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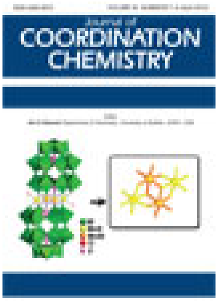

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Structures and catalytic application of carboxylate-supported copper complexes in green oxidative coupling

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Structures and catalytic application of carboxylate-supported copper complexes in green oxidative coupling

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Two new Cu(II) complexes with carboxylate ligand, $[Cu(qc)_2(H_2O)_2]\cdot(H_2O)$ (**1**) and $[Cu(qc)(bipy)(H_2O)]\cdot(H_2O)(ClO_4)$ (**2**) (Hqc = 3-hydroxy-2-quinoxalinecarboxylic acid, bipy = 2,2′-bipyridine), have been synthesized and characterized. As heterogeneous catalysts, the complexes show high catalytic activity in green oxidative polymerization of 2,6-dimethylphenol (DMP) to poly(1,4-phenylene ether) (PPE) in the presence of H_2O_2 as oxidant in water under mild conditions. Both allow reuse without significant loss of activity through four runs, which suggests that these catalysts are efficient, mild, and easily recyclable for oxidative coupling of DMP. Preliminary catalytic–structural correlations suggest that the coordination environment of the metal center have important influences on their catalytic efficiencies.

Keywords: Copper(II) complexes; Oxidative coupling; Heterogeneous catalyst; Green chemistry

1. Introduction

Copper complexes attract interest in many fields such as molecular magnetism [1], metalloproteins, and enzymes [2]. In catalysis, the unique characteristic of the Cu^{II}/Cu^{I} redox couple renders many of their complexes suited for various catalysis reactions [3], especially for green catalysis since copper is a cheap and less toxic metal.

Aerobic oxidation catalyzed by copper complexes is particularly fascinating because oxygen is an abundant and ecologically benign oxidant [4, 5]. As an important example, copper-catalyzed oxidative polymerization of 2,6-dimethylphenol (DMP) produces poly(1,4-phenylene ether) (PPE) by C–O coupling, an important engineering plastic with excellent mechanical properties and chemical resistance, and an undesirable byproduct resulting from C–C coupling, i.e., diphenoquinone (DPQ) [6–12]. However, the mechanism for the C–O/C–C coupling selectivity in DMP polymerization has not been entirely elucidated [13, 14]. Both a solvent-recovery process and an antiexplosive reactor are required for industrial production since the polymerization usually proceeds in an organic solvent under an oxygen atmosphere. For green chemistry, the use of water as a reaction medium is environmentally friendly and PPE can be easily separated

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from water due to its insolubility in water [15, 16]. Saito *et al.* [17] recently reported the oxidative coupling of DMP to form PPE with potassium ferricyanide as an oxidant in an aqueous medium. Unfortunately, the use of potassium ferricyanide is still environmentally deleterious. Green oxidative coupling of DMP in environmentally-friendly solvents with clean oxidants is extremely rare. Therefore, this reaction is still a great challenge for "green chemistry and technology." Development of efficient copper-containing catalysts for milder "green" conditions and the investigation of catalytic–structural correlations have great importance to exploiting new catalysts. For the purpose of replacing the traditional organic-medium systems by environmentally friendly processes, we prepared two new copper carboxylate adducts containing quinoxaline, $[Cu(qc)_2(H_2O)_2]\cdot(H_2O)$ (**1**) and $[Cu(qc)(bipy)(H_2O)]\cdot(H_2O)(ClO_4)$ (**2**) (Hqc = 3-hydroxy-2-quinoxalinecarboxylic acid, bipy = 2,2′-bipyridine), and explored their application as catalysts for an aqueous-medium process of oxidative coupling of DMP using hydrogen peroxide as oxidant under mild conditions.

