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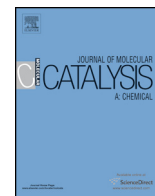


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Elucidating the role of cobalt phthalocyanine in the dehydration of carbohydrates in ionic liquids

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ABSTRACT

The cobalt(II) phthalocyanine efficiently converts glucose and cellulose into 5-hydroxymethylfurfural in [EMIm]Cl ionic liquid. From various throughout screening of metal salts, metallophthalocyanines and ionic liquids, the combination of cobalt phthalocyanine with [EMIm]Cl ionic liquid gave the best results. Co(II)Pc interacts with glucose in [EMIm]Cl ionic liquid and in situ generates the Co(I)Pc and Co(III)Pc which are confirmed from UV–visible analysis. Co(III)Pc reacts with glucose and generates five membered ring chelate complex, which subsequently isomerizes to fructose. In the reaction fructose easily dehydrates to HMF. A single-pot EMF and DFF are produced by etherification and aerobic oxidation reaction of glucose, respectively. The catalyst is easily separated from the reaction by simple filtration and recycled upto 3–5 times without the significant loss of its catalytic activity.

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1. Introduction

In recent years, the increasing consumption of natural petroleum feedstock leads us to find an alternative source. All the forest plants, woods and herbaceous energy crops contain good amount of cellulose, hemicelluloses and lignin as major constituent [1]. The presence of extensive hydrogen-bonded networks and van der Waals interactions in sugar polymers, make it difficult to hydrolyze. Therefore the replacement of petroleum feedstocks with biomass requires the development of efficient and cost-effective procedure to convert carbohydrates to a variety of useful chemical compounds [2–4].

5-Hydroxymethylfurfural (HMF) is an important organic compound which serves as a versatile intermediate between biomass-based carbohydrate chemistry [5,6] and petroleum-based industrial organic chemistry [7–9]. HMF and its derivatives potentially replace voluminous consumed petroleum-based building blocks, which are currently used to make plastics and fine chemicals. HMF is easily converted into smaller building blocks [10] like 2,5-diformylfuran (DFF) [11], 2,5-furandicarboxylic acid [12], polyethyleneterephthalate [10], 5-(ethoxymethyl)furfural (EMF)

[10], polybutyleneterephthalate [10], 2,5-dihydroxymethylfuran, [11] etc. Previously starting with glucose and fructose, many catalytic systems for the synthesis of HMF are reported in organic solvents [13], water [14], ionic liquids [15] and in microwave conditions [16]. These procedures require either protonic acid [17] or metal salt as a Lewis acid catalyst [18]. This acid catalyzed dehydration of carbohydrates leads to various side-products like levulinic acid [19], formic acid [10], furfural [20], humic acid, etc. and separation of HMF is tough from these side products. However starting with cellulose and other feedstocks, very few literature reports are available and these procedures require higher temperature with higher pressure [10].

In this paper, we have developed a simple and convenient strategy for the dehydration of cellulose and glucose to HMF by using the Lewis acidic character of cobalt phthalocyanine. Recently we have carried out various organic transformations like oxidation, reduction and dechlorination of various organic moieties [21] by using cobalt phthalocyanines as a catalyst. Thus metallophthalocyanines easily replace metal catalysts from organic transformations and provide better substitute. The unsubstituted metallophthalocyanines are insoluble in common organic solvents but they easily interact with ionic liquids. Ionic liquids have been used as a green solvent to replace the conventional organic solvents due to their unusual properties particularly low vapor pressure and flammability, highly concentrated ionic atmosphere, thermal stability, fast ion transport and ease of recyclability [22]. The combination of ionic liquids and metal salts are effective catalysts [23] for the hydrolysis

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of cellulose, therefore we have chosen the ionic liquids as a green reaction media.

Herein, we report the use of highly concentrated carbohydrate melts for the selective conversion of glucose and cellulose into HMF. Different reaction conditions for heterogeneous catalysis were investigated. The in situ generated Co(III)Pc shows better Lewis acidic character for the isomerization of glucose. In this catalytic system, the highly desirable biofuel EMF and DFF were synthesized in one pot reaction from glucose in better yield and purity.

2. Experimental

The ^1H NMR spectrum was measured in CDCl_3 at ambient temperature on a JEOL 400 MHz instrument. The chemical shifts are given in ppm related to tetramethylsilane (TMS) as internal standard. HPLC was performed in (C-18 reverse phase column); water:MeOH = 80:20, flow rate = 0.6 mL min^{-1} , monitored at 284 nm. The external standard curve method (HPLC) was employed for the quantification of the product. The standards (HMF, EMF, DFF, levulinic acid and formic acid) were obtained from Sigma–Aldrich, India. UV–vis spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis. spectrophotometer and absorption maxima have been expressed in nm. IR spectra were recorded on a Perkin-Elmer Spectrum 2000 infrared spectrophotometer. Glucose and cellulose were obtained from Spectrochem Pvt. Ltd. and was used as such as received. All the solvents are of HPLC grade. All the reactions were carried out under argon atmosphere until it is mentioned. Metallophthalocyanines (**1a–1e**) and ionic liquids (**2a–2c**) were synthesized by following the procedures [24] reported by us.

