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Porous Metalloporphyrinic Frameworks Constructed from Metal 5,10,15,20-Tetrakis(3,5-biscarboxylphenyl)porphyrin for Highly Efficient and Selective Catalytic Oxidation of Alkylbenzenes

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Supporting Information

ABSTRACT: We incorporate metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin (M-H_8OCPP), for the first time, into porous metal−organic frameworks. The self-assembled porous metalloporphyrinic frameworks $[Mn_5Cl_2(MnCl\text{-}OCPP)(DMF)_4(H_2O)_4]\cdot 2DMF\cdot 8CH_3COOH\cdot 14H_2O$ (ZJU-18; ZJU = Zhejiang University), $[Mn_5Cl_2(Ni\text{-}OCPP)(H_2O)_8]\cdot 7DMF\cdot 6CH_3COOH\cdot 11H_2O$ (ZJU-19), and $[Cd_5Cl_2(MnCl\text{-}OCPP)(H_2O)_6]\cdot 13DMF\cdot 2CH_3COOH\cdot 9H_2O$ (ZJU-20) are isostructural as revealed by their single X-ray crystal structures. The metalloporphyrin octacarboxylates (M-OCPP) (M = $Mn^{III}Cl$ for ZJU-18 and ZJU-20, M = Ni^{II} for ZJU-19) are bridged by binuclear and trinuclear metal carboxylate secondary building units to form a 3-periodic, binodal, edge-transitive net with Reticular Chemistry Structure Resource symbol **tbo** with pore windows of about 11.5 Å and pore cages about 21.3 Å in diameter. The porous nature of these metalloporphyrinic frameworks is further established by sorption studies in which different substrates such as ethanol, acetonitrile, acetone, cyclohexane, benzene, toluene, ethylbenzene, and acetophenone can readily have access to the pores. Their catalytic activities for the oxidation of alkylbenzenes were examined at 65 °C using *tert*-butyl hydroperoxide as the oxidant. The results indicate that ZJU-18 is much superior to ZJU-19, ZJU-20, and homogeneous molecular MnCl-Me_8OCPP, exhibiting highly efficient and selective oxidation of ethylbenzene to acetophenone in quantitative >99% yield and a turnover number of 8076 after 48 h.

INTRODUCTION

Porphyrin and metalloporphyrin molecules have unique chemical, physical, and electronic structures and properties and play a number of important roles in molecular binding, reaction catalysis, energy and electron transfer, and light harvesting.[1,2] Accordingly, they have been widely explored as the building blocks for the construction of diverse functional materials, ranging from photonic devices to conductive polymers, chemical sensors, receptors for selective catalysis, material for magnetic ordering, and light-harvesting materials.[3−9]

To incorporate these porphyrin and metalloporphyrin building blocks into the emerging metal−organic framework (MOF) materials (we specifically term this subclass of MOFs metalloporphyrinic frameworks (MPFs)), the three-dimensional periodical arrangements of these moieties within the frameworks have enabled them to collaboratively interact with each other and thus to enhance their functionalities.[10−16] Functionalities can be further explored beyond the traditional applications once the pore structures have been introduced into such framework materials to direct their specific and selective molecular recognitions and thus to realize their applications in gas separation, sensing, heterogeneous catalysis, bioimaging, and even drug delivery, as well established in the traditional porous MOF materials.[17−22] Although this metalloporphyrinic framework approach is very promising to target functional materials, the progress on such a research endeavor has been very slow. The first several MPFs by making use of (5,10,15,20-tetra-4-pyridyl-21*H*,23*H*-porphinato)metal (metal = Pd^{2+} and Cu^{2+}) building blocks were synthesized and structurally characterized back in the early 1990s.[23] Significant progress was only made when Suslick established the permanent porosity of the PIZA-1 constructed from cobalt(III) tetrakis-(*p*-carboxyphenyl)porphyrin by sorption studies in 2002 and later realized the catalytic properties of the PIZA-3 built from manganese(III) tetrakis(*p*-carboxyphenyl)porphyrin in 2005.[24] Over the past two decades, the explored metalloporphyrin building blocks have been mainly focused on commercially available porphyrin linkers, including the two mentioned above,

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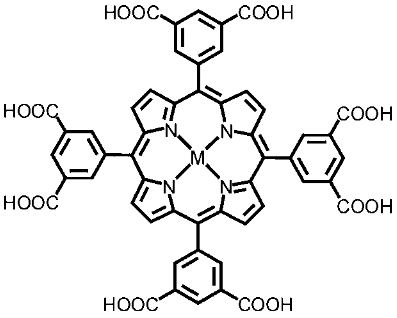
bis(4-pyridyl)porphyrin, and bis(*p*-carboxyphenyl)-porphyrin.[25−30]

