



Syntheses and structural characteristics of copper(II)-organic polymers based on N-heterocyclic ligands: A study on the importance of steric factors in the design of potent catalysts

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ABSTRACT

Two new Cu(II)-organic polymers supported by different N-heterocyclic ligands, namely $\{[\text{Cu}(\text{btx})_2]\cdot\text{Cl}_2\}_n$ **1** (btx = 1,4-bis(triazol-1-ylmethyl)-benzene) and $\{[\text{Cu}(\text{bbbm})(\text{Ac})_2]\cdot(\text{CH}_3\text{OH})_2\}_n$ **2** (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) are designed and synthesized in order to ascertain the influence of coordination polymeric structure on catalytic activity. Single-crystal X-ray diffraction shows that **1** assumes a 2D cationic rhombohedral grid network arrangement, whereas **2** features a 1D zigzag chain structural motif in which Cu atoms are bridged by μ_2 -bbbm ligands. Both of them reveal impressive catalytic capability for the selectively oxidative coupling of 2,6-di-*t*-butylphenol to the corresponding diphenoquinone in excellent yield using H_2O_2 as oxidant and KOH as co-catalyst in water and allow reuse without a significant loss of activity through three runs with the hindered phenol. Under the similar reaction conditions, the two polymers also accelerate the selectively coupling of 2,4-di-*t*-butylphenol to generate the relevant biphenol with moderate to high efficiencies. The transformation of 2,6-dimethylphenol mediated by polymers **1** and **2** proceeds smoothly with 100% and 94.5% conversion, respectively. It is found that polymer **1** offers the superior results in terms of reactivity and selectivity to **2** for such processes, indicating the crucial role of structural parameters in catalytic performance of polymers. Furthermore, the ability of **1** and **2** to undergo homogeneous oxidation couplings of these substituted phenols in 1.5:1 (v/v) methanol–toluene mixture is explored as well to demonstrate the advantages of heterogeneous catalysis.

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1. Introduction

The oxidative coupling reaction of phenol derivatives constitutes a class of broad and interesting research topic both from the biological and synthetic standpoints [1–4]. Many catalytic systems including heteropolyacids, Schiff base complexes of Co(II), Mn(II), Fe(II) and Cu(II) as well as transition metal salts of Fe, Cu, Co, Ru, Mo, etc., have been extensively employed to accomplish this transformation [5–11]. A majority of them are homogeneous systems. There are few heterogeneous catalysts despite their significant advantages of easy separation from the reaction mixture and recycling of catalysts [12]. However, the reported heterogeneous systems often require high catalyst concentrations and forced reaction conditions. Even so, the fascinating substrate conversion and product selectiv-

ity cannot be obtained simultaneously. In addition, these reaction systems are typically performed in environmentally undesirable organic solvents. Along with ever-growing environmental issues of chemical processes [13], the development of efficient and recyclable heterogeneous catalysts possessing both superior activity and selectivity that can be carried out under milder conditions in “green” reaction medium such as water is desired extraordinarily in order to provide more insight into these processes.

In the past decade, considerable effort has been focused on aspects concerning structural chemistry and material science of inorganic–organic hybrid polymers due to their potential applications in catalysis, absorption processes, photochemistry and magnetism [14–17]. In the context of catalysis, the investigation of catalytic–structural correlations aimed at understanding the structural and chemical factors that govern the activities and selectivities of these materials is of continuous interest. Although it is generally observed that hybrid materials with coordinatively unsaturated metal sites are important because they can afford competent size- or shape-selective heterogeneous catalysts for a vast

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range of chemical and biochemical processes [18], the systematic structure–reactivity relationship remains elusive. Therefore, design and synthesis of new coordinatively unsaturated inorganic–organic hybrid frameworks, especially investigation of their heterogeneous catalytic reactivity, are still meaningful. More recently, we have demonstrated that the 1D polymeric Cu(II) complex $\{[\text{Cu}(\text{Ac})_2(\text{pbbm})]\cdot\text{CH}_3\text{OH}\}_n$ (pbbm = 1,1'-(1,5-pentanediy)bis-1H-benzimidazole) was a sufficiently active homogeneous catalyst for the oxidative coupling of 2,6-dimethylphenol (DMP), while the replacement of two Ac^- anions by one SO_4^{2-} anion caused a dramatic decrease of the catalytic activity [19]. The reason might be that the coordination of SO_4^{2-} anion to copper atom increases the steric congestion around the central metal and decreases the electrophilicity of the metal, which makes the approach and binding of DMP molecules to Cu(II) centers difficult. If the steric congestion around the metal center plays an important role in the decrease of the activity of $[\text{Cu}(\text{SO}_4)(\text{pbbm})]_n$, it is to be anticipated that less crowded metal site should lead to higher catalytic efficiency in phenol derivative oxidative coupling.

To further substantiate the experimental result and extend the scope of application, we design and synthesize two new Cu(II)-organic polymers $\{[\text{Cu}(\text{btx})_2]\cdot\text{Cl}_2\}_n$ **1** (btx = 1,4-bis(triazol-1-ylmethyl)-benzene) and $\{[\text{Cu}(\text{bbbm})(\text{Ac})_2]\cdot(\text{CH}_3\text{OH})_2\}_n$ **2** (bbbm = 1,1'-(1,4-butanediyl)bis-1H-benzimidazole) containing coordinatively unsaturated Cu(II) sites and check systematically their heterogeneous reactivity for the oxidation coupling of a variety of substituted phenols. The idea behind our choice of bis-heterocyclic btx and bbbm as bridge ligands is based on their less configurational flexibility than pbbm, which benefits to produce the target complexes with relatively large voids or less steric crowding at metal center for successful catalytic behaviors. As expected, both of them can efficiently initiate the oxidation coupling of various substituted phenols, viz., 2,6-di-*tert*-butylphenol (2,6-DBP), 2,4-di-*tert*-butylphenol (2,4-DBP) and DMP in aqueous medium, and can easily be separated by the filtration and reused three times with retention of the high catalytic activity. Furthermore, the performances of the investigated polymers in the homogeneous phase as catalysts for these oxidation couplings are tested to clarify the nature of the oxidation ability.

2. Experimental

2.1. Materials and general details

All the solvents and chemicals (analytical grade) were used without further purification. 2,6-Di-*tert*-butylphenol (2,6-DBP), 2,4-di-*tert*-butylphenol (2,4-DBP) and 2,6-dimethylphenol (DMP) (99% pure) were used as obtained from J&K Chemical Ltd. NaOMe and NaOC_2H_5 were prepared following the literature procedure [20]. IR spectroscopy was performed with a PE 1710 spectrophotometer in the 400–4000 cm^{-1} region. Carbon, hydrogen and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. NMR spectra were recorded on a Bruker DPX-400 spectrometer. Scanning electron microscopy was taken on a Hitachi TM-1000 instrument.

