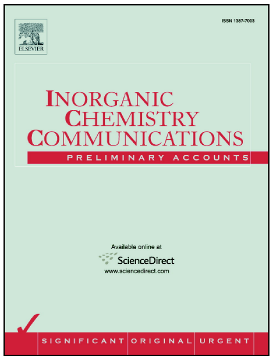

Two kinds of cobalt–based coordination polymers with excellent catalytic ability for the selective oxidation of cis-cyclooctene

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Two kinds of cobalt–based coordination polymers with excellent catalytic ability for the selective oxidation of *cis*-cyclooctene

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Keywords: coordination polymers; selective oxidation; catalysis

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Two kinds of cobalt–based coordination polymers {[Co(dsd)(H_2O)$_4$]·4,4'-bpy}(1) and {[Co(dsd)(H_2O)$_4$]·H_2O)} (2) with the chain structure possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.

The search for functional materials has emerged with a considerable importance over the last two decades, with remarkable efforts towards the design and synthesis of novel hybrid organic-inorganic compounds being performed worldwide. Coordination polymers are a notable family of hybrid materials showing infinite extended networks which usually involve two main components: inorganic nodes (metal ions or clusters) and organic linkers interconnected by coordinative bonds to afford a network arrangement with specific topology[1]. Such organic–inorganic hybrid compounds can combine the unique characteristics of the components and exhibit novel structural features, as well as new properties arising from the synergistic interplay of the two components[2]. Of particular interest are those showing potential applications in the fields of fuel gas storage[3,4], catalysis[5-7], magnetism[8-10], separation and proton conduction[11,12], etc.

Based on the similarity to metal–organic frameworks (MOFs), a logical application of coordination polymers could also be as solid catalysts, which are similar to heterogeneous catalysts and also allowed for easier post-reaction separation and recyclability than homogeneous catalysts[13]. However, despite the elevated metal content of coordination polymers, their use in catalysis is largely hampered by the relatively low stability to thermal treatments, chemical agents, and moisture, due to the presence of the organic component. Furthermore, the activity and selectivity of a catalytic reaction can be tuned by varying the size, composition and morphology of inorganic-solid catalysts[14].

In some coordination polymers, empty sites on the inorganic secondary building units can be generated through the simple removal of small neutral ligands from the metal coordination environment of the “unactivated” material (mostly H_2O, when operating under hydrothermal synthetic conditions). The preactivation of the material is expected to create open metal sites potentially available for promoting catalysis while keeping the framework crystalline texture intact. In addition, the heterogeneous nature of a coordination polymer can be very useful to separate the catalyst from the products of interest; recover it after simple filtration procedures; and finally, regenerate it for successive catalytic runs[15].

Catalysis is a core issue of chemistry and plays a significant role in current chemical industry, as well as environmental and energy problems[16,17]. Furthermore, oxidation is an important method for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities, high-value fine chemicals, agrochemicals and pharmaceuticals[18,19]. Alkene selective oxidation has attracted much attention because of the related products of epoxides are valuable and resourceful commercial intermediates. For many years, coordination polymers have been used as catalysts for a wide variety of organic reactions. The most studied reaction catalysed by coordination polymers is probably the epoxidation of olefins[20]. Although coordination polymers/MOFs could be used as catalysts with high catalytic activity in various reactions[21] (such as, cyanosilylation, hydrogenation, polymerization, oxidation, and isomerization), the studies on their application in hydrocarbon selective oxidation reactions (using t-BuOOH as oxidant) is still a huge challenge.

Here we report the synthesis of two cobalt-based coordination polymers, namely {[Co(dsd)(H_2O)$_4$]·4,4'-bpy}(**1**) and {[Co(dsd)(H_2O)$_4$]·H_2O)} (**2**) from cobalt salt with 4,4'-Diamino-2,2'-stilbenedisulfonic acid (dsd) and 4,4'-Bipyridine (4,4'-bpy). Both compound **1** and compound **2** exhibit a 3D supermolecule framework and the further selective catalytic oxidation of *cis*-cyclooctene experiments indicated that these cobalt-based coordination polymers possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.

