

# The electronic effect of 4,4'-disubstituted 2,2'-bipyridine ligands on the copper-catalysed oxidative coupling of 2,6-dimethylphenol

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## Abstract

The ligands bipyridine (bpy), 4,4'-dimethoxy-2,2'-bipyridyl (dMeObpy), 4,4'-dimethyl-2,2'-bipyridyl (dMebpy), 4,4'-dichloro-2,2'-bipyridyl (dClbpy) and 4,4'-dinitro-2,2'-bipyridyl (dNO<sub>2</sub>bpy), when combined with copper(II) nitrate render active catalysts. The highest activity was found for bpy as the ligand. The ligands dMeObpy and dMebpy, with their electron-donating substituents, render the copper ions less electrophilic than unsubstituted bpy and so decrease the oxidation rate of 2,6-dimethylphenol (DMP). One would have expected an increase in the oxidation rate of DMP with the ligands dClbpy and dNO<sub>2</sub>bpy, having electron-withdrawing substituents, which render the copper ions more electrophilic. However, probably due to a stabilisation of the copper(I) species, which retards the reoxidation to Cu(II), the overall reaction rate decreases with dClbpy and dNO<sub>2</sub>bpy. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The oxidative coupling of 2,6-dimethylphenol (DMP) was found to be catalysed by copper-amine complexes in the presence of a base in 1959 by Hay et al. [1]. The reaction yields a polymer, poly(1,4-phenylene ether) (PPE) via C–O coupling and about 5% of a diphenoquinone (DPQ, systematic name 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone)) via C–C coupling, and water, see Fig. 1.

The polymer PPE is an important engineering plastic with excellent mechanical properties and is resistant to moisture and a wide range of chemicals. Because of its exceptionally high glass-transition

temperature  $T_g$  of 205–210°C [2] the largest commercial usage of PPE is in its blend with polystyrene, which makes processing easier [3,4].

The side-product DPQ is highly coloured. It reduces the polymer properties upon further processing at higher temperatures. Also, due to the formation of DPQ, less DMP is converted into PPE [5].

Since the discovery of the polymerisation reaction by Hay et al. [1], many groups have studied the mechanism [6–20]. The first mechanistic proposals feature mononuclear copper-phenoxo species as key reacting species [4,6,21]. However, a simple radical mechanism could not explain the experimental results, as the reaction of DMP with radical initiators produces mainly DPQ [22], in contrast to the copper-catalysed polymerisation reactions of DMP, where 5% or less DPQ is formed. Only with phenols that are known to give stable radicals, e.g. 2,4,6-tri-*tert*-butylphenol [11,23], or in rapid flow techniques, radicals have been

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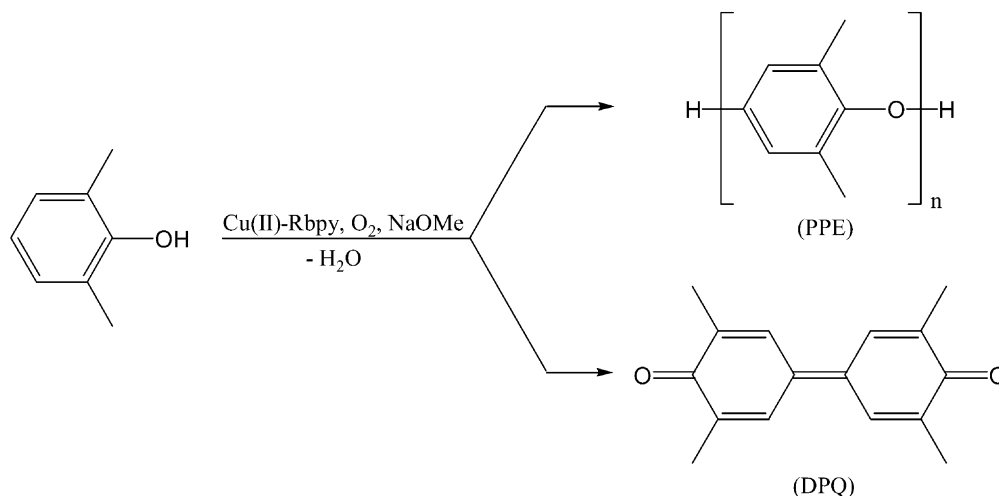


Fig. 1. Reaction scheme of the oxidative coupling of DMP to PPE and DPQ.

observed in small quantities with EPR measurements [24]. DMP radicals have been detected in larger quantities with well-known one-electron oxidants [25]. The recent mechanistic proposals feature a two-electron mechanism involving dinuclear copper(II) and the formation of phenoxonium cations [7,26–28], but up till now, this mechanism has still not been elucidated entirely.

In the present paper, the electronic effect of several 4,4'-disubstituted 2,2'-bipyridine ligands on the copper-catalysed oxidation of 2,6-dimethylphenol is reported. Various copper(II) compounds have been generated in situ with these ligands and have been tested on their activity by following the oxygen consumption in time during the coupling reaction.