2.2. Synthesis of polymer $\{[\text{Cu}(\text{btx})_2]\cdot\text{Cl}_2\}_n$ (**1**)

Well-shaped bluish-purple crystals (58% yield) suitable for X-ray diffraction were obtained from a mixture of btx (48.8 mg, 0.2 mmol), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (17.0 mg, 0.1 mmol) and H_2O (8 ml) in a 25 ml Teflon-lined stainless steel vessel at 140 °C for 3 days. The crystals are air-stable and dissolved in CHCl_3 , CH_3CN and DMF. Calc. (%) for $\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{CuN}_{12}$: C, 46.87; H, 3.93; N, 27.33; Found (%): C,

46.90; H, 3.91; N, 27.35. IR (KBr)/ cm^{-1} : 3092m, 1528s, 1280s, 1128s, 1011s, 775s.

2.3. Synthesis of polymer $\{[\text{Cu}(\text{bbbm})(\text{Ac})_2]\cdot(\text{CH}_3\text{OH})_2\}_n$ (**2**)

A solution of bbbm (29.0 mg, 0.1 mmol) in 5 ml MeOH was slowly added into a 2 ml MeOH solution of $\text{Cu}(\text{Ac})_2$ (20.0 mg, 0.1 mmol) resulting in the formation of a clear blue solution. Green crystals suitable for X-ray analysis were obtained after the solution was allowed to stand for several days (Yield 53%). Calc. (%) for $\text{C}_{24}\text{H}_{32}\text{CuN}_4\text{O}_6$: C, 53.77; H, 6.02; N, 10.45; Found (%): C, 53.74; H, 5.99; N, 10.48. IR (KBr)/ cm^{-1} : 3084w, 2924w, 1607m, 1596s, 1462s, 1383s, 1332s, 751s.

2.4. X-ray crystallographic analyses

Suitable single crystals with dimensions of 0.28 mm × 0.20 mm × 0.18 mm for polymer **1** and 0.24 mm × 0.20 mm × 0.20 mm for **2** were selected for single-crystal X-ray diffraction analysis. Data collection was performed on a Rigaku RAXIS-IV image plate area detector for study using graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation at 291(2)K using the ω -2 θ scan technique. The data were corrected for Lorentz and polarization factors and for absorption by using empirical scan data. The structure was solved with the SHELX program [21], and refined by full-matrix least-square methods based on F^2 , with anisotropic thermal parameters for the non-hydrogen atoms. The hydrogen atoms were located theoretically and not refined. Crystal data and structure refinement of the two polymers are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

2.5. Catalytic experiments

Heterogeneous catalytic experiments 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 polymer catalysts (1 mg/FW of **1** = 1.626×10^{-3} mmol, 1 mg/FW of **2** = 1.865×10^{-3} mmol) were ground well into appropriate sizes to increase the surface area, but not too small for a convenient filtration (the average particle size of 10–12 μm). Under air, the substrate 2,6-di-*tert*-butylphenol, 2,4-di-*tert*-butylphenol (0.206 g, 1 mmol) or 2,6-dimethylphenol (0.122 g, 1 mmol), base

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

Polymers	1	2
Formula	$\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{CuN}_{12}$	$\text{C}_{24}\text{H}_{32}\text{CuN}_4\text{O}_6$
Formula weight	614.99	536.08
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P-1$
<i>a</i> (Å)	7.6594(15)	8.0443(16)
<i>b</i> (Å)	21.515(4)	8.8157(18)
<i>c</i> (Å)	8.5120(17)	9.770(2)
α	90	106.13(3)
β	106.58(3)	91.07(3)
γ	90	104.41(3)
<i>V</i> (Å ³)	1344.4(5)	641.7(2)
<i>Z</i>	2	1
<i>D_c</i> (g cm ⁻³)	1.519	1.387
μ (mm ⁻¹)	1.051	0.896
<i>F</i> (000)	630	281
Reflections collected/unique	4420/2436	2001/2001
Goodness-of-fit on F^2	1.097	1.015
Final <i>R</i> indices	$R1 = 0.0356$	$R1 = 0.0514$
$[I > 2\sigma(I)]$	$wR2 = 0.0862$	$wR2 = 0.1224$

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

Polymer 1 ^a			
Cu(1)–N(1)#1	2.028(2)	Cu(1)–N(1)	2.028(2)
Cu(1)–N(6)#2	2.038(2)	Cu(1)–N(6)#3	2.038(2)
N(1)#1–Cu(1)–N(1)	180.0	N(6)#2–Cu(1)–N(6)#3	180.00(10)
N(1)#1–Cu(1)–N(6)#2	91.06(8)	N(1)–Cu(1)–N(6)#3	91.06(8)
N(1)–Cu(1)–N(6)#2	88.94(8)	N(1)#1–Cu(1)–N(6)#3	88.94(8)
Polymer 2 ^b			
Cu(1)–O(1)	1.958(3)	Cu(1)–O(1)#1	1.958(3)
Cu(1)–N(1)#1	2.012(3)	Cu(1)–N(1)	2.012(3)
O(1)–Cu(1)–O(1)#1	180.00(12)	N(1)#1–Cu(1)–N(1)	180.00(16)
O(1)–Cu(1)–N(1)#1	92.05(11)	O(1)#1–Cu(1)–N(1)	92.05(11)
O(1)#1–Cu(1)–N(1)#1	87.95(11)	O(1)–Cu(1)–N(1)	87.95(11)

^a Symmetry transformations used to generate equivalent atoms in polymer **1**: (#1) $-x, -y+1, -z+1$; (#2) $-x+1, y+1/2, -z+1/2$; (#3) $x-1, -y+1/2, z+1/2$; (#4) $-x+1, y-1/2, -z+1/2$.

^b Symmetry transformations used to generate equivalent atoms in polymer **2**: (#1) $-x, -y, -z$; (#2) $-x+1, -y, -z-1$

(1 mmol) and polymer **1** or **2** (0.005 mmol) were mixed in water (5 ml) with a magnetic stirrer and heated to 40 °C. Then, hydrogen peroxide (30% aqueous solution) was slowly added into the mixture using a syringe pump every 15 min 10 μ l for three times to minimize H₂O₂ decomposition. After 4 h, to stop the reaction, the reaction mixture was transferred into a separatory funnel, the organic materials were extracted after the addition of a few milliliters of CH₂Cl₂. This was repeated four to six times. The combined organic extracts were dried with anhydrous MgSO₄ and the solvent, after filtration, was evaporated in vacuo. The products were separated by preparative TLC performed on dry silica gel plates with petroleum ether–acetic ether (9.5:0.5, v/v) as the developing solvent for 2,6-DBP, acetic ether–hexane (1:8, v/v) for 2,4-DBP and acetic ether–petroleum ether (1:3, v/v) for DMP. The pure products TBDPQ, PQ, H₂TBDPQ, TBBP, DBQ, PPE and DPQ were collected and dried in vacuo.

