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Construction of an Asymmetric Porphyrinic Zirconium Metal–Organic Framework through Ionic Postchiral Modification

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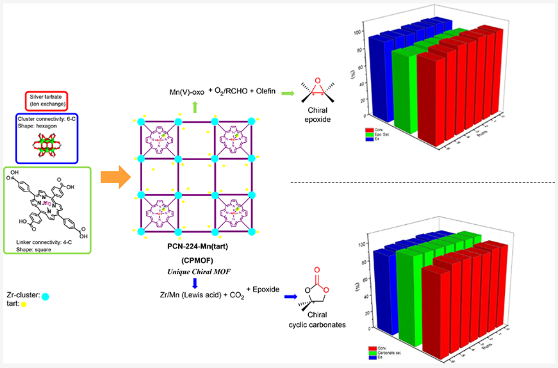
ABSTRACT: Herein, one kind of neutral chiral zirconium metal–organic framework (Zr-MOF) was reported from the porphyrinic MOF (PMOF) family with a metallolinker (Mn^{III}-porphyrin) as the achiral polytopic linker [free base tetrakis(4-carboxyphenyl)porphyrin] and chiral anions. Achiral Zr-MOF was chiralized through the exchange of primitive anions with new chiral organic anions (postsynthetic exchange). This chiral functional porphyrinic MOF (CPMOF) was characterized by several techniques such as powder X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, ^1H NMR, energy-dispersive X-ray spectroscopy, scanning electron microscopy, and Brunauer–Emmett–Teller measurements. In the resulting structure, there are two active metal sites as Lewis acid centers (Zr and Mn) and chiral species as Brønsted acid sites along with their cooperation as nucleophiles. This CPMOF shows considerable bimodal porosity with high surface area and stability. Additionally, its ability was investigated in asymmetric catalyses of prochiral substrates. Interactions between framework chiral species and prochiral substrates have large impacts on the catalytic ability and chirality induction. This chiral catalyst proceeded asymmetric epoxidation and CO_2 fixation reactions at lower pressure with high enantioselectivity due to Lewis acids and chiral auxiliary nucleophiles without significant loss of activity up to the sixth step of consecutive cycles of reusability. Observations revealed that chiralization of Zr-MOF could happen by a succinct strategy that can be a convenient method to design chiral MOFs.



INTRODUCTION

Nowadays, in industrialized societies, the preservation of the environment and reduction of energy utilization are very important issues because, unfortunately, there are various sources that produce pollutants that are harmful not only for the environment but also for human health, particularly undesirable and unwanted chemical compounds in different forms such as liquid, solid, and gas [for instance, hydrocarbons (aromatic and aliphatic) and carbon dioxide (CO_2)]. Therefore, chemical transformations should help to convert these environmental threats through chemical, photochemical, biological, and electrochemical processes. It should be said that these transformations are in the direction of green chemistry ideology: elimination of pollution or hazardous substances and reduction of energy consumption. Each day new materials as catalysts are generated and used in chemical conversion. The relationship between catalysis and the catalyst structure is an essential factor. In this regard, there is one fact that the most prevalent transformations are related to the conversion of achiral hazardous and toxic substances to achiral favorable products, for example, the transformation of CO_2 to CO, HCO_2H, and CH_4 or methanol (MeOH): the conversion of benzene to phenol and water splitting are the most complicated. However, there are many asymmetric chemical transformations as appealing methods under economical and environmental considerations with less energy consumption such as the coupling of CO_2 and epoxide or hydrocarbon oxidation to useful materials. Because of the importance of energy and environmental topics along with green chemistry, herein we report on our investigations based on green chemistry principles with an asymmetric direction. Before a further explanation is provided, it should be said that our work is divided into several steps as follows: (1) Types of catalytic reactions: hydrocarbon oxidation and CO_2 fixation are the most significant methods that are used to remove dangerous compounds, but they are commonly carried out under harsh conditions. (2) Choice of catalyst: among the catalysts, metal–organic frameworks (MOFs) as porous platforms are appropriate candidates because of their structural properties. They are constructed through strong bonds between organic and inorganic sections that can be various models, and they can act in different fields.[1−4] The tunability in the components

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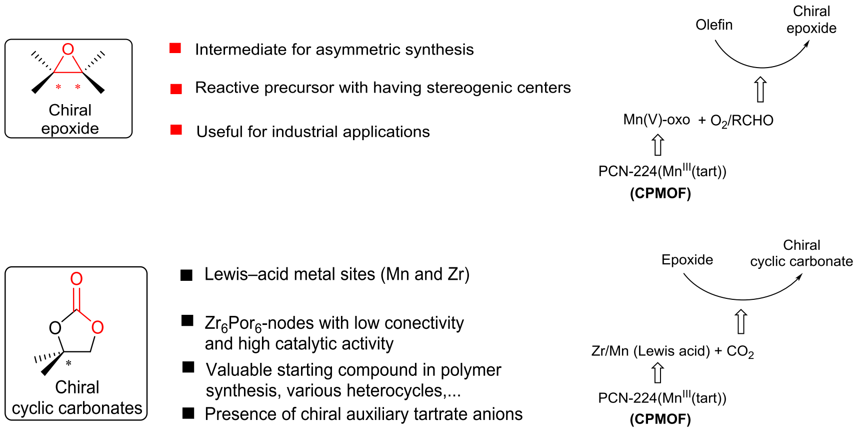
Scheme 1. General Concept of the Acidic Centers Used with the Considered Chiral Products



of MOFs has led to recent developments in the synthesis of these porous materials with novel designs.[5] The vast range of existing MOFs are electrically neutral with the usual building blocks, intriguing properties, and different uses like separation and sensing, photo- and electrocatalysis, gas sorption, and optical activity.[6−11] Ionic MOFs (IMOFs) are the other kinds of MOFs that can be classified into two types: anionic or cationic. They are similar to neutral MOFs, and they have several uses as ion-exchange materials with different applications, in particular, separation, adsorption, and catalysis (gas or ion separation/adsorption and oxidative processes), dye removal, drug delivery, and proton transfer.[12−14] It is surprising that the modulators used in the synthesis of MOFs, specifically acidic types, can also produce defects that can act as active centers. However, chirality, its relationship with MOFs, and why it is significant are important questions for researchers. Chirality is one of the important and essential features that can exist in MOFs as either neutral or ionic. This phenomenon is specifically revealed in diverse stereoselective processes, especially in biochemistry to generate enantioenriched molecules, so it is very valuable.[15] Chiral MOFs (CMOFs) are the other kinds of modified MOFs whose building blocks can be synthesized by chiral components, functionalized by chiral agents, or constructed intrinsically because of asymmetric space groups in the network. The investigations demonstrate that using the pure chiral modifier in design through a postsynthetic method is an effective procedure without complexity in the creation of CMOFs rather than others.[16] Until now, utilizing chiral molecules has been explored for suitable ability in chirality induction in MOFs such as chiral postsynthetic modification of either a metal node or an organic linker.[17] Recently, these kinds of chiral materials have attracted attention as hot topics because they have all of the applications of simple MOFs with an asymmetric direction, especially asymmetric catalysis.[18,19] Among MOFs, zirconium-based MOFs (Zr-MOFs) to a considerable extent were synthesized with specific topologies via different organic linkers and connectivities with various applications[20−23] because they have chemical, mechanical, and thermal stabilities with higher surface area and porosity than the customary MOFs. It should not be forgotten that zirconium is widely abundant at low cost.[24] Most of the organic linkers used in Zr-MOFs are bidentate carboxylic acids, but they have been newly modified with multitopic linkers such as hexatopic and tetratopic linkers, specifically by Zhou et al. In this paper, we selected a topology, among them PCN-224 [6-c(**she**)], with a porphyrin−tetratopic linker as the main platform to synthesize porphyrinic MOF (PMOF) because this framework has easily passed every test.[25,26] However, the various chiral materials were extensively synthesized to different cases by porphyrinic ligands, and few chiral Zr-MOF have also been reported, but for the first time, we reported a chiral porphyrinic Zr-MOF (CPMOF) with removal of coordinated anions by tartrate anions.[27−30] This PMOF backbone based on Zr_6 clusters (with defects such as free centers from anions or weak coordination of anions to metal sites), large channels (higher than 15 Å), and accessible pores was chiralized via coordinated anion exchange. The results showed that it can be a unique and promising chiral porous platform, which has not been reported in the Zr-MOF family. The porphyrinic metallolinkers in PMOFs can be active as catalytic centers in the various transformations to optical-related applications.[31,32] Inspired by the chemical stability and structural features of the afforded CPMOF and its extraordinary chirality, we studied its catalytic capability in enantioselective reactions. In this MOF, manganese tetrakis-(4-carboxyphenyl)porphyrin [Mn(TCPP)] units are used as 4-connected linkers, so they can simplify the substrate influence in pores during the catalytic process.[33] Besides, notably the resulting structure consists of chiral tartrates that provide the high chirality induction and acidic feature. We suggest that chiral anions interact with the cationic framework because of the exchange of chloride anions in the structure [Cl sources: $ZrCl_4$ and (Cl)Mn-porphyrin] to retain the charge neutrality of the framework. Decoration of PMOF with specific chiral molecules is necessary for improvement of the design. Our selected chiral compound is a tartrate anion that bears two effective neighboring asymmetric centers with two OH functional groups (Brønsted acid sites). Plenty of them in the resulting chiral architecture improve the chirality induction. In this work, we presented the construction of a chiral PCN-224 through postchiral modification, which is effective in synthesizing chiral functional MOFs. This ideal CMOF has advantages such as (i) having Zr clusters and Mn active sites, (ii) the majority of the defects of the framework being formed by modulators, and (iii) chiral species that can act as acidic centers (Scheme 1). Considering the present CPMOF, the relationship of structure chirality and defect activity is clearly seen. Additionally, chiral ligands can show a nucleophilic role in the considered catalytic system (CO_2 fixation into epoxides). So, the results demonstrated that designing with this degree of precision can be valuable to the development of

