

Mn^{III}(Porphyrin)-Based Porous Coordination Polymers: Synthesis, Catalytic Activities for the Oxidation of Ethylbenzene

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Abstract Six Mn^{III}(porphyrin)-based porous coordination polymers, Mn^{III}(F₅CPp)–Mn^{II} (CP1, F₅CPp=5-(pentafluorophenyl)-10,15,20-tri(4-carboxyphenyl)porphyrin dianion), $Mn^{III}(F_5CPp)-Co^{II}$ (CP2), $Mn^{III}(F_5CPp)-Ni^{II}$ (CP3), $Mn^{III}(F_{10}CPp)-Mn^{II}$ (CP4, $F_{10}CPp=5,15$ -bis(pentafluorophenyl)-10,20-bis(4-carboxyphenyl)porphyrin dianion), $Mn^{III}(F_{10}CPp)-Co^{II}$ (CP5), and $Mn^{III}(F_{10}CPp)-Ni^{II}$ (CP6), were prepared and characterized. The precursors were identified by UV-Vis, GC-MS, infrared spectra and elemental analysis in the procedures of Mn^{III}(porphyrin)-based polymers synthesis. CP1, CP4, CP3 and CP6 are amorphous aggregation supported by SEM, TEM and powder XRD. CP2 and CP5 are rod-like microcrystalline particles supported by powder XRD and SAED. These polymers exhibit high catalytic activities and selectivities toward the oxidation of ethylbenzene to acetophenone in quantitative over 70 % yields, and can be reused by filtration with only slight decreasing of catalytic activities.

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Graphical Abstract



Keywords Manganese(III) porphyrin · Ethylbenzene · *tert*-Butyl hydroperoxide · Heterogeneous catalytic · Oxidation

1 Introduction

Manganese(III) porphyrin based heterogeneous catalysts have been extensively studied in the past several decades for hydroxylation of alkanes and epoxidation of alkenes [1–7]. It would be advantageous for continuous oxidation processes to anchor and isolate catalytically active metalloporphyrins, prohibiting their self-dimerizations and oxidative degradations [2, 8-11]. Under the guidance of this idea, initially, manganese(III) porphyrins were immobilized onto organic (e.g. polymers, ion-exchange resins) or inorganic supports (e.g. zeolites, silica, clays) with the interaction of covalent organic bonds [1, 3, 4, 12–14], electrovalent bonds or van der Waals interactions (physical adsorption) [2]. Although polymer covalently-bounded Mn-porphyrin oxidation catalysts are much more stable than the inorganic supported entities, few suitable porphyrins or polymer supports could be qualified.

Recently, crystalline metal-organic frameworks (MOFs) based catalysts were proposed and experimentally demonstrated [5, 6, 15–19], such as the well known PIZA-3, a capable and robust oxidation catalyst for the hydroxvlation of a variety of linear and cyclic alkanes and the epoxidation of cyclic alkenes [15]. Despite attractive approaches to the construction of catalytic metalloporphyrins MOFs developments, for instance heterogenization of well-defined homogeneous catalysts incorporated as MOF struts [16-18], MOF-encapsulation of molecular catalysts, and post-synthesis incorporation of catalytic metal sites [10], only few metalloporphyrins MOFs have been shown to be both catalytically competent and porous with respect to chemical reactants [17, 19]. One of the problems encountered in building robust and catalytic MOFs from porphyrins or metalloporphyrins, plaguily, is that amorphous coordination polymers tend to be generated, instead of crystalline porous frameworks. To our knowledge, it is seldom literature report on amorphous coordination polymers what are combining metalloporphyrins with metal ions or clusters.

Here, we report six new Mn^{III}(porphyrin)-based porous coordination polymers, in which manganese(III) porphyrin molecules were linked by the coordination of peripheral carboxyl groups with Mn(II), Co(II), and Ni(II) ions, viz $Mn^{III}(F_5CPp)-Mn^{II}$ (CP1, $F_5CPp=5$ -(pentafluorophenyl)-10,15,20-tri(4-carboxyphenyl)porphyrin dianion), Mn^{III} $(F_5CPp)-Co^{II}$ (CP2), $Mn^{III}(F_5CPp)-Ni^{II}$ (CP3), $Mn^{III}(F_{10})$ CPp)- Mn^{II} (**CP4**, $F_{10}CPp=5,15$ -bis(pentafluorophenyl)-10,20-bis(4-carboxyphenyl)porphyrin dianion), Mn^{III}(F₁₀ CPp)-Co^{II} (CP5), and Mn^{III}(F₁₀CPp)-Ni^{II} (CP6). Considering electron-attracting group on porphyrin ring favors the oxidation reaction [8, 9, 11], pentafluorophenyl was introduced to form two new porphyrins $(H_2(F_5CPp))$ and $H_2(F_{10}CPp)$) bearing distinct coordination modes. As expected, these Mn^{III}(porphyrin)-based polymers exhibit high catalytic activities and selectivities toward the oxidation of ethylbenzene. They could be used as heterogeneous catalysts which were consecutively reused three times without detectable catalysts leaching.