The following is the standard procedure for the homogeneous oxidation: Both crystal polymer catalysts were powdered to increase the surface area for the catalysts homogeneous prior to use. Under air, the substrate 2,6-di-*tert*-butylphenol, 2,4-di-*tert*-butylphenol (0.206 g, 1 mmol) or 2,6-dimethylphenol (0.122 g, 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 molar ratio of NaOMe/catalyst were added to above solution with a magnetic stirrer. Then, hydrogen peroxide (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. All reactions were run in duplicate, and the data reported represent the average of these reactions.

3,3',5,5'-Tetra-*tert*-butyl-4,4'-diphenoquinone (TBDPQ): m.p.: 245 °C lit. 243 °C; ¹H NMR (CDCl₃, TMS) δ = 1.37 (s, 36H), 7.71 ppm (s, 4H); ¹³C NMR (CDCl₃, TMS) δ = 29.58, 36.02, 126.00, 136.12, 150.43, 186.46 ppm; IR (KBr)/cm⁻¹: 1605, 1458, 1362, 1090, 1041, 899, 883, 843, 411 cm⁻¹.

2,6-Di-*tert*-butyl-1,4-benzoquinone (PQ): m.p.: 64–66 °C; ¹H NMR (CDCl₃, TMS) δ = 1.27–1.28 (br, 18H), 6.51 (s, 2H); IR (KBr)/cm⁻¹: 1655, 1599, 1364, 1317, 1244, 1155, 1074, 922, 878, 825, 459 cm⁻¹.

4,4'-Dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (H₂TBDPQ): m.p.: 182–183 °C; ¹H NMR (CDCl₃, TMS) δ = 1.47 (s, 36H), 5.12 (s, 2OH), 7.27 (s, 4H); IR (KBr)/cm⁻¹: 3632, 2959, 1595, 1425, 1389, 1362, 1227, 1140, 1103, 1042, 870, 845, 804, 770, 619 cm⁻¹.

3,3',5,5'-Tetra-*tert*-butyl-2,2'-dihydroxybiphenyl (TBBP): m.p.: 195–197 °C; ¹H NMR (CDCl₃, TMS) δ = 1.3 (s, 9H), 1.44 (s, 9H), 4.64

(s, 1H), 7.24 (d, overlaps with solvent peak); ¹³C NMR (CDCl₃, TMS) δ = 30.3, 35.0, 36.0, 123.5, 129.5, 137.0, 144.0, 150.5; IR (KBr)/cm⁻¹: 3524, 1435, 1362, 1333, 1200, 1169, 1094, 879, 814, 650, 405 cm⁻¹.

3,5-Di-*tert*-butyl-*o*-quinone (DBQ): m.p.: 115–117 °C; ¹H NMR (CDCl₃, TMS) δ = 1.23 (s, 9H, *t*-butyl), 1.27 (s, 9H, *t*-butyl), 6.21 (d, J = 2.44, 1H, Ar), 6.93 (d, J = 2.14, 1H, Ar); IR (KBr)/cm⁻¹: 1661, 1622, 1466, 1367, 1246, 1024, 891, 812, 656, 582 cm⁻¹.

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)/cm⁻¹: ν_{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)/cm⁻¹: $\nu_{C=O}$ = 1594 cm⁻¹.

3. Results and discussion

3.1. Crystal structure of $\{[Cu(btx)_2]Cl_2\}_n$ (**1**)

Crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $p2(1)/c$ and consists of 2D cationic rhombohedral grid network. Each Cu(II) ion is quadrilaterally coordinated by four nitrogen atoms from different btx ligands, and lies on a crystallographic twofold axis. The N1–Cu1–N1A and N6B–Cu1–N6C bond angles are 180°, and the N(1)–Cu(1)–N(6)C and N(1)A–Cu(1)–N(6)C bond angles are 88.94(8)° and 91.06(8)°, respectively, so there is a ideal planarity of the CuN₄ unit. The Cu–N bond lengths (2.028(2) and 2.038(2) Å) correspond to those observed in the reported complexes $\{[Cu(fcz)_2(H_2O)]\cdot SO_4\cdot DMF\cdot 2CH_3OH\cdot 2H_2O\}_n$ (Cu–N av 2.032 Å) (fcz = 1-(2,4-difluorophenyl)-1,1-bis[(1H-1,2,4-triazol-1-yl)methyl]ethanol), $\{[Cu(L)_2(H_2O)_2]\cdot (ClO_4)\cdot (OH)\cdot (H_2O)_{2.5}\}_n$ (Cu–N av 2.025 Å) (L = 2,5-bis(4-pyridyl)-1,3,4-oxadiazole) [22] and $[Cu(pya)_2(H_2O)_2]_n$ (Cu–N 2.0324 Å) (pya = 4-pyridylacetate) [23]. Each btx ligand utilizes its triazole nitrogen to bridge two metal centers generating a 2D-layered structure with rhombohedral grid units (Fig. 1). The 2D sheets are parallel to the crystallographic *bc* plane and stack with an interpenetrating mode. In each layer, all Cu(II) ions are completely coplanar. Each rhombohedral grid is organized by four btx ligands acting as the four edges and four Cu(II) ions representing the four vertexes to give a 52-membered metallocyclic ring, the angle between two ligands is 98.2° or 81.8°, the diagonal-to-diagonal distances are 21.515 Å \times 19.533 Å, and the dimensions of the grid are 14.529 Å \times 14.529 Å. The dihedral angle between two triazole planes from the same btx is 125.9°. The network resembles the rhombohedral grids in $[Cd(btx)_2(NO_3)_2]_n$ and $[Cd(btx)_2Cl_2]_n$ derived from the same bridge ligand [24].

3.2. Crystal structure of $\{[Cu(bbbm)(Ac)_2]\cdot (CH_3OH)_2\}_n$ (**2**)

Polymer **2** features 1D zigzag chains running along *b* direction, in which Cu(II) ions are bridged by μ_2 -bbbmligands (Fig. 2). The Cu(II) ion exhibits an essentially square planar geometry, with two N-donor atoms from different bbbmligands and two oxygen atoms from two monodentate acetate ions in a linear manner with the N–Cu–N and O–Cu–O angles of 180°. The Cu–N bond length (2.012(3) Å) is shorter than that of **1** (2.028(2), 2.038(2) Å), and the Cu–O bond length of 1.958(3) is slightly shortened from those observed in the related Cu complexes, such as $\{[Cu_2L(\mu-OAc)_4](CHCl_3)_2\}_n$ (Cu–O 1.960–1.978 Å) (L = 2,5-bis(4-pyridyl)-1,3,4-thiadiazole) [25], $\{[Cu_2(bpodz)(l-OAc)_4](CH_3OH)_2\}_n$ (Cu–O 1.964–1.975 Å) (bpodz = 2,5-bis(4-pyridyl)-1,3,4-oxadiazole) [26] and $\{Cu_2-(\mu-OAc)_2([18]ane-N_6)\}(PF_6)_2$ (Cu–O 2.249 Å) ([18]ane-N₆ = 1,4,7,10,13,16-hexaazacyclooctadecane) [27]. Moreover, the

