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Effect of the N-based ligands in copper complexes for depolymerisation of lignin†

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Several organic soluble N-based ligands and their copper complexes were firstly investigated as catalysts to depolymerise organosolv lignin in the organic solvent, dimethylformamide (DMF) and an ionic liquid (1-ethyl-3-methylimidazolium xylenesulfonate, [emim][ABS]). The results of screening depolymerisation reactions in DMF and [emim][ABS] showed that all the copper–amine complexes catalysed lignin depolymerisation more efficiently in ionic liquids than in DMF. Among the seven types of ligands, copper complexes with two types of ligands (*E*)-*N*-(pyridin-2-ylmethylene)aniline and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline depolymerised the lignin more efficiently than the others. These two copper complexes with the N-based ligand were further studied to determine the most efficient conditions for the depolymerisation of the lignin. The most effective depolymerisation by conditions involved treatment at 180 °C for 12 h in [emim][ABS]. Cyclic voltammetric studies were carried out to investigate the reversible potential associated with the copper centers of their complexes with these N-based ligands. The results suggest that two types of ligands have more positive reversible potentials than those of other copper complexes.

Introduction

Lignin exists in the second cell wall of plants, and is well known as one of the most abundant renewable materials from the paper and pulp industry.[1–3] Lignin is also considered as a material with high commercial potential for producing fine chemicals. This biopolymer contains three types of primary phenylpropane units called monolignols and these creates fundamental units that combine in different ways to give various forms of the complex natural polymer known as lignin.[4–6] During the past few decades, lignin depolymerisation has become a research hotspot with many considerable methods reported, for example, depolymerisation using oxidation, reduction, biological methods and electrochemical methods.[7] The main challenge of this research is to selectively cleave different bonds in lignin in order to depolymerise lignin into fine chemicals with high value.[7]

The depolymerisation of lignin with several metallic catalysts has also been reported. However, there are drawbacks in most existing depolymerisation methods using metallic catalysts such as the need for high pressure and high temperature.[6] Pepper *et al.* investigated the catalytic ability of a number of catalysts, such as Raney® Ni, Pd/C, Rh/C and Ru/C, in the hydrogenation of softwood lignin to produce monomeric products (dihydroconiferyl alcohol), however, this method required a pressure of 3.4 MPa with a temperature of 468 K.[8] Koyama reported the hydrocracking of lignin model compounds by using Fe_2O_3–S, Fe_2O_3/Al_2O_2–S, and NiO–MoO_3–Al_2O_3 between 613 and 723 K.[9]

Some metal complexes with N-based ligands have been used for lignin oxidation and depolymerisation under mild conditions.[7] Metalloporphyrin complexes, such as trisodium tetra-4-sulfonatophthalocyanine iron(III), have been investigated to oxidize lignin.[10,11] Zucca *et al.* also utilized immobilized Fe(III)–5,10,15,20-tetrakis(pentafluorophenyl)porphyrin on a pyridyl-functionalized poly(vinyl alcohol), to oxidize lignin model compounds at room temperature.[12] The drawbacks of these metalloporphyrins are that these catalyst complexes normally have a complicated structure and lack recyclability and stability.[7] A metallosalen catalyst has also been used as a novel lignin oxidation and depolymerisation catalyst.[13] Drago *et al.* reported that Co(salen) complexes oxidised lignin model compounds rapidly with the presence of molecular oxygen to produce vanillin.[14]

Copper complexes with N-based ligands are well known oxidation catalysts for 2,6-dimethylphenol (DMP) to form an engineering thermoplastic poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and also known as catalysts to depolymerise PPO. For example, PPO was first developed by using a copper–pyridine complex and its derivatives by the oxidative polymerisation of DMP.[15,16] Some enzyme mimic complexes with N-based ligands are also applied for PPO polymerisation. Higashimura *et al.* studied the oxidative polymerisation of DMP catalysed by

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(1,4,7-triisopropyl-1,4,7-triazacyclononane)copper(II) to produce PPO.[17] We have studied the depolymerisation of PPO involving the redistribution mechanism to produce oligomeric PPO using a copper–pyridine complex.[18] This depolymerisation produced $M_n = 4.9 \times 10^2$ oligomeric PPO from PPO $M_n = 1.0 \times 10^4$.

We also reported the PPO depolymerisation mechanism as follows.[18] Under the oxidative conditions catalysed by copper complexes, two kinds of radicals (monomeric phenoxyl radical and polymeric phenoxyl radical) were generated. The redistribution was induced *via* a quinone ketal intermediate after the phenoxyl radical of PPO is attacked by the monomeric phenoxyl radical. Further study also showed that PPO can be depolymerised by copper–EDTA involving the redistribution mechanism in the ionic liquid ([emim][ABS]).[19]

Our group has applied this depolymerisation and demonstrated that lignin can be successfully depolymerised using copper–EDTA as a catalyst in both water and in ionic liquids (1-ethyl-3-methylimidazolium xylenesulfonate [emim][ABS] and 1-butyl-3-methylimidazolium methyl-sulfate [bmim][$MeSO_4$]), involving the redistribution mechanism under mild conditions (80 °C, atmospheric pressure).[20]

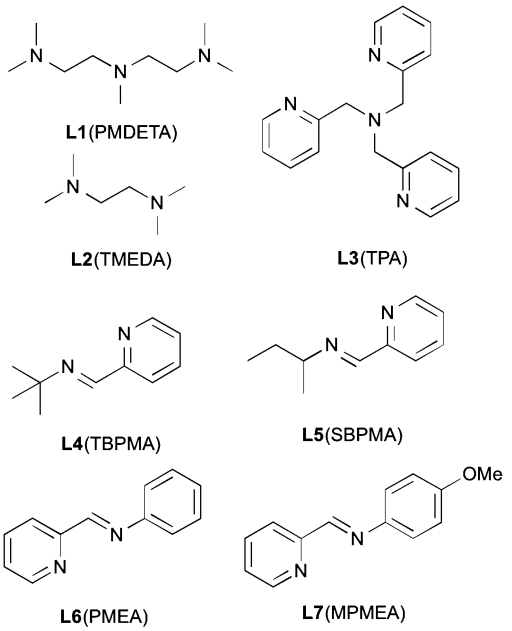
Ionic liquids, because of their non-flammability, recyclability and non-volatility, have been widely used as solvents for the organic reactions.[21,22] Binder *et al.* demonstrated that ionic liquids are excellent solvents for processing woody biomass and lignin.[23] Stärk *et al.* presented a method for oxidative depolymerisation of lignin in ionic liquid (1-ethyl-3-methylinidazolium trifluoromethanesulfonate [emim][CF_3SO_3]) using $Mn(NO_3)_2$ as a catalyst.[24] In their study, this catalyst system was shown to be an efficient reaction system as the conversion of lignin reached 66.3% after reacting for 24 h at a temperature of 100 °C, however a pressure of 84×10^5 Pa air was required. Cox *et al.* reported using an acidic ionic liquid, 1-hexyl-3-methylimidazolium chloride (HMIMCl), as both the solvent and the catalyst for lignin depolymerisation.[25] In this method, lignin, extracted from oak wood, was depolymerised in HMIMCl and proceeds by a hydrolysis reaction with alkyl–aryl ether bond cleavage.

