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Fe(Cu)-Containing Coordination Polymers: Syntheses, Crystal Structures, and Applications as Benzyl Alcohol Oxidation Catalysts

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In this paper three coordination polymers, $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (**1**), $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$ (**2**), and $\{[Cu(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (**3**) {fcz = 1-(2,4-difluorophenyl)-1,1-bis[(1*H*-1,2,4-triazol-l-yl)methyl]ethanol}, were synthesized. Crystallographic analysis reveals that polymer **1** exhibits a 2-D rhombohedral grid structure with (4, 4) nets, while polymer **2** has a 1-D double-chain framework. The structure of polymer **3** is similar to that of **1**. We found that polymers **1**–**3** could effectively catalyze the oxidation of benzyl alcohol to benzaldehyde with H_2O_2 (30 mass-%) as oxidant in aqueous medium. Various reaction conditions were studied, and optimal reaction conditions were obtained. Under the optimal conditions, the selectivity to benzaldehyde was almost up to 100 % and the conversion of benzyl alcohol was 87 % for **1**, 79 % for **2**, and 68 % for **3**. The results of the recycling test showed that the catalytic activity decreased by only about 7 % after three consecutive reaction cycles. However, under similar conditions, when we used the corresponding metal salt instead of the polymer as catalyst, or replaced the water with acetonitrile as solvent, neither the selectivity nor the conversion was the same.

Introduction

In the past decade, the investigation of coordination polymers has been intensified because of their promising perspectives toward the development of new functional materials with various structural features and properties for applications in such areas as magnetic and optical materials, gas storage, molecular recognition devices, and so on.[1–6] However, little attention has been paid to their catalytic activities.[7–9] In principle, coordination polymers would be expected to be one of the new candidates for catalysts.[10–12] First, the success of metal complexes in catalysis is largely dependent on their structures and electronic properties.[13–15] Coordination polymers offer a variety of molecular structures and electronic properties that can be obtained by changing the metal ions, ligands, anions, coordination modes, etc. For example, the d orbitals of some transition metals may interact with organic π electrons to provide a localized electronic system within a polymer.[16–19] This diversity should give one an opportunity to tune the electronic properties of the molecules, and hence to tune the catalytic activity. On the other hand, the high stability and large number of active metal centers of coordination polymers are advantageous for practical applications as catalysts.[20] Meanwhile, the structures of the catalysts should be characterized in order to fine-tune both catalytic activity and selectivity; however, the structures of the traditional heterogeneous catalysts are usually not very clear.

Benzaldehyde is a very important raw material and intermediate which is used in the perfumery, pharmaceutical, dyestuff, and agrochemical industry, and the market demands have been steadily increasing over the last years.[21–22] The selective oxidation of benzyl alcohol to benzaldehyde is one of the most fundamental reactions both for laboratory-scale experiments and in the manufacturing processes. Up to now, catalytic vapor-phase oxidation of benzyl alcohol to benzaldehyde has been widely investigated.[23–25] The few studies on the liquid-phase oxidation of benzyl alcohol mainly focus on expensive metals, such as Ru, Pd, or Pd–Ag,[26–27] heteropolyacids[28] and some Cu, Fe, and Mn complexes.[29–34] In addition, the traditional reactions are often performed in environmentally undesirable solvents.[35–36]

On the basis of the above considerations, we synthesized three coordination polymers, $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (**1**), $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$ (**2**), and $\{[Cu(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (**3**) {fcz = 1-(2,4-difluorophenyl)-1,1-bis[(1*H*-1,2,4-triazol-l-yl)methyl]ethanol}, Scheme 1], and characterized their structures as well as their catalytic activities in the oxidation of benzyl alcohol with H_2O_2 as oxidant in aqueous medium. The results show that the selectivity to benzaldehyde was almost 100% for the three polymers, and the conversion of benzyl alcohol was 87% for **1**, 79% for **2**, and 68% for **3**. When we used the corresponding metal salts as catalysts, or acetonitrile as solvent, neither the selectivity nor the conversion was the same.