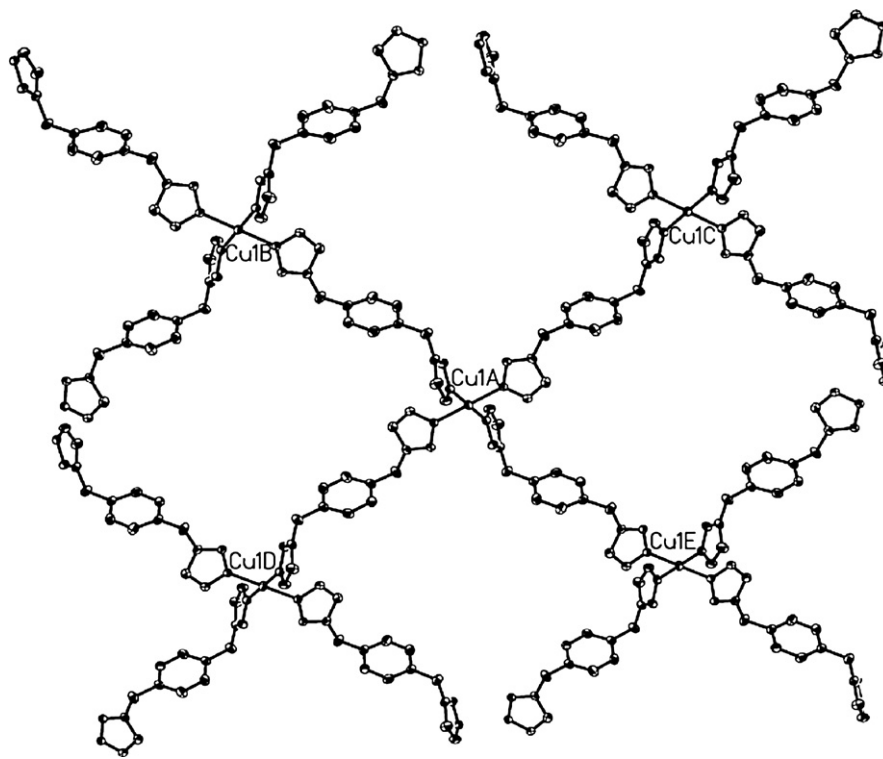


Fig. 1. The 2D-layered structure of $\{[\text{Cu}(\text{btX})_2]\text{Cl}_2\}_n$ **1** with rhombohedral grid units.

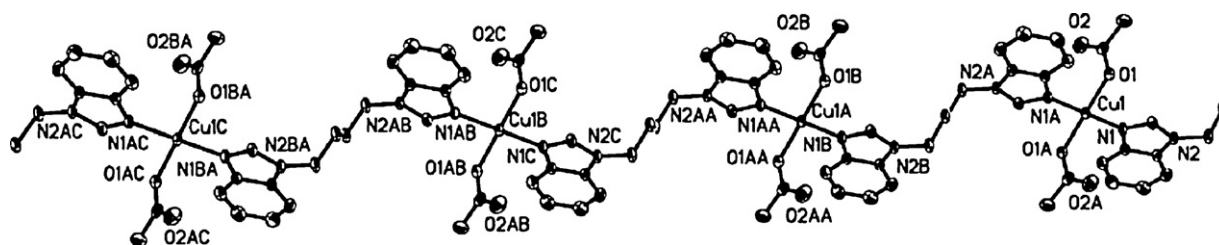


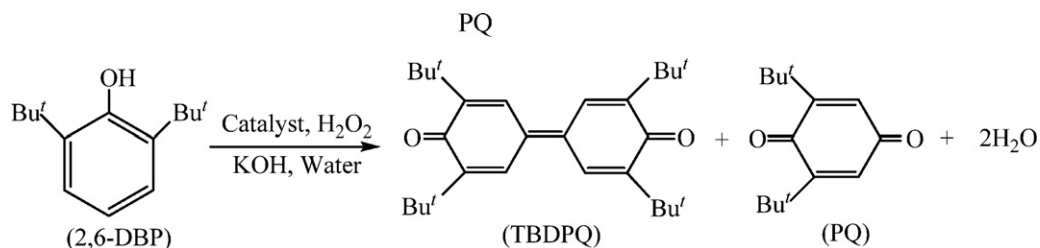
Fig. 2. The 1D zigzag chain structure of $\{[\text{Cu}(\text{bbbm})(\text{Ac})_2]\cdot(\text{CH}_3\text{OH})_2\}_n$ **2**.

Cu...Cu separation of 12.771 Å within a chain is significantly shorter than that of 14.529 Å in **1**. The bbbm ligand is twisted with the torsion angles of -67.1° and 67.1° for C9A-C9B-C8B-N2B and N2A-C8A-C9A-C9B, respectively, indicating that the two opposite benzimidazole rings are parallel to each other.

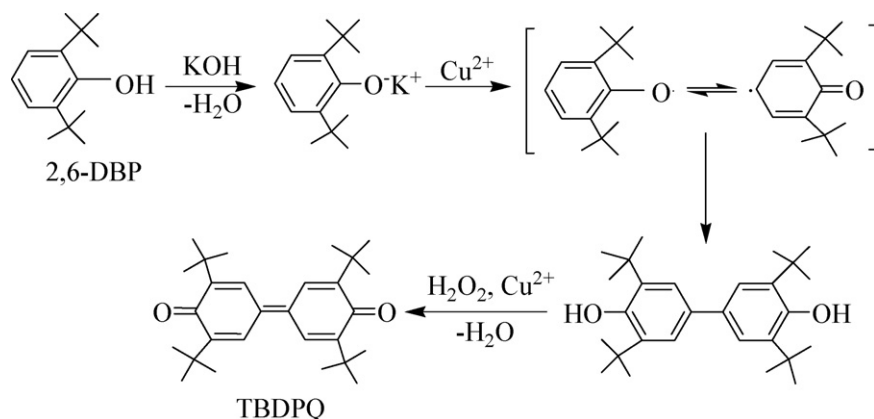
3.3. Catalytic properties of polymers

To evaluate the catalytic properties of polymers **1** and **2**, we select the oxidative coupling of 2,6-di-*tert*-butylphenol (2,6-DBP) as a probe reaction with H_2O_2 as oxidant. The selective autoxidation

of 2,6-DBP in the presence of the homogenous or heterogeneous catalyst systems has been reported previously to provide mainly the corresponding diphenoquinone TBDPQ and some of the benzoquinone PQ [28–30]. An analogous catalytic conversion can be accomplished with our species as shown in Scheme 1. The dependence of 2,6-DBP conversion and TBDPQ selectivity on various reaction parameters, including time, temperature as well as the amounts of co-catalyst, catalyst and oxidant has been determined by fixing the amount of 2,6-DBP at 1 mmol (206 mg) in 5 mL aqueous medium. Blank tests carried out in air or with H_2O_2 in the absence of polymer catalysts at room temperature result in no reac-



Scheme 1. Copper-catalyzed oxidative coupling of 2,6-DBP leading to TBDPQ and PQ.