2.1. General procedure for the conversion of glucose to HMF in neutral ionic liquids (**2a**) catalyzed by cobalt phthalocyanine (**1a**)

In a typical reaction, glucose (200 mg, 1.11 mmol) was heated to 100°C in [EMIm]Cl (324 mg, 2.22 mmol) and after 5 min catalyst **1a** (42 mg, 0.0556 mmol) was added to reaction mixture at the same temperature. The reaction was monitored by TLC. After completion of reaction, ethyl acetate (10 mL) was added to the reaction, organic layer was separated and dried over sodium sulfate. The product was analyzed by HPLC and other spectroscopic technique.

^1H NMR (400 MHz, CDCl_3): 3.16 (brs, 1H, OH), 4.7 (s, 2H, CH_2), 6.52 (d, 1H, furan H), 7.23 (d, 1H, furan H), 9.56 (s, 1H, CHO); ^{13}C NMR (75 MHz, CDCl_3): 57.02 (CH_2), 109.85 (furan CH), 123.54 (furan CH), 151.87 (furan C), 161.08 (furan C), 177.75 (CHO); HR Q-TOF MS, m/z : 127.08 ($\text{M}+1$) (calcd for $\text{C}_6\text{H}_4\text{O}_3$ 126.02).

2.2. General procedure for the hydrolysis of cellulose to HMF

In a typical reaction, cellulose (500 mg) was heated to 140°C in [EMIm]Cl (5 g) to form a homogeneous mixture and after 30 min catalyst **1a** (200 mg) was added to the reaction mixture at the same temperature. The reaction was monitored by TLC. After completion of reaction (4.5 h), the reaction mixture was extracted with ethyl acetate ($5 \times 10\text{ mL}$) and dried over sodium sulfate. Products were analyzed by HPLC. HMF was obtained in 65% yield. Ionic liquid **2a** was separated from cellulose by addition of water to reaction mixture.

2.3. Synthesis of DFF

2.3.1. Synthesis of DFF from HMF

For typical experiments, in a 50 mL round bottom flask, HMF (100 mg, 0.7936 mol), 5 wt% of the cobalt phthalocyanine **1a** (30 mg) and IL **2a** (232 mg) were heated with continuous stirring at 80°C for 1 h under oxygen atmosphere. Upon completion of reaction, the reaction mixture was cooled to room temperature. Ethyl

acetate (10 mL) was added to the reaction and organic layer was separated and dried over sodium sulfate (anhydrous). The product was analyzed by HPLC and other spectroscopic techniques.

^1H NMR (400 MHz, CDCl_3): 7.4 (s, 2H, furan H), 9.8 (s, 2H, CHO); ^{13}C NMR (75 MHz, CDCl_3): 120.4 (s, CH), 154.8 (s, qC), 179.7 (s, CHO); HR Q-TOF MS, m/z : 125.09 ($\text{M}+1$) (calcd for $\text{C}_6\text{H}_4\text{O}_3$ 124.02).

2.3.2. One-pot synthesis of DFF from glucose

In a typical reaction, glucose (200 mg, 1.11 mmol) was heated to 100°C in [EMIm]Cl (324 mg, 2.22 mmol) and after 5 min catalyst **1a** (42 mg, 0.0556 mmol) was added to reaction mixture at the same temperature. The reaction was stirred under nitrogen atmosphere until the completion of the reaction. After completion of reaction, it was cooled down and oxygen was provided to the reaction by balloon and it was further heated to 80°C . The reaction was monitored by TLC. The product was isolated in the same way as described above.

2.4. Synthesis of EMF

2.4.1. Synthesis of EMF from HMF

For typical experiments, in a 50 mL round bottom flask, HMF (100 mg, 0.7936 mol), 5 wt% of the cobalt phthalocyanine **1a** (30 mg) and IL **2a** (232 mg) in 5 mL ethanol were refluxed with continuous stirring at 90°C for 2 h using a long condenser and chilled water so that ethanol vapor can be condensed back to the liquid phase. Upon completion of reaction, the reaction mixture was cooled to room temperature and ethanol was evaporated under vacuum. To the oily residue, 10 mL distilled water was added and the product was extracted with ethyl acetate ($3 \times 10\text{ mL}$). The organic layer was dried on sodium sulfate and evaporated under vacuum to give the desired product. The product was characterized by ^1H NMR spectroscopy.

^1H NMR (400 MHz, CDCl_3): 9.59 (s, 1H), 7.19 (d, $J = 2.8\text{ Hz}$, 1H), 6.50 (d, $J = 2.8\text{ Hz}$, 1H), 4.53 (s, 2H), 3.69 (q, 2H), 1.20 (t, 3H).