CMOF chemistry. This CPMOF with these performances and without any complication was used in two catalytic reactions in an asymmetric direction: epoxidation of olefins and CO_2 cycloaddition into epoxides, which are still important and problematic, because the obtained products, epoxides and cyclic carbonates, can be used as proper intermediates or precursors in a wide range of syntheses.[32] Because of these reactions in the organic syntheses, oxygen and carbon trapping in the considered substrates can happen, so they are transformed into useful compounds. (3) Catalytic reaction conditions: ambient temperature and pressure (according to the kind of catalytic reaction) and determination of a real-time reaction to prevent hazardous byproduct formation lead us to the obtained results in the next sections.

■ EXPERIMENTAL SECTION

Syntheses. *Tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP).* H_2TCPP was prepared according to the procedure described in the research paper.[34] Briefly, a mixture of the following compounds was stirred (4 h/120 °C): pyrrole (1.16 mmol), 4-carboxybenzaldehyde (1.16 mmol), and 50 mL of propionic acid. The precipitated crystals were separated with MeOH and by using of ice bath and washed with the essential solvents (MeOH/hot H_2O). Then, a purple solid was purified through column chromatography with silica gel as the stationary phase and chloroform with a little acetone as the mobile phase.

Mn(TCPP)Cl. The metalated free-base porphyrin was prepared under the explained conditions:[35] 0.082 mmol of TCPP, 0.82 mmol of $MnCl_2$, and 20 mL of *N*,*N*-dimethylformamide (DMF) were refluxed for over 1 h. After removal of DMF, precipitated Mn(TCPP) Cl was dissolved and reprecipitated by using NaOH (0.1 M) and HCl (1 M), respectively. After recrystallization of the Mn-porphyrin, it was dried and characterized.

PCN-224-Mn^{III}(tart). PCN-224, PCN-224(Mn), and silver tartrate were synthesized based on a previous report.[26,27] Briefly, PCN-224 was synthesized in a 5 mL Pyrex vial without any Mn-porphyrin by using $ZrCl_4$, free-base porphyrin, and benzoic acid (30, 10, and 400 mg, respectively) in DMF (2 mL; 24 h/120 °C). Then, the obtained crystals were filtered and investigated. In the synthesis of PCN-224(Mn), in addition to the Zr source and benzoic acid, Mn(TCPP) was also employed (10, 250, and 10 mg, respectively). After ultrasonic dissolution of the mentioned mixture in a 5 mL Pyrex vial, it was placed in an oven with the specific conditions (2 mL of DMF, 24 h/ 120 °C). The synthesis of PCN-224-Mn(tart) was performed by adding silver tartrate to a suspension of the heterogeneous mixture [PCN-224-Mn(Cl)] in MeOH. Then, it was stirred for over 8 h under ambient conditions. For removal of the impurity, washing of the obtained PCN-224-Mn(tart) was done with DMF (3 × 2 mL) and MeOH (5 × 2 mL) several times. Finally, after solvent exchange with MeOH, it was dried at 80 °C.

Catalyses. *Epoxidation of Olefins.* The catalytic epoxidation of olefins was carried out with the described conditions: a ratio of 2.5 mmol of cocatalyst and model substrate [isobutyraldehyde (IBA)/ styrene], 0.03 g of catalyst, 1 bar of O_2, and 5 mL of solvent [acetonitrile (CH_3CN)]. Then, this reaction mixture was stirred, and the reaction proceeded for 8 h at 60 °C.

Cycloaddition of Epoxide with CO_2. This asymmetric catalytic process was performed under the explained conditions in a free solvent: a ratio of 0.08 mmol from cocatalyst and model substrate (tetrabutylammonium bromide/styrene epoxide), 0.03 g of catalyst, and 1 bar of CO_2 for 15 h at 60 ± 5 °C.

Reusability Test. To study the PCN-224-Mn(tart) reusability in both of the catalytic reactions, we separated the catalyst from the reaction mixture by centrifugation, and then we washed, dried, and reused it in a fresh reaction with a new catalytic cycle under optimized conditions. Next, the progress of the catalytic reactions was investigated by chiral gas chromatography (GC).

Hot Filtration. This general test was studied for both of the catalytic reactions: enantioselective epoxidation and cycloaddition of epoxide with CO_2. The chiral Zr-MOF catalyst was removed after reactions after 2 and 3 h, respectively. Then, the solution was stirred under optimal reaction conditions without a catalyst.

■ RESULTS AND DISCUSSION

According to our goal, we synthesized an neutral asymmetric PMOF as a chiral platform with a tetratopic ligand [manganese (chloride) tetrakis(4-carboxyphenyl)porphyrin: Mn(Cl)-TCPP]. The subsequent reaction in PCN-224(Mn(Cl)) was the stripping of Cl^- by replacement of $tart^-$ by adding a silver salt of tartrate. Tartrate ligands are also able to interact with Cl of Mn-porphyrin(s) and or most probably with unsaturated Zr cluster(s); therefore, chiral PCN-224-Mn(tart) can easily be formed postsynthetically. This catalyst could act as a chiral Zr-MOF, whereas each of the Mn^{III}-porphyrin, Zr cluster, and general framework was shielded by anionic chiral auxiliary ligands. For the first time, this work has been reported to synthesize this kind of chiral porphyrinic Zr-MOF as a significant perspective for preparing multipurpose chiral porous materials. In the preparation of this CMOF, the limitations were not observed, unlike other chiralization routes. Chirality induction to the framework can happen through a chiral transcription method (from tartrate ions to MOF). Keeping in mind that chirality and asymmetric reactions have important roles in many scientific fields, especially biosystems to produce optically pure compounds, we designed an unprecedented CMOF for asymmetric catalysis. Our system can be known as a heterobimetal material and an achiral electrophile−chiral nucleophile catalyst with unique features in both asymmetric epoxidation and CO_2 fixation. Two metallic centers, Mn and Zr can act as Lewis acids/electrophiles and a tartrate counterion as the nucleophile can act as chiral functions and Brønsted acid, too.

