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Lei Xu,^a Meng-Ke Zhai,^a Xin-Chao Lu,^a Hong-Bin Du^a*

A indium based metal-porphyrinic framework, denoted as NUPF-3, was prepared based on a new amidodecorated porphyrin ligand. NUPF-3 possesses a rarely seen 4-fold interpenetrated **pts** framework with segmented pores and dense metalloporphyrin central sites. The sturture could remain its crystallinity in common used solvents as well as acidic/alkaline solutions with pH ranging from 1 to 12 for 48 h, exhibiting a high chemical stability. Meanwhile, thermal analysis reveals that NUPF-3 possesses a relative high thermal stability. Owing to the presence of amido groups, structural interpenetration and charged framework, NUPF-3 exhibits relative high CO₂ uptakes. Moreover, NUPF-3 could be used as a good heterogeneous catalyst for cycloaddition of CO₂ and epoxides under relatively mild conditions with good recyclability.

Introduction

As a special branch of metal-organic frameworks (MOFs),¹ metal-porphyrinic frameworks (MPFs) are a resurging subfamily of crystalline porous materials that are composed of (metallo)porphyrin-decorated ligands interconnected by metal ions and/or clusters.² Since the first MPF was constructed from tetra-pyridylporphyrin in 1990s,³ MPFs have attracted evergrowing research interest. Fabricating (metallo)porphyrins into crystalline multidimensional assemblies could not only make their intrinsic characters inherited, but also introduce preferable properties to the resulting MPFs. For example, when MPFs used as heterogeneous catalysts, it could not only make the valuable (metallo)porphyrins recyclable, but also overcome the issues of self-aggregation (deactivation) or poorsolubility that (metallo)porphyrins often suffered from in homogeneous reactions.⁴ Up to date, a number of MPFs have been elaborately fabricated and demonstrated great potential in gas storage/separation,⁵ light-harvesting,⁶ sensing,⁷ photodynamic therapy,⁸ heterogeneous catalysis,⁹ etc. Nonetheless, the developments of MPFs are still in the premature stage and the exploration of novel MPFs and their potential applications are still highly desirable.^{2, 10}

In constructing MPFs, the ones with high structural stability are much desirable since these materials would provide robust platforms for various applications when subject to harsh experimental environments.^{4b} A straight-forward method to construct stable MPFs is using high-valence metal ions as structural nodes to enhance the coordination bonds between the carboxylic ligands and the metals.¹¹ In this regard, zirconium-based MPFs have been intensively investigated for their extraordinarily high stability in recent years.¹² Besides zirconium, trivalent metal ions such as Fe,¹³ Al,¹⁴ Mn¹⁵ have also been frequently used as connectors to construct stable MPFs. Since the high-coordination-number and low-toxic In³⁺ ion tends to generate structurally stable and appealing frameworks, it has been used to construct various MOF materials.¹⁶ Compared with the family of In-MOFs, the number of indium based MPFs was rather limited.¹⁷ To the best of our knowledge, only a few In-MPFs based on different porphyrin ligands have been reported so far (*i.e.* MMPF-7 and -8, UNLPF-10, In-PMOF, UNLPF-14).^{6c, 17-18}

Chemical fixation and transformation of CO₂ have recently become a hot research topic since it was promising in addressing the issue of greenhouse effect mainly caused by the excess CO₂ in the atmosphere and reusing CO₂ molecules to synthesize various valuable chemicals.¹⁹ Owing to their outstanding catalytic property in the cycloaddition of CO₂ to epoxides, metalloporphyrins have attracted extensive research interests in such area. However, these metalloporphyrin complexes generally behave as homogeneous catalysts and their separation from the reaction mixture is quite difficult, owing to the high boiling point and excellent dissolving capacity of cyclic carbonate.²⁰ Besides, the low CO₂ adsorption capacity of such homogeneous metalloporphyrin catalysts were also disadvantageous for the catalytic CO₂ fixation reactions.²¹ Using MPFs as heterogeneous catalysts could not only address the issues above-mentioned, but also could achieve a high catalytic efficiency under mild conditions.²²