Scheme 2. Oxidation dimerization of 2,6-DBP with KOH catalyzed by Cu(II) complex.

tion. When the reaction is performed in air at room temperature in the presence of polymer catalyst **1**, 37% conversion is achieved even after 24 h.

The addition of base to the reaction solvent causes the important effect on the oxidation of 2,6-DBP. It has been proved that the oxidation reaction of 2,6-DBP did not proceed in the presence of only Cu^{II} catalyst itself, but was prominently promoted by adding a base in the solvent [5]. The added base was found to have the role of generating the corresponding phenolate anion by dissociating the DBP molecule, which was known to be more oxidizable than the original phenol because of the difference between their redox potentials [31]. This finding can be expanded for our system. The influence of the kind of the base used on the catalytic activity for this transformation is thus surveyed. As shown in Table 3, the addition of base produces comparatively similar activity in the oxidation of 2,6-DBP, regardless of the kind of the base used in this study (KOH, NaOH, NaOCH₃ and NaOC₂H₅). We have hereafter employed KOH as co-catalyst in conjunction with polymer **1** to affect the oxidation coupling of 2,6-DBP. According to the proposed mechanism [5], the role of KOH in our cases is considered to be deprotonation of DBP into a potassium phenolate species, which is subsequently oxidized by Cu^{II} to supply radical intermediates of carbon–carbon coupling. A resultant Cu^I is reoxidized to Cu^{II} by H₂O₂, as shown in Scheme 2. Fig. 3 illustrates the influence of the KOH amount on the oxidation of 2,6-DBP with **1**. It is apparent that the conversion of 2,6-DBP and the selectivity to TBDPQ increase with an increase in the KOH concentration in the region of the lower KOH concentrations, and at the higher KOH concentrations, the conversion levels off whereas the selectivity descends. The optimum amount of KOH is found to be 1.2 mmol, suggesting that phenolate anion is likely to be the reactive species. Decrease of selectivity at higher amount of base could be imputed to a competing ion effect of hydroxide ion with phenolate anion [32]. It must be noted that the Cu(II) species with a KOH amount of 1.2 mmol are bluish-purple in color, but the ones in

Table 3
Effect of the kind of the base on the oxidation with **1**

Base	Conversion (%) ^a	TBDPQ (%) ^a	PQ (%) ^a	Selectivity ^b
NaOH	76	56	18	75.7
KOH	75	55	18	75.3
NaOMe	77	56	19	74.7
NaOC ₂ H ₅	74.5	54.7	18	75.2

Standard conditions: substrate (1 mmol), base (1 mmol), H₂O₂ (0.03 ml) and catalyst **1** (0.005 mmol) in H₂O (5 ml) for 4 h at 40 °C.

^a Conversions and isolated yields based on the 2,6-DBP. All isolated products were identified by ¹H, ¹³C NMR and IR spectroscopic analyses.

^b Selectivity = ([TBDPQ] × 100)/([TBDPQ] + [PQ]).

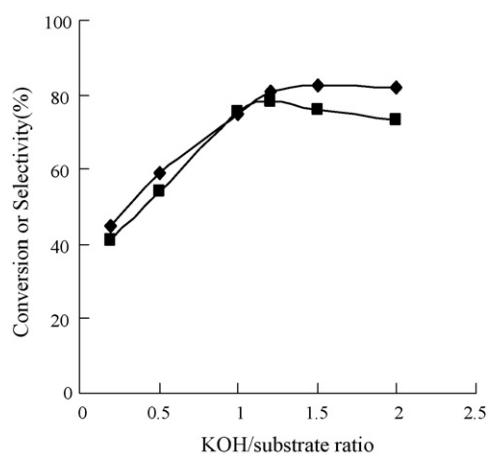


Fig. 3. Effect of various KOH-to-substrate ratios on the oxidation with **1** (standard conditions): (◆) conversion; (■) selectivity.

the amount of 2.0 mmol are rather light-brown. This may imply a change in the charge of the Cu(II) species from Cu(II) to Cu(I) due to the excess KOH in the reaction solution.

Temperature also plays a key role in driving this organic transformation. As depicted in Fig. 4, the 2,6-DBP conversion increases monotonically from 20% to approximately 90% when the temperature is increased from 25 to 50 °C, while the TBDPQ selectivity

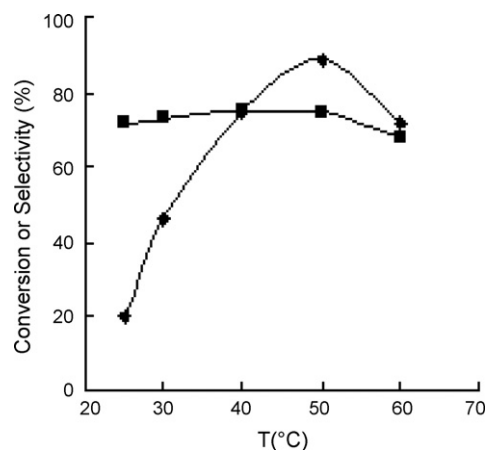


Fig. 4. Effect of temperature on the oxidation with **1** (standard conditions): (◆) conversion; (■) selectivity.

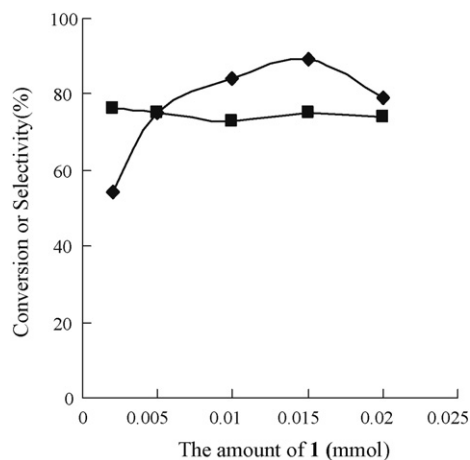


Fig. 5. Effect of the amount of **1** on the oxidation (standard conditions): (◆) conversion; (■) selectivity.

remained virtually constant at ~75%. The constant TBPQ selectivity with increasing temperature is similar to that reported previously for [*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)1,2-cyclohexanediaminato-(2-)]cobalt(II)] (Co(salen*)) in *sc*CO₂ medium [33]. The pathways to both products begin with the formation of a common radical, the phenoxy radical [34–37], which appears to be the rate-determining event. Selectivity is determined by competition between oxygenation of the first-formed radical and its dimerization. Because the activation energy is very low for radical reactions, one would not expect the product distribution to change with temperature. However, significant differences are seen at 60 °C, where the conversion to products decreases dramatically to 72% with the selectivity of 68% for TBPQ after 4 h. Meanwhile, the color of polymer **1** turns slowly from bluish-purple to dark-brown. Presumably, the color change and the activity decrease would be mainly due to partial decomposition of the catalyst during oxidation at elevated temperature. Therefore, the optimal reaction temperature is 50 °C.