Structural Characterization. PCN-224 as a porphyrinic Zr-MOF was prepared by using the previously reported procedure, and it was extensively investigated and charactrized by different methods.[26] Fourier transform infrared (FT-IR) was utilized as a primitive strategy for investigation (Figure S1). The usual characteristics in FT-IR of PCN-224-Mn(tart) have been demonstrated: C=C, around 1500 to 1620 cm^{-1}; $C-H_{deformation}$, from 720 to 1150 cm^{-1}; COO_{sy} and COO_{asy}, 1290−1714 cm^{-1}; C−H, around 2850 and 2920 cm^{-1}. The intense peak at 1714 cm^{-1} is due to the chiral tartrate anions.[28] The broad and weak peaks at about 3500 and 3300 cm^{-1} are related to OH [PCN-224 and PCN-224-Mn(tart)] and $NH_{pyrrole}$ (porphyrin base in PCN-224) bonds, respectively. UV−vis is another analysis that is used for porphyrinic compounds. So, we investigated the absorption spectra of PCN-224 and PCN-224-Mn(tart) for comparison (Figure S2). As is known, TCPP and Mn(TCPP) have two kinds of peaks in UV−vis in two different regions, Soret and Q bands. In Mn(TCPP), four Q bands of TCPP are decreased to two Q bands; this conversion is due to an increase of the symmetry. PCN-224 with a TCPP linker exhibits 1-Soret/4-Q bands: 429/518−551−591−647 nm. The number of peaks in PCN-224 is similar to that in the free-base ligand with a sensible shift toward high wavelength (L → M charge transfer due to porphyrinic ligands to Zr clusters).[36−39] PCN-224-Mn(tart) demonstrates 1-Soret/2-Q bands: 479/576−612 nm, which agree with Mn(TCPP) and confirm the insertion of Mn-porphyrin into the PCN framework.[39] To further study the

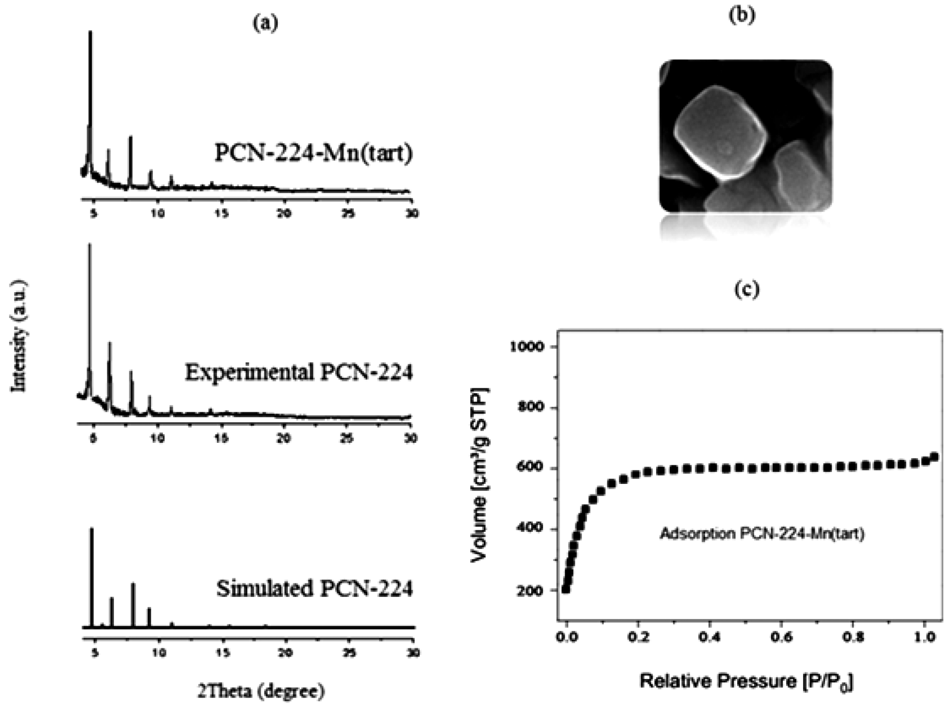
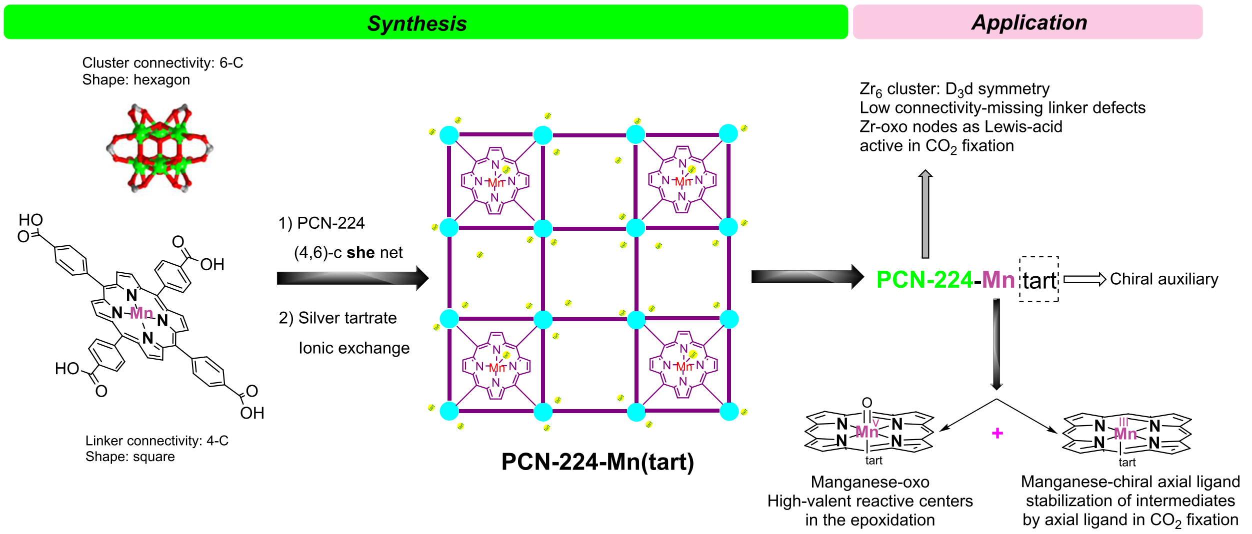


Figure 1. (a) PXRD pattern of simulated PCN-224 and experimental PCN-224 and PCN-224-Mn(tart) (from top to bottom). (b) SEM and (c) BET of PCN-224-Mn(tart).

Scheme 2. Brief Description of the Synthesis and Catalysis Processes of PCN-224-Mn(tart)



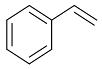
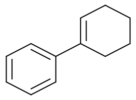
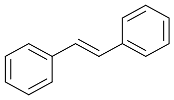
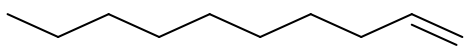
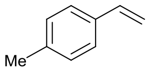
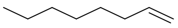
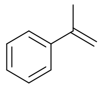
chiral Zr-MOF structure, ^1H NMR was also used (Figure S3). With this analysis, determination of the tartrate amount in the structure was done through the digested CMOF. The digestion process was accomplished in a concentrated D_2SO_4 solution. The H atoms of the tetratopic ligand appeared at around 8−9 ppm. The presence of peaks at 7−8 ppm is probably related to benzaldehyde generated from digestion of Zr-MOF and/or benzoic acid, which may not be removed sufficiently from the structure after activation. Protons of tartrate were seen at a low chemical shift (4−5 ppm) to single peak form. This confirms the existence of tartrate anions in the framework (Zr:TCPP:tart ∼3.2:1:0.7). Also, inductively coupled plasma (ICP) was used to determine the ratio of Zr to Mn in the final framework (Zr:Mn ∼ 2:1). After metalation of the PCN-224 porphyrin ligand with Mn and the addition of the tartrate anion during exchange, powder X-ray diffraction (PXRD) of the resulting compound was investigated. PXRD monitoring of the final structure, PCN-224-Mn(tart), showed that PCN-224 still maintained a crystalline structure and was not damaged during the preparation process (Figure 1a). As is known, PCN-224-Mn(tart) is prepared from two primitive substrates, PCN-224-Mn(Cl) and silver tartrate, by exiting AgCl during the preparation process. One logical reason to address the absence of AgCl in the structure is that the PXRD pattern of AgCl has clear and strong peaks from $2\theta = \sim 30$ to 50° [(111), (200), and (220) planes], which are related to the Cl^- anions and Ag^+ cations. To verify this subject, we reported the PXRD pattern of our structure until $2\theta = 50°$ (S4) and the characteristic