2 Experimental

2.1 Chemicals and Instruments

All solvents and reagents were used as received without further purification, except for pyrrole which was distilled before use. The ethylbenzene used as substrate was commercially available from ChengDu Kelong Chemical Reagent Company. The oxidant *tert*-butyl hydroperoxide (TBHP) was commercially available from Sinopharm Chemical Reagent Co., Ltd.

UV-Vis spectra were measured on a Shimadzu UV1800 spectrophotometer. The mass spectrometry analyses were carried out using a MALDI-TOF MS (Shimadzu Biotech). Infrared spectra were obtained on a BEO UZNDX₅50-FTIR spectrophotometer (Bruker) using KBr pellets. C, H, N elemental analyses were performed on a Vario EL-III apparatus (Bruker). ¹H NMR spectra were measured on a Varian INOVA-400 spectrometer (400 MHz, Varian, USA) by using tetramethylsilane (TMS) as an internal standard, with the chemical shifts relative to TMS. GC analyses were performed using a GC1100 chromatograph (PERSEE Beijing, China), nitrogen as the carrier gas $(35 \text{ cm}^3 \text{ min}^{-1})$ and equipped with a fused silica capillary 5 % phenyl 95 % dimethylpolysiloxane column (30 m \times 0.25 mm). Scanning electron microscope images (SEM) were recorded on a Quanta 400FEG microscopes. Transmission electron microscopy (TEM) and selective area electron diffraction patterns of particles were obtained using JEOL JEM-3010 microscopes. Surface area experiments were performed at 77 K on a TriStar II 3020 apparatus (Micromeritics) using nitrogen as the probing gas. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 diffractometer using graphite monochromatic copper radiation (Cu Ka) at 40 kV, 30 mA over the 2 θ range from 5° to 50°. Thermal gravimetric analysis (TGA) were performed in flowing N₂ with a heating rate of 10 °C min⁻¹ from 30 to 800 °C on a Perkin-Elmer TGA-7 instrument.

2.2 Synthesis of H₂(F₅EPp) and Mn(F₅CPp)(OAc)

Distilled pyrrole (2.7 mL, 40 mmol) with the a mixture of pentafluorobenzaldehyde (1.96 g, 10 mmol) and methyl 4-formylbenzoate (4.92 g, 30 mmol) was refluxed in propionic acid (130 mL) for 1 h. After cooling to room temperature, 80 % of the solvent was evaporated and 30 mL ethanol was added. Then the mixture was cooled for 12 h in refrigerator and filtrated under vacuum. The crude product was purified by chromatography on a silica-gel column with CH₂Cl₂ as the eluent solvent, and a desired purple solid of compound $H_2(F_5EPp)$ was obtained. Yield: 17 %; Elemental analysis Calcd. for C₅₀H₃₁F₅N₄O₆: C, 68.34; H, 3.56; N, 6.38; Found: C, 68.23 H, 3.32; N, 6.41; GC-MS observed $[M + H]^+$: 879.2 amu, calculated M: 878.2 amu; UV–Vis (nm, CH₂Cl₂) λ_{max} : 417.5 (Soret band), 513, 551, 586, 648 (Q bands); FT-IR (cm⁻¹): 3317, 2952, 1720, 1601, 1498, 1437, 1280, 1188, 1111, 983, 763. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.93–8.82 (m, 8H, Pyrrole-H), 8.40 (d, J = 7.3 Hz, 6H, Ar–H), 8.31–8.19 (d, J = 8.0 Hz, 6H, Ar–H), 1.59 (d, J = 63.8 Hz, 9H, -CH₃), -2.81 (s, 2H, N-H).

 solution was filtered, and the solvent was evaporated. The dried product was then chromatographed on a silica gel column by using CH_2Cl_2 as the eluting solvent to remove unreacted $Mn(C_2H_3O_2)_2$. Afterwards, $Mn(F_5CPp)(OAc)$ was afforded by alkaline hydrolysis of the $Mn(F_5 EPp)(OAc)$. The spectral characterization of the synthesized metalloporphyrins as follows:

Mn(F₅CPp)(OAc): yield: 85 %; M.p.: >250 °C. Elemental analysis Calcd. for C₄₉H₂₆MnF₅N₄O₈: C, 63.45; H, 2.61; N, 6.21; Found: C, 63.41; H, 2.69; N, 6.30; GC–MS observed and calculated [**Mn(F₅CPp)**]⁺: 889.1 amu; UV– Vis (nm, DMF) λ_{max} : 475 (Soret band), 575, 610; FT-IR (cm⁻¹): 3411, 2922, 1703, 1601, 1488, 1228, 1108, 972, 783.

