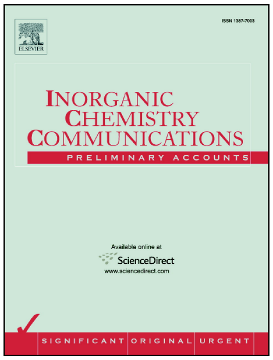

Synthesis of a pair of homochiral manganese-based coordination polymers as stable catalyst for the selective oxidation of cis-cyclooctene

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Synthesis of a pair of homochiral Manganese-based coordination polymers as stable catalyst for the selective oxidation of *cis*-cyclooctene

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Keywords: coordination polymers; selective oxidation; catalysis

A pair of homochiral manganese-based coordination polymers [Mn(H_2O)$_2$(bpy)(L-DBTA)] (**L-1**) and [Mn(H_2O)$_2$(bpy)(D-DBTA)](**D-1**): Syntheses, crystal structures and catalytic properties for the selective oxidation of *cis*-cyclooctene. The homochiral manganese-based 3D supermolecule framework exhibits high catalytic activity (38.85% conversion based on *cis*-cyclooctene and 76.13% selectivity for epoxycyclooctane) and stability for selective oxidation of *cis*-cyclooctene in the absence of solvent using TBHP as radical initiator and oxygen (in the air) as oxidant at 80 ℃.

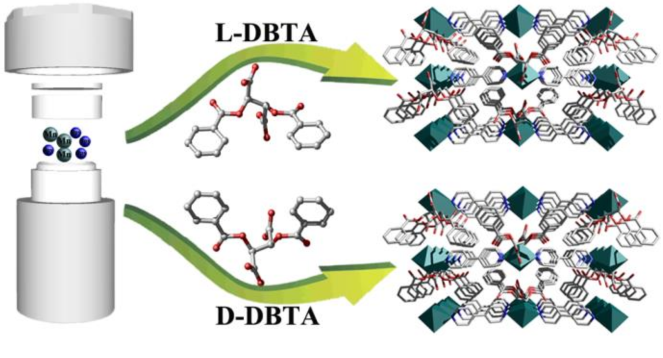
Chirality is a widespread phenomenon in nature, playing a very important role in many areas of society and science [1]. Therefore, lots of scientists focus on the topic of preparation of chiral materials [2]. In the past few years, chiral metal−organic frameworks (MOFs) or coordination polymers (CPs) are of great interest, because of their intriguing potential applications in optical resolution, enantioselective synthesis, asymmetric catalysis, and so on [3]. In general, homochiral coordination polymers can be obtained by three routes [4]. The first is using a chiral organic bridging ligand to link the metal centers in the framework [5]. The second is using a chiral molecule as an auxiliary ligand that does not bridge the metal centers but forces chirality by coordinating to the metal center [6]. The third is spontaneous resolution upon crystallization without any chiral sources [7]. Recent research has proved that the usage of chiral species as reactant precursors represent the more straightforward and effective approach toward homochiral solids for it is much easier to control the chirality of the aimed products [8].

Chiral catalysis acts as the core issues of chemistry and play significant roles in current chemical industry, as well as pharmacy and biomimetic chemistry [9-12]. To date, solid catalysts have been almost exclusively inorganic materials. Due to its crucial role in many chemical processes, heterogeneous catalysis is one of the key elements of our industrialized society, and thus has direct impact on the global economy. It is reported that approximately nine-out of-ten chemical processes utilize heterogeneous catalysts [13,14]. However, the design of more active and selective heterogeneous catalysts leading to more environmental friendly processes is still a priority and a challenge [15].

Oxidation is an important pathway to large-scale production of chemicals. However, poor efficiency is the common weakness [16]. Recently, the important concept of “green chemistry” has been associated with this type of catalytic reactions, which involves the use of molecular oxygen directly from air [17]. Among various oxidants, molecular oxygen is a cheap, clean and readily available oxidant, making it ideal for hydrocarbon oxidation from both economic and environmental perspectives [18-20]. Furthermore, oxidation is an important method for the synthesis of chemical intermediates in the manufacture of hightonnage commodities, high-value fine chemicals, agrochemicals, and pharmaceuticals [13,14]. Selective oxidation of hydrocarbons is of great interest in synthetic organic chemistry and chemical industry for the conversion of petroleum-based feedstocks to more valuable chemicals such as diols, epoxides, alcohols and carbonyl compounds [20-22]. The chemical transformations including (ep)oxidation are interesting since epoxides are key starting materials for a wide variety of products in organic chemistry.