The influence of catalyst concentration on the 2,6-DBP conversion and TBPQ selectivity is depicted in Fig. 5. The 2,6-DBP conversion increases with increasing catalyst concentration and reaches its highest value of 89% at a catalyst concentration of 0.015 mM, above which the conversion decreases. Differently, the TBPQ selectivity remains constant at 75% as the concentration of the catalyst increases. The decrease in activity at high catalyst concentrations could arise from competitive formation of catalytically inactive copper species. The accompanying loss in catalyst concentration would affect the parallel reactions that produce TBPQ and PQ equally, and this is consistent with the insensitivity of selectivity to catalyst concentration. This behavior is different from the reported observation for Co(salen*) in CO₂-expanded liquids media (CXLs) [38], where the selectivity increases with increasing catalyst concentration.

Fig. 6 illustrates the effect of time on the oxidation coupling with **1**, showing that the conversion of 2,6-DBP to products increases fast with the increase in reaction time for the first 5 h reaching a value of about 88% then gradually levels off. After 6 h, the conversion of 2,6-DBP is over 92%. Also the selectivity toward TBPQ increases fast with time in the initial stage of oxidation (about first 5 h) and nearly tends to level off at the reaction times from 5 to 6 h (maybe with a maximum around 6 h) and then gradually decreases with further reaction time. The highest TBPQ selectivity is about 85%. This behavior can be rationalized invoking an oxidative cleavage of the initially formed TBPQ into PQ

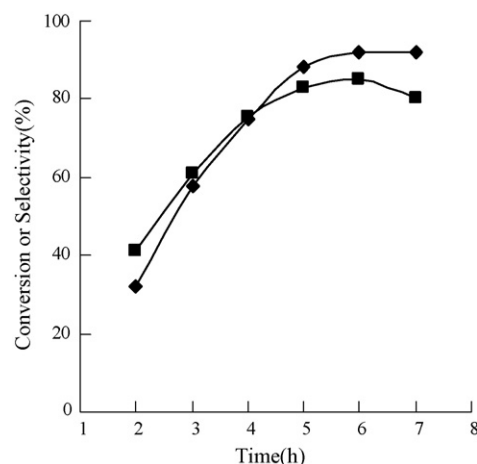


Fig. 6. Effect of time on the oxidation with **1** (standard conditions): (◆) conversion; (■) selectivity.

[4]. It should be pointed out that little amount (<5%) of 4,4'-dihydroxy-3,3',5,5'-tetra-*tert*-butylbiphenyl (H₂TBDPQ) and other unidentified products are detected in the reaction mixture after 6 h. In addition, the effect of the amount of oxidant is studied by using different volumes of H₂O₂, viz. 0.02, 0.05, 0.1, 0.2 and 0.3 ml (30 vol.%). The results indicate that a larger H₂O₂ concentration results in an increase of the conversion along with a decline in selectivity. Although excess H₂O₂ can increase the conversion, we choose 0.05 ml H₂O₂ for the reaction in order to minimize the formation of byproduct PQ.

With the optimized reaction conditions in hand, we evaluate catalytic efficiencies of the title polymers for comparison. As can be seen in Table 4, polymer **1** displaying 2D reticulation grid structure assumes the evidently superior catalytic activity to **2** exhibiting 1D zigzag chain structure, viz., the conversions of 2,6-DBP are 100% and 86% for **1** and **2**, respectively. Moreover, **1** shows a higher preference to yield TBPQ with the selectivity toward TBPQ of 90.8%. These dissimilarities are probably attributable to the differences in ligands, counteranions as well as the structures of the molecules, which have a dramatic impact on the coordination of 2,6-DBP to Cu(II) to form the proposed active copper species. As in the two polymers, the quantity of copper ions and the coordination number around metal centers are the same, the cavity dimension is probably an important factor in determining the reactivity toward the used phenolic substrate. Concretely, large cavities in **1** could accommodate more 2,6-DBP molecules binding to Cu(II) centers

Table 4

Results of oxidative coupling of 2,6-DBP with different catalysts performed under the optimized conditions

Catalyst	Conversion (%) ^a	TBDPQ (%) ^a	PQ (%) ^a	Selectivity (%) ^b
1	100 ¹	89	9	90.8
	96 ²	84	9.5	89.8
	91 ³	79	8.5	90.3
2	86 ¹	65	15	81.9
	83 ²	60	14	81
	77 ³	56	13	81.2
CuCl ₂ + 2btx	68	46	17	73
Cu(Ac) ₂ + bbbm	45	27	18	61.4
CuCl ₂	35	18.5	11	62.7
Cu(Ac) ₂	28	12	14.5	45.3
btx	0	0	0	0

Optimized conditions: substrate (1 mmol), KOH (1.2 mmol), H₂O₂ (0.05 ml) and catalyst (0.015 mmol) in H₂O for 6 h at 50 °C. The superscripts "1, 2, 3" show the results of recycling from the first (fresh), to the second, and third runs, respectively.

Table 5
Comparison with the representative catalysts carried out under their own optimized reaction conditions for the oxidative coupling of 2,6-DBP

Catalyst	Solvent	T (°C)	Time (h)	Substrate/catalyst ratio	Conversion (%)	Selectivity (%)	Ref.
Co-polymer	Cl(CH ₂) ₂ Cl	40	48	30	96	37	4
[CoPcTS] ⁴⁻	CH ₃ OH/H ₂ O	25	8	50	96	63.2	44
P-1[Co ^{II}]	CH ₃ CN	80	21	80	30	81	13
Na/Cu–Mg–Al–CO ₃	o-Xylene	130	10	–	87	70.9	29
CuSO ₄ /Al ₂ O ₃	Chloro-benzene	140	8	5	94	100	45
P–MoO ₂ (salpen)	CH ₃ OH	50	6	–	78.3	77	46
Ru(OH) _x /Al ₂ O ₃	H ₂ O	90	48	20	94	88	11
{[Cu(btx) ₂].Cl ₂] _n (1)}	H ₂ O	50	6	67	100	90.8	This work
{[Cu(bbbm)(Ac)].(CH ₃ OH) ₂] _n (2)}	H ₂ O	50	6	67	86	81.9	This work