Table 1. Effect of Various Parameters on the Oxidation of Styrene with O_2[a]

no.	catalyst	conditions	conversion (%)[b]	epoxide selectivity (%)	ee (%) (Conf.)[c]
1	CPMOF	CH_3CN/25 °C/IBA/8 h/O_2[d]	<20	65	58 (*R*)
2	*CPMOF*	*CH_3CN/60 °C/IBA/4 h/O_2*	*100*	*89*	*96 (S)*
3	CPMOF	EtOAc/60 °C/IBA/4 h/O_2	40	67	81 (*R*)
4	CPMOF	*n*-hexane/60 °C/IBA/4 h/O_2	21	42	75 (*R*)
5	CPMOF	MeOH/60 °C/IBA/4 h/O_2	0		
6	CPMOF	H_2O/60 °C/IBA/4 h/O_2	0		
7	CPMOF	CH_3CN/60 °C/IBA/4 h/air	30	79	93 (*S*)
8	no cocatalyst	CH_3CN/60 °C/4 h/O_2	0		
9	no catalyst	CH_3CN/60 °C/IBA/4 h/O_2	<10	35	
10	homogeneous form	CH_3CN/60 °C/IBA/2 h/O_2	100	75	

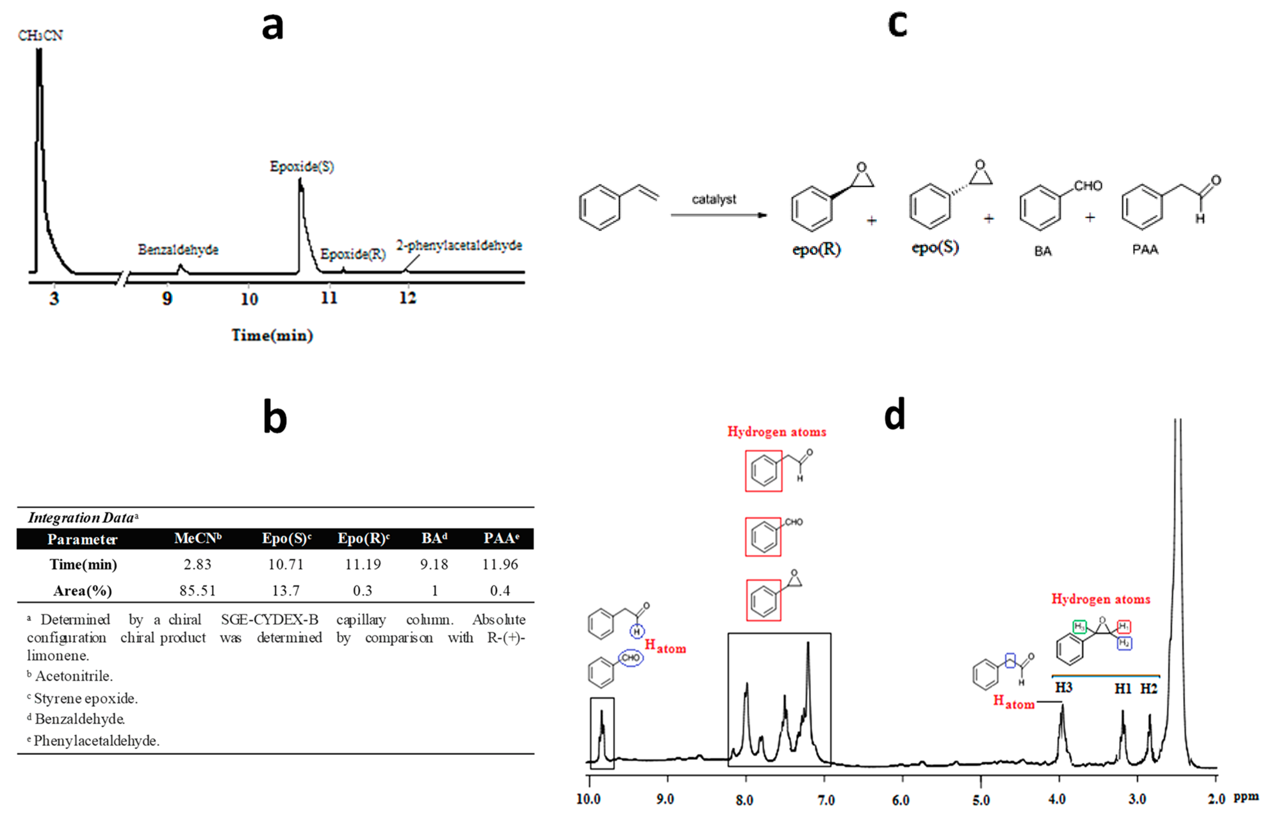
[a]Reaction conditions: catalyst, 0.03 g; styrene, 2 mmol; cocatalyst, 5 mmol; CH_3CN, 5 mL. [b]Conversions were calculated with GC/flame ionization detection (FID) by using chlorobenzene as the usual internal standard. All catalytic experiments were repeated twice. [c]Determined by GC with a chiral SGE-CYDEX-B capillary column. [d]1 atm of O_2.

Table 2. Asymmetric Epoxidation of Various Olefins by Using PCN-224-Mn(tart)[a]

Entry	Substrate	Entry	Substrate
1	 Conv.:100%, Epoxide selectivity: 89%, Ee.: 96%(S), 4h.	5	 Conv.:75%, Epoxide selectivity: 100%, Ee.: 88%(R,R), 8h.
2	 Conv.:80%, Epoxide selectivity: 100%, Ee.: 84%(R,R), 8h.	6	 Conv.:70%, Epoxide selectivity: 100%, Ee.: 96%(R), 8h.
3	 Conv.:100%, Epoxide selectivity: 86%, Ee.: 92%(S), 5h.	7	 Conv.:79%, Epoxide selectivity: 100%, Ee.: 100%(SorR), 8h.
4	 Conv.:90%, Epoxide selectivity: 83%, Ee.: 89%(S), 8h.		

[a]Reaction conditions: catalyst, 0.03 g; substrate, 2 mmol (except for *trans*-stilbene, 0.5 mmol); cocatalyst, 5 mmol; temperature, 60 °C; time, 8 h. Conversions (Conv.), epoxide selectivity, and ee were calculated with GC/FID (chiral column) by using chlorobenzene as the usual internal standard. All catalytic experiments were repeated twice.

peaks of AgCl were not seen in it. So, PXRD can confirm that AgCl, probable Cl^- anions, and coordinating Cl(s) to Mn centers do not exist in CPMOF. Besides, the obtained pattern from energy-dispersive spectroscopy (EDS) analysis of PCN-224-Mn(tart) confirmed that the displacement of Cl with tartrate happened successfully and also confirmed the PXRD data. So, the Cl anions and coordinated Cl(s) to Mn(s) that appear at less than 1 and 3 keV were not seen in the pattern of the final structure (Figure S4).[40−42] Of course, we used a simple experimental procedure (titration) based on Vogel's textbook of quantitative chemical analysis to determine chlorides of digested PCN-224-Mn(tart), in which no detectable amount of Cl was obtained. Scanning electron microscopy (SEM) of PCN-224-Mn(tart) was another reason for porphyrin Zr-MOF stability (Figure 1b). Eventually, PCN-224 has a high BET surface area in comparison to the other porphyrinic MOFs. The results demonstrated that PCN-224 after metalation and ion exchange still maintains its high surface area (1970 m^2/g) and porosity (pore size approximately 9 and 17 Å). This reduction can probably be assigned to the existence of tartrate anions that entered into the pores during the ion-exchange process (Figure 1c). Also, we provided circular dichroism (CD) of the dispersed structure to evaluate the optical activity. However, in this work, only one kind of enantiomer, as the chiral source, has been employed with a certain configuration (L-tartrate) for transmitting chirality over PCN-224. As a result, the investigation of the



Integration Data[a]

Parameter	MeCN[b]	Epo(S)[c]	Epo(R)[c]	BA[d]	PAA[e]
Time(min)	2.83	10.71	11.19	9.18	11.96
Area(%)	85.51	13.7	0.3	1	0.4

[a] Determined by a chiral SGE-CYDEX-B capillary column. Absolute configuration chiral product was determined by comparison with R-(+)-limonene.

[b] Acetonitrile.

[c] Styrene epoxide.

[d] Benzaldehyde.

[e] Phenylacetaldehyde.

Figure 2. (a and b) Chiral GC chromatogram and integration data of the styrene oxidation. (c) Aerobic oxidation reaction of styrene with O_2/IBA. (d) ^1H NMR spectrum in dimethyl sulfoxide of the oxidation of styrene as the substrate scope.

CD spectrum was not complex and similar to the CD of chiral species used (negative signal; Figure S7).