As demonstrated in the development of porous metal−organic frameworks, the exploitation of new organic linkers has played a crucial role in targeting some prototypic porous MOFs exhibiting superior properties. For example, the introduction of 1,3,5-tris(4-carboxyphenyl)benzene (H_3BTB) in 2001 led to the discovery of the extraordinarily highly porous MOF-177 in 2004 and MOF-200 in 2010.[31] Given the fact that the *m*-benzenedicarboxylate moieties are very powerful organic groups to stabilize the frameworks,[32] we expect that the metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin (M-H_8OCPP; Scheme 1) having four *m*-benzenedicarboxylate moieties will be an excellent metalloligand to construct porous MPF materials for practical applications.[33] Herein we, for the first time, explore this new type of metalloporphyrin linker and report the syntheses, structures, sorption properties, and catalytic alkylbenzene oxidation of three isostructural MPFs $[Mn_5Cl_2(MnCl\text{-}OCPP)(DMF)_4(H_2O)_4]\cdot 2DMF\cdot 8CH_3COOH\cdot 14H_2O$ (ZJU-18; ZJU = Zhejiang University), $[Mn_5Cl_2(Ni\text{-}OCPP)(H_2O)_8]\cdot 7DMF\cdot 6CH_3COOH\cdot 11H_2O$ (ZJU-19), and $[Cd_5Cl_2(MnCl\text{-}OCPP)(H_2O)_6]\cdot 13DMF\cdot 2CH_3COOH\cdot 9H_2O$ (ZJU-20). ZJU-18 exhibits highly efficient and selective catalytic oxidation of alkylbenzenes at 65 °C using *tert*-butyl hydroperoxide (TBHP) as the oxidant.

Scheme 1. Metal 5,10,15,20-Tetrakis(3,5-biscarboxylphenyl)porphyrin Metalloligands



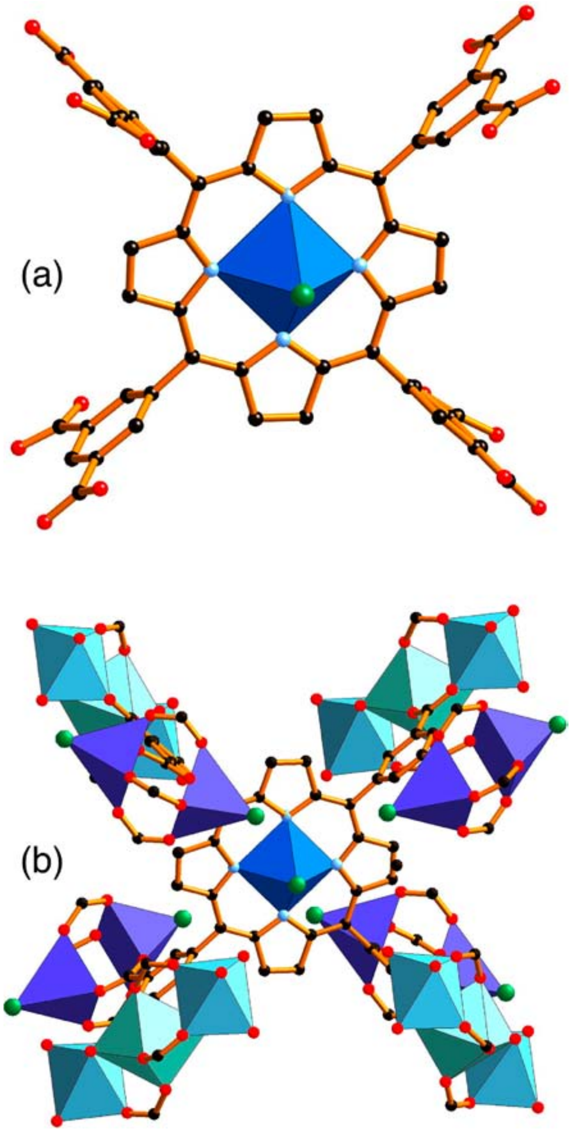


Figure 1. (a) $Mn^{III}Cl\text{-}H_8OCPP$ metalloligand centered by a MnN_4Cl square pyramid and (b) same unit connected to binuclear $Mn_2(COO)_4$ and trinuclear $Mn_3(COO)_4(\mu\text{-}H_2O)_2$ SBUs in the crystal structure of ZJU-18. Mn-centered polyhedra are shown in different shades of blue.