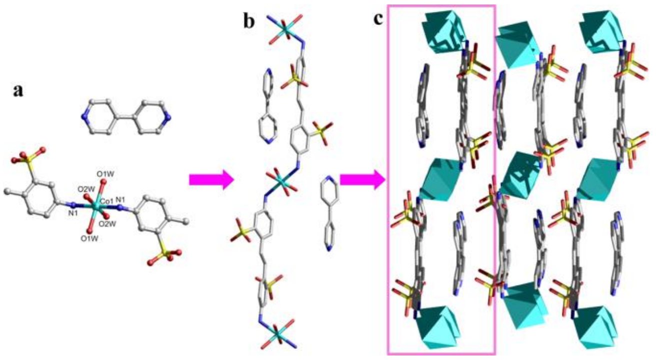


Figure 1 (a) Ball-stick view of the symmetric unit of **1**. (b) view of the 1D N–Co–N chain running along the *c* axis. (d) Stick and polyhedral view of the 3D framework.

Compound **1** crystallizes in the Orthorhombic with space group Pbcn. The symmetrical unit contains one [Co(dsd)(H_2O)$_4$] unit and one solvent 4,4'-bpy molecule for compound **1**. As shown in Figure 1a, Co atom is six-coordinated in an octahedral coordination geometry, coordinated by two nitrogen atoms from one dsd ligand and four oxygen atoms from four coordinate water molecules. Each Co atom is bridged by two amidogen N atoms to form a CoO_4N_2 unit. These Co units feature a 1D ladder along the *c* axis interconnected via dsd ligands (as illustrated in Figure 1b). The adjacent chains are further aggregated into a three-dimension (3D) network through the hydrogen bonds between the 4,4'-bpy and sulfonic acid groups oxygen atoms. As shown in Figure 1c, the neighboring chains in one row are parallel. The 4,4'-bpy ligands are filled in the free space of structure by extensive hydrogen bonding interactions to maintain the stability of the framework.

Compound **2** crystallizes in the Monoclinic with space group C2/*c*. The symmetric unit contains one [Co(dsd)$(H_2O)_4$] unit and one solvent water molecule for compound **2**. As shown in Figure 2a, Co atom is six-coordinated in an octahedral coordination geometry, coordinated by two nitrogen atoms from one dsd ligand, four oxygen atoms from four coordinate water molecules. Each Co atom is bridged by one dsd ligand to form a wave-like chain running along the *c* axis (Figure 2b). The adjacent chains are inter-linked by intermolecular hydrogen bonding interactions to afford a 3D architecture (Figure 2c). The lattice water molecules are filled in the free space of structure by extensive hydrogen bonding interactions to maintain the stability of the framework.

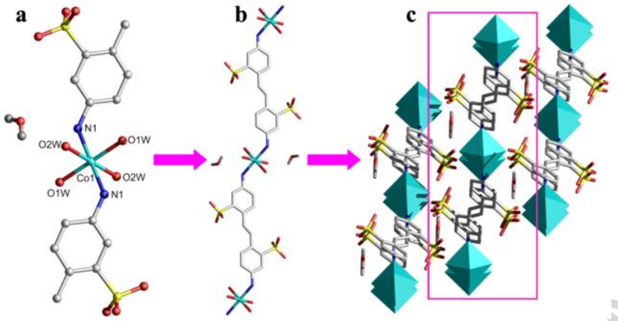
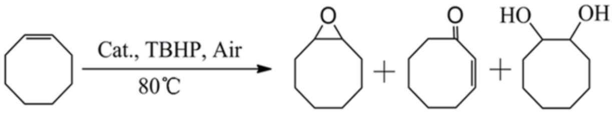


Figure 2 (a) Ball-stick view of the symmetric unit of **2**. (b) view of the 1D N–Co–N chain running along the *c* axis. (d) Stick and polyhedral view of the 3D framework.