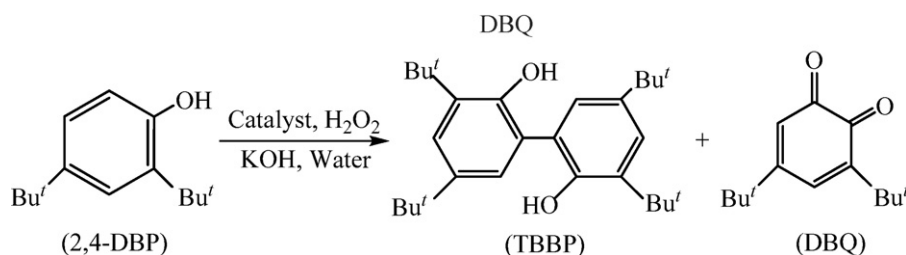
to facilitate this oxidative coupling, and thus the higher conversion and selectivity are observed. Consistent with our observation, Kol and co-workers have also testified that the structural effects on reactivity were pronounced in the zirconium series for lactide polymerization [39]. As a result, further structure modification for Cu-containing MOFs could be realized through objective molecular design and synthesis, and then enhance the catalytic properties for desired applications.

The potential benefits of heterogeneous catalysts include the facilitation of catalyst separation from reagents and reaction products, and simplification of methods for catalyst recycling [40–42]. For a truly effective heterogeneous catalyst, therefore, it is critical that recovery is simple and efficient, and that the recovered catalyst could maintain its original reactivity through multiple cycles. The recyclabilities of **1** and **2** are next examined. Upon completion of the oxidation coupling reaction, the organic materials are extracted and the catalysts are recovered by filtration. Both the solid and the aqueous phase are retained for subsequent reactions. The conversion of 2,6-DBP decreases by only about 8–9% after three consecutive cycles (Table 4). Slight decrease of the catalytic activity is presumably due to leaching of neglectable copper metal into the reaction solution during catalysis. In order to elucidate the heterogeneous nature of the present catalytic systems, we filter the catalyst and allow the filtered catalyst and the filtrate to catalyze other 2,6-DBP oxidation couplings, respectively. The filtered catalyst is subjected to the second run by charging with new reagents and then the products are again formed with about 84–90% of the original conversion. The filtrate obtained from the first filtration is also used in a new reaction with the addition of substrate. About only 6–10% conversion of 2,6-DBP is observed under similar conditions, which strongly suggests that the dominant reactive species is the heterogeneous catalyst.

Furthermore, to probe the origin of the favorable catalytic properties of the polymers, we also assess catalytic capabilities of the corresponding copper salts together with organic ligands in the mole ratios conforming to those of the polymers, copper salts alone and free ligands under the similar reaction conditions. The results obtained are collected in Table 4. We find that the activity and selectivity gained with the two polymers are better than those observed using the corresponding copper salts and organic ligands together,

and far superior to those obtained by the use of copper salts alone, and free ligands are even completely inactive, e.g., the reaction using CuCl₂ is sluggish, recording the low conversion of 2,6-DBP of only 35% with the selectivity of 62.7% to TBDPQ, and CuCl₂ together with btx provides the conversion of 68% with the selectivity of 73%, while the high conversion of up to 100% is obtained with the selectivity of up to 90.8% by the use of polymer **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 polymer. This implies that the coordination of ligands to Cu(II) ions leads to a distinct improvement of catalytic property of the polymers. That is to say, the combination of the physical and chemical properties of inorganic and organic components can allow the achievement of the targeted polymeric materials furnishing unusual catalytic characters, as has been verified by many previous studies [43–45]. This observation is very significant since it prompts us to construct new self-assembly polymers that could be efficiently used as environmentally friendly heterogeneous catalysts. In addition, it is of note that all the catalysts used in this study, including the polymers, the systems of copper salt combined with ligand as well as copper salts, show an identical product distribution for TBDPQ and PQ, signifying that all the catalysts probably carry out the oxidation coupling of 2,6-DBP by the same reaction mechanism.

Table 5 lists the best experimental results of the polymers investigated and the reported highly active heterogeneous catalysts for this process. It is found that both co-polymer and [CoPcTS]⁴⁻ give the identically exciting conversion of 2,6-DBP of 96%, but with low to moderate selectivity of 37% and 63.3% toward TBDPQ in 48 and 8 h, respectively (entries 1–2) [4,46]. The P-1[Co^{II}] and Na/Cu–Mg–Al–CO₃ catalysts deliver either a promising activity or selectivity at higher temperature (80 and 130 °C) (entries 3–4) [13,31]. In the case of CuSO₄/Al₂O₃, the excellent conversion of 94% is attained with a selectivity of 100% at higher catalyst loading and extraordinarily improved temperature of 140 °C in toxic organic solvent (entry 5) [47]. Although Ru(OH)_x/Al₂O₃ has also been proven to be specially capable of inducing this process in water, and yet inescapably suffered from rigorous conditions (90 °C,



Scheme 3. Copper-catalyzed oxidative coupling of 2,4-DBP leading to TBBP and DBQ.

Table 6
Oxidative coupling of substituted phenols in water^a or in methanol–toluene mixture^b catalyzed by polymers **1** and **2**

Catalyst	Substrate	Solvent	Conversion (%)	Major product	Selectivity (%)
1		H ₂ O CH ₃ OH/toluene	100		90.8
			89		92.2
2		H ₂ O	86		81.9
1		CH ₃ OH/toluene	78		83.5
	H ₂ O	82	62		
	CH ₃ OH/toluene	71	63.7		
	H ₂ O	68	61.5		
2		CH ₃ OH/toluene	59		62.4
H ₂ O		100	89.6		
1		CH ₃ OH/toluene	95		91.2
		H ₂ O	94.5		88.7
2		CH ₃ OH/toluene	92		90.3

^a Heterogeneous optimized conditions: substrate (1 mmol), KOH (1.2 mmol), H₂O₂ (0.05 ml) and catalyst (0.015 mmol) in H₂O for 6 h at 50 °C.

^b Homogeneous optimized conditions: substrate (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.

48 h) [11]. In sharp contrast, likewise outperforming the previous report P-MoO₂(salpen) [48], polymers **1** and **2** allow to supply both the high conversion and selectivity with the shorter reaction times and at relatively low catalyst concentrations under milder reaction conditions, thereby confirming their effectiveness as heterogeneous catalysts for this reaction (entries 8–9). These high selectivities to the *para*–*para* coupling product for the oxidative coupling of 2,6-DBP are comparable to those of the laccase and tyrosinase enzyme-catalyzed systems, where Cu²⁺ acts as a one-electron oxidant to generate the radical species from the starting phenol and Cu⁺ is reoxidized by molecular oxygen [49].