In this study, we have investigated several types of copper complexes with an N-based ligand for lignin depolymerisation involving the redistribution mechanism in two solvents DMF and an ionic liquid ([emim][ABS]). The N-based ligands shown below (Scheme 1) have been used to form copper complexes with copper halides and used as catalysts.

Some of these ligands, such as *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (**L1**), *N*,*N*,*N*′,*N*′-tetramethylenediamine (**L2**), and tris(2-pyridylmethyl)amine (**L3**), are commercially available and others are easy to synthesize and relatively stable. All these ligands in this study have been proved to coordinate with copper to form copper complexes.[26–33]

Initial screening studies with different copper complexes with N-based ligands in DMF and IL were carried out to select the most efficient N-based ligands for lignin depolymerisation.

On the basis of these results, ligands (*E*)-*N*-(pyridin-2-ylmethylene)aniline (**L6**) and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)-aniline (**L7**) were selected for further study. The novelty of this research lies in using several types of copper complexes with the N-based ligand as catalysts for lignin depolymerisation in organic solvents and an ionic liquid.



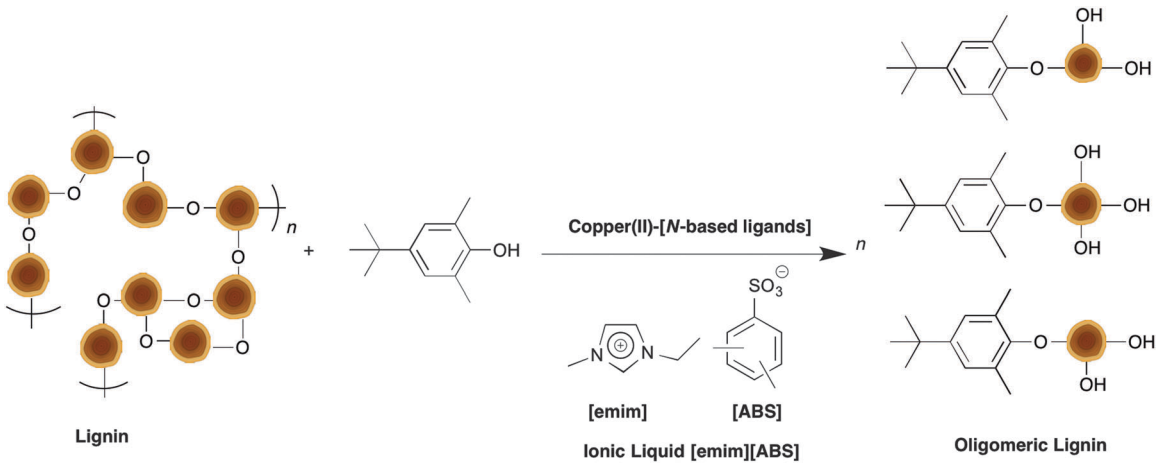
Scheme 1 N-Based ligands: **L1**: *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA); **L2**: *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMEDA); **L3**: tris(2-pyridylmethyl)amine (TPA); **L4**: (*E*)-*N*-*tert*-butyl-1-(pyridin-2-yl)-methanimine (TBPMA); **L5**: (*E*)-*N*-*sec*-butyl-1-(pyridin-2-yl)methanimine (SBPMA); **L6**: (*E*)-*N*-(pyridin-2-ylmethylene)aniline (PMEA); **L7**: (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline (MPMEA).

Results and discussion

In this study, organosolv lignin was selected as a lignin for depolymerisation research. This organosolv lignin was isolated by removing the low molecular weight fraction by stirring in methanol for 2 h to dissolve the low molecular weight fraction as we previously reported.[20] The methanol insoluble fraction, which was high molecular weight lignin, was filtered and dried. This part of lignin was defined as M-lignin used for all the depolymerisation reactions. The molecular weight and polydispersity of M-lignin were measured by GPC to give $M_n = 12\,500$ and $Đ$ (M_w/M_n) = 1.86.

Screening depolymerisation of lignin in DMF and [emim][ABS]

Initial attempts to depolymerise lignin were conducted in separate experiments, using [emim][ABS] and DMF with the seven N-based ligands (Scheme 2). DMF was chosen to enable solubilisation of the N-based ligands, monomer (TBDMP) and M-lignin. It was thought that the solubility enhanced the depolymerisation efficiency by making the solution of lignin, monomer and catalysts homogeneous. Screening reactions were carried out in DMF and [emim][ABS] at the temperatures of 120 °C and 180 °C, respectively. All the screening reactions were carried out in these two solvents using 4-*tert*-butyl-2,6-dimethyl-phenol (TBDMP) as an additive and Cu(I)/N-based ligands as catalysts under oxygen flow. These reactions were performed for 6 hours



Scheme 2 Schematic representation of the proposed lignin depolymerisation mechanism.

based on the result of previous research for lignin depolymerisation in water with copper–EDTA.[20] TBDMP was selected as a phenol additive under the conditions as it could not polymerise due to the *tert*-butyl group on the *para*-position in the redistribution process.

Table 1 summarizes the molecular weight and polydispersity changes of M-lignin under the 6 h depolymerisation reaction conditions using copper complexes with different N-based ligands.