For many years, coordination polymers/MOFs are demonstrated to be one of the most promising catalysts for the oxidation of a variety of substrates such as alkanes, olefins, alcohols, sulfides, and aromatic amines [23-26]. The most studied reaction catalysed by coordination polymers is probably the epoxidation of ole fins [27]. A significant advantage of many of these complexes is that they can be prepared from inexpensive metal sources, e.g [28]. Although coordination polymers/MOFs could be used as catalysts with high catalytic activity in various reactions [29]. (such as, cyanosilylation, hydrogenation, polymerization, oxidation, and isomerization), the search and design of highly-effective catalysts with high yields and selectivities are a challenging task for oxidation reactions, especially hydrocarbon oxidations, using tert-butyl hydroperoxide (TBHP) as radical initiator and oxygen (in the air) as oxidant [30-32].

Here we report a pair of homochiral manganese-based coordination polymers, namely [Mn(H_2O)$_2$(bpy)(L-DBTA)] (**L-1**) and [Mn(H_2O)$_2$(bpy)(D-DBTA)] (**D-1**) from manganese salt with L-DBTA=(-)-dibenzoyl-L-tartaric acid, D-DBTA=(+)-dibenzoyl-D-tartaric acid, and bpy (4,4'-Bipyridine). Both compound **L-1** and **D-1** exhibit a 3D supermolecule framework and the further selective catalytic oxidation of *cis*-cyclooctene experiments indicated that these manganese-based coordination polymers possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.



Scheme 1. Schematic representation of the synthesis of **L-1** and **D-1** assembled from manganese salt with mixed ligands bpy and L-DBTA and D-DBTA**.**

Single-crystal X-ray diffraction analyses reveal that compounds **L-1** and **D-1** are isostructural and their crystal system, space group, unit cell dimensions, related bond distances, and bond angles are only slightly different (Scheme 1), hence only the structure of **L-1** will be discussed in detail. **L-1** crystallizes in the chiral orthorhombic system with space group $P2_12_12_1$, and the flack parameter of 0.022(10) further indicates that the absolute configuration is correct. As illustrated in Fig. 1a, the asymmetric unit of **L-1** contains one crystallographically independent Mn atom, one L-DBTA ligand, one bpy ligand, and two coordinated water molecules. The Mn1 centre displays a distorted octahedral $[MnN_2O_4]$ geometry, being coordinated by two oxygen atoms from two L-DBTA ligands, two coordinated water molecules, and two nitrogen atoms from two bpy ligands. In **L-1**, the bpy bridges Mn atoms into a 1D nonlinear chain, and the whole L-DBTA acts as bidentate ligand to extend adjacent chains into 2D wavelike layer via its two monodentate carboxylate groups (Fig. 1b). There is a window in 2D layer with dimension of 11.5 ×7.9 Å based on the Zn•••Zn distances (Fig 1c). The 2D layers are extended to 3D supramolecular framework with hydrogen bondings between carboxylate oxygen atoms of the L-DBTA and coordinated water molecules (Scheme 1).

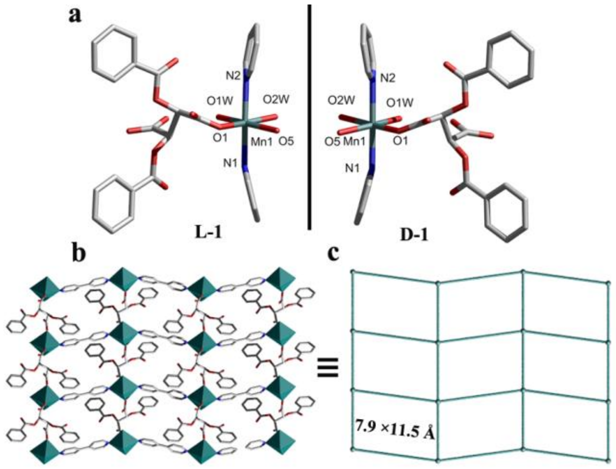


Fig. 1 The asymmetric units of **L-1** and **D-1** (a). The 2D interdigitated architecture along the *c* axes (b) and (c). Hydrogen atoms and lattice water molecules are omitted for clarity.