2.4.2. One-pot synthesis of EMF from glucose

One-pot production of EMF from glucose was carried out in ethanol by oil-bath heating. A 100 mL round-bottom flask was charged with glucose (200 mg), 5 wt% of cobalt phthalocyanine **1a** (42 mg) and IL **2a** (325 mg) catalysts in 10 mL ethanol and was refluxed with continuous stirring at 90°C for 3 h. After completion of the reaction, the oily liquid product was isolated in the same way as described above. The ^1H NMR spectrum of the isolated product revealed the presence of both EMF and EL in the reaction mixture.

2.5. Analysis

The product yields, conversion, and selectivity were determined as follows:

$$\text{Product yield, \%} = \frac{\text{weight of products}}{\text{weight of cellulose put into reactor}} \times 100$$

$$\text{Cellulose conversion, \%} = \frac{\text{moles of reacted cellulose}}{\text{moles of initial cellulose}} \times 100$$

$$\text{Product selectivity, \%} = \frac{\text{moles of product obtained}}{\text{moles of reacted cellulose}} \times 100$$

3. Results and discussion

For the dehydration of carbohydrates, metallophthalocyanines (Fig. 1) are chosen as a solid catalyst and ionic liquids (Fig. 2) as a green reaction media. The required metallophthalocyanines are synthesized from phthalonitriles by following up the procedure

Table 1
Optimized reaction conditions for the synthesis of HMF^a

S. No.	Catalyst	IL	Time (h)	Conv. ^b	HMF ^c	Levulinic acid ^c	Formic acid ^c
1	–	2a	5	20	9	4	4
2	1a	2a	3	97, 95, 89 ^d	88, 86, 78 ^d	5	3
3	1b	2a	3	92	78	8	6
4	1c	2a	3	84	66	4	2
5	1d	2a	3	29	15	6	4
6	1e	2a	3	99	61	25	10
7	Co(OAc) ₂	2a	3	60	39	9	9
8	CoCl ₂	2a	3	58	36	10	8
9	1a	2b	3	93	81	4	3
10	1a	2c	3	76	52	15	8
11 ^e	1a	2a	3	100	71	15	10

^a Reaction was performed in 1/2 molar ratio of glucose and ionic liquid at 100 °C under N₂ atmosphere.

^b Based on substrate.

^c HPLC yields.

^d Reaction was repeated with recovered catalytic system.

^e Reaction was performed at 140 °C.

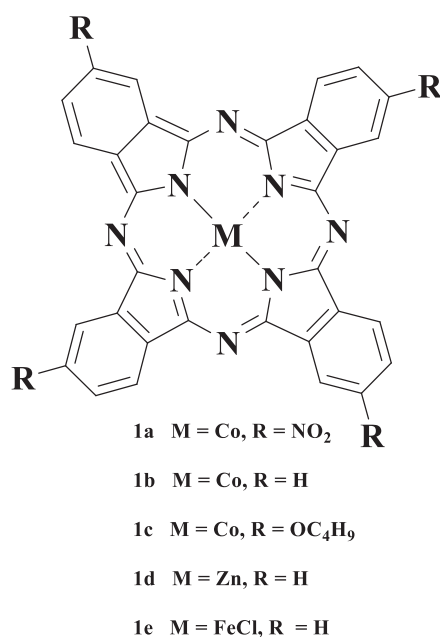
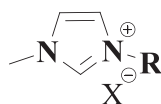


Fig. 1. Structure of metallophthalocyanines.

reported by us [24]. Ionic liquids are synthesized and purified by the literature procedures [24].

To establish the efficient catalytic conditions, glucose was selected as a model to screen the reaction parameters (Table 1, Scheme 1). Both the catalyst and solvent are crucial in the conversion of glucose to HMF. The reaction of glucose in [EMIm]Cl **2a** ionic liquid without catalyst proceeds with only 20% conversion even after 5 h (Table 1, entry 1). Our initial experiments showed that catalyst **1a** in [EMIm]Cl ionic liquid at 100 °C under nitrogen