^{a.} State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China. E-mail: hbdu@nju.edu.cn

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ARTICLE

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Moreover, previous studies revealed that amido group show high affinity towards CO₂ molecules, resulting in an enhanced CO2 uptake in MOF materials based on amido-decorated organic ligands.²³ Incorporating amido group into MPFs would improve their CO₂ adsorption capacity, and thus benefit for CO₂ fixation reactions. In this work, we report a highly stable indium-MPF, $[NH_2(CH_3)_2][In_2L(HCOO)(H_2O)](solvents)_x$ (denoted as NUPF-3, NUPF: Nanjing University Porphyrinic Framework), based on a custom-designed amido-decorated porphyrin ligand (H₄L). NUPF-3 possesses a rare 4-fold interpenetrated pts-type framework with large solventaccessible voids. The framework shows high structural stability and CO2 uptakes. Thanks to the dense metalloporphyrin centers, desired structural stability and CO₂ adsorption, NUPF-3 exhibits a high efficiency in catalyzing CO₂ chemical fixation under mild conditions.

Experimental

Chemicals

Unless otherwise specified, commercially available reagents were purchased as analytical grade and used without further purification. The porphyrin ligand (H₄L) used in this work was prepared according to our reported procedures.^{9m} In(NO₃)₃·4.5H₂O (99.99%) was obtained from Energy Chemical; 1,2-epoxypropane (99.5%), epichlorohydrin (99%), styrene oxide (98%), glycidyl phenyl ether (99%), cyclopentene oxide (98%), 1,2-epoxyhexane (96%) and allyl glycidyl ether (99%) were purchased from Tokyo Chemical Industry Co., Ltd. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of NUPF-3

H₄L (13 mg, 0.01 mmol) was transferred into *N*,*N*-dimethylformamide (DMF, 2 mL) in a small capped vial and sonicated for ten minutes for dissolution. In(NO₃)₃·4.5H₂O (20 mg, 0.052 mmol), 0.5 mL H₂O and formic acid (0.2 mL) were added into the resulting solution and further sonicated for 10 minutes. The vial was placed into a Teflon-lined acid-digestion bomb and heated at 120 °C for 3 days and then allowed to cool to room temperature naturally. Dark purple rhombic crystals of NUPF-3 were harvested (Fig. S1⁺), followed by washing several times with DMF, ethanol, respectively. Yield: ~10 mg (~75 %, based on porphyrin ligand). FT-IR (KBr pellet, cm⁻¹): v = 3404(s), 3124(w), 2366(w), 1657(w), 1599(s), 1520(s), 1398(s), 1318(m), 1251(m), 1170(m), 1102(m), 1006(m), 857(w), 701(m), 636(w), 491(w).

Characterizations

Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8-Advance diffractometer with a Cu sealed tube ($\lambda = 1.54178$ Å) at 40 kV and 40 mA. Elemental analysis (C, H and N) was performed by an Elementar Vario EL III element analyzer. Thermogravimetry analysis (TGA) was conducted on a Mettler-Toledo (TGA/DSC1) thermal analyzer under N₂ atmosphere with a heating rate of 10 °C /min. Fourier transform infrared spectra (FT-IR) were recorded as

KBr pellets on a Bruker Tensor 27 FT-IR spectrometer. Proton nuclear magnetic resonance (¹H NMR) data were collected on Bruker AVANCE 300 MHz spectrometer. The UV-Vis spectra were recorded on Varian Cary 5000 UV-Vis-NIR spectrophotometer using $BaSO_4$ as reference. Gas adsorption isotherms were collected by a volumetric method on a Micromeritics ASAP 2020 sorption analyzer. The scanning electron microscope (SEM) image was obtained on a Hitachi S-4800 at an accelerating voltage of 10 kV. Supercritical Fluid Technologies (SFT) HPR-100 reactor was used to perform supercritical CO₂ activation of the sample.

