

[Bis(catechol)salen]Mn^{III} Coordination Polymers as Support-Free Heterogeneous Asymmetric Catalysts for Epoxidation

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The formation of coordination polymers by the reaction of [bis(catechol)salen]Mn^{III} with several di- and trivalent metal ions is reported. These polymers are insoluble in a wide range of organic solvents and water but can be dissolved upon addition of excess pyrocatechol. They function as enantioselective heterogeneous epoxidation catalysts and exhibit catalytic activity comparable to that of the homogeneous [bis(catechol)salen]Mn^{III} building block alone when used for

the enantioselective epoxidation of 2,2-dimethyl-2H-chromene. After catalysis, catalyst isolation from the reaction mixture can be readily achieved by centrifugation and decantation. Under practical oxidant concentrations, the catalyst can be recycled up to ten times with little loss of activity and no loss of enantioselectivity.

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Introduction

Porous coordination polymers – especially crystalline ones – have recently received much attention for their potential applications in the areas of heterogeneous catalysis, separations, and gas storage.^[1,2] Although the coordination polymerization of chiral homogeneous catalysts has been suggested as a strategy to obtain practically useful heterogeneous asymmetric catalysts,^[3] to date there are only a few demonstrations of this approach.^[4] Among these are heterogenized catalysts for the addition of ZnEt₂ to aromatic aldehydes^[4a] and for enantioselective Michael addition.^[4b] In addition, coordination polymers have been used in asymmetric Lewis acid catalysis.^[4c,4d] Examples of coordination polymers in chiral oxidative catalysis are scarcer. Suslick and co-workers have reported that a porphyrin-based material catalyzes organic oxidations;^[4e] however, this system is not chiral. To the best of our knowledge, our recent report of the enantioselective epoxidation of 2,2-dimethyl-2H-chromene by a microporous, crystalline metal–organic framework (MOF) material constitutes the first example of chiral oxidation catalyzed by a coordination polymer.^[5] While this work successfully illustrates the translation of a homogeneous chiral (salen)Mn^{III} catalyst into the heterogeneous realm, the (salen)Mn-based MOF material has lim-

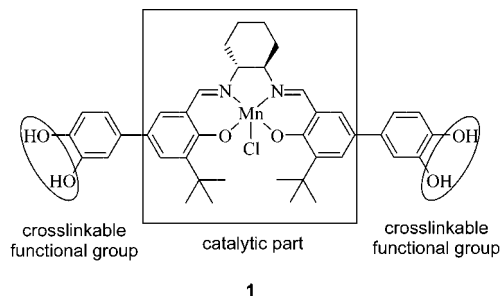
ited recyclability. Specifically, fragmentation of MOF particles and loss of the catalyst (4 to 7% per cycle) can occur during each batch reaction, reflecting the inherent weakness of the Zn^{II}–N(pyridine) bond. The required usage of zinc or similar divalent ions as framework nodes in these particular MOFs also limits the diversity of functional materials that can potentially be obtained by this approach.

If the requirement of crystallinity were relaxed, however, stronger chelate-type metal–ligand linkages (such as metal–catecholate or –semiquinone links) could be used, and the resulting amorphous coordination polymers may still exhibit heterogeneous catalytic competency.^[6] Previously, we reported the immobilization of mono-catechol-functionalized (salen)Mn^{III} complexes on alumina membranes.^[7] The modified membranes functioned well as heterogeneous asymmetric epoxidation catalysts, achieving high one-pass conversion and excellent turnover numbers, albeit with moderate recyclability due to catalyst leaching. We hypothesized that a more permanent approach to heterogenization would be coordination polymerization of [bis(catechol)salen]Mn (1). By combining 1 with various soluble metal ions, linear and/or branched coordination polymers should form, ideally as isolable solids that can be used as catalysts. While there is no precedent for the use of catechol-based coordination polymers in heterogeneous catalysis, catechol has long been known as an effective bidentate ligand for many metal ions.^[8] The redundantly chelating (salen)Mn moieties in the polymer networks might well display reduced leaching and higher stability/recyclability compared to the alumina-supported species. Herein, we report that a series of exceptionally stable enantioselective heterogeneous epoxidation catalysts can be made by the coordination po-

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lymerization of **1** and several metal ions. These catalysts can be recycled numerous times with minimal leaching and no loss of enantioselectivity.