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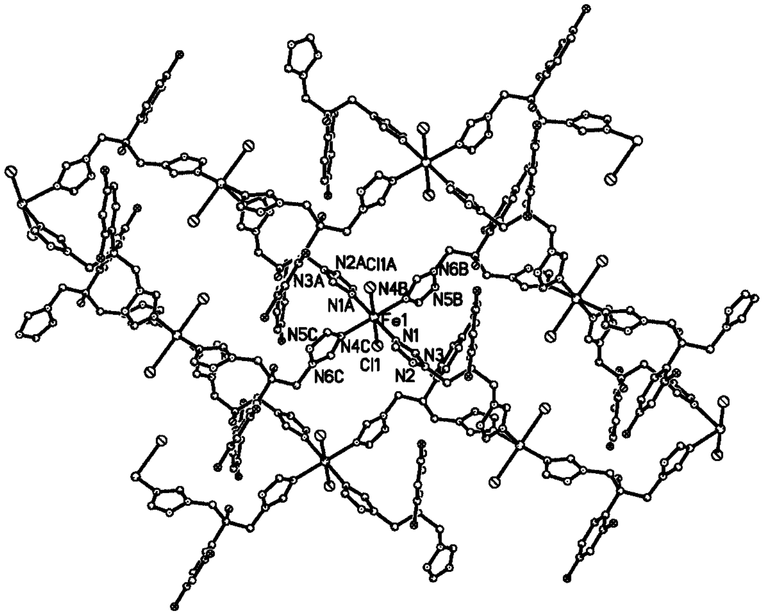
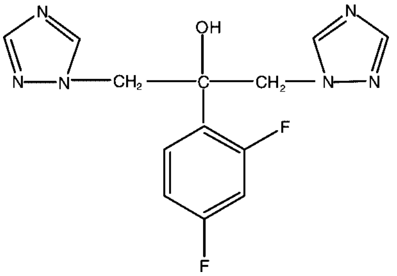


Figure 1. The two-dimensional rhombohedral grid structure of polymer **1**. Hydrogen atoms and solvent molecules have been omitted for clarity.



Scheme 1.

Results and Discussion

Crystal Structure of Polymer $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (1)

Coordination polymer **1** crystallizes in the monoclinic space group *C*2/*c* and exhibits a 2-D rhombohedral grid network structure with (4, 4) nets. Each Fe^{II} ion is located at the center of an elongated octahedron. Two chlorine anions occupy the axial positions. Four nitrogen atoms from four fcz ligands occupy the equatorial positions (Figure 1). The axial Fe–Cl bond lengths [2.560(2) Å] are substantially longer than the equatorial Fe–N bond lengths (average: 2.174 Å). The bond angles around the Fe^{II} ion are 180° (Cl1A–Fe1–Cl1, N4B–Fe1–N4C, N1A–Fe1–N1) or close to 90° (N1A–Fe1–Cl1A, N1A–Fe1–N4B, Cl1A–Fe1–N4C, etc.).

In the structure, all fcz ligands are equivalent. Every fcz ligand binds with two Fe^{II} ions leading to a rhombohedral grid unit. Each grid consists of a 40-membered ring, $Fe_4(fcz)_4$, the four Fe^{II} ions serving as four nodes and the four fcz groups acting as four sides. The rhombohedral grids have the dimensions 11.210 Å × 11.210 Å, the diagonal distances 9.430 Å × 20.337 Å, and the interior angles 49.8° and 130.2°. Two methanol molecules occupy the cavity of the (4, 4) network. Moreover, the solid-state structure of polymer **1** exhibits the layered packing mode.

Crystal Structure of Polymer $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$ (2)

Crystallographic analysis reveals that polymer **2** crystallizes in the monoclinic space group $P2_1/n$ and exhibits a 1-D polymeric double-chain structure as shown in Figure 2. Each Cu^{II} ion is at the center of a distorted tetragonal pyramid. Four nitrogen atoms from four fcz ligands occupy the basal sites, and one oxygen atom from a terminally coordinated water molecule fills the apical position. The Cu–O bond length of 2.365(4) Å is longer than the average Cu–N bond length (2.032 Å). The bond angles around the Cu^{II} ion deviate from 180° or 90° (172.6 –177.1° or 86.9–96.8°), which differs from the structure of **1**.

In contrast to polymer **1**, in polymer **2** there are two kinds of fcz ligands, fcz1 and fcz2. In fcz1, the dihedral angle between two triazole rings is 107.0°, and the dihedral angle between the triazole ring and the phenyl ring is 59.1° or 48.9°. In fcz2, the corresponding dihedral angles are 112.2° and 56.1° or 56.3°, respectively. The dihedral angle between the two benzyl rings from two different fcz ligands is 6.8°. These ligands twist to meet the requirement of steric exclusion. The torsion angles are 179.2(3) Å for N3A–C3A–C4A–C11A and 177.4(3) Å for C3A–C4A–C11A–N4A in fcz1, and 163.0(3) Å for N9A–C16A–C17A–C24A and –177.6(3) Å for C16A–C17A–C24A–N10A in fcz2.