2a R = C₂H₅, X = Cl

2b R = C₄H₉, X = Cl

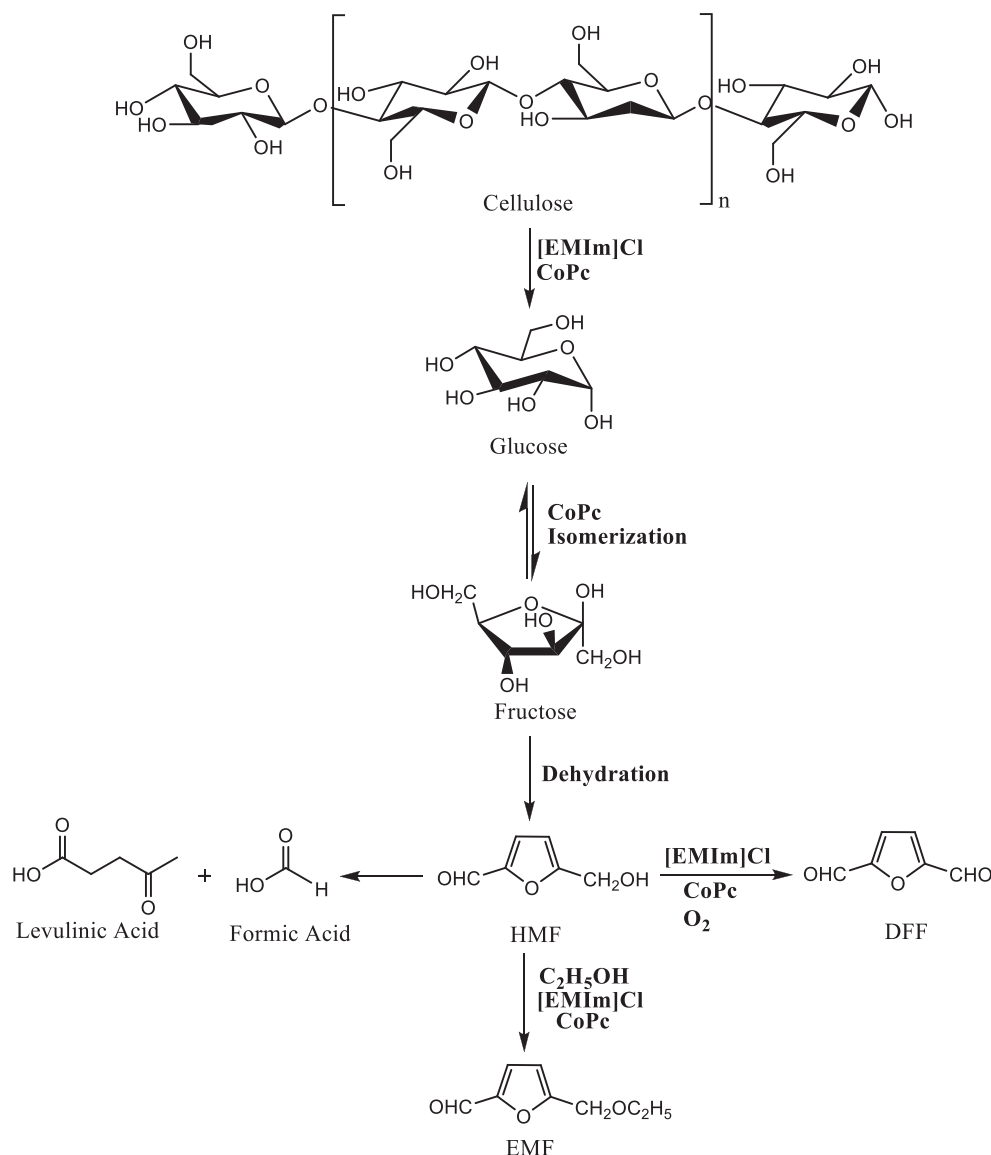
2c R = C₂H₅, X = Br

Fig. 2. Structure of imidazolium ionic liquids.

atmosphere provides 97% conversion and HMF in 88% selectivity, whereas catalyst **1b** provides 92% conversion and HMF selectivity was also decreased (Table 1, entries 2 and 3). Further catalyst **1c** in same reaction conditions showed decrease in catalytic activity (Table 1, entry 4).

From the results it is clear that, cobalt(II) phthalocyanine bearing an electron withdrawing nitro group (**1a**) exhibited better catalytic activity than those bearing electron donating groups [21a]. The catalytic activity of the cobalt phthalocyanine was governed by the variation in the redox potential of cobalt(II) phthalocyanine due to the presence of electron withdrawing and electron donating substituents [25]. Further we had changed the core metal of phthalocyanine ring with Zn(II) and Fe(III) but the catalytic efficiency and HMF yield were decreased (Table 1, entries 5 and 6) and various side-product formation had taken place in the reaction. The use of metal salts instead of metallophthalocyanine as catalyst showed quite poor activity (Table 1, entries 7 and 8). Above results demonstrate that the reaction of glucose in the presence of ionic liquid **2a** and catalyst **1a** proceeds much faster and more efficiently compared to inorganic salts which indicate the interaction of metallophthalocyanine and ionic liquids with glucose is responsible for the stabilization of the catalytic system. Ionic liquid reduces the activation barrier of the reactions by stabilizing the polar transition states or reaction intermediates [26]. By obtaining the good catalyst **1a**, we have further examined the effect of change of ionic liquids and change of temperature on the reaction. The reactivity of glucose was checked in three different imidazolium ionic liquids (**2a–2c**), and it was observed that on increasing the bulkiness on imidazolium ring, solubility of glucose was decreased and thus HMF yield was decreased. Since [EMIm]Cl (**2a**) was equivalent or better than the other two ionic liquids, we have reported the further results in this catalytic system. On increasing the temperature to 140 °C, HMF selectivity was decreased, therefore all reactions were monitored at 100 °C (Table 1, entry 11). When we used 1 mol% of catalyst **1a**, the yield of the obtained product was low, while further increasing the amount of catalyst to 5 mol%, the yield was maximum (88%). When the catalyst loading was increased to 10 mol% and 15 mol%, glucose conversion was increased but HMF selectivity was decreased. Thus the 5 mol% catalyst was used for further reactions.