Results and Discussion

The bis(catechol)-functionalized salen ligand of **1** can be prepared easily from (1*R*,2*R*)-diaminocyclohexane (see Supporting Information). Metalation with MnCl₂ under an N₂ atmosphere, followed by oxidation in air, afforded complex **1** in good yield. Coordination polymerization of **1** with Cu^{II} was accomplished under an N₂ atmosphere by adding CuCl₂ to a 1:4 mixture of compound **1** and triethylamine (TEA) dissolved in deoxygenated dimethylformamide (DMF). Vigorous stirring of the resulting reaction mixture led to a spontaneous formation of precipitates, which were then filtered and thoroughly washed with DMF to afford the Cu-linked (salen)Mn polymer **poly(Cu-1)** as a brown solid (Figure 1).^[9]

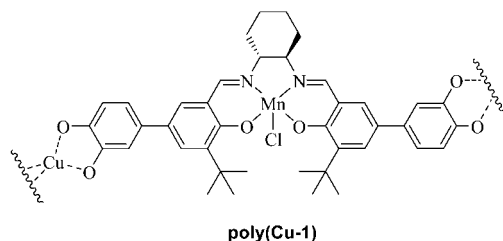


Figure 1. A schematic drawing of the coordination polymer formed between Cu^{II} and [bis(catechol)salen]Mn^{III}Cl [**poly(Cu-1)**].

Poly(Cu-1) is insoluble in a wide range of organic solvents (toluene, methanol, DMF, and dimethyl sulfoxide) and water. Inductively coupled plasma (ICP) mass spectrometric measurements performed on **poly(Cu-1)** yielded a Mn/Cu ratio of approximately 1:1.1, suggesting that **poly(Cu-1)** exhibits a quasi-one-dimensional structure, in which **1** is connected by bis(catecholate)copper linkages. The formation of **poly(Cu-1)** can be reversed: addition of excess pyrocatechol to a DMF slurry of **poly(Cu-1)** dissolves the particles within a few hours. Electrospray ionization mass spectrometry conducted on the resulting solution clearly showed mass peaks associated with the (salen)Mn building block ([M – Cl]⁺ = 703.92 and [M – Cl + DMF]⁺ = 776.56, see Supporting Information).

Thermal gravimetric analysis (TGA) performed on the as-synthesized **poly(Cu-1)** revealed a weight loss of ca. 18% between 25–200 °C, followed by several additional losses up to 700 °C (see Supporting Information). We attribute the initial weight loss to the liberation of DMF and water and the latter ones to the decomposition of the polymer. As further evidence for the initial solvent loss, TGA of a sample polymer that had been evacuated (30 mTorr) for 18 h at 80 °C showed only ca. 2% weight loss in the temperature range of 25–200 °C. The TGA trace of an evacuated polymer sample that was then resolvated showed a lower loss of solvent than the as-synthesized product (8% vs. 18%), suggesting that **poly(Cu-1)** may have undergone further aggregation upon evacuation and become less porous than freshly prepared samples. However, it still has moderate porosity (total BET surface area = 72 m² g^{−1}) and an amorphous structure as evidenced by scanning electron microscopy (SEM; Figure 2) and by the absence of peaks in powder X-ray diffraction measurements.

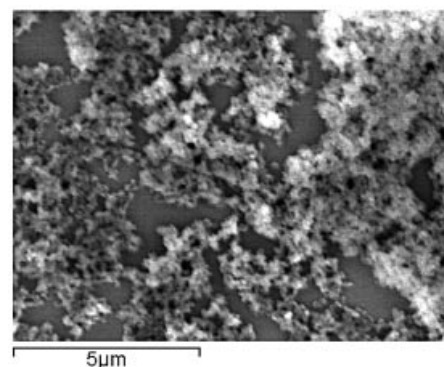


Figure 2. SEM image of **poly(Cu-1)**.

Catalytic epoxidations of 2,2-dimethyl-2*H*-chromene were carried out in dichloromethane^[10] solution under ambient conditions with **poly(Cu-1)** by using 2-(*tert*-butylsulfonyl)iodosylbenzene as the oxidant [Equation (1)]. For comparison, [bis(dimethoxyphenyl)salen]Mn^{III}Cl (**2**), the protected soluble analogue of **poly(Cu-1)**, was also tested for epoxidation activity.^[11] Although a slightly lower enantioselectivity was observed for **poly(Cu-1)** relative to **2** [76% *ee* for **poly(Cu-1)** vs. 86% *ee* for **2**], their epoxidation activities were comparable (Table 1, entries 1 and 2). As reduced enantioselectivity is often seen with homogeneous catalysts immobilized in constrained environments such as cross-linked polymers and zeolites,^[12] this slight decrease in enantioselectivity may be attributed to structural constraints resulting from the immobilization. Indeed, when **poly(Cu-1)** is dissolved in the presence of pyrocatechol (vide supra) and used as a catalyst for reaction (1), its enantioselectivity (82%) becomes quite close to that of free **1**.

