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Three novel metal-organic frameworks based on flexible porphyrin tetracarboxylic acids as highly effective catalysts

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Abstract

Targeted synthesis of metalloporphyrinic frameworks (MPFs) with Cu(II) (1), Ni(II) (2, 3) 5, 10, 15, 20-tetrakis[4-(carboxymethyleneoxy)phenyl]porphyrin (Cu(TCMOPP) and Ni(TCMOPP)) as building blocks afforded three new extended coordination polymers inter-linked by Zn(II) (1) and K(I) (2, 3). 1 shows 2D frameworks while 2, 3 are 3D frameworks. The open channel are 7-17 Å wide and accessible to other guest/solvent molecules. Besides, the thermogravimetric analyses (TGA) indicate that the framework structures of the three compounds are stable until 300 °C. In addition, the catalytic activities of 1-3 to the alkylbenzenes oxidation are examined, and the results indicate that 1 exhibit high catalytic activity to oxidation of ethylbenzene and 1,2,3,4-tetrahydronaphthalene with conversion of 64.1% and 80.3% respectively.

Keywords:Porphyrin; Cu(II) porphyrin; Ni(II) porphyrin; Crystal Structure; Catalytic oxidation.

1. Introduction

During the past decades, extensive research attention has been attracted to metal organic frameworks (MOFs) materials for its highly efficient gas storage and catalysis [1-11]. Besides the traditional solvothermal method to construct MOF, novel new synthetic methods, such as surfactant-thermal method, have been developed [12-19]. Among the MOFs, metalloporphyrinic frameworks (MPFs) has been intensively studied, mainly due to their fascinating framework topologies and potentially interesting physical and chemical properties in applications, such as

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catalysis[20-24], optics [25,26], electrics[27], gas storage and separation[28-30]. To build new MPFs with diverse structures, the choice of the peripheral substituents of porphyrins is extremely important. In the selection of porphyrins scaffolds, square-planar the tetradentatetetra(3-/4-carboxyphenyl)porphyrin (TpCPP/TmCPP) derivatives are widely employed due to their capacity to interconnect into open quadrangular supramolecular networks[31-36]. Besides, to explore more adjustable MPFs materials, in 2010 Israel Goldberg et al. introduced the flexible porphyrin tetraacids (TCMOPP, tetrakis[4-(carboxymethyleneoxy)phenyl]-porphyrin) as building blocks to construct MPFs for the first time[37]. In spite of the disposition of the carboxylic acid sites in TCMOPP is more versatile than that of TCPP, only two coordination polymers (1D and 2D) has been observed so far.

Herein, we report three new open network coordination polymers involving Cu(TCMOPP) and Ni(TCMOPP) building blocks inter-linked by external zinc and potassium metal ions (**Figure 1**). The MPFs referred to in this work include 3D supramolecular networks of Cu(TCMOPP) intercoordinated by Zn(II) ion (1:{Zn[Cu(TCMOPP)]}·2HN(CH₃)₂), and 3D networks of Ni(TCMOPP) intercoordinated by K(I) ion (2:{K₂[Ni(TCMOPP)]·DMF} and 3:{K₂[Ni(TCMOPP)]₂ (DMF)₂}·DMF·H₂O). Here we focus on not only their structural features but also their catalytic oxidation activities. The results indicate that **1** exhibit high catalytic activity to oxidation of ethylbenzene and 1,2,3,4-tetrahydronaphthalene with conversion of 64.1% and 80.3% respectively.

Figure 1

2. Experimental

2.1 Materials and methods

All reagents were purchased from Beijing Chemical Reagents Company. They were used without further purification except pyrrole and DMF, which were distilled before use. All chromatographic separations were carried out on silica gel (100–120 mesh).

Elemental analyses (C, H and N) were performed by Vario EL-III CHNOS instrument. UV-vis spectra were measured on a Shimadzu UV 1800 UV-vis-NIR spectrophotometer. FT-IR spectra were recorded on a BEQUZNDX-550 spectrometer on samples embedded in KBr pellets.

