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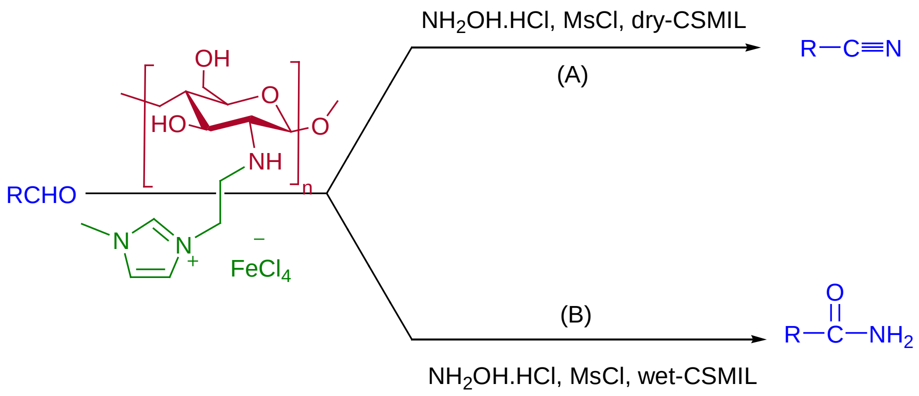

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ARTICLE TYPE

Chitosan Supported Ionic Liquid: A Recyclable Wet and Dry Catalyst for Direct Conversion of Aldehydes into Nitriles and Amides under mild conditions

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A green and highly efficient chitosan supported magnetic ionic liquid (CSMIL) was synthesized with chitosan (the most abundant biopolymers in nature and cheap industrial waste), ethyl methyl imidazole and anhydrouse/hydrouse $FeCl_3$. The heterogeneous catalyst thus obtained used for the direct conversion of aldehydes to the corresponding nitriles in the presence of NH_2OH. HCl /dry-CSMIL / $MeSO_2Cl$ and amides with NH_2OH. HCl /wet-CSMIL / $MeSO_2Cl$. A highlight of our approach is easy separation of catalyst from the reaction medium and so on recyclability of the catalyst. This simple method is applicable to access a wide range of aromatic, heterocyclic, and aliphatic aldehydes.

1. Introduction

In the recent years, development of pollution prevention research has been broad due to growing environmental concerns. In this respect, heterogeneous catalysis is generally preferred to homogeneous catalysis mainly because of the easy recovering and possible recycling of the catalyst, simple experimental procedures, mild reaction conditions and minimization of chemical wastes as compared to the liquid phase counterparts. Very recently, natural materials, in particular biopolymers for catalytic applications are attracting increasing interest as environmentally benign polymeric supports for catalysts. [1] Carbohydrates are one of the most diverse and important classes of biomolecules in nature. These renewable polymers largely used in some applications such as adhesives, absorbents, lubricants, soil conditioners, drug delivery, textiles and high strength structural materials. [2]

Among biopolymers, chitosan (CS), is the second abundant polysaccharide next to cellulose in nature and is estimated to be produced annually almost as much as cellulose and can be found in industrial waste.[3] chitosan is a potential excellent material used as support for catalytic applications in heterogeneous molecular catalysis due to its hydrophilicity, chemical reactivity, unique three-dimensional structure, presence of hydroxyl and amino groups, excellent chelating property, and mechanical properties.[4,5] Morever, chitosan is environmental friendly because it can be degraded by soil and water microorganisms. There has been much scientific and industrial interest in utilizing chitin and chitosan for different applications such as pharmaceutical, waste water treatment, cosmetics, drug delivery, heavy metal chelation, heterogeneous catalysts and many other attractive utilizations.[6],[7]

The unique and tunable physical and chemical properties of ionic liquids (IL) make this class of molecules as particularly a green solvent suitable for a range of organic reactions, and providing possibilities such as control of product distribution,[8] enhanced rates [9] and/or reactivity, [10] ease of product recovery, [11] catalyst immobilization, [12] and recycling. [13,14]

In this work, we reveal a new biopolymer supported ionic liquid based on dry $FeCl_3$ and $FeCl_3.3H_2O$ to produce both wet and dry heterogeneous catalyst.