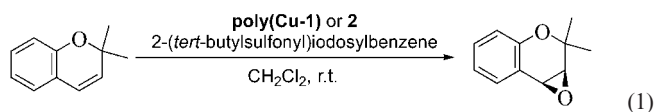


Table 1. Recyclability of **poly(Cu-1)** in the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene with 2-(*tert*-butylsulfonyl)iodosylbenzene.^[a]

Entry	Catalyst	Reuse cycle	Yield [%] ^[b]	<i>ee</i> [%] ^[c]	Leaching [%] ^[d] of Cu/Mn
1	2	1 st	87	86	not applicable
2	poly(Cu-1)	1 st	79	76	2.9:1.5
3	poly(Cu-1)	2 nd	74	76	1.8:1.6
4	poly(Cu-1)	3 rd	78	75	0.5:0.9
5	poly(Cu-1)	4 th	80	76	0.1:0.3
6	poly(Cu-1)	5 th	80	75	0.1:0.1
7	poly(Cu-1)	6 th	73	76	0.1:0.1
8	poly(Cu-1)	7 th	79	76	< 0.1: < 0.1
9	poly(Cu-1)	8 th	72	75	< 0.1: < 0.1
10	poly(Cu-1)	9 th	69	75	not detectable
11	poly(Cu-1)	10 th	70	76	not detectable

[a] Molar ratio olefin/oxidant/catalyst = 100:150:1. [b] GC yield after 2 h with undecane as an internal standard. [c] Determined by using a Supelco β -DEX 120 chiral GC column. [d] Measured by ICP mass spectrometry.

Encouraged by the persistence of catalytic activity for **poly(Cu-1)**, we examined its recyclability. Samples of **poly(Cu-1)** were easily recovered by centrifugation after catalysis and rinsed with dichloromethane and acetone before being used again for epoxidation. Remarkably, **poly(Cu-1)** can be recycled up to ten times with little loss in activity (79% \rightarrow 70% yield) and no loss in enantioselectivity (75–76% *ee*) (Table 1, entries 2–11). Evaluation of the product solutions by ICP mass spectrometry, after removing the catalyst particles, showed that 3.1% of the manganese and 4.7% of the copper initially leached out during the first two cycles (Table 1, entries 2 and 3). However, this metal loss quickly decreased during the next four cycles (Table 1, entries 4–7), and no leaching was detected in the last stages of recycling (Table 1, entries 10 and 11). Together with the retention of activity and selectivity mentioned above, it is conceivable that the initial leaching could have arisen from Cu^{II} ions and **1** that were weakly bound or entrapped in **poly(Cu-1)**. As **poly(Cu-1)** undergoes successive recycling, these weakly bound or entrapped ions and compounds are removed, leading to a substantial decrease in leaching after the second cycle.

Figure 3 compares the epoxidation activity of **poly(Cu-1)** to that of compound **2** in dichloromethane solution over a 3-h period under high-oxidant conditions (ca. 13 times the concentration used for the experiments in Table 1). As is often observed for homogeneous epoxidation catalysts, **2** is initially highly effective; however, it loses much of its activity after the first few minutes, followed by complete deactivation in less than 0.5 h. In contrast, the insoluble catalyst **poly(Cu-1)** exhibits a lifetime that is significantly greater (> 3 h) than that of **2**.^[13] In addition, the enantioselectivity of **poly(Cu-1)** stays consistent throughout the reaction, indicating that it is inherent to the nature of the system and that the Cu-coordinated **1** is probably more stable than **1** itself during the epoxidation. Although the rate of catalysis by **poly(Cu-1)** is slower than that by **2**, presumably because of the biphasic nature of its reaction, a total turnover number (TON) greater than 2000 can be obtained within

3 h. Employing a filtered homogeneous reaction mixture as catalyst in the epoxidation of chromene provides no significant TON, suggesting that the catalysis occurs heterogeneously. Interestingly, use of the recovered **poly(Cu-1)** under the same high-oxidant conditions only affords about 600 turnovers in the 3-h period and with a slightly lower *ee* (ca. 60%). These data suggest that although **poly(Cu-1)** is highly stable under practical synthetic laboratory scale (0.17 M), it is not immortal and can eventually be degraded under highly oxidative environments.