Mass spectrometry (MS) analysis were carried out on a matrix assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS, Krato Analytical Company of Shimadzu Biotech, Manchester, Britain). The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu K α) at 40 kV, 30 mA over the 2 θ range from 5 to 30°. Thermal gravimetric analysis (TGA) were performed on a Perkin-Elmer TGA-7 instrument in flowing N₂ with a heating rate of 10 °C/min from 30 to 900 °C.

2.2 Synthesis

2.2.1. Synthesis of Cu(TCMOPP) and Ni(TCMOPP).



Scheme 1Synthesis of Cu(TCMOPP) and Ni(TCMOPP).

The synthetic routes to the porphyrins Cu(TCMOPP) and Ni(TCMOPP) are shown in **Scheme 1**. 5, 10, 15, 20-tetrakis[4-(carboethoxymethyleneoxy)phenyl] porphyrin (H₂(TEMOPP)) was synthesized by a reported method [37]. Firstly, metalloporphyrins Cu(TEMOPP) and Ni(TEMOPP) were prepared by reaction of their corresponding H₂(TEMOPP) (0.1 mmol) with 0.6 mmol M(OAc)₂ (M=Cu, Ni). Then the crude products were purified by chromatography on a silica-gel column with CH₂Cl₂ as eluant. The desired Cu(TEMOPP) and Ni(TEMOPP) were obtained. Then, metalloporphyrins Cu(TCMOPP) and Ni(TCMOPP) were afforded by alkaline hydrolysis as the method reported in the literature [38].

Cu(TCMOPP): Yield: 86%. Mp:>250°C. Anal.Calcd (found) for $C_{52}H_{36}CuN_4O_{12}$ (Mol.Wt: 971.16), %: C 64.36 (64.23), H 3.80 (3.73), N 5.73 (5.76). MS:m/z 1010.12 ([M+K]⁺) amu. UV-vis (CH₂Cl₂) λ_{max} /nm: 416 (Soret band), 542 (Q-band). FT-IR (KBr): v, cm⁻¹, 3427, 2922, 1724, 1602, 1498, 1433, 1337, 1291, 1214, 1070, 997, 802, 721.

Ni(TCMOPP): Yield: 90%. Mp: >250 °C. Anal.Calcd (found) for $C_{52}H_{36}NiN_4O_{12}$ (Mol.Wt:

966.16), %: C 64.56 (64.55), H 3.80 (3.75), N 5.76 (5.79). MS:*m/z* 965.15 [M-H]⁻ amu. UV–Vis (CH₂Cl₂) λ_{max} /nm: 419 (Soret band), 531 (Q-band). FT-IR (KBr): *v*, cm⁻¹, 3427, 3032, 2922, 2854, 1726, 1633, 1604, 1502, 1433, 1352, 1286, 1213, 1174, 1074, 1002, 796, 713.

2.2.2. Synthesis of $\{Zn[Cu(TCMOPP)]\}$ ·2HN(CH₃)₂ (1).

A mixture of Cu(TCMOPP) (0.025 mmol) and Zn(CH₃COO)₂·2H₂O (0.05 mmol) was stirred in DMF (12 mL), and then sealed in a 25 mL teflon-lined stainless reactor. The solution was heated at 150 °C for 72 h, followed by slow-cooling to room temperature for 24 h. Purple block-shaped crystals suitable for X-ray crystal analyses were isolated in 45% yield. Anal.Calcd for C₅₆H₄₈CuN₆O₁₂Zn: C, 59.74; H, 4.30; N, 7.46%. Found: C, 59.82; H, 4.25; N, 7.48%. IR spectrum (KBr, ν /cm⁻¹): 3427, 2925, 1608, 1502, 1409, 1386, 1344, 1286, 1222, 1176, 1107, 1068, 999, 883, 802, 719.