2. Experimental

2.1. *General information and materials*

All solvents and chemicals (analytical grade) were used without purification. 3-Hydroxy-2-quinoxalinecarboxylic acid (Hqc), 2,2′-bipyridine (bipy), and 2,6-dimethylphenol (DMP) (99% pure) were used as obtained from J&K Chemical Ltd. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. Infrared (IR) spectra were recorded from 4000 to 400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. X-ray powder diffraction patterns (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, using a Cu-target tube and a graphite monochromator. Intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 80° with a step size of 0.02° and a scan speed of $8^\circ\ min^{-1}$.

2.2. *Synthesis of $[Cu(qc)_2(H_2O)_2]\cdot(H_2O)$ (1)*

A 5 mL aqueous solution of Hqc (19.0 mg, 0.1 mmol) was added into 5 mL methanol solution of $Cu(ClO_4)_2\cdot6H_2O$ (37.5 mg, 0.1 mmol) and then filtered to give a dark blue solution. Slow evaporation of the solvent at room temperature gave yellow needle single-crystals suitable for X-ray single-crystal analysis after *ca* 2 weeks. Yield: ~40% (based on Cu). Anal. Calcd for $C_{18}H_{18}CuN_4O_{10}$ (%): C, 42.07; H, 3.53; N, 10.90. Found (%): C, 42.02; H, 3.50; N, 10.89; IR (KBr)/cm^{-1}: 3349(m), 1688(s), 1607(s), 1467(m), 1377(m), 1276(m), 1224(m), 1158(m), 1024(w), 920(w), 885(w), 775(m), 678(w), 475(w).

2.3. *Synthesis of $[Cu(qc)(bipy)(H_2O)]\cdot(H_2O)(ClO_4)$ (2)*

The procedure was similar to that of **1**, except that bipy was added dropwise to the above mixture. The resulting dark blue solution was allowed to stand at room temperature. After a few days, green block-shaped crystals of **2** were obtained. The solid was collected by filtration and dried *in vacuo*. The sample is stable in air. Yield: 45%.

Anal. Calcd for $C_{19}H_{16}ClCuN_4O_9$ (%): C, 41.95; H, 2.94; N, 10.30. Found (%): C, 41.89; H, 2.99; N, 10.25; IR (KBr)/cm^{-1}: 3328(s), 1476(s), 1341(m), 1283(m), 1103(s), 929w, 877(w), 660(w), 622(w), 591(w), 509(w), 418(w).

2.4. *General procedure for catalytic oxidative coupling of 2,6-dimethylphenol*

All polymerizations were carried out in a 10 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 complex catalysts were ground into appropriate sizes to increase the surface area, but not too small for a convenient filtration (average particle size of 10–12 µm). DMP (122 mg, 1 mmol) was dissolved in water (5 mL). The 1.5 mol% complex was added to the solution, and the mixture was vigorously stirred under air at 50°C. Then, hydrogen peroxide (30% aqueous solution) was slowly added to the mixture using a microinjector every 15 min twice to minimize H_2O_2 decomposition. After 6 h, the reaction was stopped and the polymer product appeared as an off-white powder after salting out by the addition of sodium chloride (1.17 g, 0.02 mol). Then the mixture was transferred into a separatory funnel; the organic materials were extracted after the addition of a few milliliters of CH_2Cl_2. This was repeated thrice. The combined organic extracts were dried with anhydrous $MgSO_4$ and the solvent, after filtration, was evaporated *in vacuo*. The products were separated by preparative TLC performed on dry silica gel plates with ethyl ether : petroleum ether (1 : 3 v/v) as the developing solvents. PPE and DPQ were collected and dried *in vacuo*. We also can get the polymeric products by simple filtration after salting out, followed by reprecipitation from chloroform to methanol.

Poly(phenylene ether) (PPE): ^{1}H NMR ($CDCl_3$, TMS) $\delta = 6.44$ (s, 2 H; H_{Ar}), 2.09 ppm (s, 6 H; CH_3); ^{13}C NMR ($CDCl_3$, TMS) $\delta = 16.6$–16.8, 114.1, 114.5, 124.4, 125.0, 129.0, 131.6, 132.7, 145.6, 146.4, 151.5, 154.5, 154.8 ppm; IR (KBr): $\nu_{C\text{–}O\text{–}C} = 1186\,cm^{-1}$.