■ RESULTS AND DISCUSSION

The three MPFs were synthesized by heating a mixture of M-H_8OCPP (M = $Mn^{III}Cl$ or Ni^{II}) and manganese(II) chloride or cadmium chloride in a mixed solvent of DMF and acetic acid at 80 °C for one week. The composition of the as-synthesized MPFs was figured out on the basis of the elemental analysis, thermogravimetric analysis (TGA), and single-crystal structure. Single-crystal X-ray diffraction analysis revealed that the three compounds are isomorphous and crystallize in the orthorhombic *Fmmm* space group.[34] The representative crystal structure of ZJU-18 was discussed in detail. The structure is made up of an octatopic $Mn^{III}Cl$-OCPP metalloligand joined to two metal-containing secondary building units (SBUs), binuclear $Mn_2(COO)_4$ and trinuclear $Mn_3(COO)_4(\mu\text{-}H_2O)_2$ (Figure 1). We analyze the topology of the structure in the manner suggested by O'Keeffe and Yaghi.[35] There are three metal SBUs as shown in Figure 2. The first is a $Mn^{III}N_4Cl$ square pyramid with the four N atoms acting as points of extension. The second SBU has the composition $Mn_3(COO)_4(\mu\text{-}H_2O)_2(H_2O)_6$ with again four carboxylate C atoms as points of extension. The third one is a $Mn^{II}_2(COO)_4Cl_2$ paddlewheel with the four carboxylate C atoms forming the points of extension. A fourth node of the underlying net is the 3-coordinated branch point of the organic component (Figure 2d). These are linked together in the crystal as shown in Figure 2e to form a 3-periodic net. Remarkably the three metal-containing SBU nodes are all the same topologically, and the underlying net is the binodal, edge-transitive net with Reticular Chemistry Structure Resource (RCSR) symbol **tbo**.[36] This net was first found in an MOF structure in HKUST-1;[37a] more recently isoreticular materials of exceptional porosity and specific surface area have been reported.[37] This net in its most symmetrical realization has large cavities of about 21.3 Å (the yellow ball in Figure 2e), and the corresponding pore window in the structure of ZJU-18 is approximately 11.5 Å in diameter. Apparently, the porphyrin $Mn^{III}N_4Cl$ sites are readily accessible to the substrates. PLATON calculations indicate that ZJU-18 consists of 59.8%