Crystallography

Single crystal X-ray diffraction measurements were carried out on a Bruker D8 Venture diffractometer outfitted with a PHOTON-100 CMOS detector using monochromatic microfocus MoK α radiation (λ = 0.71073 Å) that was operated at 50 kV and 40 mA at 153 K by chilled nitrogen flow controlled by a KRYOFLEX II low temperature attachment. Single crystals were selected and mounted on a nylon loop in Paratone-N cryoprotectant. Unit cell determination was performed in the Bruker SMART APEX III software suite. The data sets were reduced and a multi-scan spherical absorption correction was implemented in the SCALE interface.²⁴ The structure was solved by direct methods and refined on F² by full-matrix least squares using the SHELXTL-2014 crystallographic software package²⁵ that imbedded in Olex^{2,26} The contribution of disordered solvent molecules was treated as diffuse using SQUEEZE procedure implemented in PLATON.²⁷ The detailed crystal data and structure refinements for NUPF-3 are given in Table S1⁺. CCDC no. 1491888.

Chemical stability tests of NUPF-3

Acidic solutions (pH = 1, pH = 2, pH = 3) and alkaline solutions (NaOH aqueous solution, pH = 10, pH = 11 and pH = 12) were firstly prepared. About 10 mg of NUPF-3 were soaked in the acidic or alkaline solutions and different organic solvents for 2 days. The samples were filtered and washed with ethanol several times and then PXRD measurements were performed immediately to check the structural stability.

SCD activation and gas sorption analysis

Super-critical carbon dioxide (SCD) activation technique was applied to activate NUPF-3. The freshly-prepared NUPF-3 was soaked in anhydrous EtOH for solvents exchanging, with EtOH refreshed every 12 hours. The procedure was repeated six times. Then the samples were transferred into an SFT HPR-100 reactor. The pressure and temperature gradually rose up to 1400 psi and 40 °C, respectively, and were maintained for 2 hours. The pressure was then released slowly during a period of 1 hour while temperature was still kept at 40 °C. This procedure was repeated three times. The activated samples were further activated in the analysis tube under vacuum using the "degas" function of the adsorption analyzer at 100 °C for 4 h.

Catalytic reactions

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Before the reaction, the catalyst NUPF-3 was activated at 120 °C under vacuum for 6 hours. For comparison, a known In-MOF ([H₂N(CH₂CH₃)₂][In(BPDC)₂]·(solvent)_x, BPDC 4,4'-= biphenyldicarboxylate) was synthesized according to the reported method (Fig. S10⁺),^{16e} and its catalytic properties were tested in a similar manner. The catalytic reactions at high pressure were carried out in a 25 mL stainless steel high-pressure reactor. The activated catalyst (45 mg, ~0.03 mmol based on porphyrinic In³⁺ center or 20 mg, ~0.03 mmol for In-MOF based on [In(COO)₄]⁻ units) together with the epoxide (25 mmol) and co-catalyst of tetra-ntertbutylammonium bromide (TBAB, 0.5 mmol) was transferred to the reactor immediately. The reactor was pressurized with CO₂ up to 2.0 MPa and stirred at 40 °C for 24 h. When the reaction was completed, the reactor was quickly cooled in ice water and the yield of product was determined by ¹H NMR. For the catalyst recycling test, the catalyst was isolated by centrifugation and washed several times with EtOH and CHCl₃ to fully remove the substrates, dried at 120 °C for 4 h under vacuum and then reused in another catalytic run.