Considering that cobalt plays an important role in current petrochemical and plastic industries, as both a hetero and homogeneous catalyst[22-25]. In the following experiments, the catalytic performance of compound **1** and **2** for the selective oxidation of *cis*-cyclooctene is further studied. In 50 ml three neck flask with a reflux condensation device, successively added 10 ml *cis*-cyclooctene, 0.020 g catalyst and 0.5 ml tertiary butyl-hydrogen peroxide, magnetic stirring, 80 ℃ constant temperature oil bath. 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). Finally, the products of the catalytic reaction were poxycyclooctane, 1,2-cyclooctanediol and cycloocten-2-one.



Scheme 1 The equation of *cis*-cyclooctene epoxidation.

When the compound **1** as catalyst **1**, the conversion rate of selective catalytic oxidation of *cis*-cyclooctene and different oxidation products change with time as shown in Figure 3a and Table 1. From the picture we can see very intuitively, when using the catalyst **1** and the reaction time is 12 h, the substrate *cis*-cyclooctene conversion rate is 14.21%, the main product is poxycyclooctane and selectivity of 74.21%. Along with the further extension of reaction time, when the reaction to 24 h, *cis*-cyclooctene conversion rate is 25.79%, the selectivity of poxycyclooctan is 79.63%, thus, *cis*-cyclooctene conversion rate and selectivity of poxycyclooctan are increasing over time. At the same time, the selectivity of 1,2-cyclooctanediol fell from 11.41% to 6.67%, the same cycloocten-2-one also fell from 14.05% to 12.95%. When the compound **2** as catalyst **2**, the conversion rate of selective catalytic oxidation of *cis*-cyclooctene and different oxidation products change with time as shown in Figure 3b and Table 2. When using the catalyst **2** and the reaction time is 12 h, the substrate *cis*-cyclooctene rate is 12.61%, the main product is poxycyclooctane and selectivity of 64.94%. Along with the further extension of reaction time, when the reaction to 24 h *cis*-cyclooctene conversion rate is 24.76%, the selectivity of poxycyclooctan is 71.40%, thus, *cis*-cyclooctene conversion rate and selectivity of poxycyclooctan are increasing over time. At the same time, the selectivity of 1,2-cyclooctanediol fell from 20.52% to 17.41%, the same cycloocten-2-one also fell from 14.22% to 10.41%.

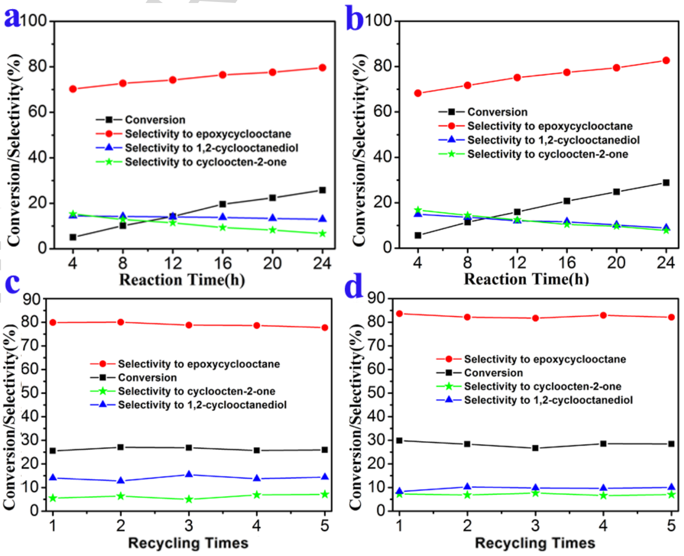
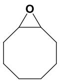
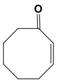
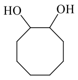


Figure 3 The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and reaction time with compound **1** (a) and **2** (b) as catalyst, respectively. The relationship between the conversion of *cis*-cyclooctene/selectivity of different products and recycling times with compound **1** (c) and **2** (d) as catalyst, respectively.