Diphenoquinone (DPQ): ^{1}H NMR ($CDCl_3$, TMS) $\delta = 8.2$ (s, 4H), 7.1 (s, 2H), 2.1 ppm (12H); ^{13}C NMR ($CDCl_3$, TMS) $\delta = 17.07$, 129.56, 135.67, 139.10, 187.21 ppm; IR (KBr): $\nu_{C=O} = 1594\,cm^{-1}$.

2.5. *X-ray structure analyses*

X-ray single-crystal diffraction measurements for **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. Determinations of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) and unit cell dimensions were obtained with least-squares refinements. SAINT [18] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS [19]. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL [20]. Copper atoms in each complex were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on $|F|^2$. Hydrogen atoms were added theoretically, riding on the atoms, and refined with fixed thermal factors. Crystal data and structure

Table 1. Crystal data and structure refinement for $[Cu(qc)_2(H_2O)_2] \cdot (H_2O)$ (**1**) and $[Cu(qc)(bipy)(H_2O)] \cdot (H_2O)(ClO_4)$ (**2**).

	1	**2**
Empirical formula	$C_{18}H_{18}CuN_4O_{10}$	$C_{19}H_{16}ClCuN_4O_9$
Formula weight	513.90	543.35
Temperature (K)	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å,°)		
a	7.2610(4)	9.7544(5)
b	7.7534(6)	10.6367(6)
c	9.5266(7)	11.6266(6)
α	72.429(7)	114.050(5)
β	82.633(5)	95.221(4)
γ	72.083(6)	103.845(5)
Volume (Å^3), Z	486.13(6), 1	1045.13(10), 2
Absorption coefficient (Mo-Kα) (cm^{-1})	1.193	1.236
Number of reflections collected [$I > 2\delta(I)$]	2864	6748
Number of independent reflections	1812	3890
Final R^a, $R_w{}^b$	0.0322, 0.0654	0.0371, 0.0840

[a] $R = \sum F_o - F_c / \sum F_o$.
[b] $R_w = [\sum (F_o - F_c)^2 / \sum_w F_o^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

1					
Cu1–O1	1.9012(15)	Cu1–O1	1.9012(15)	Cu1–N1	2.1776(17)
Cu1–N1	2.1776(17)	Cu1–O4	2.3097(17)	Cu1–O4	2.3097(17)
O1–Cu1–O1A	180.00(5)	O1A–Cu1–N1	100.65(7)	O1–Cu1–N1	79.35(7)
O1A–Cu1–N1A	79.35(7)	O1–Cu1–N1A	100.65(7)	N1–Cu1–N1	180.00(9)
O1–Cu1–O4	92.50(6)	O1A–Cu1–O4	87.50(6)	N1–Cu1–O4	88.16(6)
N1A–Cu1–O4	91.84(6)	O1–Cu1–O4A	87.50(6)	O1A–Cu1–O4A	92.50(6)
N1–Cu1–O4A	91.84(6)	N1A–Cu1–O4A	88.16(6)	O4–Cu1–O4A	180.00(7)
2					
Cu1–O2	1.9165(18)	Cu1–O1	1.9201(18)	Cu1–N3	1.985(2)
Cu1–N4	1.995(2)	Cu1–O4	2.3150(18)		
O2–Cu1–O1	92.78(7)	O2–Cu1–N3	94.32(8)	O1–Cu1–N3	170.91(8)
O2–Cu1–N4	167.60(8)	O1–Cu1–N4	90.95(8)	N3–Cu1–N4	80.95(9)
O2–Cu1–O4	94.45(7)	O1–Cu1–O4	89.95(8)	N3–Cu1–O4	95.14(8)
N4–Cu1–O4	97.38(7)				

refinement of **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of $[Cu(qc)_2(H_2O)_2] \cdot (H_2O)$ (1)*

Crystallographic analysis reveals that **1** crystallizes in the triclinic space group $P\bar{1}$. As illustrated in figure 1, Cu(II), being located at an inversion center, is six-coordinate by two nitrogen atoms (N1, N1A) and two carboxylate oxygen atoms (O1, O1A) from two