2.3 Synthesis of H₂(F₁₀EPp) and Mn(F₁₀CPp)(OAc)

Distilled pyrrole (30 mL, 434 mmol) was added in a threenecked flask, stirring at room temperature under a nitrogen atmosphere, then methyl 4-formylbenzoate (1.64 g, 10 mmol) was added dropwise. 15 min later, 2-3 drops of boron trifluoride etherate was added, the color of solution turn to yellow-green. After 25 min, 20 mL CH₂Cl₂ and 10-15 drops saturated NaOH aqueous solution were added successively, the pH of solution was about 8. And then, added anhydrous sodium sulfate to remove water. Standing 15 min, dump out the supernatant, the CH_2Cl_2 and pyrrole were evaporated respectively, and the orange oily mixture was obtained. The mixture was then passed through a silica gel column by using CH₂Cl₂ as the eluting solvent. The first pale yellow band was collected, then evaporated most of solvent, the yellow oily residual was obtained. A small amount of anhydrous ethanol was added in the yellow oily residual, then placed in the refrigerator, overnight, there was pale yellow precipitate present, and was identified as the 5-methyl benzoate-dipyrromethane. Yield: 49.6 %; M.p.: 131 °C. Elemental analysis Calcd. for C₁₇H₁₆N₂O₂: C 72.84; H, 5.75; N, 9.99; Found: C, 72.82; H, 5.68; N, 9.86.

Pentafluorobenzaldehyde (1.96 g, 10 mmol) dissolved in hot propionic acid (70 mL), and the propionic acid solution (10 mL) of 5-methyl benzoate-dipyrromethane (2.80 g, 10 mmol) was added dropwise. The solution was refluxed for 1 h. After cooling to room temperature, most of propionic acid was evaporated and 30 mL ethanol was added. Then the mixture was cooled for 10 h in refrigerator and filtrated under vacuum. The further purified by column chromatography (silica, CH₂Cl₂), and a desired purple solid of compound **H**₂(**F**₁₀**EPp**) was obtained. Yield: 6.8 %; M.p.: >250 °C; Elemental analysis Calcd. for C₄₈H₂₄F₁₀N₄O₄: C, 63.30; H, 2.66; N, 6.15; Found: C, 63.25 H, 2.58 N, 6.32; GC–MS observed [M + H]⁺: 911.2 amu, calculated M: 910.2 amu; UV–Vis (nm, CH₂Cl₂) λ_{max} : 415 (Soret band), 511, 553, 593, 652 (Q bands); FT-IR (cm⁻¹): 3317, 2947, 1722, 1609, 1434, 1278, 1107, 961, 802. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.92–8.83 (d, J = 19.0, 8H, Pyrrole–H), 8.48–8.29 (m, 8H, Ar–H), 1.57–1.43 (m, 6H, –CH₃), –2.80 (d, J = 19.8 Hz, 2H, N–H).

Mn(**F**₁₀**CPp**)(**OAc**) was prepared following the procedures described for **Mn**(**F**₅**CPp**)(**OAc**) except that H₂(F₁₀EPp) was used instead of H₂(F₅EPp). Yield: 96 %; M.p.: >250 °C. Elemental analysis Calcd. for C₄₈H₂₁ MnF₁₀N₄O₅: C, 58.91; H, 2.16; N, 5.72; Found: C, 58.75; H, 1.92; N, 5.55; GC–MS observed and calculated [**Mn**(**F**₁₀**CPp**)]⁺: 935.1 amu; UV–Vis (nm, DMF) λ_{max} : 473 (Soret band), 568, 599; FT-IR (cm⁻¹): 3434, 2919, 1704, 1609, 1499, 1272, 1119, 980, 805.

2.4 Synthesis of $Mn^{III}(F_5CPp)-M^{II}$ and $Mn^{III}(F_{10}CPp)-M^{II}$ (M = Mn, Co, Ni; CP1-CP6)

A mixture of $Mn(F_5CPp)(OAc)$ (0.009 g, 0.01 mmol), Mn(OAc)₂·4H₂O (0.007 g, 0.03 mmol), and DMF (4 mL), was stirred, and then sealed in a 10 mL Teflon-lined stainless steel reactor, kept under autogenous pressure at 90 °C for 72 h. The dark-purple precipitate of reaction was filtered and washed with water, CH₂Cl₂, DMF and ethanol to remove any unreacted monomer. The target product Mn(F₅CPp)–Mn (**CP1**) was dried at 110 °C under vacuum for 24 h. **CP2** and **CP3** were prepared following the procedure described for **CP1** except that Co(OAc)₂·4H₂O (0.007 g, 0.03 mmol) and Ni(OAc)₂·4H₂O (0.007 g, 0.03 mmol) were used instead of Mn(OAc)₂·4H₂O.

CP4–CP6 were prepared following the procedures described for **CP1–CP3** except that $Mn(F_{10}CPp)(OAc)$ (0.010 g, 0.01 mmol) was used instead of $Mn(F_5CPp)(OAc)$.

2.5 Oxidation Procedure and Catalysts Reuse

All the oxidation reactions were carried out in a sealed vial. A mixture of ethylbenzene (0.1 mmol), TBHP (0.4 mmol), and the catalyst (**CP1–CP6**, 5 mg) in acetonitrile (1 mL) was stirred at 65 °C for 12 h. When time up, the results of reaction were examined by GC. ¹H NMR and MS spectral data confirmed the identities of the product. The catalyst was recovered by centrifugation, washed with water, methanol, acetonitrile and diethyl ether successively, and dried in vacuum at 110 °C to remove the solvent for several hours before new utilization under similar reaction conditions.