Samples of every reaction were collected and the molecular weight of each sample was measured by GPC (Fig. 1 and 2). As for the initial samples, the high molecular weight peak, of which the retention time is around 14 min, is M-lignin and the low molecular weight peak with the retention time of 16.8 min is TBDMP.

After 6 h, the depolymerisation of M-lignin was observed as the molecular weight of all samples decreased (Table 1). The M_n value became smaller than the initial M_n of the M-lignin (M_n = 12 500), and the polydispersity became larger than $Đ$ of the initial M-lignin (M_w/M_n = 1.86). This indicated that all these copper complexes with N-based ligands could catalyse lignin depolymerisation with TBDMP involving the redistribution mechanism. Moreover, the GPC data (Table 1) showed that the M_n value of all the depolymerised lignin with different copper complexes is smaller for reactions conducted in [emim][ABS], compared with those conducted in DMF. This demonstrated that lignin could be depolymerised more efficiently in [emim][ABS] with all these different copper–amine complexes compared with DMF. The reason could be that the ligands were more readily soluble in [emim][ABS] other than in DMF.

Table 1 The M_n and $Đ$ values of depolymerised samples from screening reaction

	In DMF		In [emim][ABS]	
Ligands	M_n (g mol^{-1})	$Đ$ (M_w/M_n)	M_n (g mol^{-1})	$Đ$ (M_w/M_n)
L1	11 500	3.6	6000	2.5
L2	11 300	3.4	5000	2.7
L3	7000	3.0	5000	3.2
L4	7100	5.9	5700	2.4
L5	8400	3.4	6200	2.5
L6	5600	3.6	2500	3.2
L7	5200	2.6	2500	2.4

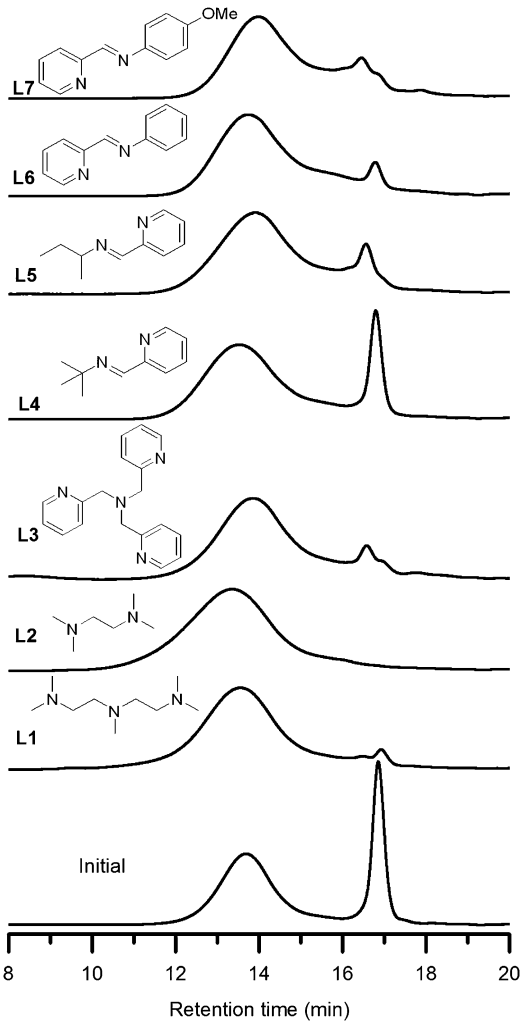


Fig. 1 GPC chromatograms of depolymerisation of M-lignin in DMF with copper complexes with different N-based ligands.

When comparing all the depolymerisation reactions, the M_n and $Đ$ (M_w/M_n) of depolymerised lignin were different to each other. This demonstrated that copper complexes with different

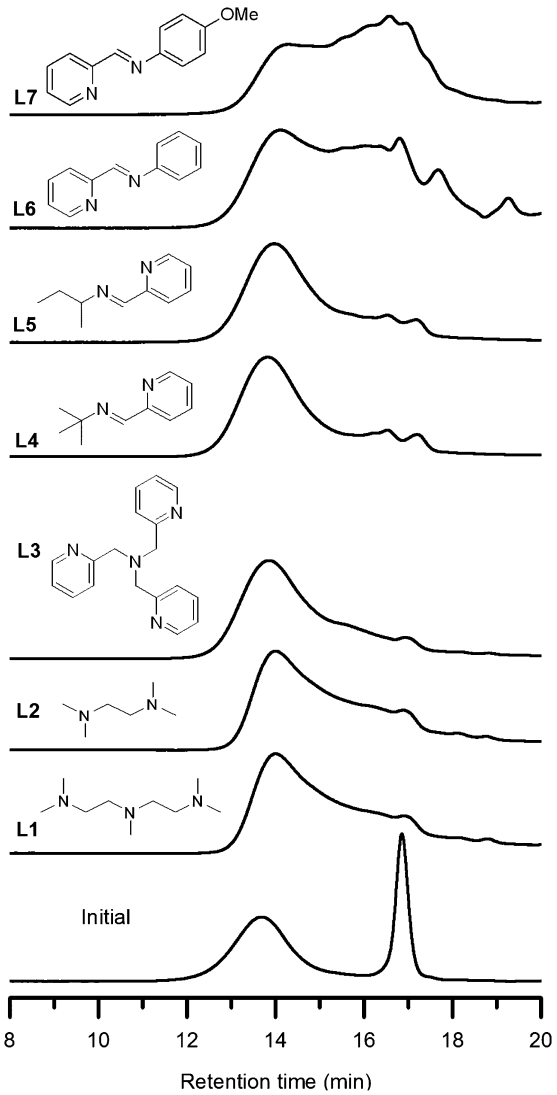


Fig. 2 GPC chromatograms of depolymerisation of M-lignin in [emim][ABS] with copper complexes with different N-based ligands.

N-based ligands showed different catalytic abilities for depolymerisation. Among all these ligands, the molecular weight of depolymerised lignin from **L6** and **L7** was lower than that of other ligands in these screening reactions and **L6** and **L7** were considered to be more efficient than other ligands.

From the results from the above screening reactions, these two N-based ligands were selected and several depolymerisation reactions were carried out in [emim][ABS] with **L6** and **L7** with different reaction times in order to find the optimum lignin depolymerisation conditions using these two N-based ligands and also to investigate the difference between these two ligands as described below.