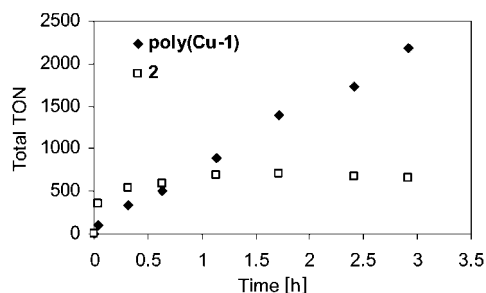


Figure 3. Plots of total turnover number (TON) vs. time for the epoxidation of 2,2-dimethyl-2*H*-chromene catalyzed by **poly(Cu-1)** (diamonds) and **2** (empty squares).

The catechol-based coordination-polymer-formation strategy is general for a wide range of metal ions, including Cr^{III}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, and Mg^{II}. Similar to the procedure for the formation of **poly(Cu-1)**, separately prepared solution mixtures of compound **1** and TEA were exposed to deoxygenated DMF solutions of CrCl₃, MnCl₂, FeCl₃, CoCl₂, NiCl₂, ZnCl₂, Cd(NO₃)₂·4H₂O, or MgCl₂. All mixtures yielded spontaneous precipitation of the desired **poly(M-1)** products as dark brown solids except for the polymer derived from Fe^{III} [**poly(Fe-1)**], which was red brown.

The catalytic activities of **poly(M-1)** were also examined through the asymmetric epoxidation of 2,2-dimethyl-2*H*-chromene with 2-(*tert*-butylsulfonyl)iodosylbenzene as the oxidant. As shown in Table 2, all **poly(M-1)** compounds catalyzed this epoxidation but to varying extents. Polymers assembled with Cr^{III}, Mn^{II}, Cd^{II}, and Mg^{II} nodes gave the highest yields ($> 70\%$; Table 2, entries 1–4) followed by those with Co^{II} and Zn^{II} (Table 2, entries 5 and 6). While enantioselectivities for **poly(Cr-1)**, **poly(Cd-1)**, **poly(Mg-1)**, and **poly(Zn-1)** were the same as that of **poly(Cu-1)** (76% *ee*), **poly(Mn-1)** and **poly(Co-1)** gave slightly lower *ee* values (60 and 52%, respectively). ICP mass spectrometric analysis for Mn was also performed for each epoxidation to estimate the extent of catalyst leaching. Similar to **poly(Cu-1)**, polymers assembled with Cr^{III}, Mn^{II}, Cd^{II}, Mg^{II}, Co^{II}, and Zn^{II} exhibited ca. 1–3% catalyst leaching during catalysis.

Polymers assembled from Fe^{III} and Ni^{II} afforded poor epoxide yields (Table 2, entries 7 and 8). These low activities are accompanied by low enantioselectivities (48% and 20% *ee*), which suggests either potential competing oxidation from the added linker ions or that the Mn-based catalytic sites of **poly(Fe-1)** and **poly(Ni-1)** are damaged or inaccessible. Notably, a large amount of manganese (19%) was

Table 2. Catalytic performance of **poly(M-1)** in the asymmetric epoxidation of 2,2-dimethyl-2H-chromene with 2-(*tert*-butylsulfonyl)iodosylbenzene.^{[a][14]}

Entry	Catalyst	Yield [%] ^[b]	ee [%] ^[c]	Manganese leaching [%] ^[d]
1	poly(Cr-1)	78	76	2.6
2	poly(Mn-1)	89	60	1.8 ^[e]
3	poly(Cd-1)	71	76	1.8
4	poly(Mg-1)	70	76	2.2
5	poly(Co-1)	49	52	2.6
6	poly(Zn-1)	66	76	2.2
7	poly(Fe-1)	22	48	19
8	poly(Ni-1)	31	20	0.5

[a] Molar ratio olefin/oxidant/catalyst = 100:150:1. [b] GC yield after 2 h with undecane as an internal standard. [c] Determined by using a Supelco β -DEX 120 chiral GC column. [d] Measured by ICP mass spectrometry. [e] Combined amount of Mn leached from complex **1** and the catechol complex.

found to leach from **poly(Fe-1)**, conceivably as a result of the displacement of Mn^{III} by Fe^{III} . A color change from dark brown to red brown [the color of (salen) Fe^{III} complexes, which are known to give lower *ee* than (salen) Mn^{III} in epoxidation]^[15] during polymerization also supports this argument. Interestingly, **poly(Ni-1)** exhibited substantially less Mn leaching than the other polymers, suggesting that its Mn-based catalytic sites are not as readily accessible, which in turn may explain its low activity and selectivity.