After the use of catalyst for three consecutive times, the acetophenone yield was no significant decline and the selectivity remained over 99 %. The leaching experiments were made in the same conditions described above, after 12 h of reaction the catalyst was isolated by centrifugation and no characteristic spectrum of the metalloporphyrin was detectable in the supernatant by UV–Vis.

3 Results and Discussion

3.1 Synthesis and Characterization of $H_2(F_5EPp)$ and $Mn(F_5CPp)(OAc)$, $H_2(F_{10}EPp)$ and $Mn(F_{10}CPp)(OAc)$

Adler synthesis is a convenient strategy for preparing porphyrin derivatives by the condensation of pyrrole and aldehyde [20-24]. As shown in Scheme 1, the metal-free 5-(pentafluorophenyl)-10,15,20-tri(4-methoxycarbonylphenyl)porphyrin, $H_2(F_5EPp)$, was synthesized firstly. Then, $H_2(F_5Pp)$ EPp) could metallize and hydrolysis generated peripheral carboxyl Mn(III)-porphyrin (Mn(F₅CPp)(OAc)), alternatively it could undergo hydrolysis first, and metallization in the opposite way. While we chose the metallization $H_2(F_5EPp)$ first and then hydrolysis route in order to get pure and high vield of Mn(F₅CPp)(OAc), because if the latter selected, it is hard to prohibit Mn(II) cations combine with carboxyl oxygen, or to produce polymers. It should be pointed out that divalent Mn(II) ions were oxidized to trivalent Mn(III) cations in the process of synthesis of manganese porphyrin compounds. Acetate anion (OAc⁻) should be combining to the center Mn(III) as a counter ion, which is supported by mass spectra and elemental analysis. The case also occur in the other Mn(III)-porphyrins (see Table 1).

It is known that 5-substituted dipyrromethanes have been used as important intermediates in the synthesis of porphyrins in [2 + 2] MacDonald synthesis [25-27], which is a useful strategy for preparing symmetrical porphyrins by the condensation of dipyrromethanes and aldehyde. Consequently, in the synthesis of the metal-free 5,15-bis(pentafluorophenyl)-10,20-bis(4-methoxycarbonylphenyl)porphyrin, $H_2(F_{10}EPp)$ in Scheme 2, methyl 4-formylbenzoate reacting with pyrrole (1:40 molar ratio) in dichloromethane under nitrogen was performed firstly, in the presence of boron trifluoride etherate at room temperature for half-hour to produce 5-methyl benzoate-dipyrromethane, and condensation of the 5-methyl benzoate-dipyrromethane with pentafluorobenzaldehyde in hot propionic acid gave a methyl ester porphyrin $H_2(F_{10}EPp)$. The next procedures are the same as $H_2(F_5EPp)$, metallization $H_2(F_{10}EPp)$ and hydrolysis obtain the product of peripheral carboxyl Mn(III)-porphyrin (Mn(F₁₀CPp)(OAc)).

All the porphyrins/Mn(III)-porphyrins derivatives in Schemes 1, 2 including $H_2(F_5CPp)$ and $H_2(F_{10}CPp)$ were isolated, and identified by UV–Vis, GC–MS, infrared spectra and elemental analysis (Table 1). In addition, $H_2(F_5EPp)$ and $H_2(F_{10}EPp)$ were identified by ¹H NMR (Table 2). UV–Vis spectroscopy is a convenient method, through which can quickly determine the formation of the porphyrin ring. The UV–Vis spectra of $H_2(F_5EPp)$, $H_2(F_{10}EPp)$, $H_2(F_5CPp)$ and $H_2(F_{10}CPp)$ have Soret band at 417.5, 415, 416 and 417.5 nm, and Q bands located at 512,550,587 and 649 nm for

 $H_2(F_5EPp)$, the others in Table 1. These characteristic spectral data of porphyrin derivatives are similar to Spellane [28] and Kadish [29] reports. The Mn(F₅EPp)(OAc), Mn(F₁₀ EPp)(OAc), Mn(F₅CPp)(OAc) and Mn(F₁₀CPp)(OAc) have Soret band at 477, 474, 475 and 473 nm, and two Q bands at 571 and 607 nm for Mn(F₅EPp)(OAc), the others in Table 1. The UV–Vis spectra provide limited information as to the formation of different porphyrin derivatives and Mn(III)-porphyrins, but these are not the case for the mass spectral data which are quite definitive. The MS data in accordance with the expected value of $H_2(F_5EPp)$, $H_2(F_{10}EPp)$, $H_2(F_5CPp)$ and $H_2(F_{10}CPp)$, which are also consistent with the elemental analysis and ¹H NMR [29–31] (see Tables 1, 2).

