

A Robust Metal-Metalloporphyrin Framework Based upon a Secondary Building Unit of Infinite Nickel Oxide Chain

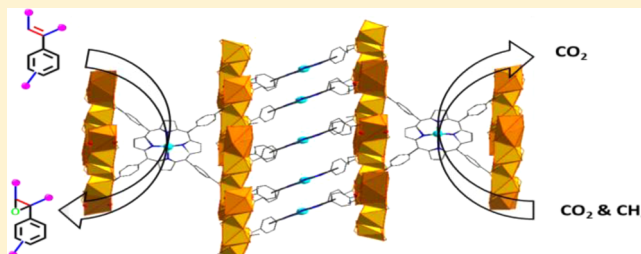
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S Supporting Information

ABSTRACT: Herein we report the construction of a robust metal-metalloporphyrin framework that is based upon a rare secondary building unit of infinite nickel oxide chain. The constructed MMPF-20 exhibits permanent porosity and selective adsorption of CO₂ over CH₄ as well as demonstrates interesting catalytic performances in the context of olefin epoxidation.



INTRODUCTION

As a subclass of metal organic frameworks (MOFs),^{1,2} metal-metalloporphyrin frameworks (MMPFs)^{3–11} have been attracting an escalating interest due to their potential applications for gas adsorption/separation,^{12–19} catalysis,^{20–33} light-harvesting,^{34–39} etc. Despite their premature stage, some challenge in the development of MMPFs as functional materials for the aforementioned applications has been recognized to be the preservation of structural integrity and permanent porosity after removal of the guest solvent molecules.^{40–43} The combined use of custom-designed multitopic porphyrin ligand and a robust secondary building unit (SBU) represents an effective approach to stabilize the MMPF structure and preserve its permanent porosity. The employment of discrete multinuclear trivalent (e.g., Al³⁺, Fe³⁺)^{44–46} or quadrivalent (e.g., Ti⁴⁺, Zr⁴⁺ and Hf⁴⁺)^{47–54} metal clusters as SBUs has afforded a series of robust and permanently porous MMPFs. Nonetheless, most MMPFs based on divalent metal ions are very fragile upon removal of guest solvent molecules.

It has been reported that MOFs with infinite metal oxide chains as SBUs can usually preserve their permanent porosities upon the removal of guest solvent molecules as well exemplified in the MOF-74 series.^{55,56} It can be envisioned that the robustness of divalent metal ion-based MMPFs will be boosted if such kinds of infinite metal oxide chain SBUs can be incorporated into their framework structures. In this contribution, we report the first MMPF based upon a SBU of infinite nickel oxide chain as illustrated in the construction of MMPF-20 which exhibits permanent porosity and selective adsorption of CO₂ over CH₄ as well as interesting catalytic performances in the context of olefin epoxidation.

RESULTS AND DISCUSSION

Crystals of MMPF-20 were formed via solvothermal reactions of the 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (H₂TCPP) ligand and NiCl₂·6H₂O in dimethylformamide (DMF) at 150 °C. The product was isolated as rod-shaped purple crystals (Figure S1) of Ni₃(Ni-TCPP)₂·1.4DMF·9H₂O at 46% yield. The overall formula was determined by X-ray crystallography, elemental analysis, and thermogravimetric analysis (TGA).

Single-crystal X-ray analysis reveals that MMPF-20 crystallizes in the space group C_{2/c} and the asymmetric unit consists of two Ni(II) ions and one Ni-TCPP ligands, which are metalated in situ (Figure 1a). Ni1 is six-coordinated by six oxygen atoms with a distorted octahedral geometry, of which two are from two bidentate bridging μ_2 - $\eta^1\eta^1$ carboxylate groups and four are from two tridentate bridging μ_2 - $\eta^2\eta^1$ carboxylate groups; Ni₂ is four-coordinated by four oxygen atoms from four different carboxylate groups with a tetrahedral geometry (Figure 1b). The binuclear Ni motifs are interconnected through the carboxylate bridges to form a rare infinite one-dimensional (1D) nanosized ribbon chain as an SBU. Alternatively, each TCPP ligand coordinates with eight Ni atoms of four neighboring Ni chains to propagate into an overall three-dimensional (3D) framework structure with 1D channels of ~4.6 Å × 12.6 Å (van der Waals radii included) along the *a* axis (Figure 1c,d). The solvent accessible volume of MMPF-20 calculated using PLATON is 38.0%.⁵⁷