Catalytic Activity. In enantioselective catalysis, the pore size, number of the active catalytic sites, and kinds of chiral ligands in the catalyst structure are important factors. Considering the PCN-224-Mn(tart) properties as a chiral porous solid, we used it to catalyze asymmetric catalytic reactions due to Mn centers at the porphyrinic rings, Zr_6 cluster defects, and neighboring hydroxyl groups in the chiral ligand as acidic catalytic sources. In Scheme 2, the synthesis and catalysis processes of PCN-224-Mn(tart) are briefly shown. Two significant benefits of our study are having (i) two distinct metallic Lewis acid centers and (ii) accessible plentiful chiral counteranions and their cooperation in the catalysis through strong hydrogen bonding as a Brønsted acid. It is notable that catalyst separation using O_2 as a friendly and healthy oxidant, mild conditions in CO_2 fixation, and the synergistic effect of Brønsted/Lewis acid are positive points of our system.

Enantioselective C=C Epoxidation Reaction. The previous experiments showed and emphasized that the oxygenation of olefins can happen over this chiral heterogeneous catalyst because of Mn metallic centers within a ring of porphyrinic linkers.[27−30] For asymmetric epoxidation catalysis, we investigated the different factors that affected the PCN-224-Mn(tart) performance such as the oxidant, temperature, solvent, time, and cocatalyst. According to the experiments that have been presented in the following, we selected O_2 as a green oxidant source, a temperature of 60 °C, the solvent CH_3CN, a time of 8 h, and the cocatalyst IBA. As shown in Table 1, the oxygenation of styrene (as an electron-rich olefin) was performed at room temperature, and the absence of catalyst (conversion <10%) and cocatalyst (reaction stopped) indicated that the reaction was not carried out in each of them. Given that the solvent is a key agent in the proceeding reaction, therefore we studied the effect of several solvents with different polarities. In most of the epoxidation reactions, CH_3CN is chosen as the most suitable solvent based on its low coordinating ability. Our results also showed that, among the solvents examined, CH_3CN can provide the proper environment for activation of the catalyst. In the optimization of the catalytic parameters, IBA was selected to reduce molecular O_2 for production of the radical oxidizing agent. The results showed that employment of a cocatalyst was necessary (entry 8). One of the optimized reactions was investigation of the PCN-224 activity without a chiral additive. As expected, unlike chiral PCN-224(Mn) [CPCN-224(Mn) or PCN-224-Mn-(tart)], achiral PCN-224(Mn) could not show any chirality induction and enantiomeric excess (ee) that were logical.

After the essential experiments, the optimal conditions were selected: temperature of 60 °C, 1 bar of O_2 (generation of the high epoxide selectivity),[43,44] catalyst of 0.03 g, cocatalyst of 5 mmol, and CH_3CN of 5 mL. Under these conditions, the substrate scope (styrene) was catalyzed, producing two stereoisomers of styrene epoxide (main product) and two inevitable different kinds of aldehydes with low percent, benzaldehyde and 2-phenylacetaldehyde (byproducts) (Table 2, entry 1; details in Figure 2). On the basis of the model substrate size (calculated by Chem3D; Figure S5a) and pore size of MOF, the reaction conversion was completed with 89% epoxide selectivity and a unique level of ee [96% (*S*)]. These results are evidences to confirm the essential role of the catalyst.

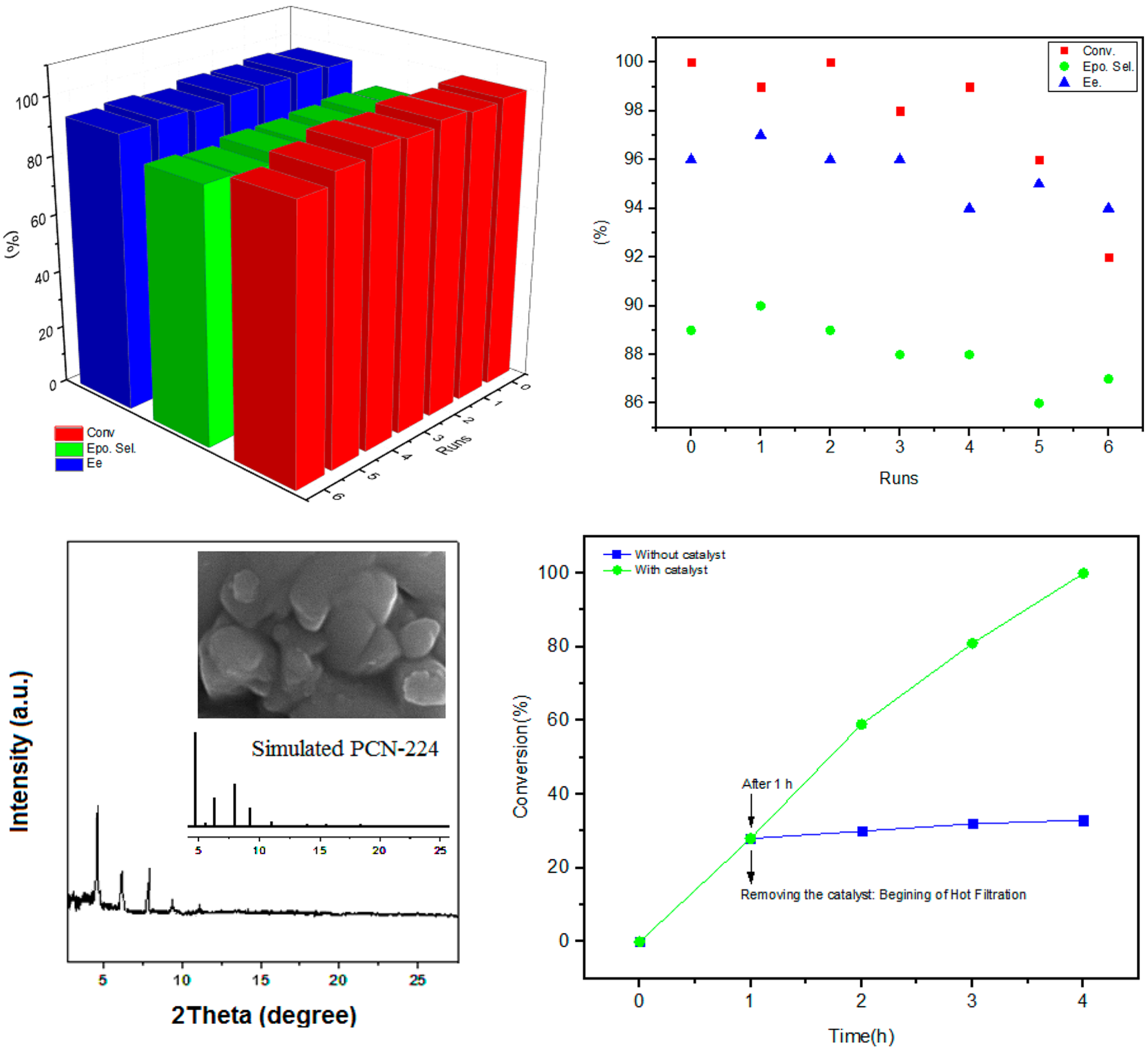


Figure 3. Recyclability of the catalyst (substrate/styrene): conversion, epoxide selectivity, and ee. (Top) Number of recycles: 0, fresh step. (Bottom left) XRD and SEM of the catalyst used in the last cycle. (Bottom right) Results of the hot filtration test.

