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Volume 54
Number 1
4 January 2018
Pages 1-112

ChemComm
Chemical Communications
rsc.li/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

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View Article Online
DOI: 10.1039/D0CC05823H

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Cu-Tetracatechol metallopolymer catalyst for three component click reactions and β-borylation of α, β-unsaturated carbonyl compounds

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The phenol-metal coordination polymers are used in applications such as catalysis, sensing and separation science. In addition, combining eco-freindly conditions with economical and handling advantages of the polymeric catalyst is of interest to the community. Here, we report a simple one pot synthesis of tetracatechol based ligand and its coordination polymer with copper ions. The Cu polymer showed electrochemical potential with the band gap of 1.01 eV. The BET surface area of the metallopolymer was 91.19 m^{2}g^{-1} with 0.14 cm^{3}g^{-1} pore volume. The polymer catalyst was used in one pot three component click reaction and in borylation of unsaturated carbonyl compounds with a maximum 99% conversion in water and good turnover efficiency even after 4 repetitive catalysis cycles. The Cu-tetracatechol catalyst offer several advantages such as high activity, easy handling, scalable, recyclable and cost effectiveness.

The metallopolymers are considered as supramolecular architecture by combining the orientation of the functional groups on organic ligand and the dimensionality of the metal coordination.[1] Due to the presence of a large number of transition metal ions with different coordination geometries, polymers with interesting structures and properties have been reported. Such polymers are used in biomedical applications, fabrication of sensors, energy storage devices and as catalysts for organic transformations.[2-5] Moreover, the structure and properties can be fine-tuned using different external stimuli such as applied potential or light to make smart stimuli responsive functional materials.[6, 7] Many higher order structures such as 2D-polymer layers, 3D-metal–organic frameworks and tunable metallopolymer based gels have been reported using metal coordination polymers.[8,9] Catechol and its derivatives are known to generate functional materials owing to their intrinsic properties such as redox behaviour, adhesiveness and strong coordinating ability with oxophilic metal ions (e.g., Fe, Cu).[10-12]

Multicomponent reactions (MCRs) are powerful tools in organic synthesis with a number of applications.[13-15] In addition, the use of water as a solvent makes the synthesis of functional molecules more eco-friendly in nature.[16] Click reaction and alkyl boronic esters are widely used in synthetic organic chemistry, polymer chemistry, biomedical sciences, synthesis of agrochemicals and pharmaceuticals.[17-19] Moreover, the catalyst which can drive these organic transformations in an environmental friendly manner with added economic benefits is fascinating for both academic and industrial perspective. In this communication, we present the design, one pot synthesis and full characterization of a tetracatechol ligand and its copper coordination polymer. Catechol derivative **1** was designed and synthesized to explore the formation of a metallopolymer through interfacial and bulk polymerizations (Scheme 1, Fig. S1-S3, ESI). For insight into the structure of the ligand, good quality single crystals were grown in DCM/MeOH mixture (1:1), with a few drops of water added, by slow evaporation. The crystal structure of the ligand is shown in Fig. 1A. As expected, the four catechol groups are organized to form a network structure through complexation with copper ions. The copper-tetracatechol complex polymer was prepared in one step and fully characterized. Copper is chosen due to its oxophilicity, biological relevance and catalytic properties.[20, 21] The Cu-tetracatechol polymer formed upon mixing the ethanolic solution of copper acetate with the ethanolic solution of tetracatechol ligand at 5 °C. Since the polymerisation was instantaneous, low temperature influences the kinetic parameters and drives the formation of the desired and reproducible structure of the polymer.

Interfacial polymerisation was carried out at the interface of the aqueous solution of copper acetate and ethyl acetate (EA) solution of tetracatechol ligand (Fig. S4, ESI).[11] After 24 h of

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Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

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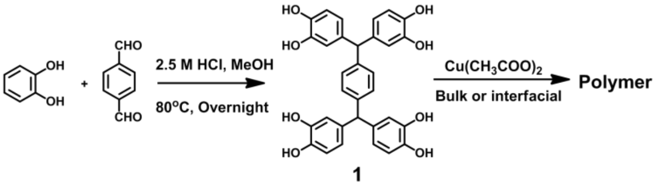
DOI: 10.1039/D0CC05835H



Scheme 1. Synthesis of tetracatechol ligand **1** and polymerisation with Cu (II) ions. The plausible structure of the polymer is given in Figure 1B.