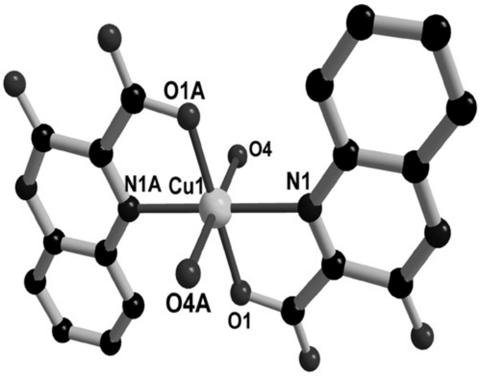


Figure 1. The coordination environment of Cu(II) of **1**. Hydrogen atoms are omitted for clarity.

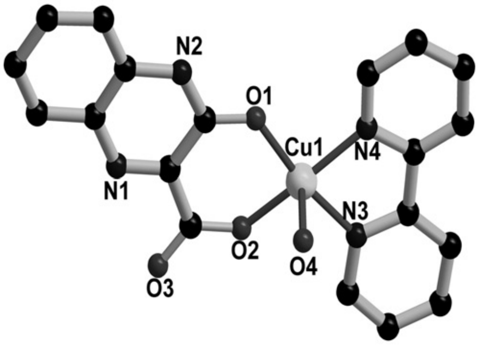
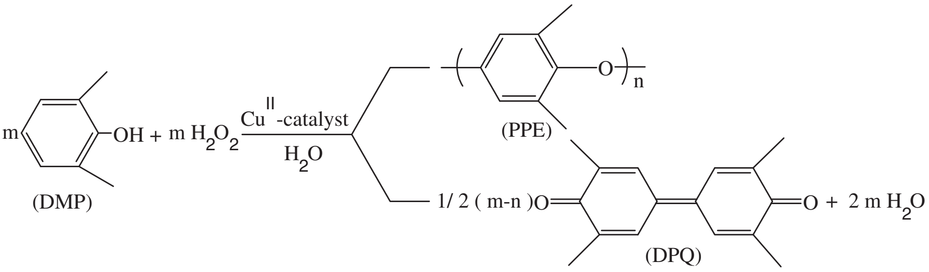


Figure 2. The coordination environment of Cu(II) of **2**. Hydrogen atoms are omitted for clarity.

qc^- ligands and two oxygen atoms (O4, O4A) from two water molecules in a nearly ideal octahedron with N1, N1A, O1, O1A composing the basal plane and O4, O4A holding axial positions. The bond angles around Cu(II) vary from 79.35(7)° to 180.00(12)°. The Cu–N bond lengths are 2.1776(17) Å and the Cu–O bond lengths are 1.9012(15)–2.3097(17) Å, which are comparable to those observed for $\{[Cu(btp)(HBTC)_2]_3 \cdot 0.5H_2O\}_n$ and $[Cu(btmb)(HBTC)]_n$ (btp = 1,3-bis(1,2,4-triazol-1-yl)propane, btmb = 4,4′-bis(1,2,4-triazol-1-ylmethyl)biphenyl, and H_3BTC = 1,3,5-benzenetricarboxylic acid) [21]. Each deprotonated qc^- serves as a two-connected node to coordinate with Cu(II) through its carboxylate and nitrogen of quinoxaline. In the solid structure of **1**, the mononuclear units are linked through hydrogen bonds formed by water molecule and carboxylate oxygen atoms of Hqc, generating a 3-D network.