After determination of the optimized conditions, our study began with various olefins, aromatic and aliphatic, like *trans*-stilbene, 4-methylstyrene, α-methylstyrene, 1-phenyl-1-cyclohexene, 1-decene, and 1-octene (Table 2). (*E*)-Stilbene (*trans*-stilbene) was chosen for asymmetric epoxidation. The C═C oxidation of *trans*-stilbene was performed for formation of the (*R*,*R*)-*trans*-stilbene epoxide isomer without any byproducts (benzaldehyde, diol, or both of them) and configuration change (entry 2).[27] So, the obtained results were very significant. The derivatives of styrene, 4-methyl, and α-methylstyrene were also tested as important industrial compounds. PCN-224-Mn(tart) could promote enantioselective epoxidation of these styrene derivatives with different conversions and ee values (entries 3 and 4). The catalytic results, under identical conditions, demonstrated that the presence of steric hindrance around or close to the double bond can be responsible for stereo- and enantioselectivity of the generated products. 1-Phenyl-1-cyclohexene[45] as a bulky substrate was another olefin whose oxidation was investigated with 75% conversion, 100% epoxide selectivity, and 88% ee (entry 5). Two aliphatic olefins were also oxidized for 8 h with the presented findings (entries 6 and 7). The moderate conversions of 1-decene (70%) and 1-octene (79%) mean that these linear terminal alkenes are less prone to oxidation compared to the other aromatic olefins.[46,47]

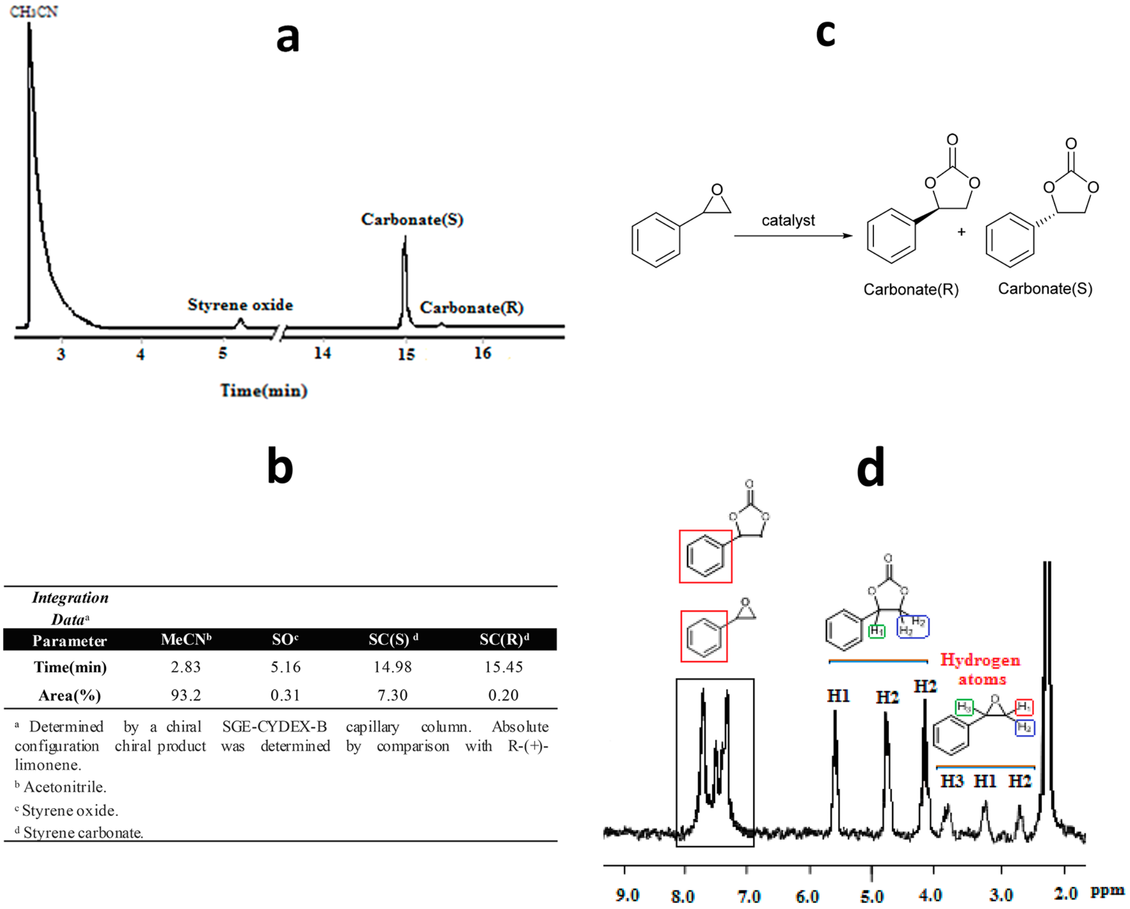
The size of the starting substrate, steric effect, or steric hindrance around of the active sites and catalyst structure–substrate interaction degree can affect the results. Regarding ee, it is interesting that, for oxidation of the considered olefins, the ee values are high (84–100%). Mn(tart)-TCPP was also tested as a homogeneous catalyst. The reaction was performed under optimized conditions with complete conversion, 74% epoxide selectivity, and 59% ee for 2 h. The ee in the heterogeneous catalytic system shows the accessible volume of chiral species in the framework. These charged species can interact with substrates inside the framework, and so this process can be effective in the product selectivity. However, tartrate anions via the outer surface of the framework confer chirality to the catalytic products with specific interactions.[48,49]

Mechanism. The probable mechanism of the oxidation of olefins by Mn^{III}/O_2/aldehyde was previously presented. The formation of an acyl radical, an acylperoxy radical, peroxy acid, and finally Mn^{V}-oxo is proposed [Mn^{III}-tart is converted to tart-Mn^{V}═O (tart as a trans-axial ligand binds to the Mn center, which is plausible)].[27] Although an understanding of the mechanism needs further studies and investigations, an

Table 3. Effect of Various Parameters on CO_2 Cycloaddition to Styrene Epoxide[a]

no.	catalyst	conditions	conversion (%)[b]	carbonate selectivity (%)[b]	ee (%) (Conf.)[c]
1	CPMOF	25 °C/Bu_4NBr/15 h/CO_2	31	45	54 (*R*)
2	no cocatalyst	60 ± 5 °C/15 h/CO_2	15	75	85 (*S*)
3	no catalyst	60 ± 5 °C/IBA/15 h/O_2	<10	42	
4	*CPMOF*	*60 ± 5°C/Bu_4NBr/15 h/CO_2*	*96*	*100*	*94 (S)*
5	PCN-224 (without Mn and tart)	60 ± 5 °C/Bu_4NBr/15 h/CO_2	81	83	
6	PCN-224-Mn (without tart)	60 ± 5 °C/Bu_4NBr/15 h/CO_2	86	84	

[a] Reaction conditions: catalyst, 0.03 g; substrate, 2 mmol; cocatalyst, 2.5 mmol; 1 bar of CO_2; time, 15 h. [b] Conversions (Conv.), cyclic carbonate selectivity, and ee were determined with GC/FID (chiral column) by using chlorobenzene as the usual internal standard. [c] All catalytic experiments were repeated two times.



Integration Data[a]				
Parameter	**MeCN**[b]	**SO**[c]	**SC(S)**[d]	**SC(R)**[d]
Time(min)	2.83	5.16	14.98	15.45
Area(%)	93.2	0.31	7.30	0.20

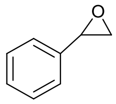
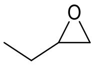
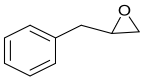
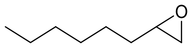
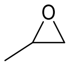
[a] Determined by a chiral SGE-CYDEX-B capillary column. Absolute configuration chiral product was determined by comparison with R-(+)-limonene.
[b] Acetonitrile.
[c] Styrene oxide.
[d] Styrene carbonate.

Figure 4. (a and b) Chiral GC chromatogram and integration data of CO_2 fixation to styrene epoxide. (c) Reaction of CO_2 cycloaddition of styrene epoxide for the production of cyclic styrene carbonate. (d) ^1H NMR spectrum in dimethyl sulfoxide of CO_2 fixation of styrene epoxide as the substrate scope.

important issue remains, that is, knowledge of how chirality induction happens and produces a superior configuration is mandatory. High enantioselectivity to epoxides is related to several points: (1) the framework pore size, (2) close vicinity of the one preferred face of the olefin (pro-*S* or -*R* face) to the active Mn center to produce a suitable configuration with high stability, and (3) the degree of noncovalent interactions of the preferred face of the prochiral substrate (H atom of the olefinic double bond) with chiral centers (interaction of the substrate with the chiral surface and pore). On the basis of the catalytic results, the *S* enantiomer is the major product in this catalytic system. This observation shows that PCN-224-Mn(tart) has the ability to discriminate between two kinds of chiral configurations, and in the prochiral alkenes examined, one face, *R* or *S*, tends to epoxidize. So, we did not see a racemic mixture in the catalytic results.

