

Catalytic applications of Cu^{II}-containing MOFs based on N-heterocyclic ligand in the oxidative coupling of 2,6-dimethylphenol

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Abstract

Two Cu^{II} complexes bearing a N-heterocyclic ligand, namely [Cu(SO₄)(pbbm)]_n (**1**) and {[Cu(Ac)₂(pbbm)]·CH₃OH}_n (**2**) (pbbm = 1,1'-(1,5-pentanediy)bis-1*H*-benzimidazole) have been synthesized with the aim of exploiting new and potent catalysts. Single crystal X-ray diffraction shows that new polymeric complex **1** features 1-D double-chain framework. The catalytic studies on **1** and **2** indicate that they are efficient homogeneous catalysts for the oxidative coupling of 2,6-dimethylphenol (DMP) to poly(1,4-phenylene ether) (PPE) and diphenoquinone (DPQ) with H₂O₂ as oxidant and NaOMe as co-catalyst at room temperature. Optimal reaction conditions are obtained by examining the effects of solvent, the reaction time, temperature as well as the amounts of co-catalyst, catalyst and oxidant. Under the optimal conditions, the selectivity to PPE is almost up to 90% for both complexes, and the conversion of DMP is 85% for **1** and 90% for **2**, comparable to those observed for highly active catalyst systems in the literature. Further comparison of their catalytic performances with those of the corresponding copper salt together with organic ligand, copper salt alone and free ligand reveals that the coordination of ligand to Cu^{II} ion plays a key role in generating the superior reactivities of complexes.

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Keywords: Cu^{II} complexes; Phenol oxidative coupling; Homogeneous catalyst

1. Introduction

Since the pioneering work of Hay and co-workers [1], oxidative polymerization of 2,6-dimethylphenol (DMP) to poly(1,4-phenylene ether) (PPE) has received extremely intensive interest because PPE is a valuable engineering thermoplastic with many industrial applications involving computer and television housings, keyboard frames, automotive parts, interface boxes, etc. (Scheme 1) [2–4]. Up to now, considerable effort has been dedicated to improve the performance and selectivity of the reaction and elucidate its mechanism. For example, several Cu-containing enzymes and some Cu, Co and Mn complexes have been utilized as homogeneous catalysts for this oxidation [5–8].

Also, diverse approaches have been adopted to obtain mechanistic details of the reaction. These include kinetic studies using various kinds of ligands, *ab initio* calculations, and studying the influence on the catalytic activity by changing the proportions of the various components (Cu, ligand, base, water, substrate) [3,4,9–11]. Despite the huge amount of impressive work published, it should be mentioned that even today this catalytic polymerization reaction is still a research field of great challenge. There seem to be the following two crucial reasons for this. Firstly, the reaction mechanism has not yet been well clarified. Secondly, this oxidative polymerization mediated by most of previously reported catalysts suffers from elevated temperatures or long reaction times, or requires high catalyst amounts. Even so, the fascinating conversion of DMP and selectivity toward PPE can not be obtained simultaneously. Therefore, the development of more effective cat-

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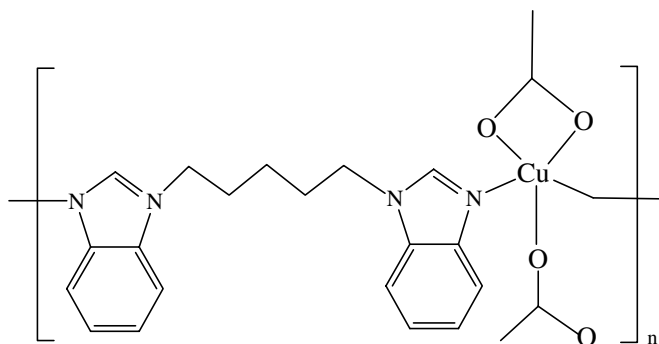


Chart 1.

time, temperature as well as the amounts of co-catalyst, catalyst and oxidant have been investigated in detail by fixing the amount of DMP at 1 mmol (122 mg) in 5 mL reaction medium.