3.2. *Crystal structure of [Cu(qc)(bipy)(H₂O)]•(H₂O)(ClO₄) (2)*

Different from **1**, each Cu(II) in **2** displays a slightly distorted square pyramidal coordination geometry comprised by two N donors from bpy and three O donors from one hydroxide O1 and one carboxylate O2 from qc^- as well as one coordinated water O4 (figure 2). Two nitrogen atoms and two oxygen atoms (O1, O2) together with the



Scheme 1. Oxidative polymerization of 2,6-dimethylphenol (DMP) in water.

central Cu(II) form the equatorial plane (the mean deviation from plane of 0.0685 Å) and O4 occupies the axial position. Unlike the Cu–N distances, the Cu–O distances here are disparate due to Jahn–Teller distortion of Cu^{II}. The axial Cu1–O4 distance (2.3150(18) Å) is much longer than the basal distances (1.9165(18)–1.9201(18) Å), which are normal compared to other Cu(II) systems [22]. Bond angles around Cu(II) vary from 80.95(9)° to 170.91(8)°.

3.3. *Catalytic oxidative coupling of DMP in water*

The overall oxidative coupling process of DMP under green reaction conditions is shown in scheme 1. Initially, **1** was selected as a catalyst model for optimization of the reaction conditions. The influences of various factors such as reaction temperature, reaction time, the amounts of catalyst, and oxidant as well as the pH of solution have been investigated.

Previous investigations have indicated that oxidative coupling of DMP in organic solvents proceeds at room temperature and higher temperatures result in more by-products (DPQ). However, in aqueous media, higher temperature is necessary because the reaction does not proceed at room temperature. Figure 3 presents the effect of reaction temperatures on polymerization with **1**, showing a significant temperature effect on the reaction. The DMP conversion increases from 66% to 88% as the temperature increases from 40°C to 70°C, and the best selectivity to PPE of 81.5% is achieved at 55°C.

In order to study the effect of time on the polymerization, product analysis was done at regular intervals of time under similar reaction conditions. DMP conversion increases quickly from about 68% to near 90% as the time changes from 4 h to 8 h (figure 4), while the selectivity to PPE increases very slowly. Further prolonging reaction time does not improve the conversion significantly but decreases the selectivity slightly. The reason for this may be that the by-product DPQ degrades the polymer upon further processing at high temperatures [23]. In addition, we find that the selectivity of PPE is not correlated for the DMP conversion, which is close to the former conclusion, since Viersen *et al.* [24] have shown that most DPQ is formed during the beginning of the reaction.

Figure 5 illustrates the effect of the amount of **1** on polymerization. The control reaction performed without any catalyst shows that the copper complex is indispensable for the reaction system. The conversion increases with increasing amount of **1**, but

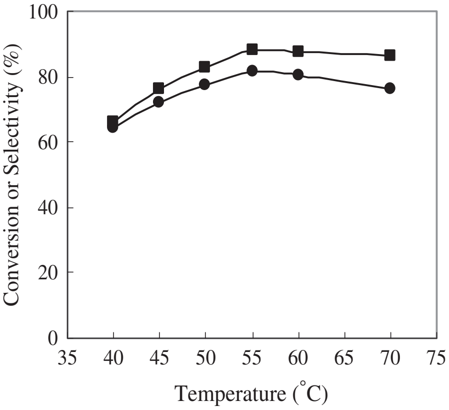


Figure 3. Effect of reaction temperature on polymerization with **1**: (■) conversion; (•) selectivity.

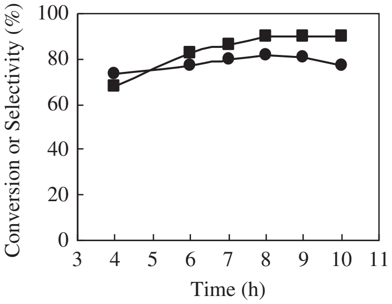


Figure 4. Effect of reaction time on polymerization with **1**: (■) conversion; (•) selectivity.