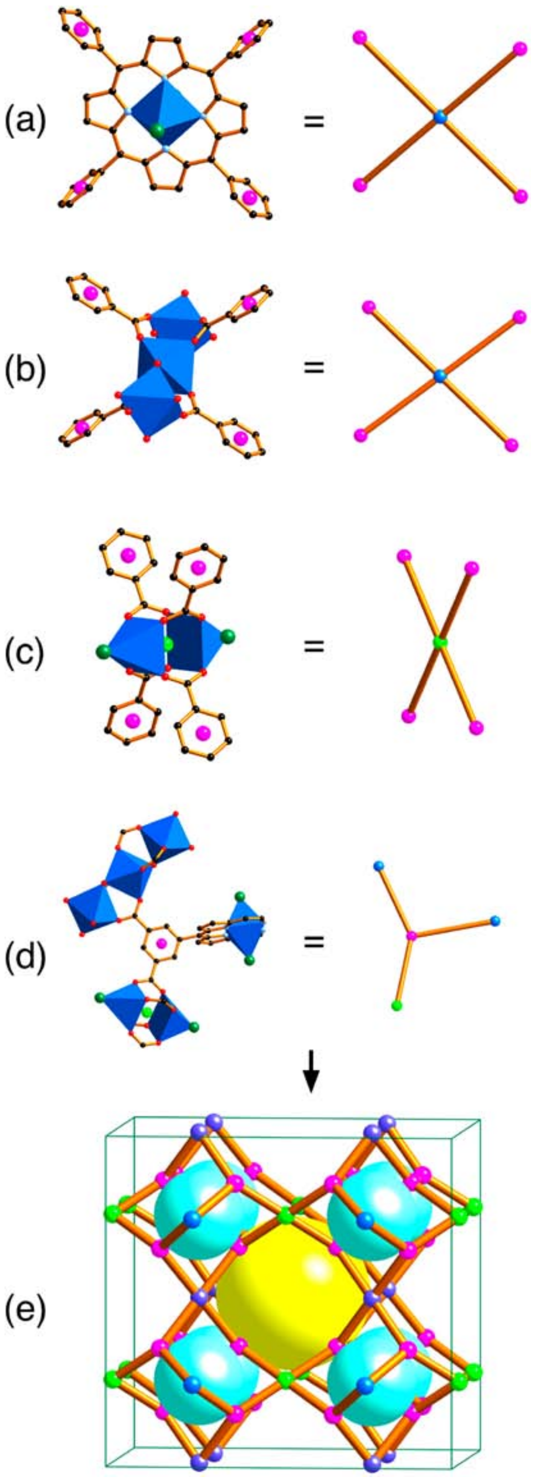


Figure 2. Mn-containing SBUs (a) $Mn^{III}N_4Cl$, (b) trinuclear $Mn_3(COO)_4(\mu\text{-}H_2O)_2(H_2O)_6$, and (c) binuclear paddlewheel $Mn^{II}_2(COO)_4Cl_2$ and (d) their linkage to the 3-coordinated node to form (e) the net from four nodes in the actual crystal structure of ZJU-18. Yellow and blue balls are centered in the large and small cavities in the structure.

void space which can encapsulate many of the solvent molecules.[38]

The access of different substrate molecules into the pores of the activated ZJU-18 was further examined by sorption studies. After the as-synthesized ZJU-18 was heated at 90 °C under vacuum for 6 h, powder X-ray diffraction (PXRD) analysis of the sample showed that the sharp diffraction pattern almost disappears. This result suggests that ZJU-18 loses its long-range order upon the removal of included solvent molecules. However, the sharp diffraction peaks can be restored by immersing the evacuated samples in DMF for 24 h. (For comparison, the evacuated sample was also exposed to the vapor of DMF at 80 °C for 24 h. The PXRD of the resulting regenerated ZJU-18 by DMF vapor sorption is basically identical to that of the regenerated ZJU-18 by immersion in DMF. See Figure S7 in the Supporting Information.) Hence, the solvent-free activated sample was immersed in various solvents for 6 h at room temperature to study the guest inclusion properties of ZJU-18 in which triphenylmethane was used as an internal standard. GC−MS analysis on the supernatants indicates that the activated ZJU-18 can readily take up a large amount of different solvent molecules such as ethanol, acetonitrile, acetone, cyclohexane, benzene, toluene, ethylbenzene, and acetophenone, as shown in Figure 3.[39]

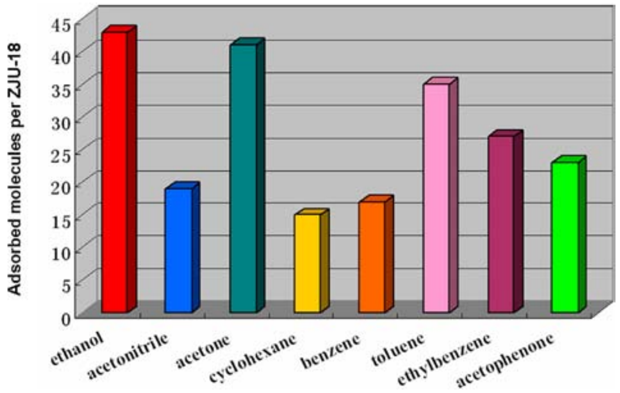
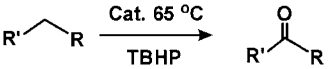
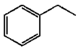
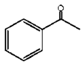
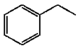
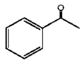
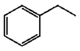
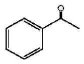
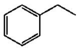
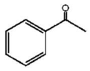
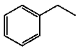
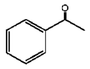
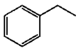
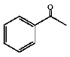
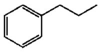
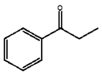
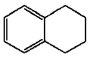
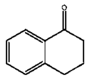
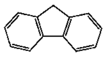
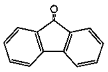
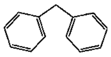
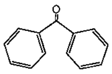
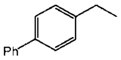
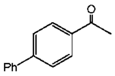
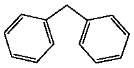
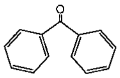
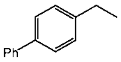
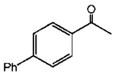
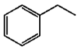
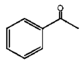
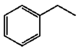
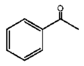


Figure 3. Illustration of the sorption ability of ZJU-18 per formula unit as probed by GC−MS.