The electronic effect of copper catalysts on the polymerisation of phenols has been studied earlier [29]. However, in that study the structures of the tested copper catalysts differ significantly from each other, resulting in mixed electronic and steric effects. In the present study, steric effects have been excluded due to the variation of substituents on the 4,4'-positions of bipyridine far away from the metal. These substituents only exert inductive effects on the coordinated copper ions.

The ligands 4,4'-dimethoxy-2,2'-bipyridine (dMeObpy) and 4,4'-dimethyl-2,2'-bipyridine (dMebpy) are electron donating, while 4,4'-dichloro-2,2'-bipyridine

(dClbpy) and 4,4'-dinitro-2,2'-bipyridine (dNO<sub>2</sub>bpy) are electron withdrawing, relative to bipyridine (bpy) itself. Electron-withdrawing ligands are expected to generate more electrophilic copper(II) ions and would therefore facilitate the oxidation of the phenolate. Electron-donating ligands make the copper(II) ions less electrophilic and thus would retard the oxidation, but may also enhance the reoxidation of the copper(I) species.

## 2. Experimental

### 2.1. General

All solvents and chemicals used were commercially available, of sufficient purity, and used without further purification unless stated otherwise. 2,6-Dimethylphenol was recrystallised from *n*-hexane. Water was demineralised prior to use.

Dioxygen-uptake experiments were performed using an in-house designed apparatus, described in detail in earlier publications [28,30].

NMR spectra were recorded on a JEOL FX-200 (200 MHz) FT-NMR spectrometer. Vis/NIR spectra were taken with a Perkin Elmer 330 double beam spectrophotometer. IR spectra were recorded as pure solid on a Perkin Elmer FT-IR Paragon 1000

Table 1  
<sup>1</sup>H NMR data of the synthesised 4,4'-disubstituted bipyridines<sup>a</sup>

	H <sub>3</sub> , H' <sub>3</sub>	H <sub>5</sub> , H' <sub>5</sub>	H <sub>6</sub> , H' <sub>6</sub>
dMeObpy <sup>b</sup>	7.92, d, 2.6 Hz	7.05, dd, 2.6/5.6 Hz	8.49, d, 5.6 Hz
dClbpy <sup>c</sup>	8.38, d, 2.1 Hz	7.67, dd, 5.1/2.1 Hz	8.69, d, 5.1 Hz
dNO <sub>2</sub> bpy <sup>c</sup>	9.22, d, 2.1 Hz	8.15, dd, 5.1/2.1 Hz	9.04, d, 5.1 Hz

<sup>a</sup> d: doublet, dd: double doublet.

<sup>b</sup> Solvent is chloroform.

<sup>c</sup> Solvent is DMSO.

spectrophotometer with a Specac single reflection diamond ATR P/N 10500. The size exclusion chromatography (SEC) measurements were carried out with multiple detection consisting of an interferometric RI-detector (Optilab DSP, Wyatt Technology) in series with a multi angle light scattering detector (Dawn-DSP-F, Wyatt Technology). With this configuration absolute molecular weights are obtained on-line. The PPE samples were measured on two Mixed-C columns (Polymer Laboratories) in chloroform with a flow of 1 ml min<sup>-1</sup>. The concentration was 10 mg ml<sup>-1</sup>; sample load was 100 μl.

## 2.2. Ligand synthesis

The ligands 2,2-bipyridine and 4,4'-dimethyl-2,2'-bipyridine were commercially available. The other disubstituted bipyridine ligands have been synthesised starting from 2,2'-bipyridine, oxidising it with peroxyacetic acid to 2,2'-bipyridine 1,1'-dioxide, and nitrating it at the 4 and 4' position to give 4,4'-dinitro-2,2'-bipyridine 1,1'-dioxide [31]. The introduced nitro group was replaced by a methoxide [32] or by a chloride substituent [33] to generate 4,4'-dimethoxy-2,2'-bipyridine 1,1'-dioxide and 4,4'-dichloro-2,2'-bipyridine 1,1'-dioxide. The oxide function at the 1 and 1' were reduced by the reaction with phosphorous trichloride, without affecting the substituents. <sup>1</sup>H NMR data are given in Table 1.

In this table the effect of the different R groups on the chemical shifts is nicely shown. The more electron withdrawing the substituents, the higher the chemical shifts are.

The synthesised ligands had been characterised by spectroscopic methods (IR and NMR) and their melting points. They appeared sufficiently pure for our purpose.