Depolymerisation of lignin in [emim][ABS] with L6 and L7

Two extended reactions were carried out with different reaction times in [emim][ABS] with the copper complexes, **L6** and **L7**.

These two reactions were undertaken over 48 h with samples collected at the following reaction times: 3 h, 6 h, 9 h, 12 h, 18 h, 24 h, 36 h, and 48 h. Samples from the different reaction times were subjected to GPC to give M_n and $Đ$ (M_w/M_n). The GPC chromatograms of depolymerised lignin are shown below (Fig. 3).

Within 3 h of reaction time, the peaks of M-lignin and TBDMP showed a molecular weight decrease from about 12 000 to about 10 000 and the $Đ$ increased from 1.8 to 1.9. After 6 h, the average molecular weight of M-lignin was reduced to M_n = 3900, with a higher $Đ$ (M_w/M_n = 2.09).

The depolymerisation reaction was continued for 12 h, and the average molecular weight decreased to M_n = 2000 with a $Đ$ value of M_w/M_n = 2.63. The depolymerisation was continued for 48 h but the molecular weight remained at about 2000 after 12 h, which indicated that the best reaction time for depolymerisation with **L6** was up to 12 h (Fig. 4).

This result showed that it was difficult to completely depolymerise lignin even using TBDMP as an additive, one reason being that the redistribution mechanism involved is an equilibrium reaction[34–36] and the low molecular weight part of depolymerised lignin can be repolymerised simultaneously with the depolymerisation.

Further depolymerisation of lignin using the copper–**L7** complex with TBDMP was carried out. All the samples of depolymerised lignin obtained from different reaction times were analysed by GPC to determine the M_n and $Đ$ (Fig. 5). Within 3 h of reaction time, the average molecular weight of lignin decreased from M_n = 12 500 to M_n = 4500 with $Đ$ increasing from M_w/M_n = 1.86 to M_w/M_n = 3.08. This indicated that depolymerisation of the mixture with the copper–**L7** complex resulted in a significant molecular weight decrease within 3 h of reaction time. After 6 h, the average molecular weight was reduced to M_n = 2700 with $Đ$ (M_w/M_n) = 2.33. The depolymerisation reaction was carried out for 48 h but there was no significant decrease in molecular weight after 9 h, with the molecular weight remaining around M_n = 2000 (Fig. 6). This reaction showed a similar result to the

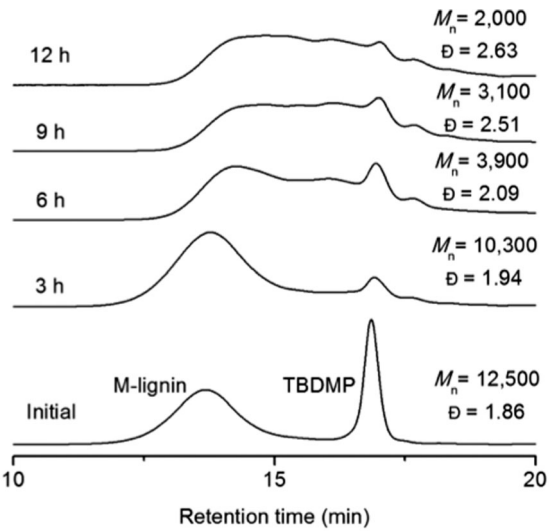


Fig. 3 GPC chromatograms of depolymerised M-lignin in [emim][ABS] using copper–**L6** with different reaction times.

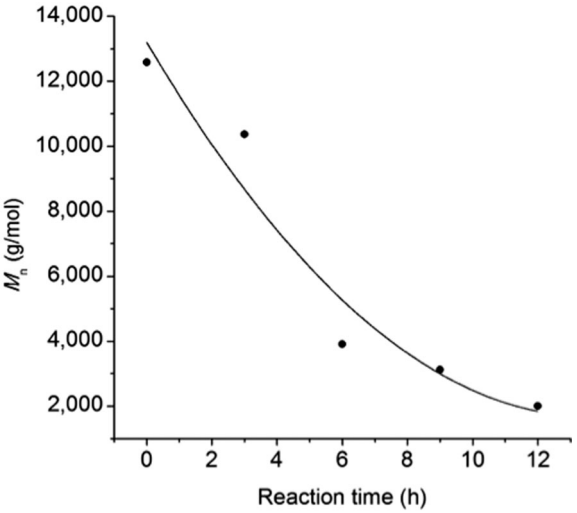


Fig. 4 M_n of samples with different reaction times of lignin depolymerisation with copper–**L6**.

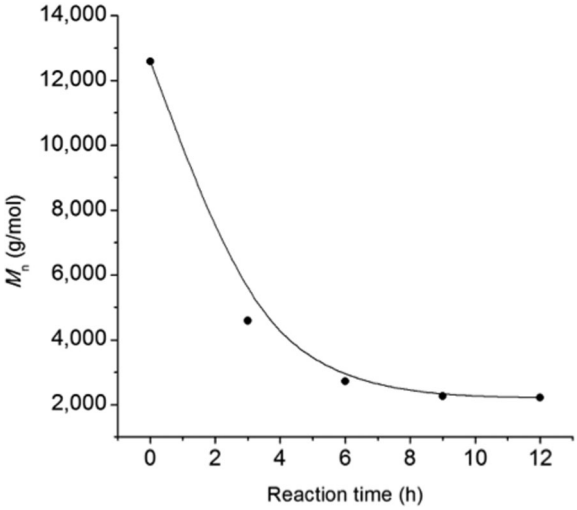


Fig. 6 M_n of samples with different reaction times of lignin depolymerisation with copper–**L7**.

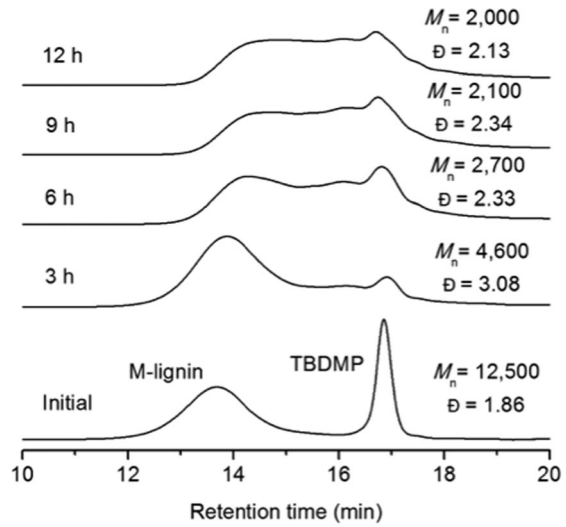


Fig. 5 GPC chromatograms of depolymerisation of M-lignin in [emim][ABS] using copper–**L7** with different reaction times.

depolymerisation using the copper–**L6** complex. The M-lignin was not completely depolymerised by the copper–**L7** complex as the low molecular weight oligomers can repolymerise concurrently with depolymerisation. Based on the results of these depolymerisation reactions, the best reaction time for **L7** was found to be 9 h.