2.2.3. Synthesis of $\{K_2[Ni(TCMOPP)] \cdot DMF\}$ (2) and $\{K_2[Ni(TCMOPP)]_2(DMF)_2\} \cdot DMF \cdot H_2O$ (3).

Ni(TCMOPP) (0.016 mmol) was dissolved in 4 mL DMF. And then two drops of aqueous solution of KOH (2 mol/L) was added, and expect to get 3D metalloporphyrinic frameworks since the potassium ions exhibited higher affinity for coordinating to the carboxylate porphyrin functions [39]. The solution was slow evaporation at 35 °C for 7 days to give X-Ray quality purple rod-like crystals of **2** in 80% yield. The solution with crystals **2** was continue evaporation at 35 °C for 5 days, 72% crystal **2** convert to purple block-shaped crystals suitable for X-ray crystal analyses of **3**. Anal.Calcd for $C_{55}H_{41}K_2N_5NiO_{13}$ (**2**): C, 58.82; H, 4.68; N, 6.62%. Found: C, 59.15; H, 3.70; N, 6.27%. IR spectrum (KBr, ν/cm^{-1}): 3431, 2925, 1664, 1604, 1504, 1467, 1434, 1409, 1384, 1353, 1294, 1228, 1176, 1109, 1072, 999, 879, 850, 800, 713. Anal.Calcd for $C_{113}H_{93}K_2N_{11}Ni_2O_{28}$ (**3**): C, 60.36; H, 4.17; N, 6.85%. Found: C, 60.41; H, 4.08; N, 6.86%. IR spectrum (KBr, ν/cm^{-1}): 3433, 2923, 1662, 1606, 1504, 1434, 1409, 1384, 1352, 1288, 1224, 1176, 1110, 1066, 1001, 881, 852, 800, 713.

2.3. Crystallographic data collection and refinement

The crystallographic data of 1, 2 and 3 were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed by using SADABS program [40]. The structures were solved by direct method and refined by full-matrix least-squares techniques using the program SHELXL-97[41, 42]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms

were placed in geometrically calculated positions. The crystal parameters of compounds **1-3** are given in **Table 1**. Selected bonds distances and angles are listed in **Table S1**. CCDC 1025961, 1025962 and 1025960 contain the supplementary crystallographic data for compounds **1-3**.

Compounds	1	2	3
Empirical formula	$C_{56}H_{46}CuN_6O_{12}Zn$	C ₅₅ H ₄₁ K ₂ N ₅ NiO ₁₃	$C_{113}H_{93}K_2N_{11}Ni_2O_{28}$
$M (g \cdot mol^{-1})$	1125.91	1116.84	2248.60
θ range (°)	1.27-25.05	2.02-25.00	1.72–25.00
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
T (K)	296(2)	296(2)	296(2)
<i>a</i> (Å)	11.4697(8)	8.4470(14)	12.6368(13)
<i>b</i> (Å)	16.1662(11)	11.1251(19)	14.4827(15)
<i>c</i> (Å)	17.1103(13)	17.581(3)	18.082(2)
α (°)	70.7630(10)	77.882(3)	83.373(2)
β (°)	80.3490(10)	88.741(3)	69.732(2)
γ (°)	74.6200(10)	79.060(3)	85.888(2)
V (Å ³)	2877.0(4)	1585.7(5)	3081.8(6)
Z	2	1	1
Calculated density (g·cm ⁻³)	1.300	1.170	1.212
F (0 0 0)	1162	576	1166
μ (mm ⁻¹)	0.850	0.495	0.445
Reflections collected/unique	14588/10095	7887/5482	15202/10714
R (int)	0.0335	0.0557	0.0208
Date/parameters	10095/692	5482/371	10714/737
R_1 (w R_2) [I >2sigma(I)]	0.0776 (0.2350)	0.1070 (0.2939)	0.0649 (0.2161)
R_1 (w R_2) (All data)	0.1154 (0.2801)	0.1981 (0.3681)	0.0789 (0.2320)
Goodness-of-fit on F ²	1.035	1.061	1.069
Largest diff. peak and hole $(e^{A^{-3}})$	1.306 and -0.551	1.409 and -0.496	1.207 and -0.440

 Table 1The crystal parameters of compounds 1-3

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CCDC	1025961	1025962	1025960		
		2 2 1/2			

 $(R_1 = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|; \quad wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

2.4. Catalytic Oxidation of Alkylbenzene

A mixture of alkylbenzene (0.4 mmol), tert-butylhydroperoxide (TBHP, 1.6 mmol), catalyst (0.02 mmol) and acetonitrile (2.5 mL) was stirred at 80 °C for 20h. After the reaction, the identity of the product was determined by using gas-chromatography (GC), compared with the 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. The structure of {Zn[Cu(TCMOPP)]}·2HN(CH₃)₂(1)

Figure 2.