The phase purity of MMPF-20 sample was verified by powder X-ray diffraction studies, which indicate that the diffraction patterns of the as-synthesized sample are consistent

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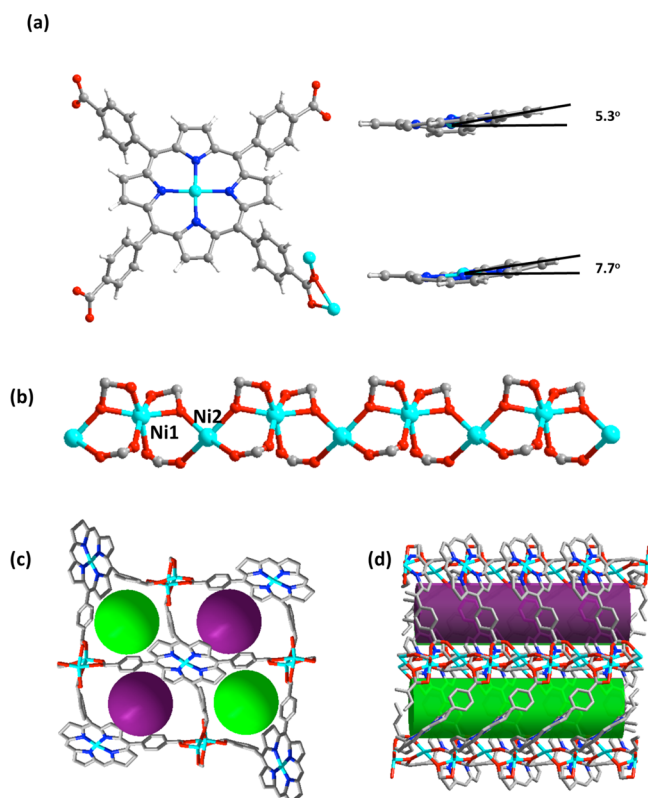


Figure 1. (a) The asymmetric unit and coplanar conformation in MMPF-20. (b) Infinite ribbon chain-shaped metal-carboxylate building unit in MMPF-20, (c) structural features of MMPF-20 along the *a* direction, and (d) the structure of MMPF-20 viewed along the *b* direction. Color scheme: Ni, turquoise; C dark gray; O, red; N, blue; H atoms are omitted for clarity.

with the calculated ones (Figure S2). Thermogravimetric analysis (TGA) studies of the fresh MMPF-20 sample (Figure S3) reveal a weight loss of 12.5% from 25 to 150 °C corresponding to the loss of guest water molecules and DMF molecules trapped in the channels. X-ray photoelectron spectroscopy (XPS) analysis shows a nickel signal at binding energies at 855.4 and 873.0 eV corresponding to peaks of Ni 2p_{3/2} and Ni 2p_{1/2} respectively (Figure S4). A very weak satellite peak at 863.1 eV is also observed in the XPS spectra, indicating the predominant diamagnetic nature for Ni(II) ions present in MMPF-20.^{58,59}

To examine the permanent porosity of MMPF-20, gas adsorption studies were performed on the activated sample. As shown in Figure 2a, the N₂ adsorption isotherm collected at 77 K indicated that MMPF-20 exhibited an uptake capacity of 259 cm³g^{−1} at the saturation pressure with typical type-I sorption behavior, as expected for microporous materials. Derived from the N₂ data, MMPF-20 has a Brunauer–Emmett–Teller (BET) surface area of 517 m²g^{−1} (*P*/*P*₀ = 0.05–0.3), which is confirmed by CO₂ adsorption isotherm at 195 K (Figure S5). Meanwhile, MMPF-20 can also preserve its crystallinity and framework integrity after activation as evidenced by powder X-ray diffraction (PXRD) studies (Figure S2).