The twisted fcz ligands link two Cu^{II} ions, resulting in a bimetallic ring as building block in which the Cu···Cu distance is 10.958 Å. The bimetallic rings are extended

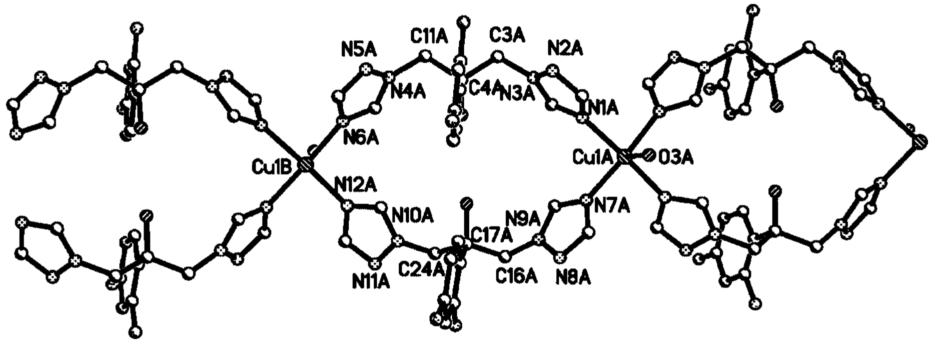


Figure 2. The double-chain structure of polymer **2** (cation part). Hydrogen atoms and solvent molecules have been omitted for clarity.

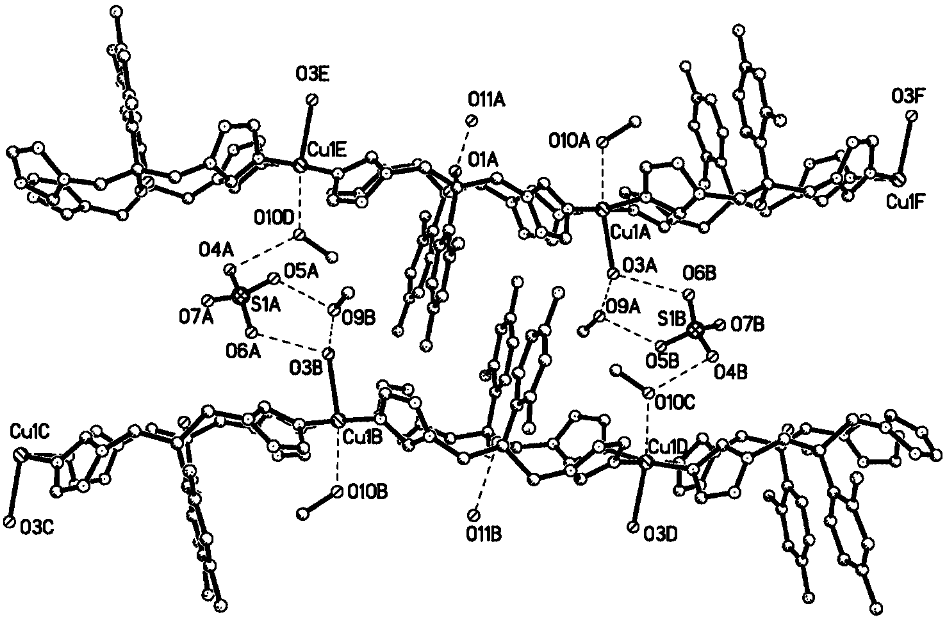


Figure 3. The crystal-packing diagram of polymer **2** with hydrogen bonds.

through co-Cu^{II} to generate an infinite double chain. These chains are further connected through intermolecular hydrogen bonds and π–π stacking interactions of the phenyl rings, as shown in Figure 3. The sulfate anions and solvent molecules are located at the vacancy among the 1-D chains and hold the cationic chains together to generate a layered architecture. In this architecture, the shortest Cu···Cu distance between adjacent chains is 9.242 Å

The structure of polymer **3**[37] is similar to that of **1**. However, the average Cu–N bond length (2.032 Å) in **3** is shorter than that of Fe–N in **1**, and the Cu–Cl bond lengths [2.793(4) Å] are longer than those of Fe–Cl because of the Jahn–Teller effect.