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The single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the triclinic *P*-1 space group. As shown in **Figure 2a**, the Cu(II) ions inserted into the porphyrin core with the coordination bonds of Cu-N (1.970 to 1.996 Å) to form a square geometry. The four pyrrole rings being slightly twisted in an alternating manner either up or down with respect to the mean plane of the saddled porphyrin macrocycle. The four pyrrole N atoms are displaced by 0.0752, -0.0936, 0.075 and -0.0747 Å from their mean N₄ plane (which may represent the average plane of the porphyrin core). The dihedral angles between adjacent pyrrole rings around the macrocycle are 10.458, 15.579, 13.394 and 14.551 °, suggesting that the macrocycle mainly adopts a saddle conformation. Each Zn(II) ion tetrahedron coordinates to four carboxylic groups of four porphyrin ligands[Zn–O coordination bonds range from 1.944(5) to 1.989(5)Å]. Each porphyrin ligand acts as a tetradentate ligand and connects four Zn(II) ions to propagate a one-dimensional bi-chains (**Figure 2c**). And the bi-chains further links each other though Zn(II) to form bilayer networks(Figure 2d). The lamellar 2D bilayered coordination polymersare packed by hydrogen bond interactions (a, b of **Figure S1**) and C-H… π (c, d of **Figure S1**) between phenyl and porphyrin macrocycle, and as a result 3D supramolecular framework is constructed.

The space-filling model of the channeled structure of **1** is shown in **Figure 3a**. The crystal architecture is characterized by extended channels that propagate through the crystal parallel to the *a* axis. These channels are approximate 13.191×7.402 Å size. And the voids are filled with a large number of dimethylamine which are not coordinated to the polymeric lattice and can be readily exchanged by other guest components. PLATON calculations indicate that **1** contains 18.6% void space. When we treat Cu(TCMOPP)²⁻ unit and Zn²⁺siteas a 4-connected node, respectively, the framework of **1** can be simplified to a binodal (4, 4)-connected(4³.6³) (**Figure 3b**).

Figure 3.

3.2. The structure of $\{K_2[Ni(TCMOPP)]DMF\}$ (2) and $\{K_2[Ni(TCMOPP)]_2(DMF)_2\}$ ·DMF·H₂O (3)

X-Ray quality purple isomorphous crystals of **2** and **3** were obtained respectively by slow evaporation from DMF solvent in the presence of the strong KOH base in different evaporation time, which both crystallize in the triclinic *P*-1 space group. The Ni(II) ions inserted into the porphyrin core reveal high propensity for a square-planar coordination environment in **2** (Ni-N = 1.948(4) Å, 1.955(4)Å) (**Figure 4a**). The four pyrrole N atoms are displaced by ± 0.0741 and ± 0.0745 Å from their mean N₄ plane. The dihedral angles between adjacent pyrrole rings around the macrocycle are 16.608, 17.592, 15.063 and 16.959 °.

