles, the yield can still exceed 90%, demonstrating the good recyclability of PCN-135(Co-TCPc) as a catalyst (Table 1, Entry 3). The PXRD pattern, Infrared and thermogravimetric analysis of the tested sample was further recorded after the photocatalytic reactions, and indicated that no framework collapse or phase transition occurred during the experiment and the structure of PCN-135(Co-TCPc) was maintained after cycling (Figures S36 – S38).

As for the reactive oxygen species (ROS) trapping tests, two individual electron paramagnetic resonance (EPR) spectroscopy experiments were employed. Firstly, a 50 µL suspension as described in Entry 1 (Table 1) was mixed with 500 µL of 2,2,6,6-tetramethylpiperidine (TEMP, 50 mM) solution, which could identify the formation of singlet oxygen ($^1O_2$) and superoxide ion ($O_2^{\cdot-}$). Then, the mixture was monitored using a Bruker EMX plus model spectrometer operating at the X-band frequency (9.4 GHz) at room temperature after being illuminated for 2 min. Secondly, similar procedures were performed except with utilization of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as the spin-trapping agent, which could identify the formation of hydroxyl radical (·OH). The EPR-trapping results show that the standard capture signal appears under visible light illumination when using TEMP as a capture agent (Figure S39a, $g = 2.0092$), verifying the generation of the nitroxide radical adduct, which proves the formation of $^1O_2$ or $O_2^{\cdot-}$.[18] As described in Figure S39b, no obvious EPR signals are detected under similar conditions in the presence of DMPO, proving the absence of ·OH in the system. Therefore, we speculated that the reaction mechanism could be that the phthalocyanine ligand captures oxygen in the air to form singlet oxygen or superoxide ion under visible light irradiation, which in turn causes the metal Co(II) center to become a high valence oxide, there-by oxidizing anthracene to anthraquinone.

In conclusion, we developed a facile one-pot synthetic strategy to incorporate multi-functionalities into MOLs via secondary ligand pillaring to form stable Zr-MOFs. Through the combination of Zr_6−BTB layer and diverse secondary ligands, 31 MOFs with multi-functionalities were obtained. Significantly, metal-phthalocyanine ligands were successfully incorporated into this Zr-MOL system as a heterogeneous catalyst for the selective oxidation of anthracene. This work not only provides a strategy for the design of heterogeneous catalysts that immobilized phthalocyanine fragments, but also opens the door to a new class of 2D coordination materials with molecular functionalities. We expect our strategy to offer a facile route to introduce multi-functionalities into stable Zr-MOFs for an extensive variety of potential applications in the near future.

Acknowledgements

The authors acknowledge the financial supports from the National Natural Science Foundation of China (Grant No. 21901084 and 21621001) and the 111 Project (Grant No. B17020). This work was also supported by the Robert A. Welch Foundation through a Welch Endowed Chair to H.-C.Z. (A-0030).

Keywords: metal-organic layers • zirconium • pore environments • heterogeneous catalysis

[1] a) S. Kitagawa, *Acc. Chem. Res.* **2017**, *50*, 514-516; b) C. S. Diercks, M. J. Kalmutzki, N. J. Diercks, O. M. Yaghi, *ACS Cent. Sci.* **2018**, *4*, 1457-1464; c) M. J. Kalmutzki, N. Hanikel, O. M. Yaghi, *Sci. Adv.* **2018**, *4*, eaat9180.

[2] a) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae, J. R. Long, *Chem. Rev.* **2012**, *112*, 724-781; b) Y. B. He, W. Zhou, G. D. Qian, B. L. Chen, *Chem. Soc. Rev.* **2014**, *43*, 5657-5678; c) Z. C. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, *43*, 5815-5840; d) J. W. Liu, L. F. Chen, H. Cui, J. Y. Zhang, L. Zhang, C. Y. Su, *Chem. Soc. Rev.* **2014**, *43*, 6011-6061; e) J. S. Qin, S. Yuan, Q. Wang, A. Alsalme, H. C. Zhou, *J. Mater. Chem. A* **2017**, *5*, 4280-4291; f) C. Gu, N. Hosono, J.-J. Zheng, Y. Sato, S. Kusaka, S. Sakaki, S. Kitagawa, *Science* **2019**, *363*, 387-391.

[3] a) M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu, H. Xu, Y. Zhao, H. Zhang, *Adv. Mater.* **2015**, *27*, 7372-7378; b) G. Lan, Z. Li, S. S. Veroneau, Y. Y. Zhu, Z. Xu, C. Wang, W. Lin, *J. Am. Chem. Soc.* **2018**, *140*, 12369-12373.

[4] a) A. Dhakshinamoorthy, A. M. Asiri, H. Garcia, *Adv. Mater.* **2019**, *31*, 1900617; b) J. Duan, Y. Li, Y. Pan, N. Behera, W. Jin, *Coord. Chem. Rev.* **2019**, *395*, 25-45; c) C. Yang, H.-F. Wang, Q. Xu, *Chem. Res. Chin. Univ.* **2020**, *36*, 10-23; d) J. Wen, Y. Li, J. Gao, *Chem. Res. Chin. Univ.* **2020**, doi: 10.1007/s40242-020-0163-6.

