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# Catalytically active metal organic framework based on a porphyrin modified by electron-withdrawing groups

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One metal free porphyrin, modified by electron-withdrawing groups, was synthesized by introduction of two peripheral pyridyl substituents and two metal coordination polymers,  $\{[Zn(C_{42}H_{16}F_{10}N_6)]\cdot 2C_2H_7N\}_n$  (1) and  $\{[Co(C_{42}H_{16}F_{10}N_6)]\cdot C_2H_7N\}_n$  (2), were synthesized solvothermally. In 1, each porphyrin connected four other porphyrin complexes to construct a 2D network through coordination bonds. Similarly, in 2 every Co(II) porphyrin coordinated with four adjacent molecules to form a 2D framework. Thermogravimetric analyses indicate that both 1 and 2 show high thermal stabilities. The fluorescence data of 1 and 2 show that 1 may be a candidate for potential inorganic-organic photoactive materials. Catalytic oxidation results show that 2 displays high activity with the only product acetophenone quantitatively in 81.4%, and after six cycles the catalytic activity slightly decreases. These features of 2, including the

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exceptional stability, and high catalytic activity, make it outstanding among MOFs reported in the literature.

Keywords: Porphyrin; Crystal structure; Alkylbenzene oxidation; Catalytic activity

# 1. Introduction

Metal-organic frameworks (MOFs), as a promising class of porous material, have attracted attention for applications in various areas of catalysis, gas storage, luminescence, magnetism, electrical conductivity, nonlinear optics and sensors [1-6]. One important application is catalysis; the large internal surface and porosity make MOFs promising catalysts. Properties of MOFs can be easily modified by tailoring the organic ligands and selecting the metal node [7-9], while that of other porous materials are difficult to change. Using building blocks, such as porphyrin which already have been proven effective as catalysts, is an attractive way to construct catalytic MOFs.

Porphyrin is a typical functional molecule and one of the most important molecules on which life is based [10]. Its properties can be easily modified by changing peripheral substituents and inserting metals into the center of the porphyrin ring [11]. Because of their functional properties, porphyrins have been building blocks for construction of functional MOFs [12-21]. MOFs can enhance the efficiency of porphyrinic catalytic centers, as described in a previous report [22]. Porphyrin with electron-withdrawing groups (such as fluorine) can greatly enhance catalytic activity for oxidative reactions, so 5,15-(4-pyridyl)-10,20-(pentafluorophenyl)porphyrin (H<sub>2</sub>Pp) was used to construct porphyrin-based MOFs. In 2009, Hupp *et al.* constructed **ZnPO-MOF** by using 5,15-(4-pyridyl)-10,20-(pentafluorophenyl)porphyrin and 1,2,4,5-tetrakis(4-carboxyphenyl)benzene as linker and Zn(II) as nodes, which could enhance ~2400-fold rate of acyl-transfer reaction [23]. In spite of MOFs constructed from 5,15-(4-pyridyl)-10,20-(pentafluorophenyl)porphyrin showing promising catalytic activities, only three such MOFs have been reported [24, 25], and there is no paper that studies MOFs constructed from  $H_2Pp$  without ancillary ligands. To further discuss features of MOFs formed by  $H_2Pp$  and exploit its catalytic activity, more  $H_2Pp$  based MOFs should be synthesized.

In this contribution, two porphyrinic MOFs,  $(\{[Zn(C_{42}H_{16}F_{10}N_6)]\cdot 2C_2H_7N\}_n$  (1) and  $\{[Co(C_{42}H_{16}F_{10}N_6)]\cdot C_2H_7N\}_n$  (2), the C<sub>2</sub>H<sub>7</sub>N is dimethylamine molecule), are constructed based upon H<sub>2</sub>Pp. Single crystal XRD data indicate that 1 and 2 are isostructural; both crystallize in the monoclinic system with C2/c space group and exhibit similar 2D layer structures. Their thermal stability is explored by thermogravimetry (TG). Here we focus on their fluorescence properties and catalytic activities to alkylbenzene oxidation. The results indicate that 2 exhibits high catalytic activities to oxidation of ethylbenzene with 81.4% conversion, while activity of 1 to ethylbenzene oxidation is only 20.1%.