In the two structures, the porphyrin moieties are interconnected to each other through the potassium ion auxiliaries. The coordination environment around the K(I) in crystals **2** can be described as distorted pentagonal bipyramid coordination geometry (**Figure 4b**) with four carboxylic/carboxylate oxygen atoms (K-O=2.766(5)–2.798(4)Å) from different [Ni(TCMOPP)]²⁻ units, two ether oxygen atoms also coordinated to the K⁺ (K-O = 2.906(4)Å, 3.096(4)Å), and the oxygen atom of DMF occupies the last coordination site (K-O = 2.804(7)Å). The coordination geometry of the two adjacent K(I) ions is shown in the **Figure 4b**.Two carboxylic groups at every Ni(TCMOPP) site are deprotonated to balance the charge of the two potassium ions. Two trans-related carboxylates bind simultaneously to two K(I) ions with two carboxylate O atoms of each group. The two other carboxylic groups bond simultaneously to two K⁺ ions with a single carboxylic O atom of each group. And all the ether oxygen atoms involved in coordination

(**Figure 4a**). Each of $[Ni(TCMOPP)]^{2}$ unit associates directly with eight different K⁺ centers results in the formation of a 2D network (**Figure 4c**), and the networks further though coordination bond between to form a 3D porous framework (**Figure 4d**) with two kinds of 1D channels (14.213×10.812 Å, 17.023×7.929 Å) along the a axis. In **2**, only one kind of the voids is found in the space-filling model. PLATON calculations indicate that **2** contains 15.4 % void space, which is accessible to the guest molecules.

Figure 4.

In the crystals **3**, the porphyrin core in **3** adopts a four-saddle conformation (**Figure 5a**), with the four pyrrole rings being slightly twisted in an alternating manner either up or down with respect to the mean plane of the saddled porphyrin macrocycle and the coordination bonds of Ni-N range from 1.9296(17) to 1.9457(15)Å. The coordination environment around the K(I) can be described as distorted quadruple prisms geometry (**Figure 5b**) with six carboxylic/carboxylate oxygen atoms (K-O = 2.700(2)-2.9892(16) Å) from different [Ni(TCMOPP)]⁻ units, wherein a ether oxygen atom also coordinates to the K(I) (K-O = 3.1349(16)Å), and the oxygen atom in DMF molecule occupy the last coordination site (K-O = 2.827(3)Å). Besides, every two adjacent K(I)ions coordinated with eight carboxylic/carboxylate from different [Ni(TCMOPP)]⁻ units. One of the carboxylic acid groups at every Ni(TCMOPP)⁻ site are deprotonated to balance the charge of the potassium ion. Each [Ni(TCMOPP)]⁻ unit associates directly with six different K(I) centers results in the formation of a1D chains structure(**Figure 5c**). The lamellar 2D networks are formed by assembly of chains through bridged K(I) ion (**Figure 5d**). And the networks further connects each other though K(I) ion to form a 3D porous framework with1D channels (14.371×10.201 Å²) along the a axis (**Figure 5e**).

The space-filling model of the channeled structure is shown in **Figure S2a** (Supporting Information). The voids are filled with some coordinated DMF molecules and a large number of uncoordinated water molecules and DMF solvent molecules which can be readily exchanged by other guest components. PLATON calculations indicate that **3** contains16.9% void space. Finally, in topological analysis for **3**, we treat porphyrin unit as a 4-connected linker and the coordination network of the two adjacent K ions as a 8-connectednode, the framework of **3** can be simplified to

a binodal $(4_2, 8)$ -connected 3D $(4^{12}.6^{12}.8^4)(4^6)$ 2 net (**Figure S2b**, Supporting Information).

Figure 5.

3.3. Structural comparison between compounds 2 and 3.

In several respects, crystal structures of 2 and 3 reveal similar features to those observed in $(Pd-TCPP)^{4} \cdot 4K^{+} \cdot 6H_2O \cdot (CH_3)_2NCHO$ the structures of the and (Pt-TCPP)⁴·4K⁺·6H₂O·C₆H₅Nreportedearlier [30]. To the best of our knowledge, this type of connection in 2 and 3 had never been reported in those MPFs based on TCMOPP or M(TCMOPP). Unexpectedly, when the crystalline samples of compound 2 were soaked in DMF, they can convert to compound **3**. Evidently, the configuration of porphyrin units and the coordination environment of K(I) in **3** is different from that in **2**. And the porphyrin core in **3** is slightly twisted to optimize the coordinative bond. It leads to the efficient offset stacking of adjacent porphyrins along the a-axis normal direction as shown in Figure 5e. Besides, the voids in 2 only contain some coordinated DMF solvent molecules. While the voids in 3 are filled with not only some coordinated DMF molecules but also a large number of uncoordinated water molecules and DMF solvent molecules which can be readily exchanged by other guest components. It also indicates that the voids in 3D networks of 2 and 3 are accessible to other guest/solvent molecules, which is need for further research.