The change of HMF selectivity was studied by changing the different molar ratio of glucose and ionic liquid **2a**. The results are summarized in Table 2. From Table 2, it is clear that the best selectivity of HMF is obtained in 1/2 molar ratio of glucose and ionic liquid. In the other combinations viscosity of the reaction medium is increased and it leads to the lesser HMF selectivity and more



Scheme 1. Direct transformation of cellulose into HMF and other products using a combination of cobalt phthalocyanine in imidazolium ionic liquid.

side-product formation. Therefore only 1/2 molar ratio combinations have sufficient interaction between glucose and ionic liquid and contain sufficient solubility of glucose.

Selective oxidation reactions of HMF are presently viewed as an attractive route for the formation of 2,5-diformylfuran (DFF) [11], which is a monomer for furan-containing polymers and materials with special properties. There are numerous reports describing various useful applications of DFF as a monomer, as the starting material for the synthesis of drugs, antifungal agents, nematocides, and ligands, in photography, as a cross-linking agent, for metal electroplating, in analytical chemistry and as a precursor for organic

metals [11]. The reaction of HMF in ionic liquid **2a** at 80 °C, catalyzed by cobalt phthalocyanine **1a** using molecular oxygen or air as an oxidant, gave DFF in 97% yield. Furthermore, we have examined the one-pot synthesis of DFF from glucose by using the same catalytic system. The reaction of glucose with **1a** in ionic liquid **2a** was carried out at 100 °C under nitrogen for 2 h followed by purging the oxygen at 80 °C for 30 min. The products were analyzed, HMF and DFF were obtained in 22% and 61% yields, respectively, along with small amount of polymeric products. Prolonged stirring of the reaction mixture caused decomposition of the product whereas the oxygen purging in shorter times, minimized the decomposition. The presence of residual water in ionic liquid also helps to obtain the DFF in trace amount under nitrogen atmosphere. This phenomenon of oxidation and polymerization by cobalt phthalocyanine in presence of residual water and molecular oxygen as oxidant was reported by us [21a].

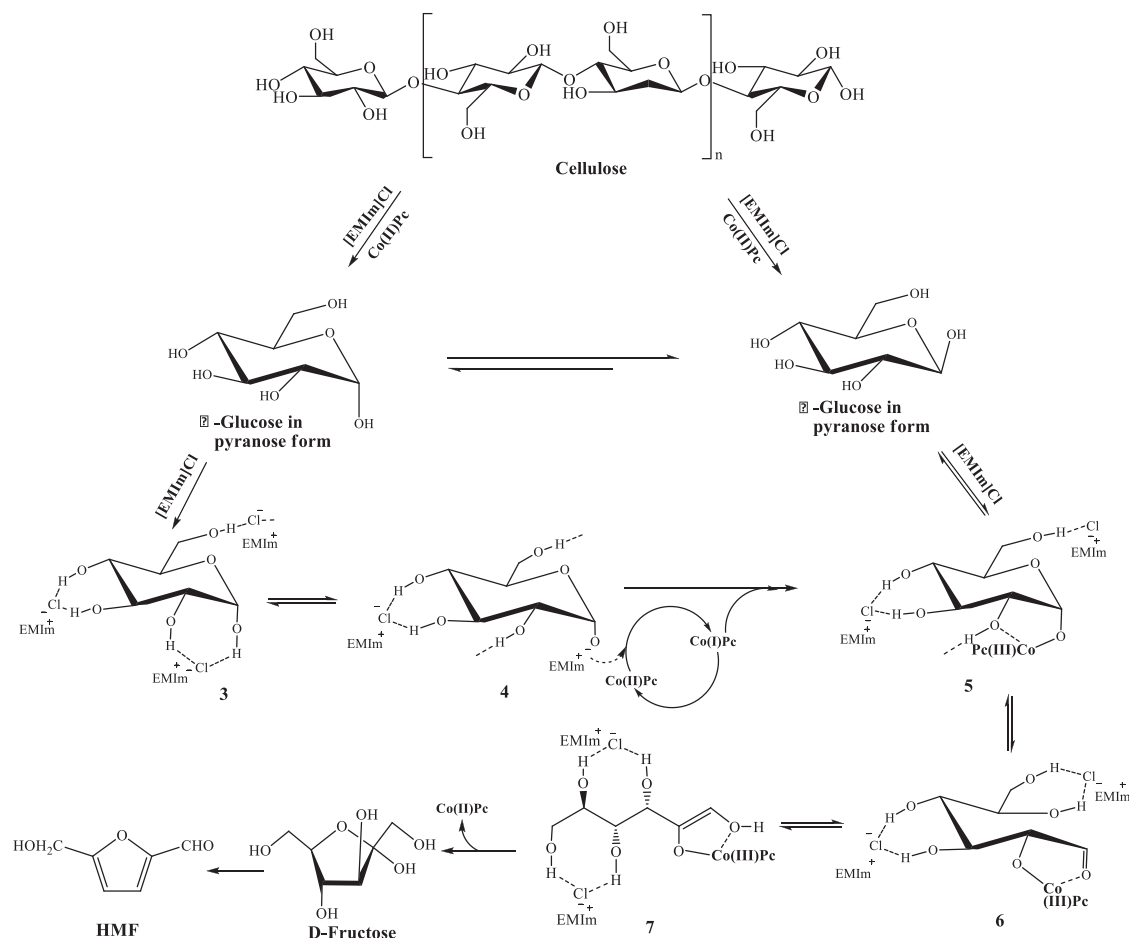
Recently 5-(ethoxymethyl)furfural (EMF) has attracted much attention as a potential biofuel alternative. It is considered as an excellent additive for diesel [13,27]. The synthesis of EMF from both HMF and fructose in ethanol has been recently reported [13,27] by various groups using various catalysts. However, glucose is a more abundant and cheaper feedstock; thus, it is of interest to prepare