We investigated the performances of MMPF-20 in selective adsorption of CO₂ over CH₄. Under 1 atm pressure, MMPF-20 can adsorb 43 cm³g^{−1} at 273 K, whereas its CH₄ uptake capacity is 12 cm³g^{−1} at 273 K under the same pressure (Figure 2b). To predict the adsorption selectivity of CO₂ over CH₄, the ideal adsorption solution theory (IAST),⁶⁰ which has been validated for calculating the adsorption selectivity of gas mixtures in MOFs,⁶¹ was employed by applying single-component adsorption isotherms. From selectivity plots of CO₂/CH₄ (50/50) shown in Figure 3, MMPF-20 is calculated to exhibit an adsorption selectivity of 8 for CO₂ over CH₄ at 273 K and 1 bar, which is comparable to that of other porphyrin-based MOFs.^{26,28,30}

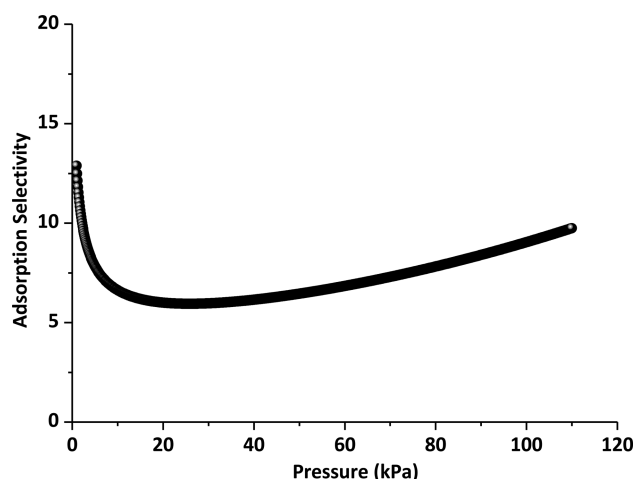


Figure 3. Gas mixture adsorption selectivity are predicted by IAST at 273 K and 100 kPa for MMPF-20.

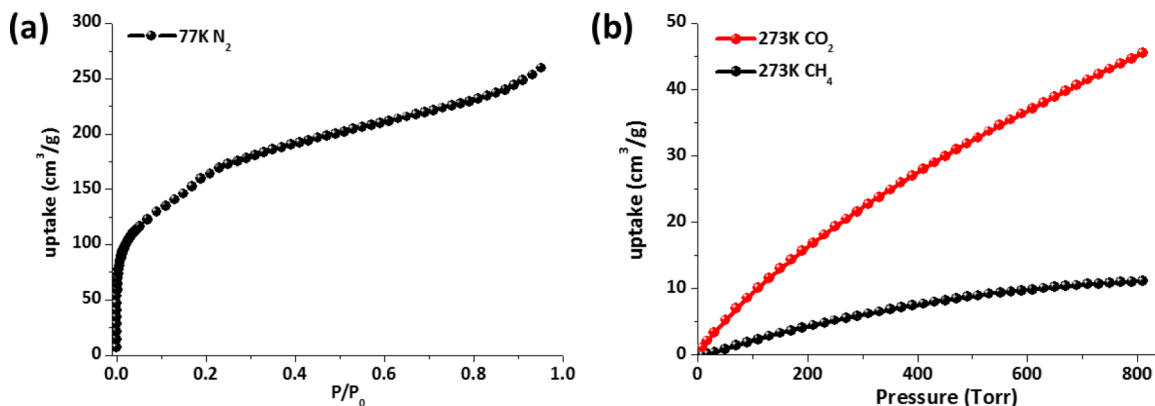
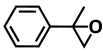
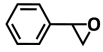
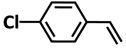
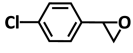
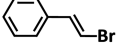
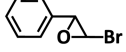
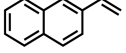
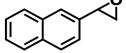
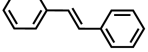
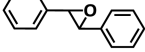
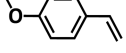
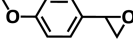
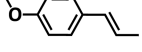
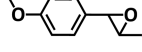


Figure 2. (a) N₂ adsorption isotherms of MMPF-20 at 77 K, (b) CO₂ and CH₄ adsorption at 273 K.