3.4. Powder X-ray diffraction, UV-vis spectra and thermogravimetric analyses

The phase purity for MPFs **1-3** is confirmed by powder X-ray diffraction (PXRD) analysis in bulk amount (**Figure S3**, Supporting Information). The PXRD results show that all of the measured peaks closely matched those in the simulated pattern generated from the single-crystal XRD data, indicating that **1-3** keeps the crystalline nature and porous structure with the pore comparable to those revealed in the single crystal. The UV-vis spectra show one Soret band and one/two Q bands (Figure S4). Compared with metal-free porphyrin, the decreased number of Q bands in **1-3** is due to the symmetry increase of porphyrin macrocycle when the metal ions coordinate with the N atoms of porphyrin ring. The Soret band position of **1** is in 389 nm while that of **2**, **3** in 420, 419 nm. The blue shift of Soret band of **1** is due to arrangement pattern. The S, Q bands of **2**, **3** are in similar position.

To study the thermal stability of **1-3**, thermogravimetric analysis (TGA, Figure **S5** Supporting Information) is carried out in the temperature range from 25 to 1000 °C under a flow of N₂ with a heating rate of 10 °C·min⁻¹. The TG curve of **1** shows an initial weight loss of 8.51% at 60-150 °C, corresponding to removal of two solvent molecules (cal. 8.02%). Significant weight loss upon 350°C is assigned to framework decomposing. Similarly, there is 7.24% weight loss for **2** at 50-180°C, corresponding to the loss of DMF molecule (cal. 6.54%), and the porphyrin framework start to decompose at 292°C. For **3**, 10.87% weight loss at 60-160°C is observed due to the loss of H₂O and DMF molecules, and the porphyrin framework start to decompose when the temperature higher than 300°C.

3.5. Catalytic Activities of Compounds

We examined 1, 2 and 3 for its catalytic oxidation to alkylbenzene. The alkylbenzene oxidation was performed in solvent of acetonitrile at 80 °C using tert-butylhydroperoxide (TBHP) as the oxidant, with GC monitored throughout the reaction. The results (Table 2) show that 1 can catalyze efficiently the conversion of ethylbenzene to the only product of acetophenone quantitatively in 64.1% yield. After reaction finished, solid 1 was easily recovered by centrifuging and filtration then subsequently used in successive runs with only slightly decreased product yields. 2 and 3 displays the basic catalytic activity with only about 21%, 13% acetophenoneproduced (Table 2). The significant difference between 1 and 2, 3in their catalytic properties clearly indicates the crucial role of the metal ion in the center of porphyrin ring. In the process of porphyrin catalyzing oxidation of ethylbenzene, according to reports [43, 44], the central metal ion will lose electron to form high oxidation state ion. It is worth to note that acetophenone is oxidized to only product acetophenone in the presence of 1-3 with the selectivity >99%. The catalytic oxidations of 1 with different substrates were also tested. And the results indicate that the 1-phenylpropane, 1,2,3,4-tetrahydronaphthalene and diphenyl methane can also be catalytic oxidized with 1, but the conversions are decreased to 40.6, 80.3 and 37.5% respectively.



Table 2. Selective oxidation of alkylbenzenes catalyzed by compounds 1-3

Entry	Substrate	Catalyst	Product	Conv.(%)	Select.(%)
1	\bigcirc	1	C ¹	64.1	> 99
2	\bigcirc	1 ^c		62.9	> 99
3	\bigcirc	2		21	> 99
4	\bigcirc	3		13	> 99
5	\bigcirc	1	C	40.6	> 99
6	$\bigcirc \bigcirc$	1	ĊĊ	37.5	> 99
7	(1)	1		80.3	95
8	\bigcirc	Cu(CH ₃ COO) ₂		6	68
9	\bigcirc	Ni(CH ₃ COO) ₂		5	71
10	\bigcirc	no		trace	-

^aConditions: Amixture of catalyst (0.02 mmol), alkylbenzene (0.4 mmol), and TBHP (1.6 mmol) in acetonitrile (2.5 mL) was stirred at 80 °C for 20 h. ^bBased on GC analysis. ^cAfter three cycles.