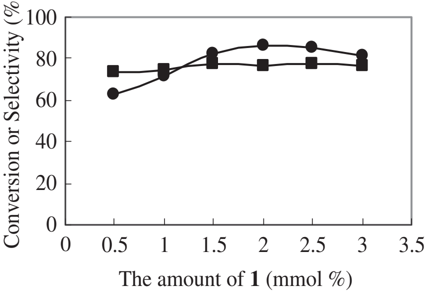


Figure 5. Effect of the amount of **1** on the polymerization: (■) conversion; (•) selectivity.

decreases for the larger amount. The maximum conversion is obtained at 0.02 mmol of **1**. However, the selectivity to PPE is stable as the concentration of catalyst increases. The decrease in activity at high catalyst concentrations could arise from competitive formation of catalytically inactive copper species. The resultant loss in catalyst

Table 3. Effect of pH on the polymerization with **1**.[a]

pH	Conversion (%)[b]	PPE (%)[b]	DPQ (%)[b]	Selectivity[c]
6.0	69	62	14	81.8
6.5	78	68	17	79.2
7.0	83	71	21	77.5
7.5	91	75	23	76.5
8.0	88	76	22	77.6
8.5	83	77	20	79.4
9.0	76	76	16	81.5

[a] Standard conditions.
[b] Conversions and isolated yields based on the DMP. All isolated products were identified by ^{1}H, ^{13}C NMR, and IR spectroscopic analyses.
[c] Selectivity = ([PPE] × 100)/([PPE] + [DPQ]).

concentration would affect the parallel reactions that produce PPE and DPQ equally, and this is consistent with the insensitivity of selectivity to catalyst concentration. The influence of the loading of oxidant is studied by using different volumes of H_2O_2 from 0 to 0.03 mL (30 vol.%). The result indicates that the addition of appropriate amount of H_2O_2 (0.02 mL) is also necessary for obtaining high conversion and selectivity. At higher amounts of H_2O_2, the substrates almost convert completely but selectivity descends correspondingly. Similar results have been found in our previous investigations [25].

The pH of solution affects the yields and distribution of products [26]. The effect of pH on the DMP polymerization is investigated in Tris-HNO_3 buffer solution from pH 6.0–9.0 by maintaining other reaction parameters. As illustrated in table 3, for the catalytic system with **1**, DMP conversion first increases and then decreases with increasing pH; maximum is at pH 7.5. The yield of PPE increases with increasing pH and remains constant above pH 7.5; pH of the solution exhibits great effect on the selectivity of PPE. The selectivity of PPE is less than 78% in a neutral aqueous solution, but about 82% in weakly acidic (pH 6.0) and weakly alkaline (pH 8.5–9.0) solutions. Because of the high conversion of DMP, good yield of PPE and the low loss of H_2O_2 in neutral aqueous solution, optimal pH is around 7.0 in practice. The pH effect on product distribution is not entirely clear. Literature reported that alkaline condition favored the formation of PPE, while acidic solution led to C–C coupling [27]. However, in this work both weakly acidic ($pH < 6.5$) and alkaline aqueous solutions ($pH > 8$) are suitable to C–O coupling in our catalytic system. On the basis of the above experimental results and previous literature [28], the phenoxy radical associated with metal complex, generated in the reaction process, is the main active species. It is possible that the pH of solution affects the state of metal complex associated with phenoxy radical, consequently influencing the association of the copper complex with phenoxy radical and induction to *p*-C atom.

With the optimized reaction conditions in hand, we then evaluated catalytic efficiencies of **1** and **2** for comparison. As shown in table 4, **1** has slightly poorer catalytic activity than **2**, namely, conversions of 93% for **1** and 97% for **2**. The dissimilarity is probably attributable to differences in coordination environments of Cu(II) centers, which have a dramatic impact on the coordination of DMP to Cu(II) to promote this oxidative coupling reaction. The lower coordination number around

Table 4. Results of the oxidative coupling of DMP with different catalysts performed under optimized conditions.[a]

Catalysts	Conversion (%)[b]	Yield (%)[b] PPE	Yield (%)[b] DPQ	Selectivity (%)[c]
1	93	75	11	87.2
2	97	92	6	93.9
$Cu(ClO_4)_2 + Hqc$	68	22	14	61.1
$Cu(ClO_4)_2 + Hqc + bipy$	69	29	16	64.4
$Cu(ClO_4)_2$	25	9	21	30.0
Hqc	0	0	0	0

[a] Optimized conditions: DMP (1 mmol), H_2O_2 (0.02 mL), and catalyst (0.02 mmol) in 5 mL of water for 8 h at 50°C.