The satisfying results of the present polymers-catalyzed oxidative coupling of 2,6-DBP and the environmentally friendly character of this methodology carried out in aqueous reaction medium, encourage us to extend it to other alkylated phenols, namely 2,4-di-*tert*-butylphenol (2,4-DBP). The 2,4-DBP oxidative coupling reaction is as follows (Scheme 3).

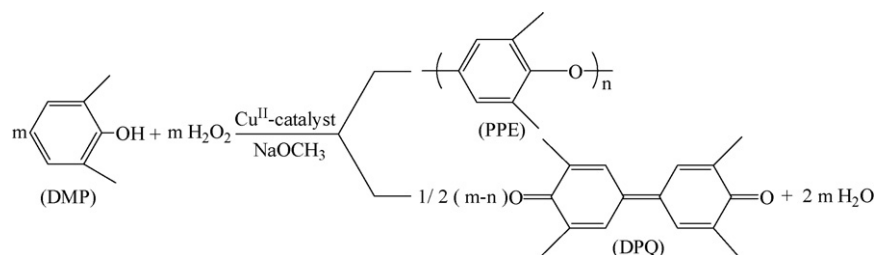
Table 6 shows the results of the oxidative coupling of 2,4-DBP in H₂O catalyzed by polymers **1** and **2**. After 5 h, 82% conversion is achieved by use of **1** with only moderate selectivity of 62% to TBBP (entry 5). Under similar conditions employing **2** as a catalyst, 68% 2,4-DBP conversion is obtained with similar product selectivity (entry 7). This contrasts the highly efficient and selective transformation of 2,6-DBP into TBDPQ mediated by these catalyst systems under identical reaction conditions, manifesting that the reactivity of the polymers correlates well with the nature of the substrate.

In an attempt to enhance the oxidation efficiency, the amount of H₂O₂ is heightened to 0.08 ml. Interestingly, using **1** as a catalyst, the reaction produces exclusively DBQ in a 71% yield but negligible amounts of TBBP. This obvious difference in product distribution could be due to the formation of different active species during the consumption of oxidant.

2,6-Dimethylphenol (DMP) is a very interesting substrate to test, because of the well known various industrial applications of its resulting polymer poly(1,4-phenylene ether) (PPE) (Scheme 4) [50–52]. Consequently, most of the recent efforts in the study of catalytic polymerization concern the design of new and efficient catalysts for such applications [20,53–55]. We think that polymers **1** and **2** display potentially the structural and chemical requirements for this catalytic reaction and could throw some light to the reaction process. The results are gathered in Table 6.

Under conditions similar to those used for 2,6-DBP and 2,4-DBP oxidations, the oxidative coupling of DMP proceeds completely in the presence of **1**, affording PPE in good yield of 88% within 5 h (entry 9), whereas the use of **2** as the catalyst for this reaction shows similar selectivity, but lower activity with the conversion of 94.5% (entry 11). It is evident from the results that such polymers would parallel the highly effective [Cu(tmeda)]·Cl₂ and K₃[Fe(CN)₆] systems introduced by Nishide and co-workers and offer the possibility of a new class of polymerization catalysts [9].

Heterogeneous catalysts offer the practical advantages of simplifying the separation and isolation of products, and of the potential for catalyst recycling [56–61]. However, it is well documented



Scheme 4. Copper-catalyzed oxidative coupling of DMP leading to PPE and DPQ.

that homogeneous catalysts often provide the better results in achieving high levels of reactivity and improved selectivity [62–65]. For the purpose of fully understanding the intrinsic advantage of heterogeneous vs. homogeneous catalysts, the oxidation couplings of the aforementioned substrates are conducted in 1.5:1 (v/v) methanol–toluene mixed solution using polymers **1** and **2** as homogeneous catalysts under the same reaction conditions as our prior study (Table 6) [19]. To our surprise, the use of the title polymers acting as homogeneous catalysts can effectively suppress benzoquinone formation in the oxidation coupling of 2,6-DBP and 2,4-DBP and diphenoquinone production in the oxidative polymerization of DMP, and improve the selectivities for TBDPO, TBBP and PPE, respectively, while decreasing distinctly the catalytic activities. For example, when utilizing **1** as heterogeneous catalyst, the oxidation coupling of 2,6-DBP occurs with high 100% conversion and 90.8% selectivity for TBDPO. Nevertheless, **1** assumes the markedly lower efficiency (89% conversion) for the reaction in methanol–toluene medium, albeit with slightly enhanced selectivity of 92.2%. The superior activities of the polymers in the heterogeneous catalytic system may be attributed to full exposure of metal sites, therefore giving an ultimately high degree of metal-dispersion [66]. On the other hand, for such transformations, **1** is found to be substantially more active than **2**. The reason for this difference in activity could be assigned to steric factor as well as variation in the chemical composition of the polymers. The beneficial property of polymer **1** is ascribed to the 2D architecture and unsaturated metal centers available for the substrate in the catalytic cycle. This view is further corroborated by the structure/activity results obtained with our previous systems of $\{[\text{Cu}(\text{Ac})_2(\text{pbbm})]\cdot\text{CH}_3\text{OH}\}_n$ and $[\text{Cu}(\text{SO}_4)(\text{pbbm})]_n$ (pbbm = 1,1'-(1,5-pentanediy)bis-1H-benzimidazole), where the $[\text{Cu}(\text{SO}_4)(\text{pbbm})]_n$ species is less effective in oxidizing DMP substrate because of the strong steric hindrance of coordination sphere, which restricts access for coupling. By comparing the reactivities of all four polymers for this oxidation coupling as catalysts, we have also observed that polymer **1** provides an open coordination site for catalysis, thereby producing the metal center to be the most active toward this process. Meanwhile, this opinion is also in accord with the idea of Kol and co-workers, who proposed that the blocking of the metal center led to the relative inertness of the complex [42]. In spite of heterogeneous or homogeneous reaction systems, the satisfactory catalytic properties seen for the two polymers, especially the remarkable behavior of **1**, suggest the high versatility of self-assembly polymers as catalysts for the oxidation coupling of a wide range of phenol derivatives.

4. Conclusions

In summary, two new Cu(II)-organic polymers containing coordinatively unsaturated metal sites have been served as effective catalysts in both heterogeneous and homogeneous reaction systems for the oxidation coupling of a series of substituted phenols. The observed notable reactivity and selectivity can be attributable to the incorporation of ligands, reflecting that combination of organic spacers and metal centers may be an effective strategy for constructing new types of potent catalysts. It is worthwhile to mention that heterogeneous catalytic oxidation is highly more active in comparison with those of homogeneous cases, illuminating clearly the enormous superiority of self-assembly polymers as recyclable catalysts. Recognizing that decreasing the steric bulkiness around the central metal should increase the reactivity of polymers, it can be expected that more studies could improve the catalytic efficiencies and selectivities of Cu(II)-containing polymers via further structural modifications by means of adjusting

the steric hindrance of the coordination sphere for practical application.

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Appendix A

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.02.025.

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