Catalytic Activities of the Polymers

To evaluate the catalytic properties of coordination polymers **1**–**3**, we selected the oxidation of benzyl alcohol as a probe reaction. The crystal polymers (1 mg/FW of **1** = $1.25\cdot10^{-3}$ mmol, 1 mg/FW of **2** = $2.08\cdot10^{-3}$ mmol, and 1 mg/FW of **3** = $1.23\cdot10^{-3}$ mmol[20]) were ground well into appropriate sizes. The effects of various reaction conditions such as temperature and amount of catalyst and oxidant H_2O_2 were investigated in detail by fixing the amount of benzyl alcohol at 4.6 mmol in 10 mL aqueous medium.

Figure 4 shows the effect of temperature on the oxidation with polymer **1**. It can be seen that the conversion of benzyl alcohol increases with increasing temperature. Especially when the temperature was raised from 30 to 40 °C, there was a significant increase in the conversion. At higher temperatures, rapid decomposition of hydrogen peroxide may take place and selectivity to benzaldehyde will decline, which are undesirable. Therefore, the optimal reaction temperature is 40 °C.

Figure 5 shows the effect of the amount of polymer **1**. When 0.005 mmol polymer **1** was employed in the reaction system, about 48% conversion of benzyl alcohol was achieved in 4 h. However, when the catalyst amount was increased to 0.01 mmol, the conversion was greatly improved and reached about 51% in 1 h and 87% in 4 h. A steady state of the catalytic reaction was observed after 4 h. Further increase in the amount of catalyst could not im-

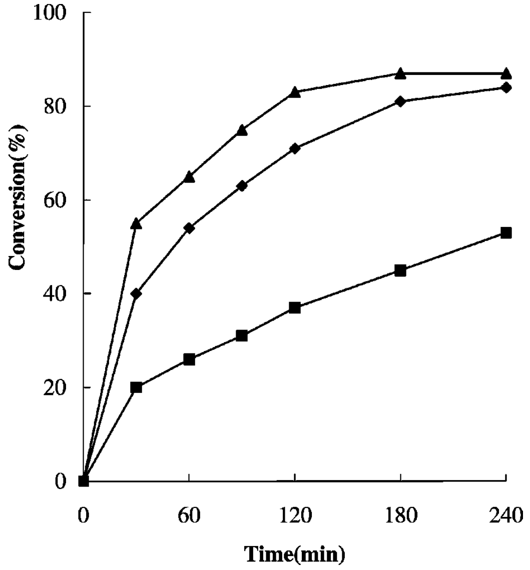


Figure 4. Effect of reaction temperature on conversion with polymer **1**: (■) 30 °C, (♦) 40 °C, (▲) 50 °C with fixed amounts of benzyl alcohol (4.6 mmol), H_2O_2 (6.0 mmol), and catalyst (0.01 mmol).

prove the conversion of benzyl alcohol significantly. The trend for polymer **2** or **3** as a catalyst was similar to that for **1**.

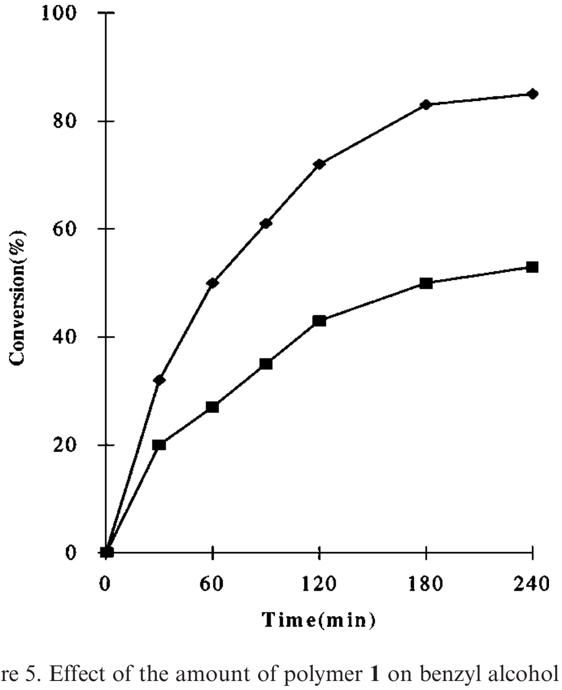


Figure 5. Effect of the amount of polymer **1** on benzyl alcohol oxidation: (■) 0.005 mmol, (♦) 0.01 mmol, with fixed amounts of benzyl alcohol (4.6 mmol) and H_2O_2 (6.0 mmol) at 40 °C in aqueous medium.