[b] Conversions and isolated yields based on the DMP, average of two runs.

[c] Selectivity = ([PPE] × 100)/([PPE] + [DPQ]).

Cu(II) in **2** may facilitate the coordination of substrate, further enhancing the catalytic efficiency. Consistent with our observation, Kol and co-workers [29] observed that structural effects on reactivity were pronounced in zirconium complexes for lactide polymerization. Comparing with Cu(II)–poly(*N*-vinylimidazole), Cu(II)–polyamidoamine catalysts giving about 95% PPE [30], the best result for copper-catalyzed synthesis of PPE in an aqueous medium so far, **2** has an obvious advantage in the oxidative polymerization with a PPE yield of 92%. The contrasting reaction using $Cu(ClO_4)_2$ as catalyst only gives trace amounts of PPE. Complexes **1** and **2** have obvious comparative advantage over the $Cu(ClO_4)_2$/Hqc and $Cu(ClO_4)_2$/Hqc/bipy catalysts under similar reaction conditions. A potential explanation for this may be inferred from the stabilizing effects [25, 31] of the organic ligand and the steric influence of the copper center. In **1** and **2**, the bidentate Hqc improves the aqueous stabilities of these complexes and also forms the open coordination geometry with less steric hindrance around the copper center which favors the coordination of DMP to Cu(II) to form the proposed active copper species [32] and the subsequent polymerization of DMP. Reedijk and co-workers [4b] have also shown that a series of Cu^{II} complexes incorporating structurally related N,O-containing ligands underwent this polymerization more efficiently than copper(II) salts.

The potential benefits of the heterogeneous catalyst include the facilitation of catalyst separation from reagents and reaction products, and simplification of methods for catalyst recycle [33]. For a truly effective heterogeneous catalyst, therefore, it is critical that recovery be simple and efficient, and that the recovered catalyst could retain its original reactivity through multiple cycles. As **2** shows higher catalytic activity, we test for its recovery and reuse. After the reaction was complete, the catalyst was recovered by filtration for consecutive runs. The recovered catalyst is used for a new reaction batch of DMP. The conversion of DMP decreases by only 7–8% after four consecutive cycles. We carried out another control reaction, because in the catalytic process the leached metal species might catalyze efficiently the oxidative coupling reaction instead of the heterogeneous catalysts [34]. To examine this possibility, we filtered catalyst **1** after the oxidative polymerization and allowed the filtered catalyst and the filtrate to react with another aliquot of DMP, respectively, as shown in the previous study [34]. The filtered catalyst is subjected to the second run by charging with new reagents and then the products are again formed with about 86–91% of the original conversion. The filtrate obtained from the first filtration is also used in a new reaction with the addition of substrate. Only 7–10% conversion of DMP is observed under similar conditions. This result strongly suggests that the dominant reactive species is the heterogeneous catalyst **2**, not species such as leached metal. However, about 7–10% conversion by the filtrate indicate that the trace amount of Cu ions might be leached during the catalysis. Powder X-ray diffraction (XRD) pattern of the filtered catalyst after the reaction revealed the same pattern as the original catalyst, suggesting that the original structure of the filtered catalyst has been retained during the reaction. Based on these results, we concluded that the heterogeneous catalyst **2** could be recycled multiple times without significant loss of activity.

4. Conclusions

We have prepared and characterized two new carboxylate-supported copper complexes. Moreover, we found that the two complexes could carry out heterogeneous catalytic oxidative polymerization of DMP in water under mild conditions. These catalyst systems constitute a promising class of environmentally-friendly heterogeneous catalysts that allow reuse without significant loss of activity through four runs and appear to be an efficient, mild, and easily recyclable method for oxidative coupling of DMP.

Supplementary material

CCDC 840030 and 840031 contain the supplementary crystallographic data for **1** and **2**, respectively. 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 associated with this article can be found in the online version at doi:10.1016/j.ica.2011.04.008.

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