To confirm the enantiomeric nature of L-1 and D-1, the circular dichroism (CD) spectra were measured in KBr pellets [33,34]. As shown in Fig. 2, the CD spectra of **L-1** and **D-1** in the solid state show that Cotton effects are in the wavelength range of 200-500 nm. Further close observation reveals that the CD spectra are mirror images of one another, which conclusively demonstrates that **L-1** and **D-1** are enantiomers. This phenomena indicated that the chiral information was transferred from chiral DBTA ligand to the metal centre and finally to the whole framework.

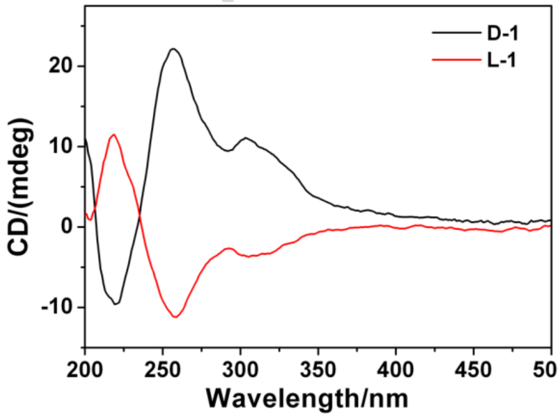


Fig. 2. Solid state CD spectra of **L-1**(red) and **D-1**(black) in KBr pellets.

On the basis of the manganese plays an important role in alkenes catalysis, as a heterogeneous catalyst [35-37]. We used **L-1** as a catalyst to study the catalytic performance of the selective oxidation of *cis*-cyclooctene. First, 10 mL of *cis*-cyclooctene and 0.020 g of **L-1** were placed in a 50 mL three-necked flask with a reflux condensation device and magnetic stirring was continued. Then 0.5 mL t-butyl hydroperoxide (TBHP) as an initiator was added dropwise to the three-necked flask, and finally the above mixed solution was stirred at 80 °C for 24 h. After the samples of 4, 8, 12, 16, 20, and 24 h were cooled to room temperature, the filter was analyzed by the gas chromatograph(GC), the products of the selective oxidation of *cis*-cyclooctene were poxycyclooctane, 1,2-cyclooctanediol, and cycloocten-2-one.

As shown in Table 1 and Fig. 3a, the detailed conversion of *cis*-cyclooctene and selectivity of oxidation products demonstrate the catalytic performance of **L-1** for the selective oxidation of *cis*-cyclooctene, which reveals that the percentage of conversion and the selectivity reach 26.42% and 61.87% after 12 h, respectively. After 24 h reaction, high conversion efficiency of 38.85% and high selectivity up to 76.13% are achieved simultaneously. With time going on, both the conversion of *cis*-cyclooctene and the selectivity of epoxycyclooctane are increased. At the same time, the selectivity of cycloocten-2-one decreases from 23.62% to 13.10%. Similarly, the selectivity of 1,2-cyclooctanediol decreases from 14.16% to 10.02%.

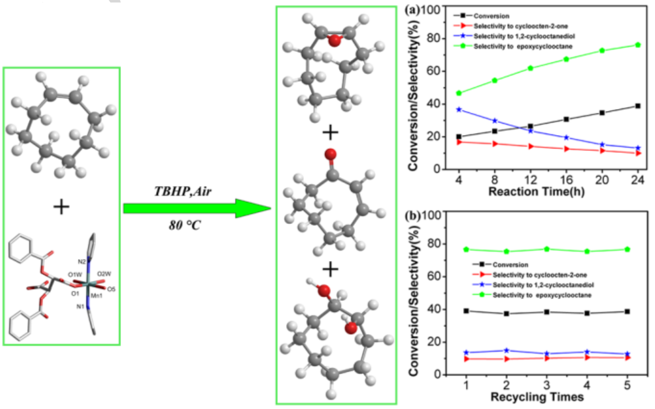
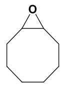
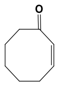
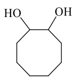


Fig. 3 The process of *cis*-cyclooctene epoxidation. (a) The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and reaction time with compound **L-1** as catalyst. (b) The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and recycling times with compound **L-1** as catalyst.

Table 1. Effect of variety of reaction time on selective oxidation of *cis*-cyclooctene using compound **L-1** as catalyst.