Previous investigations have indicated non-polar solvent as the most suitable reaction medium for the polymerization of DMP [4–6]. However, in our cases, the presence of methanol is necessary for the catalyst solubilization. A series of methanol-mixed solvents (1:1 v/v) are thus screened for this oxidation. Table 1 shows the effect of mixed solvents on the polymerization with **1**. Reaction in methanol–toluene mixed solvent provides the result in terms of the conversion of DMP and the selectivity to PPE obviously superior to those obtained in reactions conducted in other mixed solvents. Moreover, the activity and selectivity increase with the decrease in polarity of the solvent in the sequence of acetonitrile > dioxane > dichloromethane > toluene, which are in good agreement with the above literatures [4–6]. On the basis of a recently mechanistic proposal for the copper-catalyzed oxidative phenol coupling reaction (Scheme 2) [10,37], it is presumed that the decrease in polarity of the solvent should facilitate the production of phenoxonium cation intermediate, leading to the increase in conversion. Fig. 2 illustrates the effect of different ratios of methanol-to-toluene on the polymerization with **1**. It is evident that the conversion has the maximum at the volume fraction of about 60% MeOH, while the selectivity remains unchanged at approximately 80% over the entire ratio range of methanol-to-toluene. Therefore,

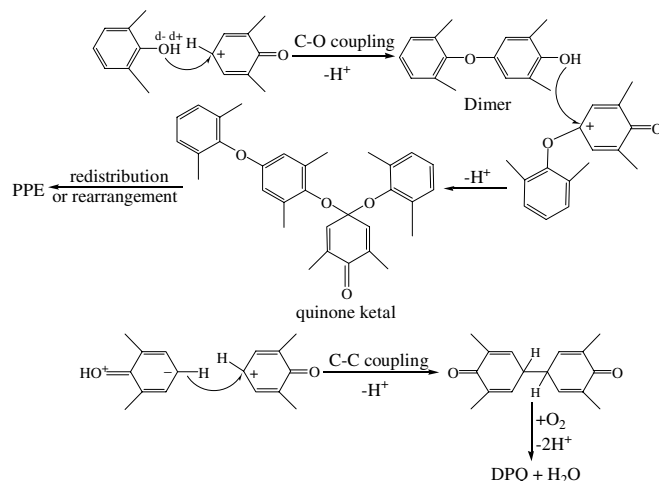
Table 1
Effect of various methanol-mixed solvents (1:1 v/v) on the polymerization with **1**^a

Solvent	Conversion (%) ^b	PPE (%) ^b	DPQ (%) ^b	Selectivity ^c
Toluene	72	55	14	79.7
Dichloromethane	65	45	18	71.4
Dioxane	47	23	20	53.5
Acetonitrile	39	15	20	42.9

^a Standard conditions.

^b Conversions and isolated yields based on the DMP. All isolated products were identified by ¹H, ¹³C NMR and IR spectroscopic analyses.

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



Scheme 2. Mechanistic pathways proposed for the oxidative coupling of DMP.

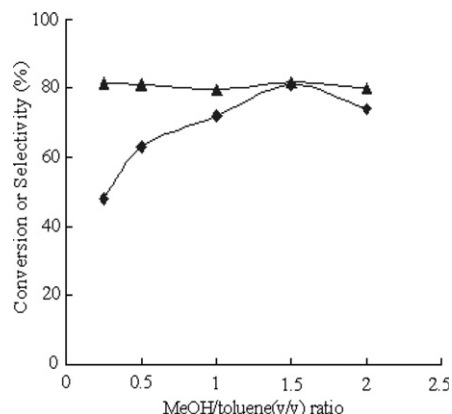


Fig. 2. Effect of various methanol-to-toluene ratios on the polymerization with **1** (standard conditions): (◆) conversion; (▲) selectivity.

the optimal mixed solvent is the 1.5:1 (v/v) methanol–toluene mixture.