polymerisation, the film was deposited on a quartz substrate (Fig. S5, ESI) and used for further characterisation.[11] As expected, the Cu-metallopolymer showed low solubility in most organic solvents and water, reflecting its high molecular weight with a network structure (Fig. 1B). The divalent character of Cu centres in the catechol complex has been established by earlier studies by different groups.[22-25] The high molecular weight of the polymer was confirmed by gel permeation chromatographic (GPC) analysis of the soluble fraction of the polymer in dimethylformamide (DMF) solvent. The analysis of GPC traces gave a molecular weight of ~ 428 kDa & ~ 568 KDa, for polymers obtained from interfacial and bulk polymerization, respectively (Fig. S6 and S7, ESI). The thermogravimetric analysis (TGA) showed the polymer is stable up to 190 °C, followed by sharp weight loss. The first derivative of the TGA curve revealed one peak at 230 °C, which corresponds to the maximum degradation temperature (Fig. 1C). The UV-Vis spectrum of polymer in DMF showed two peaks at 445 & 660 nm for the Cu-metallopolymer obtained from bulk polymerization, while maxima at 430 & 690 nm for the polymer film obtained from liquid-liquid interface polymerization (Fig. 1D). The observed peaks correspond to the absorbance of Cu-catechol complex and charge transfer peaks from catechol ligands to the Cu-metal centres along the polymer backbone.[26]

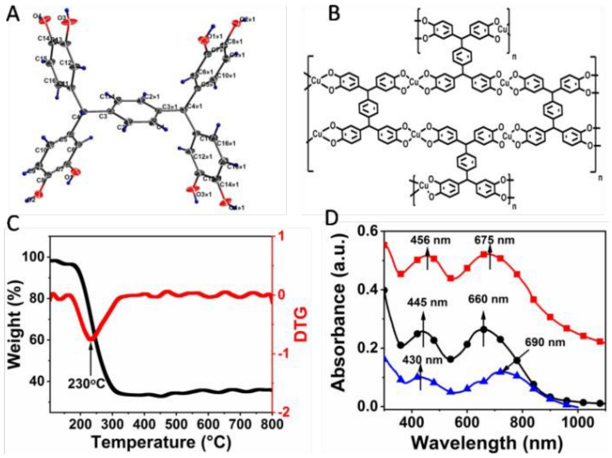
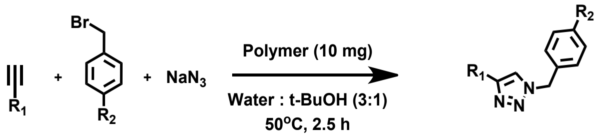


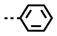
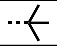
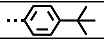
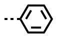
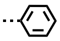
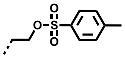
Fig. 1 Crystal structure of ligand **1** (red – oxygen, black – carbon and blue – hydrogen) (A). The plausible network structure of metallopolymer (B). TGA trace with first derivative of the polymer (C), UV-Vis spectra (D) for interfacial film - solid state (—■—), solutions of polymer film (—▲—) and bulk polymer (—●—) in DMF.

The UV-Vis spectra of solid state film showed two major peaks at 456 nm and 675 nm because of ligand to metal charge transfer (LMCT) transitions (Fig. 1D).[26] Moreover the obtained film was green in colour owing to complexation accompanied by LMCT transitions (Fig. S4, ESI).[26] The broad absorbance around 3300 cm^{-1} (-OH) in the FTIR spectra of the ligand disappeared after polymerization.[22] Also, the observed peaks at ~ 535, ~ 600 & ~ 680 cm^{-1} indicates the presence of Cu–O bonds (Fig. S8, ESI).[11, 27] They may be assigned to symmetrical stretching of Cu-O-C bond of the polymer while the peaks at 2900 cm^{-1} and 1460 cm^{-1} corresponds to aromatic C-H stretching vibrations.[28]

The copper based polymers/compounds are used in catalysis owing to redox behaviour between Cu(II) and Cu(I).[29, 30] Here, we explored the potential use of the polymer as a catalyst for a click reaction.[31] A three component [3+2] cycloaddition was tested with the help of our Cu–tetracatechol polymer. All components; catalyst, alkene, alkyl halide, sodium ascorbate and sodium azide (Table 1, entry 1a) were directly added in water/t-BuOH (3:1) mixture and stirred at 50 °C for 2.5 h. The progress of the reaction was also monitored using thin layer chromatography. After cooling the mixture, the crude product was extracted in dichloromethane (DCM) and the percentage conversion was calculated by comparing the integration of peaks of product to that of reactants in the NMR spectra of the crude products/mixture. The Cu-tetracatechol polymer catalyst showed a conversion efficiency of 99% in 2.5 h (Fig. S9, ESI).

Table 1: Three component cyclization of alkyl bromide, sodium azide, and alkyne by Cu-tetracatechol polymer.