	Product Selectivity (%)				
Reaction time (h)				Conversion (%)	$\Sigma selC_8$§
0	0	0	0	0	0
4	46.63	36.61	16.75	20.07	99.99
8	54.39	29.78	15.73	23.38	99.87
12	61.87	23.62	14.16	26.42	99.65
16	67.41	19.49	12.63	30.63	99.53
20	72.68	15.16	11.53	34.65	99.37
24	76.13	13.10	10.02	38.85	99.25

Reaction conditions: compound **L-1** (20 mg), *cis*-cyclooctene (10 mL), TBHP (0.5 mL), 80 ºC, 24 h, atmospheric pressure.

§Total selectivity to C_8 partial oxidation products.

Whether the catalyst can be recycled reliably is an important indicator to evaluate the stability of the catalyst. We used the *cis*-cyclooctene epoxidation reaction system as a model to conduct a cyclic reaction test on the catalyst. It can be seen from Fig. 3b that no significant changes are observed in the conversion rate of *cis*-cyclooctene and the selectivity of reaction products for each cycle until 24 h under the same reaction conditions for 5 cycles. The result shows that the catalyst has great recycling performance. In order to further confirm the **L-1** acts as the catalyst for this reaction, we carried out the blank control experiment (the reaction without catalyst) and the filtrate test (When the reaction was carried out for 24 h, the solid catalyst in the reaction liquid was removed by hot filtration to obtain a clear reaction solution. The clear solution was allowed to react under the same reaction conditions for 24 h. Then, the *cis*-cyclooctene conversion rate and the selectivity of reaction products was tested). The final result of the blank control experiment is that the *cis*-cyclooctene conversion rate and the selectivity of reaction products are zero. This reaction proves that the absence of the catalyst reaction is not carried out. Simultaneously, after the filtrate test, the conversion rate of *cis*-cyclooctene and the selectivity of reaction products are also still zero, which demonstrate that the filtrate does not participate in the catalytic reaction. All above-mentioned catalytic experiments show that **L-1** indeed acts as a heterogeneous catalyst in the present catalytic system.

In conclusion, a pair of homochiral manganese-based coordination polymers (**L-1** and **D-1)** with 3D supramolecular network has been constructed by the L/D-DBTA ligands and manganese salt. The catalytic experiment indicates that these manganese-based coordination polymers, directly used as a heterogeneous catalyst without any supports, possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene. Recyclability experiments shows that **L-1** is highly reusable and stabile for the catalytic performance of the selective oxidation of *cis*-cyclooctene. Significantly, this work provides an exciting prospect for the application of coordination polymer in catalytic reactions. Further work is underway in our laboratories.

Acknowledgments

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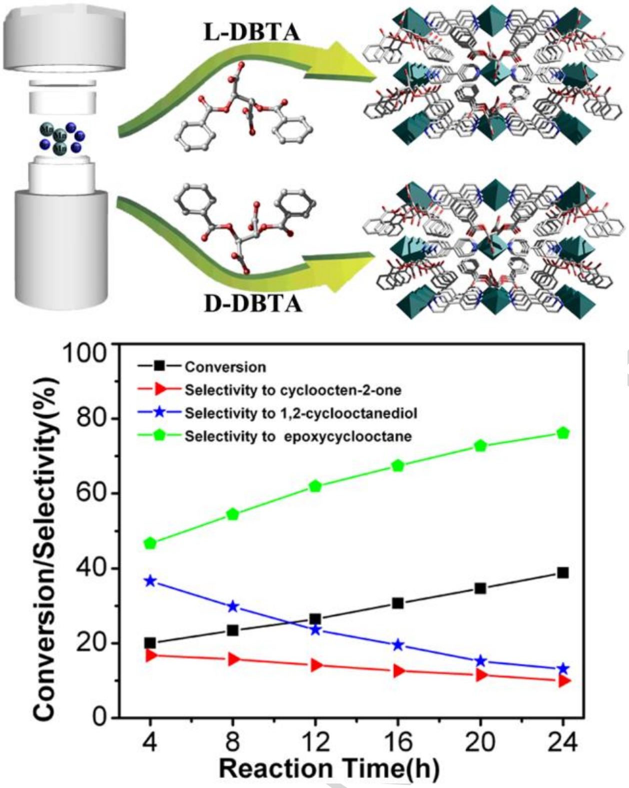
Graphical abstract



A pair of homochiral manganese-based coordination polymers possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.

Highlights

> A pair of homochiral Manganese-based coordination polymers exhibit 3D supermolecule framework.

> Catalytic ability for the selective oxidation of *cis*-cyclooctene.