We examine these three MPFs for their catalytic oxidation of alkylbenzenes. The ethylbenzene oxidation by MPFs was performed in a mixed solvent of acetonitrile, acetic acid, and water at 65 °C for 18 h using TBHP as the oxidant. GC−MS analysis after the reaction showed that ZJU-18 efficiently catalyzes this chemical transformation in which ethylbenzene was converted to the only product acetophenone quantitatively in >99% yield (Table 1, entry 1), while ZJU-19 having Ni^{II}-OCPP porphyrin centers displayed basically negligible catalytic activity in which only 9% acetophenone was formed (entry 2). The significant difference between ZJU-18 and ZJU-19 for their catalytic transformation of ethylbenzene to acetophenone clearly indicates the crucial roles of the $Mn^{III}Cl$-OCPP sites within ZJU-18 as the efficient catalytic sites. We speculate that the manganese sites on the SBU nodes $Mn^{II}_3(COO)_4Cl_2$ and $Mn^{II}_3(COO)_4(\mu\text{-}H_2O)_2(H_2O)_6$ within ZJU-18 might also be partially responsible and work collaboratively with $Mn^{III}Cl$-OCPP sites to enforce such efficient catalytic activity, given the fact that ZJU-20's catalytic activity is much lower than that of ZJU-19 (entry 3, conversion of 69%; in the structure of ZJU-20, the SBUs are $Cd^{II}_2(COO)_4(H_2O)_2$ and $Cd^{II}_3(COO)_4Cl_2(H_2O)_4$). We also studied the catalytic activity of $MnCl_2$, Mn-Me_8OCPP, or Ni-Me_8OCPP (entries 4−6) for comparison, again to confirm that $Mn^{III}Cl$-OCPP sites within ZJU-18 play the most important roles for highly efficient and selective oxidation of ethylbenzene. ZJU-18 can also catalyti-

Table 1. Selective Oxidation of Alkylbenzenes Catalyzed by MPFs for the Formation of Phenyl Ketones[a]



Entry	Substrate	Catalyst	Product	Conv.(%)[b]	Select.(%)[b]
1		**ZJU-18**		>99	>99
2		**ZJU-19**		9	80
3		**ZJU-20**		69	95
4		MnCl-Me$_8$OCPP		16	86
5		Ni-Me$_8$OCPP		trace	-
6		MnCl$_2$		5	79
7		**ZJU-18**		74	>99
8		**ZJU-18**		58	>99
9		**ZJU-18**		42	>99
10		**ZJU-18**		18	>99
11		**ZJU-18**		16	>99
12		MnCl-Me$_8$OCPP		26	>99
13		MnCl-Me$_8$OCPP		28	>99
14		**ZJU-18**		92	90[c]
15		MnCl-Me$_8$OCPP		trace	-[d]

[a] Alkylbenzene (0.1 mmol), TBHP (0.15 mmol), catalyst (0.005 mmol), acetonitrile (1.0 mL), acetic acid (0.2 mL), and water (0.2 mL) were stirred at 65 °C for 18 h. [b] Conversion (%) and selectivity (%) were determined by GC–MS on an SE-54 column. [c] Fifteenth cycle, and the byproduct is 1-phenylethanol. [d] Third cycle.

cally oxidize various alkylbenzenes (Table 1, entries 7–11) under the above-mentioned reaction conditions. The conversion of substrate decreases gradually when the size of the substrate increases. The much lower catalytic conversion for the larger substrates (entries 10 and 11) might be attributed to their difficult access to the interior pores of ZJU-18, so the catalytic reaction mainly occurs on ZJU-18 exterior surfaces. In fact, ZJU-18 exhibits even lower catalytic activity than the molecular MnCl-Me$_8$OCPP catalyst for the catalytic oxidation of larger substrates diphenylmethane and 4-ethylbiphenyl (Table 1, entries 12 and 13 versus 10 and 11) because of the difficult access of these larger substrates into the interior pores of ZJU-18. It needs to be mentioned again that ZJU-18 displays much higher catalytic activity than the molecular MnCl-Me$_8$OCPP catalyst for the catalytic oxidation of smaller substrate ethylbenzene (entry 4 versus 1). These results clearly indicate that catalytic properties of ZJU-18 for the oxidation of alkylbenzenes are substrate size-selective, as well established in other types of solid porous catalysts,[40] though steric constraint and the electronic effect of the different reactant substrates might also have some effects.

We intentionally interrupted the catalytic reaction after 5 h and collected the catalyst ZJU-18 solid to study the chemical species adsorbed inside the pores. GC−MS analysis of the desorbed species from this reacted ZJU-18 suggests that it incorporates about seven ethylbenzene and two acetophenone molecules per ZJU-18. This study clearly demonstrates that the catalytic oxidation of ethylbenzene into acetophenone does occur inside the pores of ZJU-18. However, when the same procedure was applied for the oxidation of larger substrate 4-ethylbiphenyl, only trace substrate and product molecules were detected by GC−MS. These results further confirm the substrate size-selective property of ZJU-18 for the oxidation of alkylbenzenes. The easy access of small substrate ethylbenzene into the pore space of ZJU-18 has maximized the catalytic activity and efficiency of the immobilized catalytic Mn^{III} sites inside the pores, while the large substrate 4-ethylbiphenyl is very difficult to diffuse into the pores of ZJU-18, so the catalytic oxidation of 4-ethylbiphenyl mainly takes place on the surface of ZJU-18, leading to the much lower catalytic activity.