S.No	R$_1$	R$_2$	% Conversion
1a		- -H	99
2a		- -H	58
3a		- -H	99
4a		- -NO$_2$	15
5a		- - -I	30
6a		- -H	51

Standard reaction condition: alkyne (0.5 mmol), sodium azide (0.5 mmol), alkyl bromide (0.5 mmol), in water and *t*-butyl alcohol (1.5/0.5 mL each) with Cu polymer (10 mg). % conversion was calculated using NMR spectroscopy.

Even though a small amount (3 mg) of the catalyst was sufficient to achieve a conversion efficiency of 99%, we selected an optimum amount of catalysts (10 mg) to offer maximum recovery and reusability of the polymer. Control experiments without the polymer catalyst did not convert the reactants into product fully within 2.5 h (Fig. S10, ESI).

The surface charge density (zeta potential) of the solid polymer particles dispersed in water was -9.32 mV, indicating an electron rich polymer backbone (Fig. S11, ESI). To further support the high catalytic activity of the electron rich polymer, the same click reaction was carried out without sodium ascorbate (Table1, entry 1a) and achieved 99% conversion

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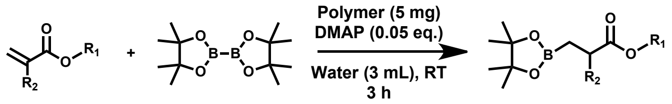
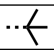
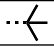
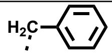
efficiency (Fig. S12, ESI). Also, the effect of substituents on the reactants was explored and showed that aromatic alkynes gave a better product yield as compared to aliphatic *t*-butyl alkyne (Table 1, entry 1-3). In addition, a significant reduction in the conversion efficiency was observed in the presence of electron withdrawing and bulky groups (Table 1). The reproducibility and reusability of the polymer were also tested in successive reactions. After each experiment (Table 1, entry 1a), the solid polymer catalyst was collected by centrifugation and used for the next reaction. The polymer showed 99% conversion efficiency for 4 repeated cycles (Fig. S12, ESI). Two positive control reactions were also carried out with $CuSO_4$ and sodium ascorbate, and Cu(I) without reducing agent. All reactions give the same product confirming the catalysis by Cu ions (Fig. S13, ESI).

It is known that copper catalyses the β-borylation of α,β-unsaturated carbonyl compounds to yield alkyl boronates.[32] To further prove the ability of designed Cu-tetracatechol polymer as a catalyst, all reactants- acrylate, boronpinacolate and amine base (Table 2) along with 5 mg polymer, were mixed in 3 mL of water and stirred at room temperature in air for 3 h.

Table 2: **β-borylation of α,β-unsaturated carbonyl compound by Cu – tetracatechol polymer in water**



S.No	R_1	R_2	% Conversion
1b		- -H	99
2b	- -CH_3	- -CH_3	99
3b	- -CH_2CH_3	- -H	99
4b		- -CH_3	98
5b		- -H	89

Standard reaction conditions: bis(pinacolato)diboron (1.0 equ.), acrylate (1.0 equ.), and DMAP (0.05 equ.) in water (3 mL) with 5 mg of solid Cu – tetracatechol polymer and stirred at RT for 3 h. % conversion was calculated using % conversion was calculated using NMR spectroscopy.

NMR spectra were taken at different time periods to monitor the product formation and to calculate the % conversion. The alkene protons of acrylate starting material disappeared from the spectrum and two new triplets appeared in the upfield region of the spectrum, indicating the product formation (Fig. S14 and S15, ESI). The NMR calculations showed 99% conversion of reactant (Fig. S14, ESI). Different acrylates were used to explore the variability of the reaction and excellent % conversion was observed for all acrylates indicating efficient catalysis (Table 2). The reusability and reproducibility of the catalyst was checked by collecting the products and reactants from the reaction mixture by liquid-liquid extraction followed by adding fresh reagents (Table 2, entry 1a) without any processing to regenerate the catalyst. The catalyst gave >99 % conversion up to four cycles as monitored by NMR spectroscopy (Fig. S15, ESI). The use of catalyst was quantified with respect to control reaction with no catalyst added. Control reaction did not proceed with high conversion of reactants to product (Fig. S16, ESI). Our Cu-tetracatechol polymer showed good catalytic activity, high conversion rate, good reproducibility and high recycling efficiency for the two important organic reactions (click and borylation, Fig. 2).

Since LMCT transitions are accompanied with the shift in partial electron density from ligand to metal, redox potential is expected to differ for polymer from its monomer. The cyclic voltammogram (CV) of tetracatechol showed reversible redox properties of the molecule with the reduction peak at -1.12 V and oxidation at 0.99 V (Fig. 3A). Only one type of redox potential can be attributed to the symmetry of the molecule, where all the catechol groups behave in the same manner. The HOMO-LUMO calculations for the tetracatechol ligand (**1**) gave a band gap of 2.11 eV. Subsequently, the corresponding positions of HOMO and LUMO orbitals of the tetracatechol ligand (**1**) were calculated as -5.34 eV and -3.23 eV, respectively (Fig. 3A).