[5] W. Shi, L. Cao, H. Zhang, X. Zhou, B. An, Z. Lin, R. Dai, J. Li, C. Wang, W. Lin, *Angew. Chem. Int. Ed.* **2017**, *56*, 9704-9709.

[6] L. Cao, Z. Lin, F. Peng, W. Wang, R. Huang, C. Wang, J. Yan, J. Liang, Z. Zhang, T. Zhang, L. Long, J. Sun, W. Lin, *Angew. Chem. Int. Ed.* **2016**, *55*, 4962-4966.

[7] J. Mack, M. J. Stillman, *The Porphyrin Handbook* **2003**, *16*.

[8] a) A. B. Sorokin, *Chem. Rev.* **2013**, *113*, 8152-8191; b) M. Urbani, M.-E. Ragoussi, M. K. Nazeeruddin, T. Torres, *Coord. Chem. Rev.* **2019**, *381*, 1-64; c) M. Urbani, G. de la Torre, M. K. Nazeeruddin, T. Torres, *Chem. Soc. Rev.* **2019**, *48*, 2738-2766.

[9] F. Dumoulin, M. Durmuş, V. Ahsen, T. Nyokong, *Coord. Chem. Rev.* **2010**, *254*, 2792-2847.

[10] M. Pica, A. Donnadio, M. Casciola, *Coord. Chem. Rev.* **2018**, *374*, 218-235.

[11] a) Y. Bai, Y. B. Dou, L. H. Xie, W. Rutledge, J. R. Li, H. C. Zhou, *Chem. Soc. Rev.* **2016**, *45*, 2327-2367; b) S. Yuan, J. S. Qin, C. T. Lollar, H. C. Zhou, *ACS Cent. Sci.* **2018**, *4*, 440-450.

[12] a) R. Wang, Z. Wang, Y. Xu, F. Dai, L. Zhang, D. Sun, *Inorg. Chem.* **2014**, *53*, 7086-7088; b) J. Ma, A. G. Wong-Foy, A. J. Matzger, *Inorg. Chem.* **2015**, *54*, 4591-4593.

[13] S. Yuan, J. S. Qin, L. F. Zou, Y. P. Chen, X. Wang, Q. Zhang, H. C. Zhou, *J. Am. Chem. Soc.* **2016**, *138*, 6636-6642.

[14] a) S. Yuan, Y. P. Chen, J. S. Qin, W. G. Lu, L. F. Zou, Q. Zhang, X. Wang, X. Sun, H. C. Zhou, *J. Am. Chem. Soc.* **2016**, *138*, 8912-8919; b) S. Yuan, J. S. Qin, J. Li, L. Huang, L. Feng, Y. Fang, C. Lollar, J. Pang, L. Zhang, D. Sun, A. Alsalme, T. Cagin, H. C. Zhou, *Nat. Commun.* **2018**, *9*, 808; c) S. Yuan, J. S. Qin, J. Su, B. Li, J. Li, W. Chen, H. F. Drake, P. Zhang, D. Yuan, J. Zuo, H. C. Zhou, *Angew. Chem. Int. Ed.* **2018**, *57*, 12578-12583.

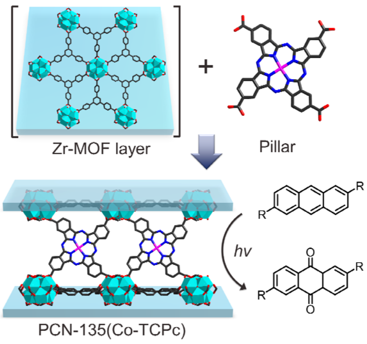
[15] J. S. Qin, D. Y. Du, W. L. Li, J. P. Zhang, S. L. Li, Z. M. Su, X. L. Wang, Q. Xu, K. Z. Shao, Y. Q. Lan, *Chem. Sci.* **2012**, *3*, 2114-2118.

[16] a) M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature* **2009**, *461*, 246-249; b) D. T. Lee, J. D. Jamir, G. W. Peterson, G. N. Parsons, *Small* **2019**, *15*, e1805133.

[17] F. Ghani, J. Kristen, H. Riegler, *J. Chem. Eng. Data* **2012**, *57*, 439-449.

[18] a) H. Wang, S. Jiang, W. Shao, X. Zhang, S. Chen, X. Sun, Q. Zhang, Y. Luo, Y. Xie, *J. Am. Chem. Soc.* **2018**, *140*, 3474-3480; b) Z. Wang, W. Ma, C. Chen, H. Ji, J. Zhao, *Chem. Eng. J.* **2011**, *170*, 353-362.

Entry for the Table of Contents



A facile one-pot synthetic strategy was explored to incorporate multi-functionalities into stable zirconium metal-organic layers (MOLs) through the functionalization of Zr_6–BTB (BTB = benzene-1,3,5-tribenzoate) layers via secondary ligand pillaring. Significantly, a metal-phthalocyanine fragment was successfully incorporated into this Zr-MOL system, giving rise to an ideal platform for the selective oxidation of anthracene.