Results and discussion

The dark-purple rhombic crystals of NUPF-3 were prepared by heating an acidic (HCOOH) solution of DMF/H₂O containing $In(NO_3)_3$ ·4.5H₂O and porphyrinic ligand H₄L^{9m} in sealed vials at 120 °C for 3 days (Fig. S1⁺). Single-crystal X-ray crystallographic analysis revealed that NUPF-3 crystalizes in monoclinic P21/c space group (Table S1⁺). As depicted in Fig 1a, the porphyrin macrocycle in NUPF-3 is almost planar without obvious out-ofplane deformation, and the porphyrinic central sites were insitu metallized by In³⁺ ions during the solvothermal process. Such central In³⁺ ions were coordinated to four pyrrolic N atoms, one water molecule and one formate anion, resulting in a six-coordinated octahedron geometry. The adjacent phenyl rings in each side-arm of the porphyrin linker, which are linked by amido groups, are non-coplanar and mutually tilted by 5.04 °, 19.66°, 17.68° and 31.37 °, respectively. The benzoic acid moieties of the porphyrinic linker are fully deprotonated and coordinate to four In³⁺ ions, which serve as structural building nodes in NUPF-3. Meanwhile, each In³⁺ nodes are eight-coordinated via chelation in a bi-dentate manner by four carboxylate groups from four different porphyrin ligands, resulting in a typical 4-connected [In(COO)₄]⁻ structural building unit (SBU) (Fig. 1b).



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Fig. 1 (a) The 4-connected porphyrin carboxylate ligand used in NUPF-3. (b) The 4-connected mononuclear $[In(COO)_4]^{\circ}$ SBU in NUPF-3. (c) The 4-fold interpenetrating **pts** framework of NUPF-3. (d) Solvent accessible pores in NUPF-3, the connolly surfaces were calculated using a 1.7 Å probe radius in a 2×2×1 unit cell.

The 3D framework of NUPF-3 is constructed by a 4connecting porphyrinic ligand and a 4-connecting [In(COO)₄] SBU. Each planar porphyrinic L ligand links four [In(COO)₄] SBUs through its four benzoate arms, while each [In(COO)₄] SBU is tetrahedrally connected by four porphyrinic ligands. This gives rise to a highly porous framework with **pts** topology. The large voids formed by the linkage of elongated porphyrin linker and mononuclear [In(COO)₄] SBU lead to the known phenomenon of interpenetration,²⁸ forming a 4-fold interpenetrated three-dimensional framework in NUPF-3 (Fig. 1c and S6⁺). Despite the interpenetration, NUPF-3 is still highly porous, and rhombic channels of 12.6imes15.5 Å $_{ imes}$ 13.9 imes13.5 Å and 21.6 imes 11.9 Å in diagonal dimensions propagate along the *b*-axis (Fig. S5⁺). The solvent accessible pore volume comprises of 59.7 % of its unit cell volume as calculated by PLATON (Fig. 1d). $^{\rm 27}$ The framework of NUPF-3 is anionic, like many other In-based MOFs.^{16a, 16h, 29} The negatively-charged framework is balanced by the $[NH_2Me_2]^+$ cations that were formed through the hydrolysis of DMF.³⁰ The anionic nature of NUPF-3 could be further confirmed by dye adsorption experiments (S7⁺).^{6c}



Fig. 2 PXRD patterns of the samples soaked in common used solvents (a) and acidic/alkaline solutions (b) for 2 days. (c) TG profile of NUPF-3 under N₂ atmosphere from room temperature to 800 °C. (d) Comparison of the adsorption (solid symbols) and desorption (open symbols) isotherms of CO₂ at 273 (blue line) and N₂ at 77 K (red line) for NUPF-3.

As many other indium-based MOFs, NUPF-3 exhibits high chemical and thermal stabilities. As shown in Fig. 2a and 2b, after the samples immersed in common used solvents such as MeOH, H_2O , CH_3CN , THF, DMSO, EtOH and acidic/alkaline solutions with pH ranging from 1 to 12 for 2 days, the PXRD patterns of the samples remained, verifying the high chemical stability of NUPF-3. The strong acid/alkali resistance of NUPF-3 is comparable to some highly stable Fe³⁺ or Zr⁴⁺ based MPFs.^{7a,} Published on 31 October 2016. Downloaded by University of California - San Diego on 01/11/2016 06:10:56.