Conclusion

We have demonstrated that heterogeneous asymmetric catalysts can be formed by the coordination polymerization of chiral [bis(catechol)salen] Mn^{III} catalysts and any of several di- or trivalent metal ions. These catalysts show catalytic activity comparable to their homogeneous counterpart, complex **1**, when used for epoxidation and exhibit great potential as recyclable catalysts. This polymerization approach provides a facile and efficient strategy for support-free heterogenization of molecular catalysts.

Experimental Section

Materials and Methods: Please see Supporting Information.

Preparation of poly(M-1): In a 20-mL vial equipped with a magnetic stir bar were combined **1** (30 mg, 4.1×10^{-2} mmol), TEA (19.0 mg, 0.16 mmol), and degassed DMF (10 mL) under a nitrogen atmosphere. In another vial was prepared a DMF solution of corresponding metal salts (0.10 M). To the DMF solution of **1** was added the salt solution in appropriate amount ($[\textbf{1}]/[\text{salts}] = 1:1$ for dicationic salts or $[\textbf{1}]/[\text{salts}] = 3:2$ for tricationic salts) over 10 min with vigorous stirring. Precipitates formed instantaneously, and the resulting slurry was left to stir for an additional 2 h under a nitrogen atmosphere. The solids were collected by filtration in air, washed with DMF (3×10 mL), and dried under vacuum overnight. The samples were stored under N_2 prior to being used.

General Procedure for the Asymmetric Epoxidation of 2,2-Dimethyl-2H-chromene: To a 2-mL conical vial were added 2,2-dimethyl-2H-chromene (17.6 mg, 1.1×10^{-4} mol), undecane (9.8 mg), and dichloromethane (1 mL). Catalyst (1.1×10^{-6} mol) was next placed in the vial along with a micro magnetic stir bar. The oxidant, 2-(*tert*-butylsulfonyl)iodosylbenzene (18.7 mg, 5.5×10^{-5} mol), was then added as a solid to the mixture to start the reaction. The same quantity of oxidant was added twice more at 20-min intervals (total amount added = 1.7×10^{-4} mol). Aliquots (40 μL) of the reaction mixture were taken, filtered through a silica gel plug (120 mg), and washed with CH_2Cl_2 (5 mL). The combined filtrate was analyzed by GC and chiral GC for yield and enantioselectivity, respectively.

General Procedure for Recycling of poly(Cu-1): After being used for the catalytic reaction, the mixture was centrifuged on a Hermle Z230MA centrifuge at 12,000 rpm for 1 min. The supernatant solution was decanted for analysis by GC. The remaining solid was washed with acetone (3×1 mL) followed by dichloromethane (3×1 mL) before being dried in air for 0.5 h prior to being reused.

General Procedure for the Asymmetric Epoxidation of 2,2-Dimethyl-2H-chromene under High-Oxidant Conditions: To a 3.7-mL screw-threaded vial (15 mm \times 45 mm) were added a dichloromethane solution of 2,2-dimethyl-2H-chromene (2.25 mmol, 2 mL, 5.5×10^{-3} mol) and undecane (100 mg) as an internal standard. The catalyst (1.1×10^{-6} mol) was next placed in the vial along with a micro magnetic stir bar. The oxidant, 2-(*tert*-butylsulfonyl)iodosylbenzene (136 mg, 4.0×10^{-4} mol), was then added as a solid to the reaction mixture to start it. The same quantity of oxidant was added 10 more times at 10 min intervals (total amount added = 4.4×10^{-3} mol). Aliquots (20 μL) of the reaction mixture were taken periodically over 3 h, filtered through a silica gel plug (60 mg), and washed with CH_2Cl_2 (5 mL). The combined filtrate was analyzed by GC and chiral GC for yield and enantioselectivity, respectively.

Supporting Information (see footnote on the first page of this article): Synthetic procedures and characterization data for **1** and **2**; ESI-MS, FTIR, TGA, and BET isotherm data for **poly(Cu-1)**; ICP mass spectroscopic analysis of **poly(M-1)**; and procedure for catalyst dissolution.

Acknowledgments

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