Reusability Test. Also, the reusability of the catalyst was investigated. The catalyst recovered in each run was washed (CH_3CN), dried, and employed in a fresh catalytic reaction to the sixth step. 100% conversion, 89% epoxide selectivity, and 96% ee were decreased to 92% conversion, 87% epoxide selectivity, and 94% ee. It is interesting that chiral PCN-224 was not destroyed and was stable after successive catalytic reactions (SEM and PXRD in Figure 3 and BET in Figure S8). The minor decrease in the conversion of the sixth cycle rather than a fresh step depends on the negligible leaching of Mn from the framework. Therefore, the Zr-based framework can give stability to the porphyrin and prevent leaching/aggregation of Mn(TCPP). All of recycle solutions at the

Table 4. CO_2 Cycloaddition to Various Olefin Epoxides[a]

Entry	Substrate	Entry	Substrate
1	 Conv.:96%, Cyclic carbonate selectivity:100%, Ee.: 94%(S)	4	 Conv.:91%, Cyclic carbonate selectivity:100%, Ee.: 97%(R)
2	 Conv.:87%, Cyclic carbonate selectivity:100%, Ee.: 90%(S)	5	 Conv.:78%, Cyclic carbonate selectivity:100%, Ee.: 96%(R)
3	 Conv.:99%, Cyclic carbonate selectivity:100%, Ee.: 98%(S)		

[a] Reaction conditions: catalyst, 0.03 g; substrate, 2 mmol; cocatalyst, 2.5 mmol; 1 bar of CO_2; temperature, 60 ± 5 °C; time, 15 h. Conversions (Conv.), cyclic carbonate selectivity, and ee were determined with GC/FID (chiral column) by using chlorobenzene as the usual internal standard. All catalytic experiments were repeated two times.

end of the reaction were investigated with UV−vis, and it was confirmed that no Mn-porphyrin has been leached (Figure S6).

Finally, hot filtration was also investigated as a main strategy to show the catalyst effect, which is commonly performed with a heterogeneous catalyst. In the epoxidation reaction of the model substrate, after 1 h, the catalyst was removed by centrifugation. Then, the remaining solution was stirred under optimized conditions, and it was monitored with GC every 1 h. The reaction progress was not acceptable and satisfactory (Figure 3). So, the presence of a catalyst that helps the catalytic reaction proceed is essential. These results showed that this CMOF with these achievements is known as a robust and stable CMOF catalyst from the PCN family.

Enantioselective CO_2 Cycloaddition to Epoxide Reaction. Recently, Zr-MOFs are candidates for significant applications because of their high stability.[50,51] One essential reason for their selection is the presence of random defects, which are very important in these structures for different goals.[51,52] Modulators, missing linker and cluster, can produce defects that lead to vacancies and open Zr centers as active Lewis acids with low connectivity. These accessible Lewis acid centers, particularly defects, can induce catalytic ability into the framework for use in various catalytic reactions such as CO_2 chemical fixation. Usually, this reaction is carried out with low yields under rough conditions (high temperature, pressure, and time). Thus, the design of powerful and stable catalysts is of great interest.[53] Given that PCN-224 had been previously extensively identified in detail, we found that our CMOF as a chiral acid catalyst can be wonderfully used in the asymmetric CO_2 cycloaddition to epoxide.[54] This reaction was also carried out with styrene epoxide as the scope substrate (Figure S5b) that could enter the framework with large pores. However, the external surface of MOFs as defects can effect the development of the catalytic reaction. We started our goal in the chiral environment with styrene epoxide as a racemic substrate and PCN-224-Mn(tart), which replete with Zr/Mn centers as Lewis acids and tartrate species as Brønsted acids. After primitive investigations, the selected conditions were as follows: temperature 60 ± 5 °C; 1 bar of CO_2; Bu_4NBr as the cocatalyst. The main investigated catalytic reactions are denoted as (a) PCN-224 (without Mn), (b) PCN-224-Mn (without tart), and (c) PCN-224-Mn(tart) (details in Table 3).

To demonstrate the auxiliary effect of the tartrate anions as nucleophiles, in addition to chirality induction and acidity, we investigated PCN-224-Mn without tart. In the first and second cases, the conversion of styrene epoxide to styrene carbonate was carried out (81% and 86%, respectively). The results of the metalated and nonmetalated PCN-224 showed that Zr nodes are more effective than Mn as active sites. The low performance of Mn(TCPP) can be assigned to the reported findings that (i) the interaction of CO_2 molecule with Mn(TCPP) and (ii) the distance of CO_2 with Mn(TCPP) are weaker and longer than those of the CO_2-Zr cluster.[55] Thus, the obtained data agree with the structural properties. When a chiral ligand was used in the framework, it was found that tartrate anions could be the active catalytic centers and they could increase the activity of PCN-224 due to a synergistic effect with the other acidic centers. The low conversion of PCN-224-Mn without tart rather than the PCN-224-Mn(tart) catalyst showed that the present chiral anions could accelerate the rate of reaction through the production of ring-opened alkoxide. Notably, the excessive amount of tart anions can play an important and key role in the reaction development. In the third case, PCN-224-Mn(tart), the chiral auxiliary ligand (tartrate), can act as both a nucleophile and a Brønsted acid because of its nature (Conv. 96%; details in Figure 4). A remarkable point is that additional product such as diol was not seen during the reaction. This kind of product (diol) is usually generated at temperatures above 90 °C in this kind of catalytic process, while our catalytic system has mild conditions (free solvent and 60 ± 5 °C).[56] Meanwhile, the high selectivity of styrene carbonate can be related to its lack of thermal degradation.[57]

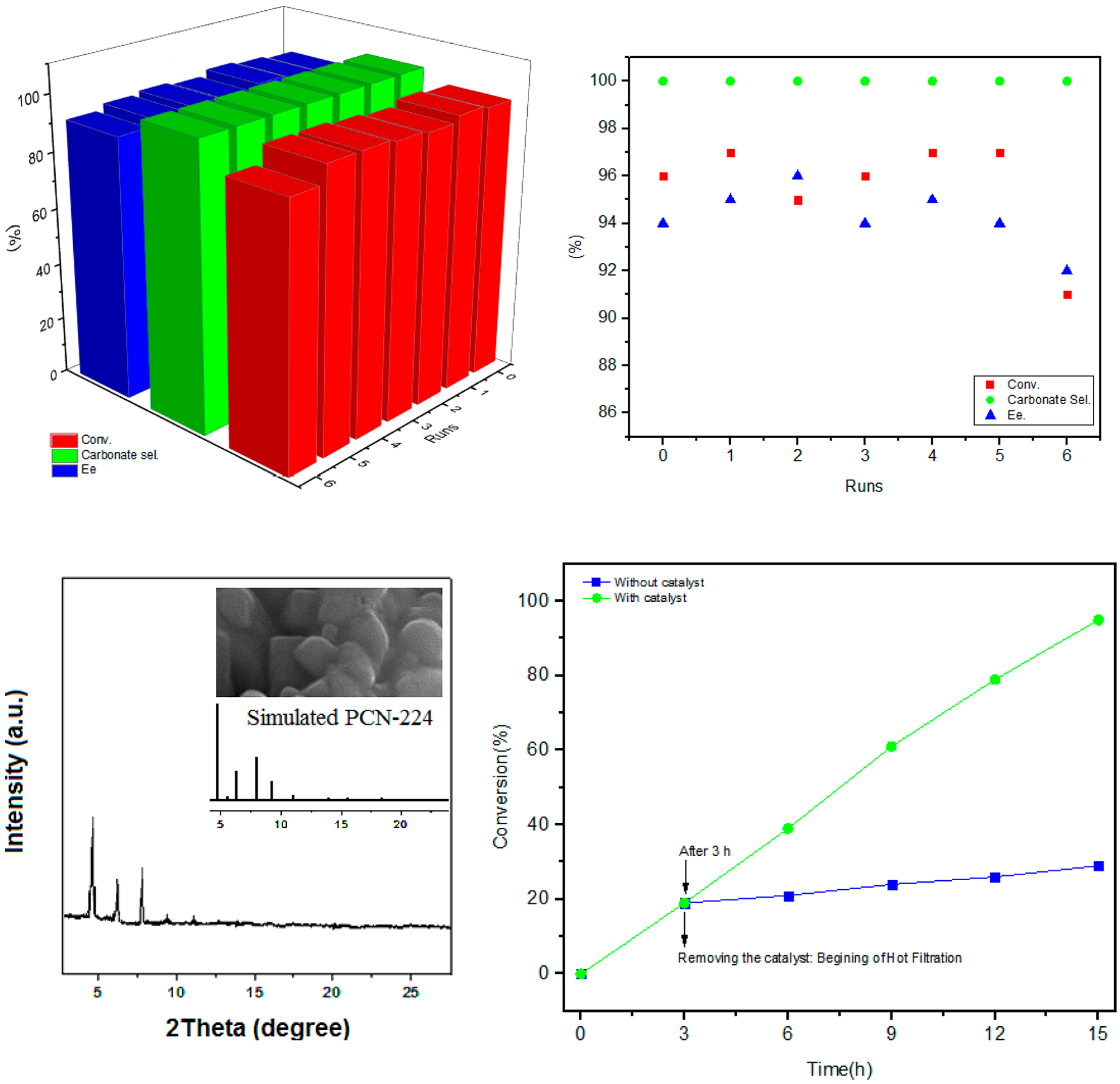


Figure 5. Recyclability of the catalyst (substrate/styrene epoxide): conversion, cyclic carbonate selectivity, and ee. (Top) Number of recycles: 0, fresh step. (Bottom left) XRD and SEM of the catalyst used in the last cycle. (Bottom right) Results of the hot filtration test.