Table 2
Reaction in different concentrations of glucose and ionic liquid **2a** catalyzed by **1a**^a

S. No.	Glucose/IL 2a ratio	HMF ^b	Levulinic acid ^b	Formic acid ^b
1	1/2	88	5	3
2	2/2	79	12	5
3	3/2	66	4	2
4	4/2	9	4	4

^a Reaction was performed at 100 °C and checked after 3 h.

^b HPLC yields.



Scheme 2. Chemical pathway for the direct transformation of cellulose into HMF.

EMF from glucose. The reaction of HMF in ionic liquid **2a** at 90 °C, catalyzed by cobalt phthalocyanine **1a**, along with ethanol gave EMF in 92% yield in 2 h. Whereas further continuing the reaction (3 h), did not affect the selectivity of the product. Furthermore, we have examined the one-pot synthesis of EMF from glucose by using the same catalytic system. The reaction of glucose with catalyst **1a** in ionic liquid **2a** and ethanol (10 mL) at 90 °C was carried out under nitrogen atmosphere for 3 h. The obtained products were analyzed and EMF was obtained as a major product (80%) along with ethyl levulinate as a side product (5%). Thus this catalytic system offers the synthesis of highly valuable EMF in higher selectivity from the cheaper starting material glucose. When the characterization was performed without doing workup, minor amount of acetal (2%) was detected. It was concluded that during the usual extractive work up procedure, the minor amount of acetal formed is hydrolyzed to the corresponding aldehyde [27c] and therefore was not detected in the final product.

Since cellulose is an abundant renewable polysaccharide consisting of a linear chain of (1–4) linked β -glucopyranose units, therefore it requires an effective catalytic system for its hydrolytic degradation. The direct transformation of cellulose into HMF involves three steps: (1) hydrolysis of polymeric cellulose into monosaccharides, (2) isomerization of glucopyranose to fructofuranose, and (3) dehydration of fructofuranose to HMF [28]. The $[EMIm]Cl$ and $[BMIm]Cl$ ionic liquids hydrolyzed the cellulose at 100 °C, whereas in $[EMIm]Br$ ionic liquid hydrolysis of cellulose was very less. The Cl^- ions of ionic liquids **2a** and **2b** interact with the hydrogen bonded cluster of cellulose and are responsible for breaking the hydrogen bonds of cellulose [29]. The complete dissolution

of cellulose in $[EMIm]Cl$ makes the cellulose chains accessible to be contacted with catalyst for the chemical transformation. The cellulose hydrolyses into glucose and its further conversion to HMF is similar to glucose. It is found that the yield of HMF increases gradually during the reaction from 2 h to 4.5 h. When the time is extended to 4.5 h or even longer, the yield of HMF decreases which indicates the formation of byproducts. Addition of catalyst **1a** increases the yield up to 35%. Further on increasing the temperature of the reaction mixture from 100 °C to 140 °C HMF yield increases and maximum yield (65%) was observed at 140 °C, whereas on increasing the temperature to 160 °C, HMF yield was decreases to 60%. The reason for the promotional effect of the catalyst is the cobalt coordination interaction.

Glucose is mainly present in the pyranose form and its conversion to HMF involves open chain structure and ene-diol intermediates **7** (Scheme 2). In pyranose form, both the α and β -glucose are present in equilibrium mixture and its interaction with ionic liquid **2a** and catalyst **1a** are explained with 1H NMR spectroscopic studies (Fig. 3). When $[EMIm]Cl$ interacts with glucose at room temperature, the intensity of the peaks of hydrogen atom in hydroxyl groups of glucose decreases, indicating that the Cl^- ions of $[EMIm]Cl$ interacts with these hydrogens and abstracts the proton to generate the intermediate **4**. Further these peaks disappear on addition of catalyst **1a** to this system and formation of five member ring chelate intermediate **5** takes place. On increasing the temperature of this mixed system to 100 °C, a new peak at 4.98 ppm was observed, which shows the further interaction of glucose in this system [7]. This suggests that heating would enhance the interaction between catalyst and oxygen atom of glucose, leading to