## 2. Experimental

# 2.1. Synthesis of 5,15-(4-pyridyl)-10,20-(pentafluorophenyl)porphyrin (H<sub>2</sub>Pp)

The method to generate **H<sub>2</sub>Pp** was that reported [26, 27]; 0.80 g (7.37 mmol) 4-pyridinecarboxaldehyde was mixed with 100 mL propionic acid. Then, 2.30 g (7.37 mmol) meso-(pentafluorophenyl)dipyrrole dissolved in 15 mL propionic acid was added dropwise to the mixture. The reaction mixture was heated at 145 °C for 50 min. After completing the reaction, the solvent was removed under vacuum and 20 mL C<sub>2</sub>H<sub>5</sub>OH was added. Then the mixture was cooled overnight and crude product precipitated. The crude product was purified by using silica chromatography with dichloromethane and acetone (4:1) as eluent; the main purple band was collected. After removing solvent, a purple-black solid of **H<sub>2</sub>Pp** was obtained. Yield: 5.8%. m.p. >250 °C; Anal. Calcd. for C<sub>42</sub>H<sub>18</sub>F<sub>10</sub>N<sub>6</sub> (Mol. wt: 796.14), %: C, 63.32; H, 2.28; N, 10.55. Found: C, 63.25; H, 2.38; N, 10.62. MS, *m*/z: 797.2([M+1]<sup>+</sup>) amu. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS),  $\delta$  9.01 (d, 4H, 2, 6-H on pyridine); 8.79-8.85 (dd, 8H, β-H on porphyrin), 8.10 (d, 4H, 3-H on pyridine), -2.99 (s, 2H, NH). UV-vis (CHCl<sub>3</sub>)  $\lambda_{max}/mm$ , 413 (Soret band), 509, 539, 584, 640 (Q bands). FT-IR *v*, cm<sup>-1</sup>, 3437, 2923, 1650, 1596, 1521, 1499, 1403, 1348, 1149, 1072, 1046, 987, 922, 812, 778, 749, 730, 668. At the next stage, 0.02 mmol (0.016 g)  $H_2Pp$  was dissolved in 8 mL mixture of dichloromethane and 2 mL of ethanol, and then kept at room temperature; three days later, purple prismatic crystals of  $H_2Pp$  were obtained.

**2.2.** Synthesis of  $\{[Zn(C_{42}H_{16}F_{10}N_6)] \square C_2H_7N\}_n$  (1) and  $\{[Co(C_{42}H_{16}F_{10}N_6)] \square 2H_7N\}_n$  (2) A solution of  $H_2Pp$  (0.015 mmol) and metal salts ( $Zn(NO_3)_2 \cdot 4H_2O$  or  $Co(NO_3)_2 \cdot 6H_2O$ ) (0.03 mmol) in 6 mL DMF (N,N-dimethylformamide) was transferred to a 25 mL polytetrafluoroethylene lined stainless steel container. The vessel was then heated to 120 °C and

kept for 96 h. After cooling to room temperature at 5  $^{\circ}$ C·h<sup>-1</sup>, purple prismatic crystals were obtained. Crystals were very stable in air.

**2.2.1.** {[Zn(C<sub>42</sub>H<sub>16</sub>F<sub>10</sub>N<sub>6</sub>)]·2C<sub>2</sub>H<sub>7</sub>N}<sub>n</sub> (1). Yield: 70.0%. Elemental analyses Calcd (%) for C<sub>44</sub>H<sub>23</sub>F<sub>10</sub>N<sub>7</sub>Zn (905.06): C, 58.39; H, 2.56; N, 10.83. Found: C, 58.35; H, 2.62; N, 10.86. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 413 nm, 477 nm, 529 nm; IR(KBr)  $\nu$ / cm<sup>-1</sup>: 3431, 2932, 1600, 1474, 1212, 975, 801, 564.

**2.2.2.** {[Co(C<sub>42</sub>H<sub>16</sub>F<sub>10</sub>N<sub>6</sub>)]·C<sub>2</sub>H<sub>7</sub>N<sub>3</sub>n (2). Yield: 67.0% Elemental analyses Calcd (%) for C<sub>44</sub>H<sub>23</sub>F<sub>10</sub>N<sub>7</sub>Co (898.62): C, 58.81; H, 2.58; N, 10.91. Found: C, 58.86; H, 2.62; N, 10.96. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 409 nm, 538 nm; IR(KBr)  $\nu$ / cm<sup>-1</sup>: 3435, 2925, 1600, 1485, 975, 797.

# 2.3. Crystallographic data collection and refinement

Appropriate crystals were placed on a Bruker Smart Apex CCD crystal X-ray diffractometer with graphite monochromated Mo K<sub>a</sub> radiation ( $\lambda = 0.7107$  Å) at 298 K. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$  using SHELXTL-97 crystallographic software package [28, 29]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogens were placed in calculated positions with fixed C-H bond lengths. The crystal parameters of **H**<sub>2</sub>**Pp**, **1** and **2** are given in table 1.