Table 1. Epoxidation of Conjugated Olefins with Different Electron-Donating and Withdrawing Groups Catalyzed by MMPF-20^a

Entry	Substrate	product	Yield (%)	Selectivity (%)
1			66/65 ^[b]	85/85 ^[b]
2			55	58
3			51	50
4			0	-
5			63	60
6			59	68
7			72	92
8			92	>99

^aSubstrate (0.2 mmol), TBHP (0.4 mmol), catalyst (0.002 mmol), acetonitrile (10 mL), and bromobenzene 100 mg as internal standard sealed in a Teflon-lined screwcap vial were stirred at 80 °C. ^bAfter three cycles.

It has been well documented that metalloporphyrins are capable of catalyzing the epoxidation of alkenes.⁶² Considering the rare studies on the electronic effect on transforming conjugated olefins into epoxides, we decided to evaluate the performances of MMPF-20 as heterogeneous catalyst in the context of epoxidation of conjugated olefins with different electron-donating and withdrawing groups on double bond or phenyl ring. Catalytic assays for the epoxidation of isopropenylbenzene were first carried out. As shown in Table 1, MMPF-20 exhibits good catalytic activity in terms of both yield (66%) and selectivity (85%). It is obvious that the methyl group connected to the double bond of styrene can effectively enhance the yield of epoxide, as compared to the substrate styrene (Table 1, entry 2). In contrast, withdrawing groups on the phenyl rings or double bond can reduce the epoxide yield. For instance, a decrease in epoxide yield is observed when the substrate changes to 4-chlorostyrene (Table 1, entry 3); moreover, virtually no product was detected even after 24 h when 2-bromoethenylbenzene with bromine substituent group on double bond was employed as the substrate (Table 1, entry 4). On the other hand, extending the conjugation of substrate molecules can afford higher the epoxide yields (Table 1, entry 5 and 6) given the electron donating effect of phenyl ring. It is worth mentioning the slightly lower yield observed for *trans*-stilbene compared with 2-vinylnaphthalene should be presumably due to the steric hindrance. From the above results, it can be hypothesized that the effect of donating groups around double bond can enhance the epoxide yield to a certain extent, and the position of the donating groups also plays a crucial role

in the overall yield and selectivity. To further verify this hypothesis, we strategically select another two substrates with electron-donating group adjacent to the double bond, such as 4-methoxystyrene and 1-methoxy-4-[(1*E*)-1-propenyl] benzene (Table 1, entry 7 and 8). As expected, the epoxidation turns out to be very effective, with up to distinctly higher yield particularly for the substrate 1-methoxy-4-[(1*E*)-1-propenyl] benzene. This can be tentatively interpreted that a higher electron density on double bond usually increases the nucleophilicity of conjugated olefins toward electrophilic oxygenating intermediates.⁶³

No detectable leaching of active site was observed in the reaction solution for the oxidation of isopropenylbenzene after removal of MMPF-20 by filtration, confirming the heterogeneous nature of the catalyst. Moreover MMPF-20 can retain its structural integrity (Figure S3) and can be reused for three cycles without significant drop in its catalytic activity (Table 1, entry 1). A BET analysis after catalysis showing a slight reduction in Figure S6 demonstrates the robustness of MMPF-20.

CONCLUSION

In summary, we have demonstrated the employment of infinite metal-oxide chain-based SBU for the construction of a robust metal-metalloporphyrin framework as exemplified by MMPF-20 that is based upon the SBU of infinite nickel oxide chain. The robustness of MMPF-20 has been assessed by gas adsorption and PXRD studies, which show that MMPF-20 possesses permanent porosity and retains crystallinity/frame-

work integrity after activation as well as exhibits selective adsorption of CO₂ over CH₄. In addition, the performances of MMPF-20 as heterogeneous catalyst have also been evaluated in the context of epoxidation of conjugated olefins with different electron-donating and withdrawing groups. Our work herein thus provides a new approach to developing robust MMPFs as functional materials for various applications. Ongoing work in our laboratories includes the design of new robust MMPFs for applications in gas separation and catalysis.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.cgd.5b01548](https://doi.org/10.1021/acs.cgd.5b01548). CCDC reference number 1005654 for MMPF-20.

Experimental procedures for powder X-ray diffraction patterns, TGA plots, crystal data of MMPF-20 (PDF)

Accession Codes

CCDC 1005654 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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