As to Mn(III)-porphyrins, the elemental analysis are consistent with composition of the isolated compounds, Mn(F₅ EPp)(OAc), $Mn(F_5CPp)(OAc)$, $Mn(F_{10}EPp)(OAc)$ and $Mn(F_{10}CPp)(OAc)$, respectively (Table 1). In addition, the mass data of the isolated Mn(III)-porphyrins which lost acetate anions in the process of mass spectra identification are also consistent with the structure of $Mn(F_5EPp)^+$, $Mn(F_{10})$ EPp)⁺, Mn(F₅CPp)⁺ and Mn(F₁₀CPp)⁺ cations, respectively. Although most of the absorption bands observed in the infrared spectra of the isolated Mn(III)-porphyrins are due to the porphyrins themselves, the subtle differences between the spectra of the custom-designed porphyrins and Mn(III)-porphyrins suggest that the structure distinction of them. An infrared spectral feature common to all of the isolated porphyrin derivatives is a wagging vibration absorption band of $\omega_{\rm N-H}$ in the region of 960 cm⁻¹ (Table 1). This band is present in each spectrum of metal-free porphyrin and absent from that of the Mn(III)-porphyrin. Meanwhile, a stretching vibration absorption band of v_{Mn-N} in the region of 980 cm⁻¹ is present in each spectrum of Mn(III)-porphyrin and absent from that of the metal-free porphyrin (Table 1) [32]. These subtle differences between the infrared spectra of the porphyrins and Mn(III)-porphyrins indicate that Mn(III) cations are locating at the core of porphyrins and coordinating to four nitrogen atoms in Mn(III)-porphyrins.

All the above discussion, indicating the isolated porphyrins and Mn(III)-porphyrins, H₂(F₅EPp), H₂(F₁₀EPp), H₂(F₅CPp), H₂(F₁₀CPp), Mn(F₅EPp)(OAc), Mn(F₁₀ EPp)(OAc), Mn(F₅CPp)(OAc) and Mn(F₁₀CPp)(OAc), are consistent with the structures illustrated in Schemes 1, 2.

3.2 Synthesis and Characterization of $Mn^{III}(F_5CPp)-Mn^{II}$ (CP1), $Mn^{III}(F_5CPp) Co^{II}$ (CP2), $Mn^{III}(F_5CPp)-Ni^{II}$ (CP3), $Mn^{III}(F_{10}CPp)-Mn^{II}$ (CP4), $Mn^{III}(F_{10}CPp)-Co^{II}$ (CP5), and $Mn^{III}(F_{10}CPp)-Ni^{II}$ (CP6)



Table 1 Data of element analyses, UV-Vis, FT-IR and GC-MS spectra of porphyrins/Mn(III)-porphyrins

Compd.	Element analyses						UV–Vis	IR		GC-MS	
	С		Н		N		λ_{max} , nm (CH ₂ Cl ₂)	$\omega_{\rm N-H}$	v _{Mn-N}	Found	Calcd.
	Found	Calcd.	Found	Calcd.	Found	Calcd.		(cm ⁻¹)	(cm ⁻¹)	(amu)	(amu)
H ₂ (F ₅ EPp)	68.23	68.34	3.32	3.56	6.41	6.38	417.5, 512, 550, 587, 649	966		879.2 ^a	878.2
$H_2(F_{10}EPp)$	63.25	63.30	2.58	2.66	6.32	6.15	415, 511, 553, 593, 652	961		911.2 ^a	910.2
$H_2(F_5CPp)$	67.52	67.47	3.23	3.01	6.62	6.70	416, 512, 546, 590, 647	966		835.2 ^b	836.2
$H_2(F_{10}CPp)$	62.52	62.59	2.23	2.28	6.52	6.35	417.5, 512, 547, 585, 652	962		881.1 ^b	882.1
Mn(F5EPp)(OAc)	63.32	63.04	3.33	3.26	5.75	5.65	477, 571, 607		983	931.1 ^c	931.1 ^c
Mn(F ₁₀ EPp)(OAc)	58.63	58.72	2.41	2.46	5.51	5.48	474, 592, 622.5		985	963.1 ^c	963.1 ^c
Mn(F ₅ CPp)(OAc)	63.41	63.45	2.69	2.61	6.21	6.30	475, 575, 610		972	889.1 ^c	889.1 ^c
$Mn(F_{10}CPp)(OAc)$	57.85	57.96	2.21	2.13	5.55	5.63	473, 568, 599		980	935.1°	935.1°

^a [M + H]⁺ charged

^b [M–H]⁻ charged

^c $Mn(F_5EPp)^+$, $Mn(F_{10}EPp)^+$, $Mn(F_5CPp)^+$ and $Mn(F_{10}CPp)^+$ ions

 $Mn^{III}(F_{10}CPp)-Mn^{II}$ (**CP4**), $Mn^{III}(F_{10}CPp)-Co^{II}$ (**CP5**), and $Mn^{III}(F_{10}CPp)-Ni^{II}$ (**CP6**), were prepared from Mn(III)-porphyrins of Mn(F₅CPp)(OAc) and Mn(F₁₀ CPp)(OAc) and nodes of Mn(II), Co(II) and Ni(II) ions in DMF under solvothermal. In Fig. 1, the profiles of the UV– Vis spectra of **CP1–CP6** maintain the characteristics of

manganese(III) carboxyphenylporphyrin precursors. The Soret bands of **CP2**, **CP5**, and **CP6** blue shift, respectively, to 408, 415 and 408 nm, and those of **CP1**, **CP3**, and **CP4** red shift slightly to 482, 481 and 479 nm. It is suggests that complexes of **CP1–CP6** are mainly composed of $Mn(F_5 CPp)/Mn(F_{10}CPp)$ units. The infrared spectra of