Moreover, the effect of the amount of oxidant was studied by using different concentrations of H_2O_2, viz. 4.6, 6.0, and 6.9 mmol (the molar ratio of H_2O_2 to benzyl alcohol was 1:1, 1:1.3, and 1:1.5). When the amount of H_2O_2 was increased from 4.6 to 6.9 mmol, the conversion of benzyl alcohol increased. Although excess H_2O_2 can increase the conversion, we chose 6.0 mmol H_2O_2 as the oxidant in order to avoid the formation of byproducts. In addition, the solvent was also taken into consideration for the oxidation of benzyl alcohol. The selectivity and conversion are better in aqueous medium than in acetonitrile, as shown in Table 1. The results are consistent with those in the literature,[38] in which benzyl alcohol was used as the substrate for the oxidation in a triphase using water with about sevenfold increase in conversion as compared with that obtained in a biphase using acetonitrile as solvent with titanium silicate catalyst.

Table 1. Results of oxidation of benzyl alcohol to benzaldehyde.[a]

Catalysts	Solvent	Conversion (%)	Selectivity (%)
Polymer **1**	H_2O	87^a	100
		85^b	100
		81^c	100
	CH_3CN	38	62
Polymer **2**	H_2O	79^a	100
		77^b	100
		73^c	100
	CH_3CN	29	56
Polymer **3**	H_2O	68^a	100
		66^b	100
		63^c	100
	CH_3CN	36	59
$FeCl_2{\cdot}4H_2O$	H_2O	32	85
$CuCl_2{\cdot}2H_2O$	H_2O	34	82
$CuSO_4{\cdot}5H_2O$	H_2O	35	84

[a] The superscripts "a, b, c" show the results of recycling from the first (fresh), to the second, and third runs, respectively.

Finally, the recycling of the catalysts was investigated. The organic phase was separated when the oxidation of benzyl alcohol was over. The aqueous phase and catalysts were reused for the subsequent oxidation reaction. The conversion of benzyl alcohol decreased by only about 7% after three consecutive cycles (Table 1). In order to prove that the Fe(Cu)-containing coordination polymers were heterogeneous catalysts, we filtered the catalysts and allowed the filtered catalysts and the filtrate to catalyze other benzyl alcohol oxidations. About 80–85% of the original conversion was achieved by using the filtered catalyst, while the filtrate showed only 10–15% conversion under similar conditions. This result suggests that the dominant reactive species is the heterogeneous catalyst.

Figure 6 presents the conversions of benzyl alcohol using polymers **1**–**3** as catalysts under optimized conditions. Obviously, polymer **2** exhibits the best catalytic activity in the first 2 h. However, the catalytic activity of polymer **1** improves later and surpasses that of polymer **2**. All relevant data, i.e. the conversion of benzyl alcohol and the selectivity to benzaldehyde, are collected in Table 1. We can find that the catalytic activities of these polymers are better than those of the corresponding salts. For example, the selectivity of polymer **1** to benzaldehyde was almost 100%, while the selectivity with $FeCl_2$ reached only 85%. This may be explained by the stabilizing effect of the fcz ligands. On the other hand, free metal ions resulted in rapid decomposition of hydrogen peroxide, and poor selectivity was observed. Also, it can be seen that the conversion of benzyl alcohol using Fe-containing polymer **1** as catalyst is higher than those using Cu-containing polymers, and the Cu-containing polymers **2** and **3** exhibit different catalytic activities, which can be ascribed to the difference in the coordination environment of their Cu^{II} centers. The results suggest that both the central metals and the structures of the polymers have great influence on their catalytic activities.