As shown in Figure 3, the pores within ZJU-18 are large enough to take up both ethylbenzene and acetophenone molecules. After the activated ZJU-18 was immersed into the mixture of ethylbenzene and acetophenone (v/v = 1/1) with a triphenylmethane internal standard for 6 h at room temperature, GS−MS analysis showed that ZJU-18 preferably takes up ethylbenzene (23 molecules) over acetophenone (5 molecules) per formula unit of ZJU-18. Such preferred sorption of substrate reactant over the product will significantly facilitate the recognition of the substrate and the release of the product, which is certainly also responsible for the remarkable catalytic activity of ZJU-18 for the oxidation of ethylbenzene.

After a mixture of ZJU-18 and TBHP in a mixed solvent of acetonitrile, acetic acid, and water was heated at 65 °C for 18 h under stirring, ethylbenzene and additional TBHP were subsequently added into the filtered hot filtrate, which was further heated at 65 °C for another 18 h. GC analysis only detects a trace of product, which is identical to that of the background reaction. This result demonstrates the heterogeneous catalytic nature of ZJU-18. ZJU-18 is easily recovered by centrifugation to remove the supernatant, washed with acetonitrile several times, and subsequently used in the successive runs for 15 cycles (Table 1, entry 14; Figures S8 and S9, Supporting Information). The remarkable stability of ZJU-18 further encouraged us to study the kinetic behavior by using a large amount of substrate. As shown in Figure S10 in the Supporting Information, the turnover number (TON) reaches 8076 with a turnover frequency (TOF) of 168 h^{-1} after 48 h without loss of catalytic activity in the following runs. ZJU-18 is significantly superior to other reported heterogeneous catalysts such as polyoxometalates, metal oxides, immobilized metalloporphyrins, mesoporous materials, and others for the oxidation of ethylbenzene.[41] These known catalysts suffer from a lower oxidation selectivity, which leads to a certain amount of side products 1-phenylethanol and benzaldehyde; while the highest TON is up to 90. The high selectivity of ZJU-18 for the oxidation of ethylbenzene to exclusively produce acetophenone at high yield and extremely high TON of the ZJU-18 catalyst is really remarkable.

The PXRD patterns of the recovered solid ZJU-18 showed that the structural integrity of the catalyst was maintained during the catalytic process (see Figure S11 in the Supporting Information), leading to its high catalytic activities even after 15 cycles. This is significantly different from the homogeneous counterpart. The recovered homogeneous catalyst MnCl-Me_8OCPP basically lost its catalytic activity after three cycles (Table 1, entry 15). It is speculated that the mechanism of the catalytic reaction inside the pores of ZJU-18 is similar to those of reactions catalyzed by homogeneous metalloporphyrin catalysts: the formation of reactive oxometalloporphyrin intermediates and hydrogen abstraction from a benzylic carbon atom (see Scheme S1 in the Supporting Information).[42] However, the homogeneous metalloporphyrin catalysts have very high suicidal inactivation because of the formation of catalytically inactive μ-oxometalloporphyrin dimers.[43] The incorporation of these catalytically active metalloporphyrin species into the porous metalloporphyrinic framework solid catalysts has not only heterogenized the catalysts, but also significantly enhanced and sustained their catalytic activities by blocking the formation of the catalytically inactive dimetalloporphyrinic species.

■ CONCLUSION

To make use of the new metalloporphyrin ligands metal 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin (M-H_8OCPP) (M = Mn^{III}Cl and Ni^{II}), we, for the first time, have successfully constructed three porous metalloporphyrinic frameworks whose structures are 3-periodic, binodal, edge-transitive nets with RCSR symbol **tbo**, having intercrossed pore windows of about 11.5 Å and pore cages about 21.3 Å in diameter. Because of the immobilization of Mn^{III}-porphyrin catalytic sites onto the pore surfaces of the resulting porous metalloporphyrinic frameworks, the developed catalyst ZJU-18 exhibits highly efficient and selective oxidation of alkylbenzene in which 99% yield has been realized for the transformation of ethylbenzene to acetophenone. ZJU-18 is very superior to the molecular Mn^{III}Cl-Me_8OCPP counterpart in terms of their catalytic activities, indicating that such a porous metalloporphyrinic framework approach has not only heterogenized the homogeneous catalysts, but also significantly sustained and enhanced their catalytic activities by blocking the formation of the catalytically inactive dimetalloporphyrinic species and by making use of their substrate-selective properties. The new metalloporphyrin ligands M-H_8OCPP have multicarboxylates to stabilize the porous frameworks; it is expected that this work will facilitate much more extensive research on these metalloporphyrin ligands for their construction of functional porous metalloporphyrinic frameworks; thus, more functional MPF materials for gas separation, sensing, light harvesting, and heterogeneous catalysis will be emerging in the near future.