 13c Thermogravimetric (TG) analyses in the N₂ stream demonstrated that the framework of NUPF-3 could be maintained before 350 °C, indicating a relatively high thermal stability (Fig. 2c). Such high chemical and thermal stabilities can be ascribed to the strong coordination bonds between In³⁺ ions and the carboxylic porphyrin ligands.³¹

Despite high chemical and thermal stabilities, NUPF-3 showed limited N₂ uptake at 77 K after activation (Fig. 2d and Fig. S6⁺). The limited N₂ adsorption is likely due to the low affinity of the NUPF-3 framework toward N₂, similar to other reported porous MPFs such as NUPF-1,^{9m} ZnMn-RPM,³² UNLPF-1,³³ MMPF-7^{18a} and so on.³⁴ However, NUPF-3 exhibited large uptake for CO₂ at 273 K. When the pressure gradually approached 101 kPa, the CO₂ uptake reaches 82 cm³/g at 273 K. The relatively high CO₂ adsorption capacity could be attributed to the presence of acylamide group in NUPF-3, which could enhance the affinity of the framework toward CO₂.²³ Besides, the interpenetrated structure and charged framework of NUPF-3 could also contribute to the high CO₂ uptakes.^{18a, 22c, 35}

Recently, it has been reported that In³⁺ sites in indiumbased MOFs could serve as Lewis acidic centers for CO2 fixation.^{31b} Considering the high structural stability, large CO₂ uptakes as well as the high density of accessible metalloporhyrin centers, we evaluated the catalytic performance of NUPF-3 as a Lewis acid catalyst to catalyze cycloaddition of CO₂ and epoxides to form cyclic carbonates under relatively mild conditions. As shown in Table 1, the yields were very low (<13%) when the reactions performed with no catalyst or solely catalyzed by NUPF-3 or TBAB (entries 1-3) under the conditions of 40 °C and 2.0 MPa for 24 h. However, the yield was increased to 95% (entry 4) under the identical conditions when NUPF-3 and TBAB were used together in the catalytic system. This phenomenon has been known for the cycloaddition of epoxides with CO₂ in many other catalytic systems, which is attributed to the synergistic effect between the solid catalysts and quaternary ammonium salts.²² To evaluate the contribution of [In(COO)₄]⁻ SBU to the catalytic reaction, control experiments were conducted over In-MOF with coordination-saturated $[In(COO)_4]^2$ SBUs. The vield of the coordination-saturated In-MOF catalyzed reaction was 14% (entry 5), comparable to TBAB catalyzed reaction (entry 3). The results showed that coordination-saturated [In(COO)₄]⁻ SBUs have a negligible contribution to the cycloaddition of CO₂ reaction. Thus, the high catalytic activity of NUPF-3 should be mainly ascribed to the high density of unsaturated metalloporphyrin sites confined in the accessible voids, the large CO₂ uptakes, and the activation effect for epoxide of acylamide groups presented in porphyrin ligand, as demonstrated by previous reports.²²

Table 1 NUPF-3 catalyzed cycloaddition of CO₂ and epoxides.



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				2	
				(%) [°]	
1	Blank	ݣ	ب ک	0	0
2	NUPF-3	Å	ý L	9	75
3	TBAB	ڴ	Ŷ	13	
4	NUPF- 3/TBAB	ڴ		95	791
5	In-MOF /TBAB	ڴ	۲	14	116
6	NUPF- 3/TBAB	Å	کے	93 ^b	775
7	NUPF- 3/TBAB	cı		91	758
8	NUPF- 3/TBAB	\bigtriangleup	j L	24	200
9	NUPF- 3/TBAB	\checkmark		87	725
10	NUPF- 3/TBAB	\sim	\sim i	76	633
11	NUPF- 3/TBAB	so <u>Å</u>		69	575
12	NUPF-	\bigwedge^{Δ}		63	525

^a Reaction conditions: epoxide (25.0 mmol), TBAB (0.5 mmol), and NUPF-3 (45 mg, ~0.03 mmol based on metalloporphyrin core) or In-MOF (20 mg, ~0.03 mmol based on $[In(COO)_4]$ SBU), under 2 MPa of CO₂ at 40 °C for 24 h. The yield was determined by ¹H NMR. ^b4th catalytic run. ^{c.} Moles of epoxide consumed per mole of catalyst.