Scheme 2 Scheme of reaction for the synthesis of $H_2(F_{10}EPp)$ and $Mn(F_{10}CPp)(OAc)$



Mn(F₅CPp)(OAc), Mn(F₁₀CPp)(OAc) and **CP1–CP6** are shown in Fig. 2, where it can be seen the C=O stretch bands of Mn(F₅CPp)(OAc) and Mn(F₁₀CPp)(OAc) in the region of 1700 cm⁻¹, which are absent from spectra of **CP1–CP6**. Meanwhile, v_{COO}^{as} , v_{COO}^{s} and v_{Mn-N} absorption bands of **CP1–CP6** are present in the region of 1660, 1400 and 980 cm⁻¹, respectively. These indicate that the peripheral carboxylates of Mn(F₅CPp)/Mn(F₁₀CPp) are ligating the nodes of metal ions (Mn(II), Co(II) and Ni(II)), and the core Mn(III) ions of the porphyrins remained which is consistent with the UV–Vis spectra. Consequently, the recommended structures of **CP1–CP6** complexes are shown in Fig. 3, metalloligands of Mn(F₅CPp)/Mn(F₁₀. CPp) combine with nodes of metal ions (Mn(II), Co(II) and Ni(II)) forming the extension structure.

Figures 4, 5 show the SEM and TEM images of CP1– CP6. It is interesting to note that the particles morphologies of polymers are correlated with nodes of the metal ions in CP1–CP6. CP1 and CP4 are spherical particles in which Mn ions as nodes, the sizes of CP1 particles are larger than that of CP4. The powder XRD patterns and TEM images indicate that CP1 and CP4 are amorphous aggregations (see Figs. 4d, 5d and 6). Similar to CP1 and

Table 2 ¹H NMR parameters for $H_2(F_5EPp)$ and $H_2(F_{10}EPp)$, ppm

Porphyrins	$\delta_{\rm N-H}$	$\delta_{\mathrm{Pyrrole-H}}$	$\delta_{ m Ar-H}$	δ -CH ₃
H ₂ (F ₅ EPp)	-2.81	8.82-8.93	8.40, 8.19-8.31	1.59
$H_2(F_{10}EPp)$	-2.80	8.83-8.92	8.29-8.48	1.43–1.57



Fig. 1 UV-Vis spectra of CP1-CP6 in solid



Fig. 2 IR spectra of CP1-CP6

CP4, **CP3** and **CP6** are also amorphous aggregations in which Ni ions as nodes, while the shapes of the particles are irregular which accord with the powder XRD pattern. **CP2** and **CP5** are rod-like microcrystalline particles in which Co ions as nodes, which were analyzed using selected area electron diffraction (SAED) and powder XRD patterns as shown in Figs. 4e, 5e and 6.

BET specific surface areas and most probable pore-sizes of the **CP1–CP6** based N₂ adsorption data are summarized in Table 3. **CP1–CP6** have similar isotherm profiles, and show type II ones with moderate hysteresis loops (Figs. S28–S33 in Supplementary Material). Moreover, the wide ranges of pore-sizes of **CP1–CP6** indicate that the pores are primarily attributed to the accumulation of particles, which can also be seen from the SEM and TEM images. These suggest that the adsorption occurred mainly on the external of particles. In addition, all three **CP1–CP3** show relatively low pore-size distributions in narrow ranges, 4.0–4.5, 4.0–4.6 and 4.0–4.6 nm for **CP1**, **CP2** and **CP3** respectively, compared to **CP4–CP6**. These pores of **CP1–CP3** are likely to be arisen from $Mn(F_5CPp)$



Fig. 3 Illustration of $Mn(F_5CPp)-M$ (CP1-CP3, a) and $Mn(F_{10}$ CPp)-M (CP4-CP6, b), assembled from metalloligands and metal ions nodes (M = Mn(II), Co(II), Ni(II))

coordinating with nodes of Mn(II), Co(II) and Ni(II) ions, since the coordination mode of custom-designed $H_2(F_5 CPp)$ is distinct from that of $H_2(F_{10}CPp)$. So, presumably, catalytic reactions occur on the surface of the complexes.

Thermogravimetric analysis (TGA) was taken to examine the thermal stability of the polymers **CP1–CP6**. As can be seen in Fig. 7, the first weight loss of the **CP1– CP6** should be attributed to solvent molecules. With the temperature increased, the second weight loss began in 350 and 300° C for the **CP1–CP3** and **CP4–CP6**, respectively, which should correspond to decomposition of polymers structures. So that stable state can be maintained for the **CP1–CP3** below 350 °C, and for the **CP4–CP6** below 300 °C.