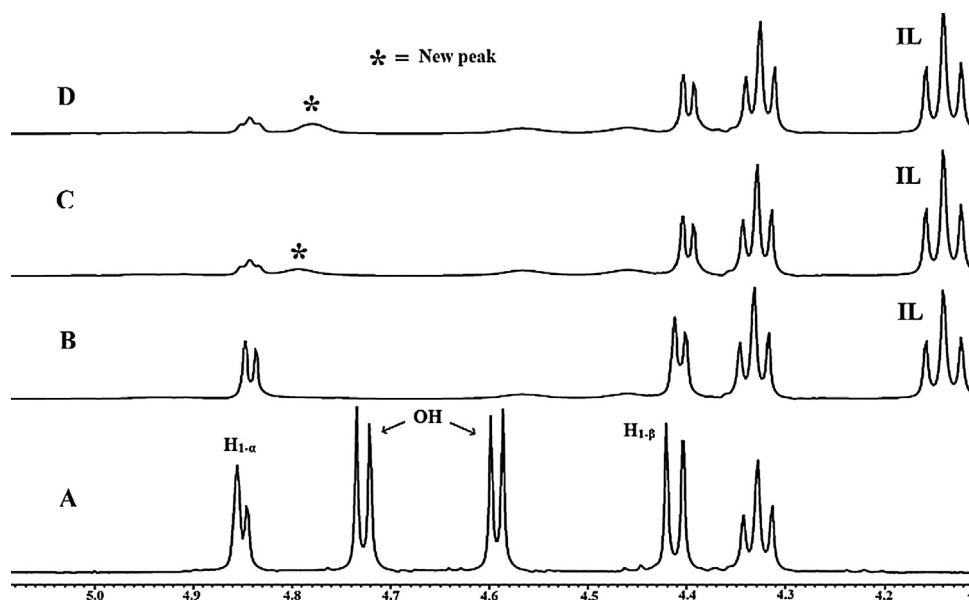


Fig. 3. ^1H NMR spectra of glucose in d^6 -DMSO: (A) Glucose (0.2 M). (B) Glucose (0.2 M) in [EMIm]Cl (0.5 M). (C) Glucose (0.2 M) and catalyst (0.1 equivalent) in [EMIm]Cl (0.5 M). (D) Glucose and catalyst in [EMIm]Cl (after 5 min heating at 100°C).

the generation of an open chain structure **6**. Intermediate **6** is further converted to ene-diol intermediate **7** which is transformed into fructose and in the presence of catalyst **1a**, it dehydrates to form HMF.

The interaction of cobalt(II) phthalocyanine **1b** with glucose in [EMIm]Cl ionic liquid was studied by UV–vis spectroscopy (Fig. 4). The UV–vis spectra of catalyst **1b** in DMSO showed a Q band at 658.78 nm [21c]. When glucose was stirred in [EMIm]Cl ionic liquid at 90°C for 10 min and was added to the catalyst **1b**, a new band at 465 nm accompanied by a red shift in the Q band from 665 to 703 nm was generated which are characteristic peaks for Co(I)Pc [21b]. The Cl^- ion of ionic liquid abstracts the proton from glucose and generate the species **4**, which transfers the electron to Co(II)Pc and reduce it to Co(I)Pc as an intermediate in the reaction. The red shift in Q band of catalyst **1b** is due to the tendency of metallophthalocyanine to take up the electrons reversibly in the d_{z^2} orbital of central metal [30] from the alkoxy group of glucose. This gives a clear cut evidence for the interaction of alkoxy group

of glucose with catalyst **1b**. On standing the solution for 10 min, Q band was blue shifted from 703 nm to 661 nm along with the disappearance of the peak at 465 nm, a characteristic peak for Co(III)Pc [21]. Co(III)Pc act as a Lewis acid and catalyze the isomerization reaction faster than Co(II)Pc. The stability and rate of formation of Co(I)Pc and Co(III)Pc were found to be affected by changing the ionic liquids, justifying the role of the ionic liquid in the reaction. The generation of alkoxide ion by ionic liquid was further confirmed by treating ethanol with [EMIm]Cl ionic liquid in the similar way. When only ethanol was added to Co(II)Pc and UV spectrum was recorded, no change was observed (ESI†). Whereas on addition of equimolar mixture of [EMIm]Cl and ethanol, peaks corresponding to Co(I)Pc was slowly generated. Similarly on addition of sodium ethoxide solution to Co(II)Pc, peaks corresponding to Co(I)Pc was generated. It gives a clear cut evidence for the generation of alkoxide ion of glucose by [EMIm]Cl ionic liquid in the reaction.

In situ FT-IR spectroscopy was further used to get information about the hydrogen bond promoted effect of [EMIm]Cl on cellulose and glucose (ESI†). An OH-stretching vibration of glucose approaches the lower frequency region in the presence of [EMIm]Cl. This is understandable because the interaction of Cl^- ions of ionic liquid may weaken the OH-stretching vibration. The FT-IR study proves the involvement of Cl^- ions in the reaction medium by showing the hydrogen bonding with hydroxyl group of cellulose and glucose, thus reduces the OH-stretching frequency.