The addition of base to the reaction solvent causes the important effect on the DMP polymerization. It has been demonstrated that the oxidation reaction of DMP did not proceed in the presence of Cu^{II} catalyst alone, but was promoted significantly by adding base such as NaOMe in the reaction mixture [32]. The added base was found to have the role of generating the corresponding phenolate anion by dissociating the DMP molecule, which was critical in the whole catalytic process [38]. This finding can be expanded for our system. The effect of NaOMe is thus surveyed by maintaining other reaction parameters. Fig. 3 presents the effect of various NaOMe-to-catalyst ratios on the polymerization with **1**. It is apparent that the continuously improved conversion and selectivity are obtained in the region of the lower amounts of base, and at the higher amounts of base, the selectivity reaches saturation whereas the conversion descends. The trend for **2** as a catalyst is similar to that for **1**, as shown in Fig. 4. The favorable

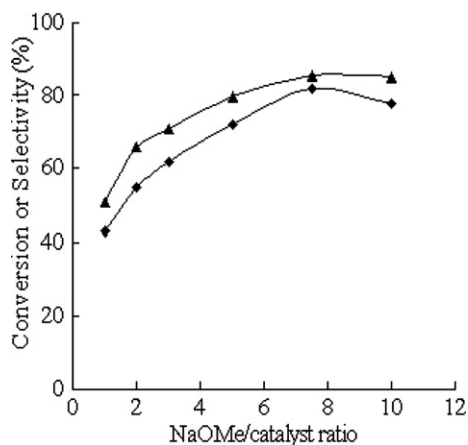


Fig. 3. Effect of various NaOMe-to-catalyst ratios on the polymerization with **1** (standard conditions): (◆) conversion; (▲) selectivity.

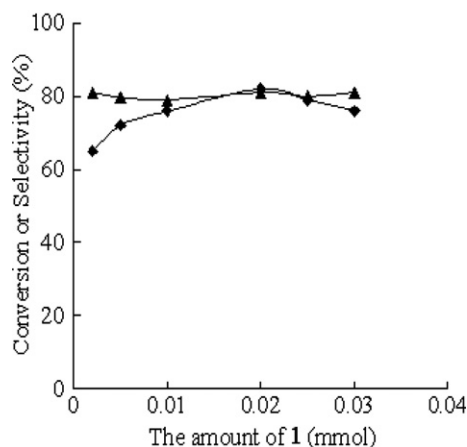


Fig. 5. Effect of the amount of **1** on the polymerization (standard conditions): (◆) conversion; (▲) selectivity.

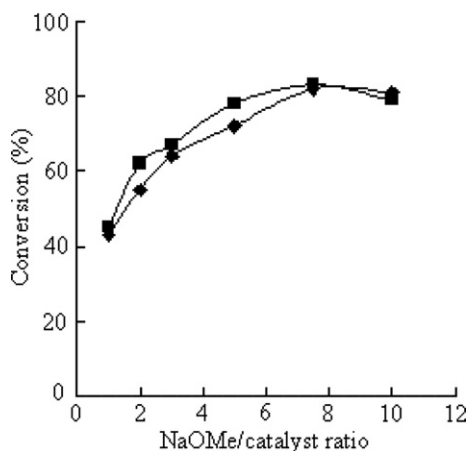


Fig. 4. Effect of various NaOMe-to-catalyst ratios on the conversion with **1** and **2** (standard conditions): (◆) **1**; (■) **2**.

effect on the conversion reaches the maximum of 83% at a 7.3 NaOMe-to-catalyst ratio for **1** and 85% at a 7.1 ratio for **2**. The aforementioned data, taken together with the previous finding of the probably partial decomposition of complex with an excess of basicity [9], allow a 7 ratio of NaOMe-to-catalyst for optimization. Similarly, Camus et al. also obtained an optimum activity using a 7 KOH-to-Cu^{II} ratio [8].