In summary, the GPC chromatogram of the lignin depolymerisation in Fig. 3 shows that lignin could be depolymerised into oligomers with an average molecular weight of about M_n = 2000 in [emim][ABS] using copper–**L6** and copper–**L7** complexes within 12 h and 9 h, respectively. Comparing the results of the depolymerisation catalysed by the copper–**L6** complex with those of the copper–**L7** complex, the copper–**L7** complex could catalyse lignin depolymerisation more efficiently. These copper complexes were used as catalysts to generate radicals on phenols to perform the depolymerisation process. The hypothesis for this result is that the reversible potential of the copper–**L7** complex could be more positive than that of the copper–**L6** complex. The reversible potentials of different copper complexes are known to change due to the structure of the coordinated ligand and different N-based ligands in copper complexes can affect the radical generation rate that can affect the lignin depolymerisation rate.[36–38]

The yields of depolymerised products using copper–**L6** and copper–**L7** were both *ca.* 90%. The ^{1}H NMR spectrum (ESI,† Fig. S3) of separated depolymerized lignin was analysed and showed peaks in the range of 6.2 to 9.0 ppm (δ values) resulting from the aromatic protons in lignin units and peaks at 1.3 ppm from the *tert*-butyl group resulting from TBDMP. However, there were also several unidentified peaks in the ^{1}H NMR spectrum because of the nature of the lignin structure and we were not able to identify or isolate individual depolymerized products.

Recovery and reusability of [emim][ABS]

The recovery and reusability of [emim][ABS] have been studied. First, the method reported by Tan *et al.* was followed to recover the ionic liquid.[39] Next, the ionic liquid was analysed by ^{1}H NMR to confirm its original structure remaining after the reaction (ESI,† Fig. S1 and S2). As a result, *ca.* 75% of the ionic liquid was recovered after each reaction and was able to reuse for the depolymerisation reactions. In addition, catalysts were not able to recover and reuse.

Electrochemical measurements

In the depolymerisation reactions, Cu(I)Cl was added to coordinate with different ligands to form copper complexes, in which the Cu^+ center was then oxidized to Cu^{2+} under air flow. Cyclic voltammetric measurements were carried out to determine the reversible potentials of the copper centers of the copper complexes with different N-based ligands. This part of work aimed to study if the differences in the reversible potentials of copper complexes could correlate with the different depolymerising ability of copper complexes with each ligand in [emim][ABS].

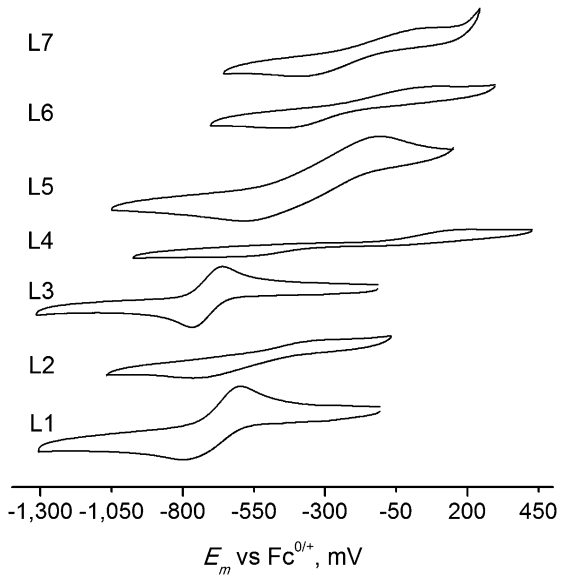


Fig. 7 Cyclic voltammograms of copper complexes with different ligands.

Table 2 E_m of copper complexes with different ligands *vs.* $Fc^{0/+}$

Ligands	L1	L2	L3	L4	L5	L6	L7
E_m/mV	−695	−523	−760	−210	−320	−193	−152

The $Cu^{+/2+}$ redox processes associated with the copper complexes are shown in Fig. 7. At a more negative potential region, the reduction of Cu^+ to metallic Cu is evident since a characteristic copper stripping peak was observed in the reverse anodic sweep (results not shown). In addition, the ligands without copper were also analysed by cyclic voltammetry (ESI,† Fig. S4). There were no detected signals or visible reductive or oxidative potential peaks from the cyclic voltammetry of all these ligands from −800 mV to −100 mV.

The E_m (reversible potential) values (taken as the average of the reduction and oxidation peak potentials) of copper complexes with different ligands *vs.* $Fc^{0/+}$ are shown in Table 2. The copper centers of different copper complexes with different N-based ligands show different E_m values. The E_m values (Table 2) of copper–**L6** and copper–**L7** are more positive than those with other ligands, indicating that they are stronger oxidizing agents than other copper complexes coordinating with other ligands. Based on the depolymerisation mechanism, this result could explain why copper–**L6** and copper–**L7** more efficiently depolymerise lignin compared to the other ligands. The reversible potential of copper–**L7** is more positive than that of copper–**L6**, which is consistent with the fact that copper–**L7** is the best copper complex for lignin depolymerisation involving the redistribution mechanism among the seven ligands.

Conclusions

Seven N-based ligands were found to coordinate with copper to form copper complexes and were firstly used to catalyse lignin depolymerisation in DMF and the ionic liquid, [emim][ABS], as solvents. Among all these seven ligands, both **L6** and **L7** were the most efficient ligands to catalyse lignin depolymerisation in [emim][ABS]. Lignin can be depolymerised into oligomers with TBDMP under oxidative conditions involving the redistribution mechanism with the average molecular weight M_n = 2000 in [emim][ABS] using copper–**L6** and copper–**L7** complexes within 12 h and 9 h, respectively. Cyclic voltammetric results showed that copper–**L6** and copper–**L7** have more positive reversible potentials than other copper complexes and this could be the reason for the high depolymerisation efficiency of these two ligands compared to the other five ligands.