On the basis of above observations, a reaction mechanism has been proposed (Scheme 2). It is generally accepted that the two successive steps are required during the conversion of glucose to HMF, namely isomerization of glucose into fructose and followed by dehydration of fructose to HMF [31]. The conversion of glucose to HMF can be explained by interaction [31] of catalyst **1a** with both α and β -glucose. When the glucose interacts with ionic liquid **2a**, Cl^- ion of ionic liquid abstracts the proton from the hydroxyl group of glucose and generates the alkoxide type of anionic intermediate **4** [32]. The anionic intermediate **4** transfers the electron to catalyst Co(II)Pc and reduces it to Co(I)Pc. The Co(I)Pc further interacts with intermediate **4** and generate the stronger Lewis acid Co(III)Pc with intermediate **5** having more stable five member ring chelate complex [7]. The intermediate **5** undergoes ring opening and generates the open chain intermediate **7** which further cyclizes to form the furanose form of fructose. The Lewis acidic character of Co(III)Pc is

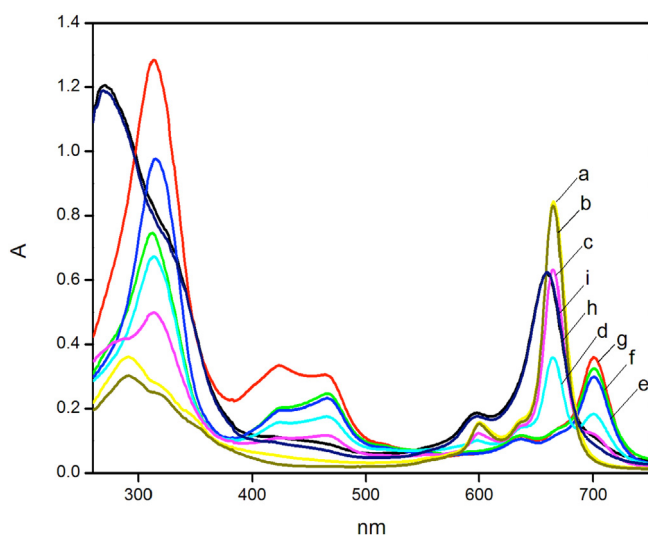


Fig. 4. UV–vis spectra of **1b** (a) in DMSO, (b–i) on addition of glucose and [EMIm]Cl in DMSO at an interval of 1 min.

responsible for the activation of the reaction via a Lewis acid–base interaction [33] and glucose is converted to furanose form of fructose. In the catalytic system fructose easily dehydrates to HMF.

A typical time profile was recorded for the conversion of glucose to HMF using catalyst **1a** in [EMIM]Cl ionic liquid at 100 °C. The reaction proceeds with high conversion and higher selectivity (ESI†) in 1 h of the reaction; whereas further prolonging the reaction conversion becomes slow. From the graph it is clear that the reaction follows the nonzero order reaction pathway. A similar phenomenon was also observed in another report [7].

Apart from the mild reaction conditions and its excellent results, the simplicity of product isolation and the possibility to recycle the ionic liquid and catalyst offer a significant advantage. Because ionic liquids (**2a–2c**) are immiscible in ethyl acetate and the desired product is soluble in ethyl acetate, the products can be directly separated by adding ethyl acetate into the synthetic system after the completion of the reaction. The catalyst **1a** remained in IL **2a** and can be reused up to three to five times (Table 1, entry 2).

After completion of the reaction, stability of the catalytic system was checked with ¹H NMR, FT-IR, UV–vis and X-ray powder diffraction (XRD) techniques. It was found that the ionic liquid and catalyst both are stable in this catalytic system. XRD of reused catalyst **1a** was recorded and it was quite similar with fresh catalyst **1a**, which shows the stability of catalyst in this catalytic system (ESI†). Catalyst does not undergo decomposition during reaction but the decrease in the yield of product after 3rd run is due to the unexpected removal of the ionic liquid during extraction process resulting in leaching of the ionic liquid and catalyst. The presence of an unchanged UV–vis spectrum of the catalyst **1a** after the reaction (after 3 runs) further confirms its stability in this catalytic system.

4. Conclusions

The unique ability of cobalt phthalocyanine to catalyze the dehydration of carbohydrates to HMF critically depends on the oxidation state of the metal. Co(III)Pc is much more active than Co(II)Pc for the isomerization of glucose to fructose as well as in the subsequent fructose dehydration. It is an effective catalytic system for the direct conversion of cellulose and glucose to HMF, DFF and EMF which are valuable intermediates in the various organic transformations. The present method offers various advantages over conventional methods such as high selectivity, higher yield of product, shorter reaction time, lower temperature, simple work-up procedure and reusability of the catalyst.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2014.07.014>.

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