Fig. 5 depicts the effect of the amount of **1** on the polymerization. The conversion increases with the increased amounts of **1**, but decreases for the larger amounts. The maximum conversion is obtained at a 0.02 mmol amount of **1**. However, the selectivity to PPE remains constant at 80% as the concentration of catalyst increases. Busch and co-workers also reported the similar observations in the O₂ oxidation of 2,6-di-*tert*-butylphenol and 3,5-di-*tert*-butylphenol by {[*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminato]cobalt(II)} in supercritical carbon dioxide medium [39]. The decrease in activity at high catalyst concentrations could arise from competitive for-

mation of catalytically inactive copper species. The resultant loss in catalyst concentration would affect the parallel reactions that produce PPE and DPQ equally, and this is consistent with the insensitivity of selectivity to catalyst concentration.

Fig. 6 illustrates the effect of the reaction time on the polymerization with **1**, showing that the conversion and selectivity increase gradually as the reaction time prolongs. A steady state of the catalytic reaction is observed after 3 h. Further increase in the reaction time can not improve the conversion and selectivity significantly. On the other hand, the effect of the amount of oxidant is studied by using different volumes of H₂O₂, viz. 0.02, 0.05, 0.1 and 0.2 ml (30 vol.%). The results indicate that a larger H₂O₂ concentration induces an increase of conversion, but a marked decline in selectivity. So, we choose 0.05 ml H₂O₂ for the reaction in order to minimize the formation of byproduct DPQ. In addition, temperature is also taken into account for this polymerization. A slight increase of temperature favors the C–C coupling process. Also, the decomposition

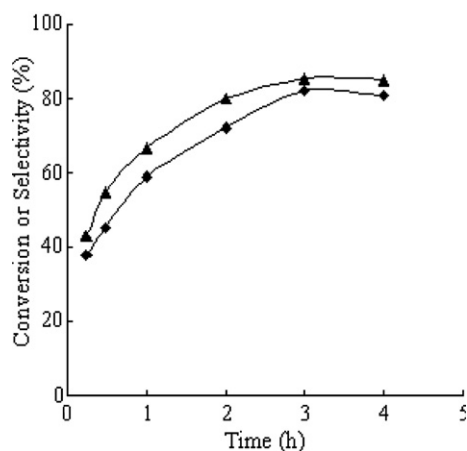


Fig. 6. Effect of the reaction time on the polymerization with **1** (standard conditions): (◆) conversion; (▲) selectivity.

of hydrogen peroxide may take place. Both account for the decline in selectivity, which is undesirable.

With the optimized reaction conditions in hand, we then evaluate catalytic efficiencies of the title complexes for comparison. As can be seen in Table 2, polymer **2** showing 1-D wave-like linear chain structure assumes the slightly superior catalytic activity to **1** exhibiting 1-D double-chain structure, viz., the conversions of 90% and 85% for **2** and **1**, respectively. The dissimilarity is probably attributable to the differences in counteranions and the structures of complexes, which have a dramatic impact on the coordination of DMP to Cu^{II} to form the proposed active copper species [3,40]. Concretely, the less steric hindrance around Cu^{II} center in polymer **2** may ease more DMP molecules binding to Cu^{II} centers to promote this oxidative coupling reaction, and the higher conversion is observed. In addition, both complexes perform identically the good selectivity of almost 90%, which is comparable to that found for enzymes such as laccase and tyrosinase [41,42]. As a result, further structure modification for Cu-containing MOFs could be obtained through objective molecular design and synthesis, and then enhance the catalytic properties for desired applications.