Experimental

Materials

Organosolv lignin, DMP, Cu(I)Cl, sodium dodecyl sulfate (SDS), 1-ethyl-3-methylimidazolium chloride, PMDETA, TMEDA, TPA, dichloromethane (DCM), 2-pyridinecarboxaldehyde, aniline, and *p*-anisidine were purchased from Sigma-Aldrich. Hydrochloric acid (32%) was obtained from Ajax Finechem. High purity oxygen purchased from Air Liquid, Australia, was used for experiments that required oxygen gas. Dimethylformamide (DMF), for gel permeation chromatography (GPC) analysis, chloroform ($CDCl_3$), deuterium oxide (D_2O), and methanol were purchased from Merck. All reagents were used as purchased from the supplier without any further purification.

Measurements

^1H NMR spectra were recorded on a Bruker DRK-400 spectrometer operating at 400 MHz as solutions in $CDCl_3$ and D_2O. The molecular weight of isolated lignin and depolymerised samples was measured by GPC performed on a Tosoh EcosHLC-8320 Gel Permeation Chromatograph equipped with both refractive index (RI) and ultraviolet (UV) detectors (UV detection, λ = 280 nm) using Tosoh alpha 4000 and 2000 columns. DMF (with 10 mM LiBr) was used as the mobile phase with a flow rate of 1.0 mL min^{-1}. A UV detector in GPC chromatograms set at 280 nm was used to analyze all the depolymerised samples and isolated lignin. Calibration curves were obtained using polystyrene standards.

Syntheses

4-*tert*-Butyl-2,6-dimethylphenol (TBDMP). TBDMP was prepared from DMP by following the reported literature procedure.[40] ν_{max} (KBr)/cm^{-1} 3403 (O–H), 2917 (C–H), 1617 (C═C). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.03 (s, 2H, ArH), 2.28 (s, 6H, CH_3), 1.32 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 16.3, 31.7, 34.0, 122.5, 125.7, 143.0, 150.0. MS (+ESI); *m*/*z*; 178.14 [M+].

Ionic liquid 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS]). [emim][ABS] was prepared using the reported procedure.[39] ν_{max} (KBr)/cm^{-1} 3053, 2964, 2924, 2855, 1654, 1465, 1327, 969, 771. ^1H NMR (400 MHz, D_2O) δ_H 8.55–8.45 (s, [emim] ArH), 8.21–8.19 (s, [ABS] ArH), 7.80–6.90 (m, [ABS]

ArH), 4.15–4.00 (q, [emim] $-CH_2-CH_3$), 3.73 (s, [emim] $-CH_3$), 3.00–2.75 (m, [ABS] $-CH_3-CH-CH_3$), 2.65–2.55 (q, [ABS] $-CH_2-CH_3$), 2.53–2.40 (m, [ABS] CH_3–Ar), 2.28 (s, [ABS] $-CH_3$–Ar), 2.24–2.12 (m, [ABS] $-CH_3$–Ar), 1.45–1.25 (t, [C_2mim] $-CH_2-CH_3$), 1.20–1.11 (m, [ABS] $-CH_2$ $-CH_3$, $CH_3-CH-CH_3$). ^{13}C NMR (100 MHz, D_2O): δ_C 139.40, 137.21, 130.01, 128.24, 122.81, 123.04, 42.01, 27.22, 21.3 *m*/*z* (+ESI) 282.1.

(*E*)-*N*-*sec*-Butyl-1-(pyridin-2-yl)methanimine (L5). The *N*-alkyl-(2-pyridyl)methanimine ligand was synthesized using the reported procedure.[41] B.p. 74 °C at 5.0 Torr. ν_{max} (KBr)/cm^{-1} 1630, 1571, 1454. ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.50 (d, 4.56 Hz, 1H), 8.24 (s, 1H), 7.86 (d, 7.68 Hz, 1H), 7.57 (t, 7.36 Hz, 1H), 7.14 (dd, 4.92, 6.32 Hz, 1H), 3.17 (sext, 6.32 Hz, 1H), 1.50 (m, 7.72 Hz, 2H), 1.13 (d, 6.28 Hz, 3H), 0.72 (t, 7.36 Hz. 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 161.60, 154.49, 149.16, 136.29, 124.38, 120.96, 69.36, 29.27, 22.50, 10.90. *m*/*z* (ESI) 163.1.

(*E*)-*N*-*tert*-Butyl-1-(pyridin-2-yl)methanimine (L4). This compound was obtained as a yellow liquid (322.2 mg, 85%) following the reported procedure.[42] ν_{max} (KBr)/cm^{-1} 1637, 1569, 1451. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.63(d, 4.0 Hz, 1H), 8.36 (s, 1H), 8.02 (d, 7.9 Hz, 1H), 7.73 (t, 7.7 Hz, 1H), 7.29 (ddd, 7.5, 4.9, 1.2 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C 157.04, 156.69, 150.01, 137.05, 125.26, 120.74, 57.94, 10.8. *m*/*z* (ESI) 163.1.

General procedure[41] for (*E*)-*N*-(pyridin-2-ylmethylene)aniline (L6) and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline (L7). To a solution of pyridine carboxaldehyde (1.2 equiv.) in dichloromethane DCM were added dry $MgSO_4$ (5 g, 41.5 mmol) followed by N-based ligands (1.0 equiv.). The reaction mixture was stirred at room temperature for 24 hours, and filtered and the solvent was removed *in vacuo*. Ligands were then purified by distillation at reduced pressure.

(*E*)-*N*-(Pyridin-2-ylmethylene)aniline (L6). 2-Pyridinecarboxyaldehyde (0.32 g, 3.0 mmol, 1.2 equiv.), aniline (0.23 g, 2.5 mmol, 1.0 equiv.) and dichloromethane (20 mL) were subjected to the general procedure[41] for the synthesis of ligands. Purification by vacuum distillation resulted in dark orange oil (0.45 g, 2.5 mmol, 99%); ν_{max} (neat, cm^{-1}) 3053, 1627, 1591, 1485; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.72 (1H, d, 4.8 Hz), 8.61 (1H, s), 8.21 (1H, d, 7.7 Hz), 7.82 (1H, td, 7.7, 1.6 Hz), 7.45–7.40 (2H, m), 7.37 (1H, ddd, 7.7, 4.8, 1.0 Hz), 7.32–7.24 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 160.7, 154.6, 151.0, 149.7, 136.7, 129.3, 126.8, 125.2, 121.9, 121.1; *m*/*z* (ESI) 183.1.