As the stability and recyclability of the catalyst are very important for heterogeneous catalysis, the recycling experiments were carried out over the used NUPF-3 catalyst recovered from the cycloaddition reaction by a washing and drying process. Experimental results indicated that the high catalytic activity was maintained after 4th run (entry 6 and Fig. S8⁺). Moreover, the PXRD pattern of the recycled NUPF-3 showed no change in the peak intensity and position, demonstrating the high stability of NUPF-3 under experimental conditions (Fig. S9⁺).

Encouraged by the high catalytic activity, we further examined the performances of NUPF-3 in chemical fixation of CO_2 with different functional group substituted epoxides. A high yield of 91% was observed for cycloaddition of 2chlorooxirane using CO_2 (entry 7). However, when gradually increasing the molecular sizes of epoxide substrates, the yields correspondingly decreased (entry 9-12), *i.e.* from 87% yield of 4-ethyl-1,3-dioxolan-2-one (entry 9) to 63 % yield of 4-phenyl-1,3-dioxolan-2-one (entry 12). The internal epoxide 1,2epoxycyclopentane gave a low yield of 22% (entry 8), which is likely due to the intrinsic inert nature of the substrate.³⁶ The Published on 31 October 2016. Downloaded by University of California - San Diego on 01/11/2016 06:10:56

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shape-selective phenomenon over NUPF-3 may be attributed to the limited diffusion of large-sized epoxide molecules into the pores of NUPF-3, proved that the catalytic reactions mainly occurred in the pores of the structure rather than on the external surface.³⁷

According to previous studies, 22b, 22d, 38 a tentative mechanism was proposed for the cycloaddition of epoxides and CO₂ to form cyclic carbonate catalyzed by NUPF-3. As illustrated in Scheme 1, the central porphyrinic In atoms in the pores of desolvated NUPF-3 might be activated and can serve as Lewis acid catalytic sites to activate the epoxy ring via interactions with the oxygen atom of epoxide. Besides, epoxide may also be activated by forming hydrogen bond between the acylamide groups of porphyrin linker and the oxygen atom of epoxide. The less-hindered methylene carbon atom of the activated epoxide is then attacked by the Br⁻ from TBAB to open the epoxy ring. Subsequently CO₂ interacts with the oxygen anion of the activated epoxide intermediate to form an alkylcarbonate anion, which is then converted into the corresponding cyclic carbonate through a ring closing step. From a mechanistic point of view, the dense central porphyrinic In sites and high CO₂ uptakes of NUPF-3 could facilitate the cycloaddition reaction, resulting in a high efficiency for converting CO₂ into cyclic carbonates under mild conditions.



Scheme 1 The schematic representation of the tentatively proposed catalytic mechanism for the cycloaddition of epoxides and CO_2 over NUPF-3. The coordinative formic acid anions were omitted for clarity.

Conclusions

In summary, a novel indium-based MPFs, denoted as NUPF-3, has been constructed and characterized. NUPF-3 possesses a rare 4-fold **pts** topology with segmented pores and dense metalloporphyrin central sites. The structure could maintain its crystallinity in commonly-used organic solvents and aqueous solutions with pH ranging from 1 to 12, exhibiting high chemical stability. After activation, NUPF-3 exhibits a high CO₂ uptake. Moreover, NUPF-3 could be used as a good catalyst for

cycloaddition of CO_2 and epoxides in the presence of TBAB under relatively mild conditions.

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