Furthermore, to ascertain the origin of the favorable catalytic properties of complexes, we also assess catalytic capabilities of the corresponding copper salt together with organic pbm ligand in a 1:1 molar ratio, copper salt alone

Table 2
Results of the oxidative coupling of DMP with different catalysts performed under the optimized conditions^a

Catalyst	Conversion (%) ^b	PPE (%) ^b	DPQ (%) ^b	Selectivity (%) ^c
1	85	70	8.8	88.8
2	90	75.3	9.3	89
CuSO ₄ + pbm	36	21	12	63.6
Cu(Ac) ₂ + pbm	39	25	13.4	65.1
CuSO ₄	15	10	13.2	43.1
Cu(Ac) ₂	35	18	14.5	55.4
pbm	0	0	0	0

^a Optimized conditions: DMP (1 mmol), NaOMe (0.14 mmol), H₂O₂ (0.05 ml) and catalyst (0.02 mmol) in a 1.5:1 MeOH/toluene mixture for 3 h under the ambient temperature.

^b Conversions and isolated yields based on the DMP. All isolated products were identified by ¹H, ¹³C NMR and IR spectroscopic analyses.

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

Table 3
Comparison with the representative catalysts carried out under their own optimized reaction conditions for the oxidative coupling of DMP

Catalyst	Solvent	T (°C)	Time (h)	Substrate/catalyst ratio	Conversion (%)	Selectivity (%)	Reference
Co(SMDTP)	Toluene	25	24	384	100	43	[36]
[Cu ₂ (OH) ₂ (hexpy)] · (CF ₃ SO ₃) ₂	CH ₂ Cl ₂ /MeCN	25	5	50	91	50.6	[33]
[Cu(tmeda)] · Cl ₂	H ₂ O	50	6	10	69	99.7	[32]
MnO ₂	H ₂ O	50	6	10	25	100	[32]
K ₃ [Fe(CN) ₆]	H ₂ O	25	6	0.5	99	23.7	[32]
Ru(OH) _x /Al ₂ O ₃	H ₂ O	90	48	20	98	0	[32]
[Cu ^I ₂ (MeCN) ₂ (L)] · (ClO ₄) ₂	CH ₂ Cl ₂ /MeCN	25	6	10	96	27.1	[34]
[Cu(SO ₄)(pbm)] _n (1)	CH ₃ OH/toluene	25	3	50	85	88	This work
{[Cu(Ac) ₂ (pbm)] · CH ₃ OH} _n (2)	CH ₃ OH/toluene	25	3	50	90	89	This work

and free pbm ligand under the similar reaction conditions (Table 2). We find that the activity and selectivity obtained with the complex are better than those observed using the corresponding copper salt and organic ligand together, and far superior to those obtained by the use of copper salt alone, and free pbm ligand is even completely inactive, e.g., CuSO₄ records the low conversion of DMP of only 15% with the selectivity of 43% to PPE, and CuSO₄ together with pbm provides the conversion of 36% with the selectivity of 63.6%, while the high conversion of up to 85% is obtained with the selectivity of up to 90% by the use of complex **1**. The advantageous catalytic capability of copper salt together with ligand over that of copper salt itself suggests the weak and incompact interactions between copper salt and ligand in the reaction system. Contrastively, coordination interactions between Cu^{II} center and organic ligand are firmly established in the complex. This implies that the coordination of ligands to Cu^{II} ions leads to a distinct improvement of catalytic property of complex. That is to say, ligands may permit the possibility of optimizing catalytic property and enhance the catalytic capability of metal salt attached. Important roles of coordinating ligands are supposed to include stabilizing effects and governing activity and selectivity by electronic and steric influences. Likewise, Reedijk and co-workers have also shown that a series of Cu^{II} complexes incorporating structurally related N,O-containing ligands or dinucleating phenol-based “end-off” compartmental N,O,S-ligands underwent this polymerization more efficiently than copper(II) salts [43,44]. Consistent with our view, Hirao et al. pointed out that the bidentate or multidentate coordination of flexible N-heterocyclic ligands was considered to be a key factor for the construction of efficient oxygenation systems [45].