■ EXPERIMENTAL SECTION

Materials and Methods. All of the chemicals were obtained from commercial sources and were used without further purification, except 5,10,15,20-tetrakis(3,5-biscarboxylphenyl)porphyrin was prepared according to the literature.[44] IR spectra were collected from KBr pellets on an FTS-40 spectrophotometer. Thermogravimetric analyses (TGA) were carried out under a N_2 atmosphere on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 °C min^{-1}. Elemental analyses were performed on a ThermoFinnigan Flash EA 1112 element analyzer. GC−MS spectra were recorded on a SHIMADZU GCMS-QP2010. PXRD data were recorded on a RIGAKU D/MAX 2550/PC for Cu Kα radiation (λ = 1.5406 Å). ^{1}H NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ solution, and the chemical shifts were reported relative to the internal standard TMS (0 ppm).

Synthesis of ZJU-18. MnCl-H_8OCPP (5.3 mg, 0.005 mmol) and $MnCl_2\cdot4H_2O$ (9.9 mg, 0.05 mmol) were dissolved in a mixture of DMF (2.0 mL) and HOAc (0.2 mL). The mixture was sealed in a screw cap vial and heated at 80 °C for one week. Brown crystals of ZJU-18 were filtered, washed with DMF, EtOH, and Et_2O, and dried at room temperature. Yield: 85%. Anal. Calcd for $C_{86}H_{130}Cl_3Mn_6N_{10}O_{56}$: C, 39.19; H, 4.97; N, 5.31. Found: C, 39.36; H, 4.76; N, 5.32. IR (KBr pellet, ν/cm^{-1}): 1656(s), 1613(s), 1560(s), 1498(w), 1437(s), 1367(s), 1334(w), 1242(m), 1207(w), 1144(w), 1111(m), 1058(w), 1013(m), 943(w), 915(w), 819(w), 780(s), 737(w), 712(s), 688(w), 669(w), 617(w), 570(w), 536(w), 457(w), 438(w), 414(w).

Synthesis of ZJU-19. Ni-H_8OCPP (5.1 mg, 0.005 mmol) and $MnCl_2\cdot4H_2O$ (9.9 mg, 0.05 mmol) were dissolved in a mixture of DMF (2.0 mL) and HOAc (0.2 mL). The mixture was sealed in a screw cap vial and heated at 80 °C for one week. Brown crystals of ZJU-19 were filtered, washed with DMF, EtOH, and Et_2O, and dried at room temperature. Yield: 80%. Anal. Calcd for $C_{85}H_{131}Cl_2Mn_5N_{11}NiO_{54}$: C, 39.64; H, 5.13; N, 5.98. Found: C, 40.79; H, 5.09; N, 5.94. IR (KBr pellet, ν/cm^{-1}): 1611(s), 1561(s), 1437(s), 1370(s), 1249(m), 1147(w), 1110(w), 1081(w),1055(w), 1013(m), 934(m), 802(w), 781(s), 736(w), 712(s), 688(w), 669(w), 653(w), 611(w), 537(w), 438(w), 415(w).

Synthesis of ZJU-20. The preparation procedures are similar to those of ZJU-18, except $CdCl_2\cdot2.5H_2O$ was used instead of $MnCl_2\cdot4H_2O$. Brown crystals of ZJU-19 were filtered, washed with DMF, EtOH, and Et_2O, and dried at room temperature. Yield: 73%. Anal. Calcd for $C_{95}H_{149}Cd_5Cl_3MnN_{17}O_{48}$: C 37.77; H, 4.97; N, 7.88. Found: C, 38.02; H, 5.09; N, 7.85. IR (KBr pellet, ν/cm^{-1}): 1654(s), 1611(s), 1561(s), 1501(w), 1436(s), 1367(s), 1301(w), 1251(w), 1207(w), 1145(w), 1105(m), 1055(w), 1014(m), 944(w), 918(w), 804(w), 779(s), 736(w), 715(s), 669(m), 611(w), 410(w).