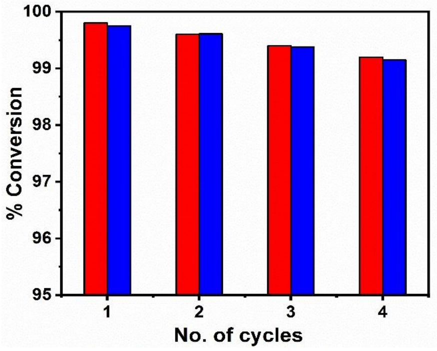


Fig. 2 % conversion of reactant into product during repetitive catalytic cycles for three component click reaction (🟥) and for β-borylation of α,β-unsaturated acrylate (🟦) using Cu-tetracatechol polymer.

Cyclic voltammetry (CV) studies have been conducted with solution of Cu-tetracatechol polymer in DMSO. CV traces showed an oxidation potential at 0.205 V, while the 1st reduction at -0.81 V and 2nd reduction potential at -1.21 V (Fig. 3B). Two reduction potentials can be assigned to the redox chemistry of catechol ligand.[33] Using the CV data, HOMO and LUMO orbital of the Cu-tetracatechol polymer was calculated as -4.55 eV and -3.54 eV, respectively (Fig. 3B). Similarly, band gap for the polymer gave an interesting low value of 1.01 eV. This is due to the strong interactions of orbitals of both partners and enhanced LMCT between the ligand and metal centre along the polymer backbone. Such low band gap also suggests that electrons can reach LUMO easily and can participate in the catalytic reactions. The plausible mechanism for the observed catalytic activity is shown in Fig. S17, ESI. Cu (I) species is required for the reaction to proceed and formed *in situ* via electron transfer from ligand to Cu (II) centres along the polymer chain.[34] The Cu (I) formed reacts with the alkyne group to form Cu acetylide, which then reacts with the azide group in a [3+2] cycloaddition to give Cu-triazole adduct. During the work up, the Cu-triazole gets protonated and release the copper ion, which becomes available for continuing the catalytic cycle.[29]

DOI: 10.1039/D0CC05823H

To further gain the details of the mechanism, the porosity of the polymer was measured using Brunauer–Emmett–Teller (BET) isotherm, which showed a surface area of 91.19 m^2g^{-1} with 0.14 cm^3g^{-1} pore volume (Fig. S18, ESI). This suggests that the catalytic reactions are taking place at the catalytic sites along the pore surfaces of the Cu-tetracatechol catalyst. The mechanism for the borylation reaction is given in the earlier literature reports.[32] This includes the role of amine added to *in situ* deprotonate nucleophilic water-boron adduct and form activated sp^2-sp^3 diboron which transmetalate with copper and undergoes the boryl conjugate addition.[32]

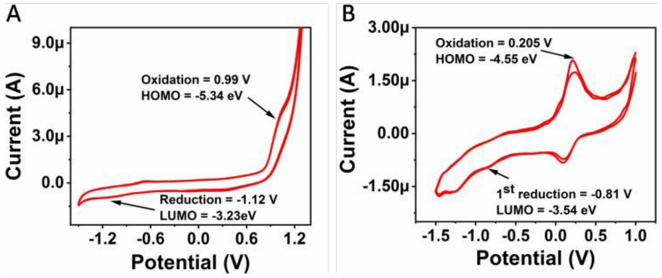


Fig. 3 Cyclic voltammetry for tetracatechol ligand (A) and polymer (B) in DMSO.

In conclusion, we synthesized and characterised Cu-tetracatechol polymer and investigated its properties. The optical spectra indicate strong charge transfer from catechol ligand to the Cu-metal centres along the polymer backbone. The band gap of polymer (1.01 eV) and pure ligand (2.11 eV) was calculated from the reduction and oxidation potentials obtained from the CV measurements. The BET analysis gave a surface area of 91.19 m^2g^{-1} and 0.14 cm^3g^{-1} pore volume for the polymer. The synthesized Cu-tetracatechol polymer was used as a catalyst for three component click reaction and borylation of unsaturated carbonyl compounds. In both cases, a maximum (>99 %) conversion efficiency of reactant into product was observed in repeated cycles indicating a high catalytic turnover efficiency of the polymer. The catalyst is eco-friendly, easy to synthesize, recyclable and showed wide applicability. Such low cost tendering catalysts are useful and needed in many water based organic transformations.

We gratefully acknowledge funding support from the National University of Singapore under the IITK-NUS joint degree program. Sandeep Verma thanks SERB for JC Bose Fellowship.

Conflicts of interest

"There are no conflicts to declare".

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