Table 3 lists the best experimental results of the complexes investigated and the reported highly active catalysts for this process. It is found that Co(SMDTP), [Cu₂(OH)₂(hexpy)] · (CF₃SO₃)₂ (hexpy = 1,2-bis[2-di-(2-pyridyl)methyl-6-pyridyl]ethane) and [Cu^I₂(MeCN)₂(L)] · (ClO₄)₂ (L = a,a'-bis[(N-methyl-2-pyridyl)ethylamino]-2-fluoro-*m*-xylene) give the excellent conversions of DMP of 100%, 91% and 96%, but with only moderate selectivities of 43%, 50.6% and 27.1% toward PPE in 24 h, 5 h and 6 h, respectively (entries 1, 2 and 7) [33,34,36]. In the case of [Cu(tmeda)] · Cl₂

(tmeda = *N,N,N',N'*-tetramethylethylenediamine), the conversion of 69% is attained with a selectivity of 99.7% at higher temperature (entry 3) [32]. The heterogeneous MnO₂, K₃[Fe(CN)₆] and Ru(OH)_x/Al₂O₃ catalysts also reveal either a promising activity or selectivity at higher catalyst concentration (entries 4–6) [32]. In contrast, complexes **1** and **2** allow to offer both the high conversion and selectivity with the shorter reaction times and at relatively low catalyst concentrations under mild reaction conditions (room temperature), thereby confirming their effectiveness as catalysts for this reaction (entries 8 and 9). It is well believed that these systems have significant potential for the development of a new class of potent catalysts in the future.

3. Conclusions

The present work indicates that the complexes **1** and **2** are potent catalysts for the oxidative coupling of 2,6-dimethylphenol to poly(1,4-phenylene ether) and diphenoquinone. The observed remarkable activity and selectivity can be ascribed to the incorporation of ligands, which permits the possibility of optimizing catalytic properties and enhances the catalytic capabilities of metal salts attached. Recognizing that counteranions, the structures of complexes as well as the reaction conditions may be responsible for their catalytic behaviors, it can be expected that more studies could improve the catalytic efficiencies and selectivities of Cu^{II}-containing MOFs via further structural modifications and judicious choices of reaction conditions for practical application.

4. Experimental

4.1. Materials and general details

All the solvents and chemicals (analytical grade) were used without further purification. 2,6-Dimethylphenol (DMP) (99% pure) was used as obtained from J&K Chemical Ltd. NaOMe was prepared following the literature procedure [7]. IR spectroscopy was performed with a PE 1710 spectrophotometer in the 400–4000 cm⁻¹ region. NMR spectra were recorded on a Bruker DPX-400 spectrometer.

4.2. Synthesis of [Cu(SO₄)(pbbm)]_n (**1**)

Well-shaped bluish-purple crystals (55% yield) suitable for X-ray diffraction were obtained from a mixture of pbbm (60.8 mg, 0.2 mmol), CuSO₄ · 5H₂O (49.8 mg, 0.2 mmol) and H₂O (8 ml) in a 25 ml Teflon-lined stainless steel vessel at 150 °C for 4 days. The crystals are air-stable and dissolved in CHCl₃, CH₃CN and DMF. IR (KBr)/cm⁻¹: 3111m, 2936m, 1572s, 1509w, 1391s, 1200w, 749s.

4.3. Synthesis of {[Cu(Ac)₂(pbbm)]CH₃OH}_n (**2**)

Complex **2** was synthesized according to the literature procedure [31].

4.4. X-ray crystallographic analysis

Crystallographic data for **1** was performed on a Bruker ApeX CCD diffractometer with graphite monochromatic Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz-polarization effects and for absorption by using empirical scan data. All calculations were performed using the SHELXL-97 crystallographic software package [46], 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 parameter and the crystal data for **1** are summarized in Table 4, and selected bond lengths and bond angles are listed in Table 5.