3.3 Ethylbenzene Oxidation with *tert*-Butyl Hydroperoxide (TBHP) Catalyzed by CP1–CP6

To assess the catalytic properties of the new heterogeneous catalysts, the oxidation of ethylbenzene was carried out using TBHP as the oxidant (Scheme 3). In Table 3 are summarized the results catalyzed by **CP1–CP6**, homogeneous Mn-porphyrin counterparts and metalloporphyrin. M^{II} polymers (Ni^{II}(F₅CPp)–Mn^{II}, Ni^{II}(F₅CPp)–Ni^{II}, Co^{II} (F₁₀CPp)–Mn^{II} and Co^{II}(F₁₀CPp)–Co^{II}). These results show not only higher activities of the **CP1–CP6** than homogeneous ones for ethylbenzene oxidation, but the



Fig. 4 SEM images of CP1 (a), CP2 (b) and CP3 (c). TEM images of CP1 (d), CP2 (e) and CP3 (f)



Fig. 5 SEM images of CP4 (a), CP5 (b) and CP6 (c). TEM images of CP4 (d), CP5 (e) and CP6 (f)



Fig. 6 Powder XRD pattern of CP1-CP6

Table 3	Oxygenation	of ethylbenzene v	vith TBHP	catalyzed by	CP1-CP6,	Mn-porphyrins	compounds	and metalloporphyrin-M	complexes
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Complexes	Yield ^a (%)	Selectivity ^a (%)	Cycles	Specific surface area ^b (m ² g ⁻¹)	Most probable pore size ^b (nm)
Mn(F5EPp)(OAc)	23	>99	1		
$Mn(F_5CPp)(OAc)$	46	>99	1		
CP1	75	>99	1	124.1	29
CP2	71	>99	1	194.2	19
CP3	80	>99	1	305.1	25
$Mn(F_{10}EPp)(OAc)$	53	>99	1		
Mn(F10CPp)(OAc)	53	>99	1		
CP4	80	>99	1	177.3	16
CP5	72	>99	1	112.7	30
CP6	82	>99	1	189.1	30
Ni(F5EPp)	5	>99	1		
Ni(F5CPp)	5	>99	1		
Ni ^{II} (F ₅ CPp)-Mn ^{II}	12	>99	1	107.9	19
Ni ^{II} (F ₅ CPp)-Ni ^{II}	12	>99	1	190.2	25
Co(F ₁₀ EPp)	21	>99	1		
Co(F ₁₀ CPp)	22	>99	1		
Co ^{II} (F ₁₀ CPp)-Mn ^{II}	67	>99	1	114.7	26
$Co^{II}(F_{10}CPp)Co^{II}$	68	>99	1	133.7	22

Reaction conditions: ethylbenzene (0.1 mmol), TBHP (0.4 mmol), catalyst (5 mg), CH₃CN (1 mL), temperature 65 °C, time 12 h

^a GC yield based on starting ethylbenzene

 $^{\rm b}\,$ BET specific surface area, N_2 adsorption isotherm measurements at 77 K



Scheme 3 Oxidation of ethylbenzene with TBHP catalyzed by CP1-CP6

selectivities were over 99 % indicating the products were almost acetophenone. The higher activities of the CP1-**CP6** could be attributed to the two factors as follows, (i) $Mn(F_5CPp)/Mn(F_{10}CPp)$ are the catalytic active units which are immobilized by ligating to nodes of metal ions (Mn(II), Co(II) and Ni(II)) in the polymers of CP1-CP6, and prevent their self-dimerization and oxidative degradation, however, the metal ions nodes were not involved in the catalytic reaction. (ii) Both of the $Mn(F_5CPp)/$ Mn(F₁₀CPp) units and metal ions nodes were involved in the catalytic reaction, moreover, lead to synergy probably. As shown in Table 3, the homogeneous catalysts of $Mn(F_5EPp)(OAc), Mn(F_5CPp)(OAc), Mn(F_{10}EPp)(OAc)$ and $Mn(F_{10}CPp)(OAc)$ exhibit catalytic activities, so that the abilities of catalytic activities of CP1-CP6 must be connected with those of homogeneous counterparts. Furthermore, the yields of CP1-CP6 catalyzed reactions are vary in little ranges to different metal nodes (Mn(II), Co(II) and Ni(II), in Table 3), which are approximately coincident with the specific surface areas of the polymers. These suggest that the metal nodes were not involved in the catalytic reactions.

In order to further examine whether the metal ions nodes are also involved in the catalytic reactions or donnot,

nickel- and cobalt-porphyrin complexes and polymers were isolated, and identified as well as CP1-CP6 counterparts. As expected, the yields of ethylbenzene oxidation reactions which were catalyzed by Ni^{II}(F₅CPp)-Mn^{II}, Ni^{II}(F₅CPp)-Ni^{II}, Co^{II}($F_{10}CPp$)-Mn^{II} and Co^{II}($F_{10}CPp$)-Co^{II} are also vary in very little ranges to different metal nodes (Mn(II), Co(II) and Ni(II), in Table 3), these indicating that the catalytic activities of metal-porphyrin units are dominant. whereas the metal nodes were not involved in the catalytic reactions in both CP1-CP6 and nickel-, cobalt-porphyrin polymers.