# 2.4. Typical procedure for catalytic oxidation

Alkylbenzene (0.1 mmol), *tert*-butylhydroperoxide (TBHP, 0.5 mmol), catalyst (0.005 mmol) and H<sub>2</sub>O (2.0 mL) were added into a flask and stirred at 80 °C for 20 h. When the reaction finished, the identity of the product was determined by using gas chromatography (GC), compared with authentic samples analyzed under the same conditions. The yield of product was also obtained by GC analysis with a flame-ionization detector (FID) using a capillary SE-54 column.

# 3. Results and discussion

# 3.1. Crystal structure of H<sub>2</sub>Pp

The crystal structure of  $H_2Pp$  is shown in figure 1a; crystal data and refinement parameters are given in table 1. The single crystal X-ray diffraction analysis reveals that  $H_2Pp$  crystallizes in the monoclinic space group *C2/c*. They have flexible central backbone and four peripherally positioned binding sites oriented laterally in different directions. The porphyrin macrocycle in  $H_2Pp$  displays a planar configuration with four pyrrole rings almost coplanar. The dihedral angles between the neighboring pyrrole rings in  $H_2Pp$  are 7.105°, 4.614°, 6.221° and 5.687°, respectively. The distance between pyrrole nitrogen and porphyrin main plane (formed by 20 C atoms) is within ±0.0143 Å, indicating that four nitrogens are almost coplanar.

Porphyrin molecules self-assemble through C-H…F interactions to form step-ladder chains. The distance between two porphyrin macrocycle planes is 4.2777 Å. The chain further connects to each other by  $\pi$ … $\pi$  interactions between pyridine rings and C-H…F interactions to construct a 3D supermolecular configuration.

In **1**, the Zn(II) resides at the center of the porphyrin macrocycle by coordinating with four pyrrole nitrogens and forms octahedral geometry through coordinating with two nitrogens of two *trans*-pyridyl molecules in axial positions (figure 2a). The values of Zn-N bond lengths are generally close. The displacement of each 20-membered ring atom is from -0.158(9) to

+0.158(9) Å from the equatorial mean N4 plane, while that of four pyrrole nitrogens is 0 Å from their mean N4 plane, indicating that atoms of the porphyrin macrocycle are almost coplanar.

Each porphyrin connects two adjacent units through coordination bonds formed by its pyridyl substituents and Zn(II) of adjacent porphyrins, and it links another two porphyrins through Zn(II) coordinating with pyridyl. Every porphyrin molecule connects four adjacent molecules through coordination bonds to self-assemble into a two-dimensional (2D) layer (figure 2b). The neighboring layers further packed into a 3D supermoleculer framework in a parallel model with interlayer distance of adjacent layers about 12.2 Å (figure 2c). If porphyrin is considered to be a four-connected node in the square geometry, the net of 1 can be simplified as a  $\{4^46^2\}$  network (figure S1, Supporting Information). Because of the large size of the square-planar molecules, the networks formed by porphyrin are porous. These voids account for 11.9% of the crystal volume and are accessible to guest solvent components (dimethylamine) as estimated by PLATON analyses.

As shown in figure 3a, Co(II) coordinates with four nitrogens of the porphyrin macrocycle and two pyridyl substituent groups to form an octahedral geometry. The atoms of the porphyrin macrocycle are almost coplanar. The porphyrin connects two adjacent porphyrins through coordination bonds between its pyridyl substituents and Co(II) of adjacent porphyrins, and links another two porphyrins through Co(II) coordinating with pyridyl to form a 2D metalloporphyrin framework (figure 3b). The 2D networks further arrange through  $\pi \cdots \pi$ interactions in ABAB stacking pattern (figure 3c), generating a microporous 3D supermolecular structure with pore size of 7.9 × 7.9 Å. If one considers the porphyrin building block to be a four-connected node, the net of **2** can then be rationalized as a {4<sup>4</sup>6<sup>2</sup>} network topology (figure **S2**, Supporting Information). The potential solvent accessible void space accounts for 10.1% of the whole crystal volume as estimated by PLATON.