(*E*)-4-Methoxy-*N*-(pyridin-2-ylmethylene)aniline (L7). 2-Pyridinecarboxyaldehyde (0.32 g, 3.0 mmol, 1.2 equiv.) and *p*-anisidine (0.31 g, 2.5 mmol, 1.0 equiv.) in dichloromethane (20 mL) were subjected to the general procedure[41] for the synthesis of ligands. Purification by vacuum distillation resulted in dark orange oil (0.45 g, 2.12 mmol, 86%); ν_{max} (neat, cm^{-1}) 3051, 2834, 1624, 1579, 1503, 1242; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.62 (1H, d, 4.7 Hz), 8.55 (1H, s), 8.10 (1H, d, 7.8 Hz), 7.71 (1H, td, 7.8, 1.6 Hz), 7.31–7.21 (3H, m), 6.94–6.81 (2H, m), 3.76 (3H, s, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 158.3, 157.6, 154.3, 149.0, 143.1, 136.0, 124.2, 122.1, 121.0, 113.8, 54.9; *m*/*z* (ESI) 213.1.

Isolation of the high molecular weight fraction of lignin using a solubility method

5.98 g of dried organosolv lignin was added to methanol (600 mL) and the suspension was stirred (500 rpm) using a magnetic stirrer for 2 h at room temperature (23 °C), and then filtered through a pre-dried (105 °C overnight) weighed cellulose filter paper. The solid lignin residue together with the filter paper was then oven-dried overnight at 105 °C. After cooling in a desiccator, the dried solid methanol-insoluble residue (M-lignin) was weighed and collected. Evaporation of solvent from the filtrate under vacuum afforded a soluble fraction. The percentage of the insoluble material was calculated based on the dry weight. The molecular weight distribution of the methanol-insoluble fraction of M-lignin was determined by GPC.

Depolymerisation

Screening depolymerisation of lignin in DMF. A typical lignin depolymerisation procedure is summarized as follows: for each reaction, lignin (0.31 g), TBDMP (0.45 g, 2.5 mmol), Cu(I)Cl (0.025 g, 0.25 mmol) and pyridine/ligands (2 mL, 0.25 mmol) were added to DMF (20 mL). The reaction mixture was stirred under oxygen at 120 °C and samples of the reaction mixture (5 mL) were withdrawn at the following time intervals: 1 h, 3 h and 6 h. At the end of 6 h, the reaction was stopped by dropwise addition of 1 M HCl until pH 2 was reached, causing precipitation of the depolymerised product. The suspension was centrifuged several times with distilled water until the pH of the supernatant reached 7. The precipitate was then dried under vacuum at room temperature. The initial acidified supernatant was then extracted with 3 volumes of dichloromethane and dichloromethane was removed under vacuum to give a residue. The molecular weight of all of the products obtained in this way was analysed by GPC. A control reaction was carried out without TBDMP (monomer) or catalyst (Cu(I)-Cl/ligands) under the same conditions in order to compare the results.

Screening depolymerisation of lignin in 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS]). M-lignin (0.005 g), TBDMP (7 mg, 4×10^{-2} mmol), $CuCl_2 \cdot 2H_2O$ (0.7 mg, 4×10^{-3} mmol) and ligands (4×10^{-3} mmol) were added to [emim][ABS] (0.5 g). The reaction mixture was stirred under oxygen at 180 °C for 6 h. At the end of 6 h, the pH of the mixture was adjusted to 2 by dropwise addition of 1 M HCl. The resulting precipitate was collected and washed by centrifugation with distilled water until the pH of the supernatant reached 7. The washed precipitate was dried under vacuum at room temperature. The molecular weight distributions of the depolymerised products were characterized by GPC. A control reaction was carried out in the absence of TBDMP and the catalyst (Cu(II)Cl/ligands) as described above in order to compare the results.

Lignin depolymerisation in 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS]). M-lignin (0.04 g), TBDMP (0.056 g, 0.33 mmol), $CuCl_2 \cdot 2H_2O$ (0.0033 g, 0.033 mmol) and ligands (0.66 mmol) were added to [emim][ABS] (4 g). The reaction mixture was stirred under oxygen at 180 °C for 48 h. And samples

were taken from the mixture at the following reaction time: 3 h, 6 h, 9 h, 12 h, 18 h, 24 h, 36 h and 48 h. After every sample had been taken from the mixture, we followed the previous screening procedure for purification and characterisation.

Recovery of [emim][ABS]. After each depolymerisation reaction, the mixture was acidified with 1 M HCl and centrifuged with distilled water to precipitate and remove depolymerised lignin. The acidic aqueous filtrate containing ionic liquid, copper chloride, and hydrochloric acid was neutralised using 1 M NaOH. Next, the mixture was left under high vacuum at the temperature of 70 °C overnight to remove water. Acetonitrile (100 mL) was added to the mixture to dissolve only the ionic liquid and to remove all the insoluble residue (copper chloride and sodium chloride) by filtration. The ionic liquid was recovered by removing acetonitrile at 70 °C under high vacuum. The recovered ionic liquid was then analysed by ^{1}H NMR to confirm its structure.

Electrochemical measurement. Electrochemical experiments were carried out at the temperature of 23 ± 2 °C in a standard three-electrode cell configuration using a Bioanalytical Systems (BAS West Lafayette, Indiana) Model 100B potentiostat at a scan rate of 100 mV s^{-1}. A glassy carbon disc electrode (1 mm diameter, eDAQ) was used as the working electrode. A platinum wire was employed as the reference electrode and another platinum wire as the counter electrode. The reference potential was calibrated against that of the Fc/Fc^+ (Fc = ferrocene) redox couple as an internal reference from measurements made on the oxidation of 1 mM Fc present in the same solution.[43] The voltammetric investigation was carried out in 0.5 mL of [emim][ABS] in the presence of 0.0165 mmol Cu(I)Cl, and 0.33 mmol ligands. Prior to voltammetric experiments, the glassy carbon electrode was polished with 0.3 μm alumina slurry on a clean polishing cloth (Buehler, USA), rinsed with deionized water, washed with acetone and finally dried with nitrogen gas.