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

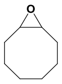
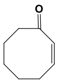
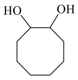
Reaction time (h)	Product Selectivity (%) 	 	  	Conversion (%)	ΣselC$_8$§
0	0	0	0	0	0
4	70.23	14.48	15.27	5.08	99.98
8	72.73	14.22	12.88	10.16	99.83
12	74.21	14.05	11.41	14.21	99.67
16	76.44	13.78	9.34	19.58	99.56
20	77.63	13.33	8.22	22.37	99.38
24	79.63	12.95	6.67	25.79	99.25

Reaction conditions: compound **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.

Table 2. Effect of variety of reaction time on selective oxidation of *cis*-cyclooctene using compound **2** as catalyst **2**.

Product Selectivity (%)

Reaction time (h)				Conversion (%)	ΣselC$_8$§
0	0	0	0	0	0
4	68.28	14.92	16.79	5.63	99.99
8	71.70	13.68	14.46	11.49	99.67
12	75.17	12.04	12.47	15.94	99.56
16	77.47	11.61	10.45	20.78	99.44
20	79.49	10.21	9.69	24.82	99.36
24	82.66	8.83	7.73	28.86	99.24

Reaction conditions: compound **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.

In order to further confirm the two compounds for this reaction of the catalyst, we were carried out two groups of blank test (no compounds, other experimental conditions unchanged) and the filtrate experiment (when the experiment to 24 h after the catalyst removed, the remaining filtrate continued to react for 24 h to verify that the filtrate did not participate in the catalytic reaction). The conversion rates of the two blank sets were all 0, indicating that the reaction was not carried out when catalyst was not involved in the reaction. The conversion rates of the two groups of filtrate experiments were all 0, indicating that the filtrate after the reaction did not participate in the reaction. It can be shown that compound **1** and compound **2** act as heterogeneous catalyst in the experiments of *cis*-cyclooctane catalytic oxidation. In order to test the stability of the two kinds of catalysts, we did five times the same repeated trials under the same conditions with the catalysts which were separated from the reaction solution, washed several times with dichloromethane to remove the physisorbed molecules and dried after the first catalytic run. As shown in Figure 3c and 3d, *cis*-cyclooctene conversion rate and selectivity of reaction products are no change with almost. All above-mentioned catalytic experiments show that compound **1** and compound **2** indeed act as heterogeneous catalyst in the present catalytic system.

In summary, two new compounds based on dsd ligands and 4,4'-bpy ligands with Co metal salts have been synthesized and characterized. The catalytic experiment indicates that compound **1** and compound **2**, directly used as a heterogeneous catalyst without any supports, possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene. Considering that there are a large number of possible organic ligands and metal ions that can be used in this synthetic strategy, the results presented here may open a promising route for the design and fabrication of other novel coordination polymers with high catalytic performance. 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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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC-1572057 for compound **1** and CCDC-1572058 for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data containing XRPD, IR, TG and together with tables of compounds **1** and **2**.

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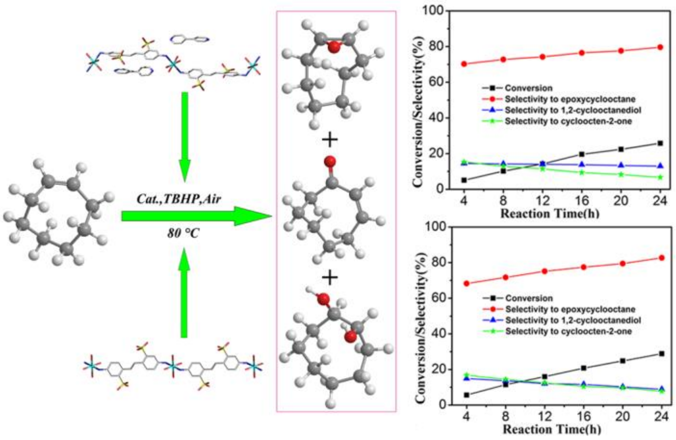
Graphical Abstract



Cobalt-based coordination polymers possess excellent catalytic ability for the selective oxidation of *cis*-cyclooctene.

Highlights

> Two cobalt-based coordination polymers exhibit a 3D supermolecule framework.

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