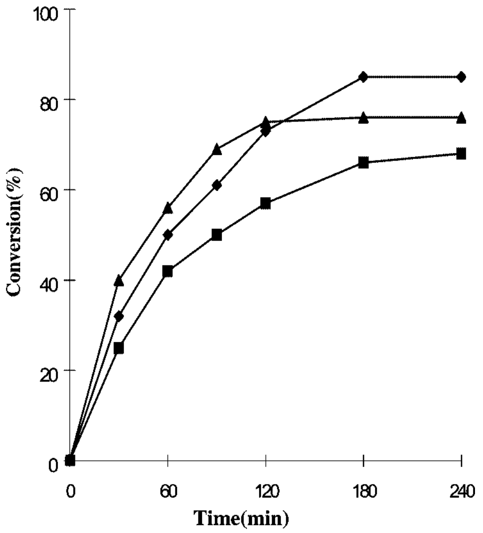


Figure 6. Dependence of the conversion of benzyl alcohol on the reaction time with different polymers: (♦) polymer **1**, (▲) polymer **2**, (■) polymer **3**, under the optimized conditions with fixed amounts of benzyl alcohol (4.6 mmol), H_2O_2 (6.0 mmol), and catalyst (0.01 mmol) at 40 °C in aqueous medium.

Conclusions

The present study shows that polymers **1**–**3** are potential catalysts for the oxidation of benzyl alcohol to benzaldehyde. In addition, central metals and structures of the polymers have great influence on their catalytic activities.

Experimental Section

Materials and General Details: Fcz was supplied by Zhongshuai Pharmaceutical Sci. & Tech. Development Co. Ltd., Henan Province, China. All the solvents and chemicals were used without further purification. IR spectroscopy was performed with a PE 1710 spectrophotometer in the 400–4000-cm^{-1} region. Carbon, hydrogen, and nitrogen analysis were performed with a Carlo–Erba 1106 elemental analyzer.

Synthesis of Polymer $\{[Fe(fcz)_2Cl_2]\cdot 2CH_3OH\}_n$ (1): A methanol solution of fcz (0.2 mmol, 6 mL) was added dropwise into an aqueous solution of $FeCl_2\cdot 4H_2O$ (0.1 mmol, 1 mL) to give a clear solution. The resulting solution was allowed to stand at room temperature for two weeks. Yellow crystals formed; yield 56 mg (ca. 70 %). The crystals are insoluble in water and most organic solvents. $C_{28}H_{32}Cl_2F_4FeN_{12}O_4$ (803.41): calcd. C 41.84, H 3.98, N 20.92; found C 41.72, H 4.07, N 20.76. IR (KBr): $\tilde{\nu}$ = 3446 (s), 1619 (s), 1502 (s), 1277 (s), 1129 (s), 967 (m), 677 (m) cm^{-1}.

Synthesis of Polymer $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$ (2): A mixture of methanol and DMF solution of fcz (0.2 mmol, 6 mL) was slowly added into an aqueous solution of $CuSO_4\cdot 5H_2O$ (0.1 mmol, 1 mL) to give a clear solution. The resulting solution was allowed to stand at room temperature for two weeks. Blue crystals formed; yield 30 mg (ca. 60 %). The crystals are insoluble in water and most organic solvents. $C_{31}H_{45}CuF_4N_{13}O_{12}S$ (963.40): calcd. C 38.61, H 4.67, N 18.89; found C 38.52, H 4.67, N 18.76. IR (KBr): $\tilde{\nu}$ = 3445 (s), 3131 (s), 1620 (s), 1500 (m), 1279 (m), 1130 (s), 675 (m) cm^{-1}.

Table 2. Crystal data and structure refinement for polymers **1** and **2**.

	1	2
Empirical formula	$C_{28}H_{32}Cl_2F_4FeN_{12}O_4$	$C_{15.5}H_{22.5}Cu_{0.5}F_2N_{6.5}O_6S_{0.5}$
Formula weight	803.41	481.70
Temperature [K]	291(2)	291(2)
Radiation	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*P*2$_1$/*n*
Crystal dimensions [mm^3]	0.20 × 0.18 × 0.18	0.20 × 0.18 × 0.18
a [Å]	23.423(5)	12.006(2)
b [Å]	9.4356(19)	18.014(4)
c [Å]	20.826(4)	18.953(4)
α [°]	90	90
β [°]	125.66(3)	93.81(3)
γ [°]	90	90
V [$Å^3$]	3739.8(13)	4092.2(14)
Z	4	8
F(000)	1648	1996
ρ [$g\,cm^{-3}$]	1.427	1.564
μ [mm^{-1}]	0.616	0.679
Data/restrains/parameters	2375/0/235	7548/0/599
Goodness-of-fit on F^2	0.966	1.047
$R_1 = [I > 2\sigma(I)]$	0.0792	0.0553
wR_2 (all data)	0.2008	0.1292

Synthesis of Polymer {[Cu(fcz)$_2$Cl$_2$]·2CH$_3$OH}$_n$ (3): Polymer **3** was synthesized according to the literature[37] as blue crystals; yield 50 mg (ca. 60%). The crystals are insoluble in water and most organic solvents. $C_{28}H_{32}CuCl_2F_4N_{12}O_4$ (811.10): C 41.43, H 3.95, N 20.72; found C 41.49, H 3.90, N 20.74. IR (KBr): $\tilde{\nu}$ = 3448 (s), 1619 (s), 1501 (s), 1278 (s), 992 (m), 673 (m) cm^{-1}.