Single-Crystal X-ray Data Collection and Structure Determination. The determination of the unit cells and data collection for the crystals of ZJUs-18, -19, and -20 were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphite-monochromatic enhanced ultra Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[45] The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with the SHELX-97 program package.[46] The solvent molecules in these compounds are highly disordered; the SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.[47] The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically.

Deconstruction of the Structure. We analyze the topology of the structure in the manner suggested by O'Keeffe and Yaghi.[35] The metal-containing SBUs and their points of extension are identified. Nodes of the underlying net are then placed at the center of the SBUs. The valence (coordination number or "connectivity") of these nodes is the same as the number of points of extension. Further nodes are placed at branch points (if any) of the organic component.

Typical Procedure for Substrate Adsorption Experiments. A sample of ZJU-18 (0.03 mmol) was treated under vacuum at 90 °C for 6 h. The evaluated sample was subsequently immersed in ethylbenzene (0.25 mL) with triphenylmethane as an internal standard at room temperature. The mixture was determined by analyzing an aliquot of the bulk solution using GC−MS with a flame ionization detector (FID) using a capillary SE-54 column and compared with the authentic sample analyzed under the same conditions. We have further performed additional experiments to confirm that the ethylbenzene was adsorbed in the void space. After the solid was thoroughly washed with ethyl ether to remove surface-adsorbed molecules, the solid was subsequently submersed in $CDCl_3$ for 12 h. The supernatant liquid was used for ^{1}H NMR study. The ethylbenzene peak is clearly visible from the NMR spectra.

Typical Procedure for Oxidation of Alkylbenzenes. Ethylbenzene (0.1 mmol), TBHP (0.15 mmol), catalyst (0.005 mmol), acetonitrile (1.0 mL), acetic acid (0.2 mL), and water (0.2 mL) were stirred at 65 °C for 18 h. The identity of the product was determined by analyzing aliquots of the bulk solution using GC−MS and compared with the authentic samples analyzed under the same conditions, while the conversion and selectivity were obtained by GC analysis with an FID using a capillary SE-54 column. The used ZJU-18 was recovered by centrifugation to remove the supernatant, washed with acetonitrile several times, and subsequently used in the successive runs.

Typical Procedure To Study the Chemical Species Adsorbed inside the Pores of ZJU-18 during Oxidation of Alkylbenzenes. Ethylbenzene (0.2 mmol), TBHP (0.3 mmol), catalyst (0.01 mmol), acetonitrile (2.0 mL), acetic acid (0.4 mL), and water (0.4 mL) were stirred at 65 °C for 5 h. After the reaction mixture was cooled to room temperature, the solid was recovered by filtration and thoroughly washed with acetonitrile three times. The solid was digested by using dilute aqueous ammonia solution, which was extracted with ethyl ether. The aliquot of the bulk solution was subjected to GC−MS analysis and compared with the authentic samples analyzed under the same conditions.

Study of the TONs for Oxidation of Ethylbenzene Catalyzed by ZJU-18. Ethylbenzene (20 mmol), TBHP (30 mmol), ZJU-18 (0.002 mmol), acetonitrile (8 mL), acetic acid (1.6 mL), and water (1.6 mL) were stirred at 65 °C for 48 h. The solid catalyst was centrifugated and washed with acetonitrile three times. The aliquots were regularly taken out for GC analysis to determine the conversion of ethylbenzene, the yield of acetophenone, TONs (TON is defined as the mole ratio of the substrate converted to the catalyst), and TOFs (TOF is defined as the moles of substrate converted per mole of catalyst per hour).

Typical Procedure for the Reuse of MnCl-Me_8OCPP in the Catalytic Oxidation of Ethylbenzene. MnCl-Me_8OCPP (0.005 mmol), ethylbenzene (0.1 mmol), TBHP (0.15 mmol), acetonitrile (1.0 mL), acetic acid (0.2 mL), and water (0.2 mL) were stirred at 65 °C for 18 h, and the liquid was subsequently evaporated under vacuum. The resulting solid was washed with ethyl ether three times. The combined Et_2O solution was subjected to GC−MS analysis, while the recovered MnCl-Me_8OCPP solid was subsequently used in the successive runs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic, IR, TGA, and PXRD data, catalytic study data including turnover figures, MS and NMR spectra of the products, and CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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c = 31.833(9) Å, V = 22435(11) Å^3, Z = 8, μ = 9.375 mm^{-1}, R1 = 0.1054, wR(F^2) = 0.1821 ($I > 2\sigma(I)$), and S = 0.804.

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