4.5. Catalytic experiments

The following is the standard procedure for the polymerization: Both crystal complex catalysts (1 mg/FW of **1** = 2.16×10^{-3} mmol, 1 mg/FW of **2** = 1.93×10^{-3} mmol) were powdered to increase the surface area prior to use. Under air, 2,6-dimethylphenol (1 mmol) was dissolved in the 1:1 (v/v, 5 ml) mixture of methanol–toluene in a 10 mL flask, and a 0.5% molar ratio of catalyst/substrate and a 5 M ratio of NaOMe/catalyst were added to above solution with a magnetic stirrer. Then, hydrogen peroxide

Table 4
Crystal data and structure refinement for [Cu(SO₄)(pbbm)]_n (**1**)

Formula	C ₁₉ H ₂₀ CuN ₄ O ₄ S
Formula weight	463.99
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.6751(13)
<i>b</i> (Å)	10.3435(13)
<i>c</i> (Å)	10.9898(14)
α (°)	89.4990(10)
β (°)	68.6450(10)
γ (°)	68.316(2)
<i>V</i> (Å ³)	941.7(2)
<i>T</i> (K)	291(2)
<i>Z</i>	2
μ (Mo K α) (cm ⁻¹)	1.636
Number of reflections collected [<i>I</i> > 2 σ (<i>I</i>)]	6855
Number of independent reflections	4098
Final <i>R</i> ^a , <i>R</i> ^w	0.0343, 0.0765

Table 5
Selected bond distances (Å) and bond angles (°) for [Cu(SO₄)(pbbm)]_n (**1**)^a

Cu(1)–N(4) 1.966(2)	Cu(1)–N(1)#1 1.988(2)
Cu(1)–O(2) 2.0123(18)	Cu(1)–O(1) 2.0012(19)
Cu(1)–O(4)#2 2.324(2)	
N(4)–Cu(1)–N(1)#1 102.49(9)	N(4)–Cu(1)–O(1) 93.00(8)
N(1)#1–Cu(1)–O(1) 160.72(9)	N(4)–Cu(1)–O(2) 158.65(9)
N(1)#1–Cu(1)–O(2) 91.04(8)	O(1)–Cu(1)–O(2) 70.97(7)
N(4)–Cu(1)–O(4)#2 98.12(9)	N(1)#1–Cu(1)–O(4)#2 84.96(9)
O(1)–Cu(1)–O(4)#2 104.34(8)	O(2)–Cu(1)–O(4)#2 99.47(8)

^a Symmetry transformations used to generate equivalent atoms: #1 $-x + 2, -y + 1, -z + 1$ #2 $-x + 1, -y + 1, -z + 2$.

(30% aqueous solution) was slowly added into the mixture using a syringe pump every 15 min 10 μ l for five times to minimize H₂O₂ decomposition. After 2 h, the sample was concentrated *in vacuo*, and the products were separated by preparative TLC performed on dry silica gel plates with acetic ether–petroleum ether (1:3 v/v) as the developing solvents. PPE and DPQ were collected and dried *in vacuo*. All reactions were run in duplicate, and the data reported represent the average of these reactions.

Poly(phenylene ether) (PPE): ¹H NMR (CDCl₃, TMS) δ = 6.44 (s, 2H; H_{Ar}), 2.09 ppm (s, 6H; CH₃); ¹³C NMR (CDCl₃, TMS) δ = 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): $\bar{\nu}_{C-O-C}$ = 1186 cm⁻¹.

Diphenoquinone (DPQ): ¹H NMR (CDCl₃, TMS) δ = 8.2 (s, 4H), 7.1 (s, 2H), 2.1 ppm (12H); ¹³C NMR (CDCl₃, TMS) δ = 17.07, 129.56, 135.67, 139.10, 187.21 ppm; IR (KBr): $\bar{\nu}_{C=O}$ = 1594 cm⁻¹.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.01.010](https://doi.org/10.1016/j.jorganchem.2007.01.010).

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