Crystal-Structure Determination: Crystallographic data for the polymers **1** and **2** were collected with a Rigaku R-AXIS-IV image plate area detector with graphite-monochromatized Mo-K_α X-radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects and for absorption by using empirical scan data. All calculations were performed using the SHELXL-97 crystallographic software package,[39] and refined by full-matrix least-squares methods based on F^2 with isotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically. Processing parameters and the crystal data for polymers **1** and **2** are summarized in Table 2, and selected bond lengths and bond angles are listed in Table 3.

Table 3. Selected bond lengths [Å] and angles [°] for polymers **1** and **2**.[a]

Polymer **1**			
Fe(1)–N(1)	2.162(6)	Fe(1)–N(4)#2	2.185(7)
Fe(1)–Cl(1)	2.560(2)	N(1)–Fe(1)–N(1)#1	180.0(3)
N(4)#2–Fe(1)–N(4)#3	180.000(1)	N(1)–Fe(1)–N(4)#2	90.7(2)
N(1)#1–Fe(1)–N(4)#2	89.3(2)	N(1)–Fe(1)–Cl(1)	90.61(17)
N(1)#1–Fe(1)–Cl(1)	89.39(17)	N(4)#2–Fe(1)–Cl(1)	90.32(18)
N(4)#3–Fe(1)–Cl(1)	89.68(18)	Cl(1)–Fe(1)–Cl(1)#1	180.00(9)
Polymer **2**			
Cu(1)–N(7)	2.022(3)	Cu(1)–N(12)#1	2.031(3)
Cu(1)–N(6)#1	2.032(3)	Cu(1)–N(1)	2.043(3)
Cu(1)–O(3)	2.365(4)	N(7)–Cu(1)–N(12)#1	86.94(12)
N(7)–Cu(1)–N(6)#1	172.64(13)	N(12)#1–Cu(1)–N(6)#1	95.53(12)
N(7)–Cu(1)–N(1)	90.19(12)	N(12)#1–Cu(1)–N(1)	177.12(12)
N(6)#1–Cu(1)–N(1)	87.34(12)	N(7)–Cu(1)–O(3)	96.81(15)
N(12)#1–Cu(1)–O(3)	90.60(13)	N(6)#1–Cu(1)–O(3)	90.11(14)
N(1)–Cu(1)–O(3)	89.58(13)		

[a] Symmetry transformations used to generate equivalent atoms: Polymer **1** # $1 - x, -y + 2, -z$; #2 $-x - 1/2, -y + 3/2, z - 1/2$; #3 $-x + 1/2, y + 1/2, -z + 1/2$; Polymer **2** #1 $x + 1/2, -y + 3/2, z + 1/2$.

CCDC-262170 and -262172, for polymers **1** and **2**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Catalytic Experiments: Catalytic experiments were carried out in a 50-mL, three-necked, round-bottom reaction flask fitted with a water condenser. One neck of the flask was equipped with a mercury thermometer for measuring the reaction temperature. The crystal polymer catalysts were ground well into appropriate sizes to increase the surface area, but not too small for a convenient filtration. Benzyl alcohol and water were mixed in the reactor with a magnetic stirrer and heated to a given temperature. Then, hydrogen peroxide (concentration determined by iodometric titration before use) was added to the reaction system. Samples of 0.2 mL were removed every 30 min and diluted (1:10) with CH_3OH to be analyzed by HPLC (HP 1100 high-pressure liquid chromatogram analyzer). A reversed-phase Eclipse × DB-C8 (4.6 × 150 mm) column was used at ambient temperature, and a methanol/water mixture (70:30 vol-%, 0.5 mL·min^{-1}) was used as the eluent. The UV detector was employed at 253 nm. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. Commercial products were used for all chromatographic standardizations.

Acknowledgments

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