In view of only acetophenone was formed as a main product and no other product was found to be forming, as shown in Scheme 4, ethylbenzene oxidation with TBHP should follow a free radical mechanism in the presence of CP1-CP6 catalysts. Possibly, the CP1-CP6 catalysts act as an initiator in the homolysis of t-BuOOH into free alkoxy (t-BuO·) and alkylperoxy radicals (t-BuOO·) [34, 35]. Subsequently, oxidation takes place at the α -carbon of the ethylbenzene [36]. Formation of the product acetophenone has been illustrated in Scheme 4.

The catalysts examined in the present work and the other catalysts used for oxidation of ethylbenzene with TBHP as the oxidant, under different conditions in previous literatures, are compared in Table 4. When the ethylbenzene conversion (82 %) and selectivity to acetophenone (>99 %) obtained in this work were compared with other published data, it can be observed that the catalysts employed here behaves in a comparable way, or even better, in most cases with respect to other catalysts.

3.4 Catalysts Reuse and Stability

The stabilities of the heterogeneous catalysts CP1-CP6 were examined through repeated oxidations of ethylbenzene using TBHP. The catalysts were isolated, washed exhaustively with water, methanol, acetonitrile and diethyl

1) 2 *t*-BuOOH $\xrightarrow{\text{CP1-CP6}}$ *t*-BuOO· + *t*-BuO· + H₂O Scheme 4 The probable free radical mechanism for oxidation of ethylbenzene with TBHP (t-BuOOH) over CP1-CP6 acetophenone t-BuOOH, CP1-CP6 -H⁺ t-BuOH t-BuOO· t-BuO 2) - t-BuOH 1-phenyl-ethyl-tert-butyl-peroxide ethylbenzene

catalysts

Table 4	Oxygenation	of ethylbenzene	with TBHP	catalyzed by	y CP1-CP6 and	other catalysts
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Catalysts	Ethylbenzene conversion	Selectivity (%)	Temperature	Time	
	(%)	Acetophenone	Other products	- (°C)	(h)	
CP1	75	>99	_	65	12	
CP2	71	>99	-	65	12	
CP3	80	>99	-	65	12	
CP4	80	>99	-	65	12	
CP5	72	>99	-	65	12	
CP6	82	>99	-	65	12	
$[(pymox-Me_2)RuCl_2]^+BF_4^-$ [33]	95	83 ^a	-	20	16	
5 wt% Ag/SiO ₂ [34]	38	88	12 ^b	120	12	
CeO ₂ nanorods [35]	88	65	35 ^e	105	120	
Si/Al- <i>pr</i> -NH- <i>et</i> -N=methyl-2-pyridylketone-Mn [36]	67	93	2.7 ^c , 4.3 ^d	80	24	
Pd-nanoparticles [37]	92.3	93.5	0.5 ^c , 6.0 ^d	130	24	
MnSBA-15 [38]	25	37	62 ^d	80	8	
Mn-MCM-41 [39]	60	39	10 ^c , 50 ^d	80	24	
CNCr-2 [40]	45	69	30 ^d	70	8	
Co/MCM-41 [41]	26	85	9.1 ^c , 5.9 ^d	80	24	
Zr-K-OMS-2 [42]	62	98	2.0 ^d	65	10	
NMC [43]	88.3	53.4	-	80	24	
[Co(TCPp)]·2DMF [44]	83.1	>99	-	80	20	
ZJU-18 [45]	>99	>99	-	65	48	
CoZnAl-MMO/Al ₂ O ₃ [46]	69.5	80.4	12.1 ^c , 7.5 ^d	120	12	

^a Isolated product yields

^b 1-Phenylethanol

^c Benzaldehyde

^d Other products

^e 1-Phenyl-ethyl-tert-butyl-peroxide

NMC nitrogen-doped mesoporous carbons

ether, and dried before being used for fresh ethylbenzene and TBHP. The catalysts were consecutively reused three times with only slight decreasing of catalytic activities, however, without detectable catalysts leaching.

4 Conclusion

This work presents six heterogeneous catalytic coordination polymers of **CP1–CP6** based on Mn(III)-porphyrins, which were very easily prepared from commercially available compounds, able to selectively oxidize ethylbenzene exclusively to acetophenone. The higher catalytic efficiency observed for **CP1–CP6** in comparison with the homogeneous manganese porphyrins counterparts may be attributed to Mn(F₅CPp)/Mn(F₁₀CPp) units immobilized in the polymers, owing to prohibit their self-dimerization and oxidative degradation. The catalysts are robust toward the oxidation reactions of ethylbenzene and easily recovered by simple filtration at the end of the reactions. Moreover, three times reuse of the catalysts in the oxidation reactions of ethylbenzene provided no significant decrease of acetophenone yields.

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