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Notes and references

1 F. S. Chakar and A. J. Ragauskas, *Ind. Crops Prod.*, 2004, **20**, 131–141.
2 M. P. Pandey and C. S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29–41.
3 J. H. Grabber, *Crop Sci.*, 2005, **45**, 820–831.
4 J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P. F. Schatz, J. M. Marita, R. D. Hatfield, S. A. Ralph and J. H. Christensen, *Phytochem. Rev.*, 2004, **3**, 29–60.
5 D. S. Argyropoulos, in *Biotechnology in the Pulp and Paper Industry*, ed. Karl-Erik L. Eriksson, Springer, Heidelberg, 1st edn, 1997, ch. 3, pp. 127–158.
6 P. Azadi, O. R. Inderwildi, R. Farnood and D. A. Kin, *Renewable Sustainable Energy Rev.*, 2012, **21**, 506–523.
7 J. Zakzeski, P. C. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
8 J. M. Pepper and Y. W. Lee, *Can. J. Chem.*, 1969, **47**, 723–727.
9 M. Koyama, *Bioresour. Technol.*, 1993, **44**, 209–215.
10 N. A. Stephenson and A. T. Bell, *J. Mol. Catal. A: Chem.*, 2007, **275**, 54–62.
11 C.-M. Che and J.-S. Huang, *Chem. Commun.*, 2009, 3996–4015.
12 P. Zucca, F. Sollai, A. Garau, A. Rescigno and E. Sanjust, *J. Mol. Catal. A: Chem.*, 2009, **306**, 89–96.
13 K. C. Gupta, A. K. Sutar and C.-C. Lin, *Coord. Chem. Rev.*, 2009, **253**, 1926–1946.
14 R. Drago, B. Corden and C. Barnes, *J. Am. Chem. Soc.*, 1986, **108**, 2453–2454.
15 A. Hay, H. Blanchard, G. Endres and J. Eustance, *J. Am. Chem. Soc.*, 1959, **81**, 6335–6336.
16 W. Brackman and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, 1955, **74**, 1021–1039.
17 H. Higashimura, K. Fujisawa, M. Kubota and S. Kobayashi, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1955–1962.
18 K. Saito, T. Masuyama, K. Oyaizu and H. Nishide, *Chem. – Eur. J.*, 2003, **9**, 4240–4246.
19 S. Nanayakkara, A. F. Patti and K. Saito, *Aust. J. Chem.*, 2013, **66**, 60–66.
20 S. Nanayakkara, A. F. Patti and K. Saito, *Green Chem.*, 2014, **16**, 1897–1903.
21 Z. C. Zhang, *Adv. Catal.*, 2006, **49**, 153–237.
22 H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal., A*, 2010, **373**, 1–56.
23 J. B. Binder, M. J. Gray, J. F. White, Z. C. Zhang and J. E. Holladay, *Biomass Bioenergy*, 2009, **33**, 1122–1130.
24 K. Stärk, N. Taccardi, A. Bösmann and P. Wasserscheid, *ChemSusChem*, 2010, **3**, 719–723.
25 B. J. Cox and J. G. Ekerdt, *Bioresour. Technol.*, 2013, **134**, 59–65.
26 A. J. Clark, A. E. Collis, D. J. Fox, L. L. Halliwell, N. James, R. K. O'Reilly, H. Parekh, A. Ross, A. B. Sellars and H. Willcock, *J. Org. Chem.*, 2012, **77**, 6778–6788.
27 D. M. Haddleton, D. J. Duncalf, D. Kukulj, M. C. Crossman, S. G. Jackson, S. A. Bon, A. J. Clark and A. J. Shooter, *Eur. J. Inorg. Chem.*, 1998, 1799–1806.
28 A. J. Clark, D. J. Duncalf, R. P. Filik, D. M. Haddleton, G. H. Thomas and H. Wongtap, *Tetrahedron Lett.*, 1999, **40**, 3807–3810.
29 A. J. Clark, G. M. Battle, A. M. Heming, D. M. Haddleton and A. Bridge, *Tetrahedron Lett.*, 2001, **42**, 2003–2005.
30 D. K. Seth and S. Bhattacharya, *Polyhedron*, 2011, **30**, 2438–2443.
31 S. Dehghanpour, N. Bouslimani, R. Welter and F. Mojahed, *Polyhedron*, 2007, **26**, 154–162.
32 A. J. Clark, *Chem. Soc. Rev.*, 2002, **31**, 1–11.
33 T.-H. Huang and M.-H. Zhang, *Inorg. Chim. Acta*, 2014, **410**, 150–155.
34 K. Saito, N. Kuwashiro and H. Nishide, *Polymer*, 2006, **47**, 6581–6584.
35 K. Saito, T. Masuyama and H. Nishide, *Green Chem.*, 2003, **5**, 535–538.

36 R. Bailey, S. Kozak, T. Michelsen and W. Mills, *Coord. Chem. Rev.*, 1971, **6**, 407–445.
37 E. T. Adman, *Adv. Protein Chem.*, 1991, **42**, 145–197.
38 E. A. Ambundo, M.-V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. Ochrymowycz and D. Rorabacher, *Inorg. Chem.*, 1999, **38**, 4233–4242.
39 S. S. Tan, D. R. MacFarlane, J. Upfal, L. A. Edye, W. O. Doherty, A. F. Patti, J. M. Pringle and J. L. Scott, *Green Chem.*, 2009, **11**, 339–345.
40 G. A. Olah, M. W. Meyer and N. A. Overchuk, *J. Org. Chem.*, 1964, **29**, 2313–2315.
41 D. M. Haddleton, M. C. Crossman, B. H. Dana, D. J. Duncalf, A. M. Heming, D. Kukulj and A. J. Shooter, *Macromolecules*, 1999, **32**, 2110–2119.
42 K. Kloc, E. Kubicz, J. Młochowski and L. Syper, *Synthesis*, 1987, 1084–1087.
43 J. Zhang and A. M. Bond, *Anal. Chem.*, 2003, **75**, 2694–2702.