The production of cyclic carbonates as fine chemicals with other racemic epoxides was also examined under the current conditions. Two racemic aromatic epoxides and three aliphatic epoxides were our selection (Table 4, entries 1−5). Styrene epoxide and its derivative showed conversions of 96% and 87%, respectively. The catalyst exhibited more activity in CO_2 fixation to styrene epoxide than its derivative, which can be ascribed to the molecular size and steric hindrance. In propylene epoxide catalysis, high conversion was observed rather than those of its two derivatives with conversions of 99%, 91%, and 78%, respectively (entries 3−5). The obtained results are evidence to show the superiority of PCN-224-Mn(tart). However, the results revealed that PCN-224-Mn(tart) has a capability to generate high ee values (90−98%).

As expected, tartrate groups are more around the clusters and linkers, so they can transfer chirality to the environment and directly activate epoxide or probably CO_2.[58−61] Of course, free carboxylic acid groups of TCPP can also act as Brønsted acids in promoting the reaction.[62] Three catalyzed substrates produced *S*-cyclic carbonates. It can be inferred that the chiral component direction can affect the main product optical activity. Certainly, the size of the substrate and MOF pores can affect the conversion and cyclic carbonate selectivity. However, it should be noticed that the selected substrates are in racemic form (50:50) and PCN-224-Mn(tart) has the potential to discriminate between *S* and *R* enantiomers of epoxide. So, in addition to the major enantiomer of the chiral cyclic carbonate produced, a chiral epoxide (*R*, *S*, and or both of them) that has not been used as a reactant in the CO_2 fixation catalytic reaction is also seen. Several MOFs have been reported in which their cation and anion sites could act in CO_2 fixation into propylene oxide but under harsh conditions like a pressure of 20 bar and a temperature of 120 or 140 °C.[63−66]

The best results of asymmetric epoxidation and CO_2 fixation are listed in Table S1. It is noticed that asymmetric CO_2 cycloaddition into epoxide reactions have been done less, especially by using chiral heterogeneous catalysts.

Mechanism. The mechanism of this reaction and chirality induction happen based on the interaction between the active acidic center (Zr; on the basis of the defect hypothesis in the Zr cluster), Mn as the acid-assisted site, and auxiliary OH groups of tartate with O atom of the epoxide ring (pro-*S* or -*R* face).[67] Then, the present cocatalyst as a nucleophile ($\bar{Br}$) attacks the activated epoxide ring, and then ring opening happens. It is interesting that chiral tartrate anions can help with ring opening of epoxide.[68] So, the reaction without a nucleophile and with a counteranion can proceed, although with low conversion. After attachment of CO_2 to the negatively opened ring, cyclic carbonate is produced. Another significant point is that, during the reaction development (for 15 h), byproducts are not observed.[69] With development of the reaction, increasing ee is seen, which could be related to interaction of the chiral centers and substrate pro-*R*/*S* face.

Reusability Test. The conversion, cyclic carbonate enantioselectivity, and ee results of the PCN-224-Mn(tart) catalyst for six steps were investigated (Figure 5). A small reduction in these findings was observed that was not related to the catalyst ability but was due to the lost mass of the catalyst during the recyclability test because, in per cycle, the catalyst is separated from the reaction mixture, washed, and dried. Again, the catalyst is employed in the next run. Findings did not show the noticeable changes in SEM and PXRD (Figure 5) and BET (Figure S8). Therefore, it can be said that this chiral catalyst maintained its physical and chemical properties. ICP analysis was also utilized to study recycle solutions, and Zr leaching was not identified. A hot filtration method was also investigated in this catalytic process; its diagram is shown in Figure 5 (plot of the conversion versus time). After removing catalyst from the solution mixture (after 3 h) and returning the temperature of the catalytic solution to the optimized temperature, the solution was stirred under optimal experimental conditions. Every 3 h, the progress of the catalytic reaction was studied using GC. The findings gained in this process were previously confirmed in the olefin epoxidation section and reflect the catalyst importance.

One-Pot Asymmetric Epoxidation/CO_2 Cycloaddition Catalysis Reactions. Finally, it should be said that, for the production of chiral cyclic carbonate, we investigated these one-pot catalysis reactions via tandem reaction (asymmetric epoxidation/CO_2 cycloaddition) with styrene as the first substrate [*reaction pathway:* (1) starting substrate, prochiral styrene; (2) generated chiral epoxide, semiintermediate (as the second substrate); (3) chiral cyclic carbonate, main product]. The obtained results were suitable in conversion (80%), selectivity of carbonate (89%), and ee [93% (*S*)], and they were close to the separated reaction results.

However, observations proposed that, in the asymmetric tandem, from the second step, the reaction is performed easily.[70] Because the starting substrate of the second stage is enantioriched epoxide (*R* or *S*), that CO_2 addition leads to cyclic carbonate asymmetrically with high ee, which it is expected. On the other hand, in this manner, enantiodiscrimination of styrene epoxide by the catalyst is not necessary. So, we maneuvered over asymmetric epoxidation and CO_2 fixation, separately. Of course, there is no difference in the kind of the chiral styrene cyclic carbonate created because PCN-224-Mn(tart) gave the *S* enantiomer in nontandem fixation, and, in contrast, in a tandem reaction, the *S* enantiomer was also generated.

■ CONCLUSION

In the present research topic, the foregoing findings show that, because of engineering of the synthesis process and manipulation of the MOF framework by chiral anions, a CMOF can be synthesized. For the first time, we report a neutral chiral Zr-MOF, PCN-224-Mn(tart), that can be considered to be a combinatorial multipurpose catalyst: *achiral electrophile–chiral nucleophile–chiral functional groups*. Our suggestion is the synthesis of a CMOF with unique chemical stability through postchiral modification. In this method, chiral ionic exchange happens in the outer and inner regions of the framework. The ease of PCN-224-Mn(tart) preparation is the first positive point. PCN-224-Mn(tart) having two different metallic active sites (Zr/Mn: Lewis acid), abundant chiral functional groups, and centers (Brønsted acid: to activate the epoxide ring) can be selected as a unique chiral porous catalyst. To ascertain that a CMOF has a pivotal role with heterogeneous nature in the environmental catalysis with less energy utilization, a series of olefins and epoxides with the various sizes were used in the enantioselective oxidation and CO_2 fixation. The results show that PCN-224-Mn(tart) can catalyze the catalytic reactions at low energy and ambient pressure and temperature. Meanwhile, high selectivity to an enantiomer in the asymmetric processes demonstrates that high energy has not been employed for enantioseparation. In fact, in the catalytic and reusability tests, PCN-224-Mn(tart) exhibited excellent efficiency with ee to 100%. In total, the presence of the accessible catalytic sites such as Mn centers, Zr clusters, chiral functional groups, and hydrogen bonds is useful in the catalyst structure. These reasons are the second positive points of our catalyst. In the end, our comprehensive study not only shows a simple strategy for the design of a new renewable chiral Zr-based MOF as a chiral heterogeneous catalyst that agrees well with green chemistry but also demonstrates a unique vision to develop new chiral structures as asymmetric platforms based on the MOF structure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02811.

Details of materials and instrumentation, FT-IR and UV–vis spectra, ^1H NMR, EDS, PXRD, Chem3D data, CD analysis, Barrett–Joyner–Halenda pore-size distributions, and N_2 adsorption isotherms (PDF)

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Notes

The authors declare no competing financial interest.

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