4. Conclusions

Three novel MPFs (1-3) were synthesized by the coordination of metal ions with tetracarboxylic acid metalloporphyrinsligands Cu(TCMOPP) and Ni(TCMOPP).TheMPFsobtained workinclude 2D networks ofCu(TCMOPP) in this intercoordinated by Zn(II) (1), and 3D networks of Ni(TCMOPP) intercoordinated by K(I) (2 and **3**). Compound **1** reveals the binodal (4, 4)-connected 2D network with $4^3.6^3$ topological structure, and compound **3** is the binodal $(4_{2,8})$ -connected 3D $(4^{12}.6^{12}.8^4)(4^6)$ 2 net offlu-type topology. PLATON calculations indicate that compounds 1-3 contain 18.6%, 15.4% and 16.9% void space,

respectively. The open channel-type, 7-17Å wide, architecturesare accessible to other guest/solvent molecules. Besides, thermogravimetric analyses indicate that the framework structures of MPFs **1-3** are stable until 300 °C. In addition, **1** shows highly catalyticactivity to oxidation reaction of alkylbenzene.

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Figure Captions

Figure 1 The chemical structure of the flexible metalloporphyrins tetra-acid as building blocks.

Figure 2. Crystal structure of **1** (a) Coordination environments of Cu(II) and Zn(II) ions; (b) The distorted tetrahedral coordination geometry of Zn(II); (c) The 1D Zn-bridged bi-chain porphyrin assemblies; (d) The 2D bilayer constructed from 1D bi-chain. (The dimethylamine trapped in the interporphyrin voids and hydrogen atoms are omitted for clarity).

Figure 3 (a) The space-filling model of the channeled structure viewed down the a axis. It shows the hollow architecture, with channel voids accessible to other components that propagate parallel to this axis. (b)The simplified network structure of **1**. The Cu(TCMOPP)²⁻ units and the peripheral Zn^{2+} sites are indicated by pinkand blue, respectively.

Figure 4.Crystal structure of **2**(a) Coordination environments of Ni(II) and K(I) ions. Note that each porphyrin unitis in direct coordination contact through its carboxylic/carboxylate groups with eight K(I)ions, two at every carboxylic/carboxylate end; (b) The distorted pentagonal bipyramid coordination geometry of K(I) and the coordination geometry of the two adjacentK ions; (c) The K-bridged 2Dmetalloporphyrinic layer (K(I) linkersare seven-coordinate).(d) The 3Dporous metalloporphyrinic frameworks constructed from layers. (The hydrogen atoms are omitted forclarity).

Figure 5. Crystal structure of 3(a) Coordination environment of Ni(II) and K(I) ions; (b) The

distorted quadruple prisms coordination geometry of K(I); (c) The1D porphyrin chain bridged by K(I); (d) The2D network formed by porphyrin chain;(e) The 3D porous framework constructed by porphyrin network. (The water molecules and DMFsolvent molecules trapped in theinterporphyrin voids and hydrogen atoms are omitted forclarity).

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Figure 1



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Figure 2.







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Figure 4.







Three novel metal-organic frameworks based on flexible porphyrin

tetracarboxylic acids as highly effective catalysts

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Three novel metalloporphyrinic frameworks (**1**, **2**, **3**) were synthesized based on tetracarboxylic Cu(II) (**1**), Ni(II) (**2**, **3**) metalloporphyrin inter-linked by Zn(II) (**1**), K(I) (**2**, **3**), and **1** shows high catalytic activity to oxidation reaction of alkylbenzenes with conversion 80.3%.

Accepted