The frameworks of **1** and **2** are directly constructed through porphyrin units, which is different from those observed in **ZnPO-MOF** [24], constructed from 1,2,4,5-tetrakis(4-carboxyphenyl)benzene and 5,15-dipyridyl-10,20-bis(pentafluorophenyl)-

porphyrin. X-ray diffraction analysis shows that 1 and 2 are isostructural and have similar crystal structures: first, both 1 and 2 crystallize in the monoclinic system with C2/c space group and exhibit a 2D layer structure; second, the configuration of porphyrin units and the coordination environment of metals in 1 and 2 are similar; third, there are the same solvent molecules (dimethylamine) in the pores of 1 and 2. The metal to metal distance between porphryin units in different layers of 1 is 11.179 Å, while the distance for 2 is 11.979 Å, slightly shorter than that of reported MOFs from H<sub>2</sub>Pp [24]. Due to different metals in the macrocycle of porphyrin, the size of pores in 1 and 2 are  $9.9 \times 9.9$  Å and  $7.9 \times 7.9$  Å, respectively, which lead to different potential solvent accessible void space (11.9% for 1 and 10.1% for 2). Owing to different center metal of porphyrin units in 1 and 2, which determine catalytic activity of MOFs, 1 and 2 show quite different catalytic properties with conversion 20.1% for 1 and 81.4% for 2, respectively.

# 3.2. Thermogravimetric analysis and powder XRD

Thermogravimetric analyses (TGA, figure S3) of **1** and **2** were performed by heating the samples from 20 to 800 °C under N<sub>2</sub> with a heating rate of 10 °C·min<sup>-1</sup> (figure S3a). There is 5% weight loss from room temperature to 220 °C, corresponding to loss of dimethylamine and decomposition of **1** framework occurred at 450 °C. For **2**, 2.5% weight loss around 200 °C corresponds to loss of two dimethylamine molecules, at 400 °C decomposition occurred. The thermal behaviors characterized by TGA display that these two materials exhibit high thermal stabilities. The phase purity for **1** and **2** is confirmed by powder X-ray diffraction (PXRD) analysis in bulk (figure S4) with all of the measured peaks closely matching those in the simulated pattern generated from the single-crystal XRD data, indicating that **1** and **2** retain the erystalline nature and porous structure with the pores comparable to those revealed in the single crystal.

#### **3.3.** Fluorescence property

The fluorescence of **1** and **2** was examined in the solid state at room temperature as shown in figure 4. Free **H<sub>2</sub>Pp** displays two medium-intensity emission peaks at 665 and 708 nm upon excitation at 424 nm. For **1**, there is only one emission at 672 nm upon excitation at 368 nm, which is ascribed to protonation of the ligand and the heavy-atom effect. After Zn ion inserts into the porphyrin macrocycles, the N of pyrrole form coordination bonds with Zn(II) and Zn(II) forms back donation  $\pi$  bond with nitrogens by donating electrons in *d* orbital. The formation of back donation  $\pi$  bond between Zn(II) and porphyrin enhances the electrons density of porphyrin macrocycle. Therefore, the symmetry and aromaticity of porphyrin macrocycle are decreased, resulting in larger HOMO-LUMO energy gap, therefore blue-shifted peaks were observed [30-32]. These results indicate that the emission behavior can be effectively modulated by protonation and metal coordination, suggesting that **1** may be a candidate for potential hybrid inorganic-organic photoactive materials.

#### **3.4.** Catalytic activity

We examined **1** and **2** for their catalytic oxidation of ethylbenzene. The ethylbenzene oxidation was performed using *tert*-butylhydroperoxide (TBHP) as the oxidant in H<sub>2</sub>O at 80 °C, with GC monitoring of reaction. The results (table 2) show that **2** efficiently catalyzes conversion of ethylbenzene to acetophenone in 81.4% yield, while **1** shows negligible activity with conversion of 20.1%. After reaction completion, solid **2** was easily recovered by centrifuging, and subsequently used in successive runs with only slightly decreased product yields. The conversion after three cycles is 74.5%. When the substrate was changed to 1-phenylpropane, 1,2,3,4-tetrahydronaphthalene and diphenyl methane, the conversion decreased to 38.6, 43.7 and 15.6%, respectively. The catalytic activity of **2** is slightly lower than Mn(III)/Fe(III) porphyrin MOFs in previous reports [15, 16, 33], with Mn(III)/Fe(III) exhibiting higher activity than that of **2** (Co(II)). However, the catalytic ability of **2** is superior to MOFs constructed by Co(II) porphyrin [34].



