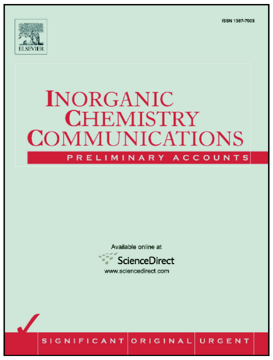

Synthesis of a pair of homochiral manganese-based coordination polymers as stable catalyst for the selective oxidation of cis-cyclooctene

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PII: S1387-7003(18)30083-2
DOI: doi:10.1016/j.inoche.2018.03.009
Reference: INOCHE 6913

To appear in: *Inorganic Chemistry Communications*

Received date: 26 January 2018
Revised date: 24 February 2018
Accepted date: 9 March 2018

Please cite this article as: Guangju Zhang, Yang Shi, Ying Wei, Qingguo Zhang, Yanping Zhang, Kedi Cai, Siqi Xiu , Synthesis of a pair of homochiral manganese-based coordination polymers as stable catalyst for the selective oxidation of cis-cyclooctene. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Inoche(2017), doi:10.1016/j.inoche.2018.03.009

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

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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 ℃.

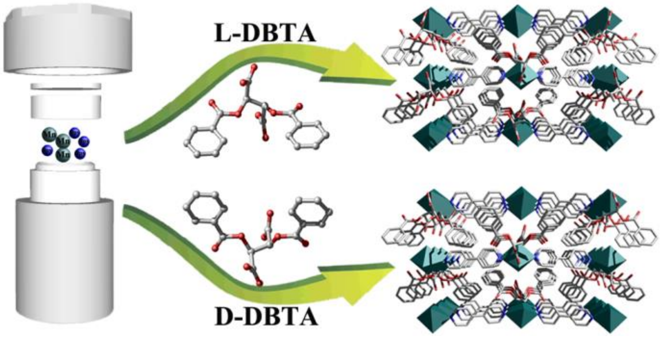
Chirality is a widespread phenomenon in nature, playing a very important role in many areas of society and science [1]. Therefore, lots of scientists focus on the topic of preparation of chiral materials [2]. In the past few years, chiral metal−organic frameworks (MOFs) or coordination polymers (CPs) 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.