## 2.3. Dioxygen-uptake experiments

A common solvent mixture used for the oxygen-uptake experiments in industry is toluene/alcohol. Due to the poor solubility of the compounds used in this research in these mixtures, acetonitrile was chosen as the solvent, as in the research of Gamez et al. [34] The oxygen-uptake experiment has been performed as follows. In a special reaction vessel, divided into two compartments, one compartment was filled with a 5 ml acetonitrile solution containing 0.05 mmol Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 0.05 mmol of the ligand, while the other compartment was filled with 10 ml acetonitrile, containing 3.0 mmol DMP and a small amount of a highly concentrated solution of 0.1 mmol of NaOMe in methanol. The resulting reaction mixture was 3.33 mM in copper(II) nitrate and 0.20 M in DMP, the DMP-to-copper ratio 60. Prior to the beginning of the reaction, the system was flushed with pure dioxygen. Subsequently, the reaction vessel was shaken vigorously in a thermostated bath at 25°C, allowing the two reactant solutions to mix instantly and intimately with each other and with dioxygen. After the experiment, the reaction mixture was diluted with acetonitrile and the amount of DPQ formed was measured spectrophotometrically. Since PPE and DPQ are virtually the sole products of the reaction, the amount of PPE formed can be calculated from the amount of dioxygen consumed, corrected for the amount of DPQ formed. A more detailed description of the dioxygen-uptake equipment and the handling of the data has been described earlier [28,30]. To determine the molecular weight of the polymers produced, the reaction mixture was evaporated to dryness, dissolved in 1 ml of chloroform and poured into 200 ml of methanol. The precipitated polymer was filtered off, washed with methanol and analysed with SEC.

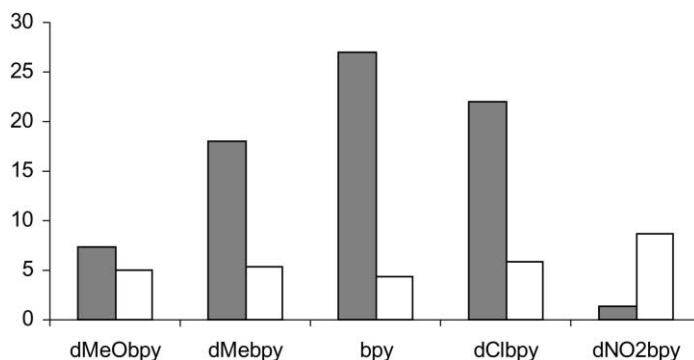


Fig. 2. Initial reaction rates ( $R_0$ ) expressed in  $10^{-5}$  mol/l s (dark) and DPQ quantities in percentage (white).

### 3. Results and discussion

In all experiments a ligand-to-copper ratio of 1:1 has been used, because with higher ratios lower activities were observed. This appears to be in contrast to the results of Baesjou et al. who used up to 30 equivalents of the monodentate ligand Nmiz to obtain an optimum activity [28]. Apparently, the chelating bpy ligand binds stronger to the copper ion than Nmiz and, when used in larger ratios, hampers the binding of the substrate. Also, the base-to-copper ratio has been kept equal to one, because higher ratios resulted in lower activities and more DPQ. The latter can be rationalised by realising that more base in a slow catalytic system generates a high amount of dehydrated DMP, which, because it is not directly reacted to PPE, will give larger amounts of DPQ.

All copper nitrate complexes with the 4,4'-disubstituted-2,2'-bipyridine ligands have been found to be active in the oxidative coupling reaction. The resulting activities are given in  $10^{-5}$  mol/L s in Fig. 2. The amount of DPQ formed is given in percentages of the initial amount of DMP.

In most cases, the amount of DPQ formed lies in the same range, except for the systems with very low activity, where the quantity of DPQ appeared to be substantially larger.

The ligands dMeObpy and dMebpy, both with electron-donating substituents, gave less active catalysts than bpy itself as the ligand. These ligands render the copper ions less electrophilic and therefore decrease the oxidation rate of the phenolate. The more electron-donating the ligand, the less active the catalyst.

For the ligands dClbpy and dNO<sub>2</sub>bpy, both with electron-withdrawing substituents which therefore render the copper ions more electrophilic, one would expect an increase of the oxidation rate of the phenolate. However, a lower activity than with bpy as ligand was observed. Most likely, the electron-withdrawing ligands stabilise copper(I) and thereby retard the oxidation reaction.

There seems to be a correlation between polymer length and catalytic activity, because the lower the activity of the catalyst, the lower the molecular weight of the polymers produced, see Table 2.

Table 2  
Results of the polymerisation of DMP

Ligand	$R_0$ ( $10^{-5}$ mol/L s)	DMP converted (%)	Reaction time (s)	DPQ (%)	$M_w$ (Da)
dMeObpy	7.4	57	7440	5.0	NP <sup>a</sup>
dMebpy	18	68	2235	5.3	8.400
bpy	27	61	800	4.3	13.100
dClbpy	22	48	1005	5.9	6.200
dNO <sub>2</sub> bpy	1.4	45	10000	8.6	NP <sup>a</sup>

<sup>a</sup> NP: No PPE precipitate could be obtained.

In the case of very low activity, namely with the ligands dMeObpy and dNO<sub>2</sub>bpy, a PPE precipitate could even not be obtained, most likely because the molecular weight was too low.

#### 4. Conclusions

All 4,4'-disubstituted-2,2'-bipyridines were found to give active catalysts with copper(II) nitrate for the oxidative coupling of DMP. Compared to bpy, the more electron-donating bipyridine ligands dMeObpy and dMebpy decrease the activity of the catalyst, by making the copper ions less electrophilic. The more electron-withdrawing bpy ligands dClbpy and dNO<sub>2</sub>bpy should increase the oxidation of DMP, but apparently do not increase the activity (in contrast to the expectation), because of a much slower reoxidation of copper(I). Low activity results in a higher amount of the side product DPQ and a lower molecular weight of PPE.

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