# 4. Conclusion

One metal free porphyrin,  $H_2Pp$ , was synthesized by the introduction of two peripheral pyridyl substituents and their two metal coordination polymers ({[ $Zn(C_{42}H_{16}F_{10}N_6)$ ]·2 $C_2H_7N$ }<sub>n</sub> (1) and {[ $Co(C_{42}H_{16}F_{10}N_6)$ ]· $C_2H_7N$ }<sub>n</sub> (2)) were synthesized solvothermally. In both 1 and 2, each porphyrin connected to four adjacent porphyrins to construct a 2D network through coordination bonds. Thermogravimetric analyses indicated that 1 and 2 show high thermal stabilities. 1 exhibited strong luminescence, indicating it would be a good candidate for luminescent materials. Catalytic oxidation results show that 2 displayed high catalytic activity with acetophenone the only product in 81.4%; after six cycles the catalytic activity slightly decreases. These features of 2 including the exceptional stability and catalytic activity make it outstanding among the MOFs reported in the literature.

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Figure 1. (a) The molecular structure of **H**<sub>2</sub>**Pp**; (b) self-aggregated step-ladder; (c) supermolecular structure of **H**<sub>2</sub>**Pp**.



Figure 2. (a) Zn(II) coordination environment of **1** (hydrogens are omitted for clarity). Symmetry transformations used to generate equivalent atoms: a, -x+1/2,-y+3/2,-z; b, -x+1/2,y-1/2, -z+1/2; c, x, -y+2, z-1/2). (b) 2D network in **1** (coordination environment around Zn ion is shown as turquoise polyhedron). (c) Perspective views of the packing diagram of **1** along the *a*-axis. (All hydrogens and solvent molecules are omitted for clarity.)





Figure 3. (a) Co(II) coordination environment of **2** (symmetry transformations used to generate equivalent atoms: a, -x+1/2, -y+3/2, -z; b, -x+1/2, y-1/2, -z+1/2; c, x, -y+2, z-1/2). (b) 2D network of **2** (coordination environment around Co is shown as violet polyhedron). (c) Packing framework of **2** along the *a*-axis. (All hydrogens and solvent molecules are omitted for clarity.)



Figure 4. Photoluminescence spectra of  $H_2Pp$ , 1 and 2 in the solid state at room temperature.

# Graphical abstract



	H <sub>2</sub> Pp	1	2
Empirical formula	$C_{42}H_{18}F_{10}N_6$	$C_{44}H_{23}F_{10}N_7Zn$	$C_{44}H_{23}F_{10}N_7Co$
Formula weight	796.62	905.06	898.62
CCDC number	981137	981135	1448878
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
<i>a</i> (Å)	20.598(6)	23.107(5)	22.637(5)
<i>b</i> (Å)	7.061(2)	13.906(3)	14.201(3)
<i>c</i> (Å)	23.997(7)	14.106(3)	14.275(3)
α (°)	90	90	90
β (°)	91.832(7))	102.36(3)	102.71
γ (°)	90	90	90
$V(Å^3)$	3488.4(18)	4427.5(15)	4476.5(15)
Z	4	4	2
D <sub>calc</sub> (Mg/m <sup>3</sup> )	10.538	1.358	1.300
F(0 0 0)	10608	1824	1760
μ (mm <sup>-1</sup> )	1.599	0.635	0.461
$R_1, wR_2 [I > 2\sigma(I)]$	0.0896, 0.2131	0.1057, 0.3817	0.1391, 0.3810
$R_1$ , $wR_2$ (all data)	0.2024, 0.2877	0.1094, 0.4028	0.1910, 0.4443
$GOOF(F^2)$	1.147	1.065	1.049

Table 1. The crystal parameters of  $H_2Pp$ , 1 and 2.

Entry	Substrate	Catalyst	e Product	Conv. $(\%)^b$	Select. (%)
1	$\bigcirc$	1	Ů	20.1	> 99
2	$\bigcirc$	2	C <sup>1</sup>	81.4	> 99
2	$\bigcirc$	<b>2</b> <sup>c</sup>		74.5	> 99
3	$\bigcirc$	2	<u>C</u>	38.6	>99
4	$\bigcirc \bigcirc$	2		15.6	>99
5	$\bigcirc$	2		43.7	82
6	$\bigcirc$	ZnCl <sub>2</sub>		2.7	75
7	$\bigcirc$	CoCl <sub>2</sub>	CI	> <sub>4.8</sub>	71
8	$\bigcirc$	no		trace	-

Table 2. Selective oxidation of alkylbenzenes catalyzed by porphyrin complexes<sup>*a*</sup>.

<sup>*a*</sup> Conditions: a mixture of catalyst (0.01 mmol), alkylbenzene (0.1 mmol), and TBHP (0.5 mmol) in H<sub>2</sub>O (2.0 mL) was stirred at 80 °C for 20 h. <sup>*b*</sup> Based on GC analysis. <sup>*c*</sup> The sixth cycle.