The nitrile moiety is an important constituent in different natural products, and considerable precursor for the synthesis of amines, amides, ketones, carboxylic acids and esters. There are diverse methods for the synthesis of nitrile groups from different organic functional groups.[15] Among these, the direct conversion of aldehydes into corresponding nitriles has been shown to be an attractive and important strategy for the preparation of nitriles in organic transformations.[16] Until now, several methods have been reported for the conversion of aldehydes to nitriles via dehydration of aldoximes such as using $Pd(OAc)_2/PPh_3$,[17] N-(*p*-toluenesulfonyl) imidazole (TsIm),[18] $[RuCl_2$(*p*-cymene)$]_2$/molecular sieves,[19] 2-chloro-1-methyl pyridinium iodide,[20] triethyl amine/SO_2,[21] PPh_3/CCl_4,[22] acetic anhydride,[23] Vilsmeier reagent,[24] Burgess reagent,[25] cyanuric chloride,[26] di-2-pyridylsulfite,[27] AlI_3,[28] $TiCl_3(OTf)$,[29] $AlCl_3$. $6H_2O/KI$,[30] chlorosulfonic acid,[31] and S,S-dimethyl dithiocarbonate.[32]

Although all of these methods are valuable, most of them have one or more of the following drawbacks: less readily available reagents, harsh reaction conditions, low yields, refluxing for a prolonged period of time, tedious workup of the reaction mixture, use of expensive metals and toxic oxidants. Hence, it is of great

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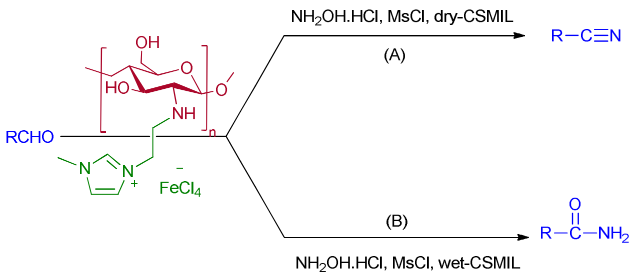
practical importance to develop a more efficient and also environmentally benign method that avoids all of these drawbacks for the conversion of aldoximes into nitriles.

Herein, as part of our ongoing study on the application of this new green catalyst in organic synthesis,[33] we would like to present the direct oxidative conversion of aldehydes into the corresponding nitriles and amides by treatment with hydroxyl amine hydrochloride and mesyl chloride under solvent free condition at 70 ºC in the presence of dry and wet chitosan supported magnetic ionic liquid (CSMIL) (Scheme 1).



Scheme 1. Direct conversion of aldehydes into the corresponding nitriles (method A), and amides (method B) in the presence of CSMIL

Result and discussion

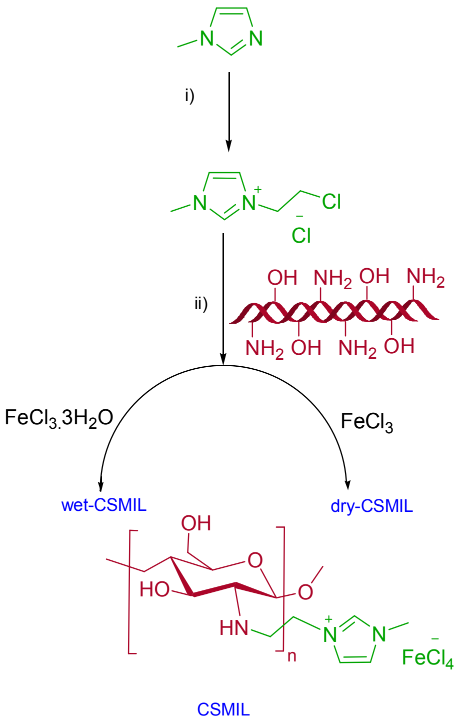
Catalyst preparation

Dry and wet catalyst was prepared and characterized based on the following procedure (Scheme 2) (see the *supporting information*).

Optimization of reaction

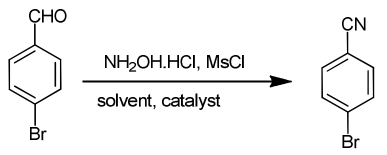
In our initial studies, effect of different catalyst on the outcome of the reaction was considered. For this reason, the conversion of *p*-bromobenzaldehyde to the *p*-bromobenzonitril, as standard model, was considered. The reaction was performed using mixture containing 1 mmol of *p*-bromobenzaldehyde, 1.2 mmol of hydroxylamine hydrochloride, 1.2 mmol of mesyl chloride, and different amounts of catalysts (Table 1). It was confirmed by the results that no product is obtained when the reaction is carried out without catalyst (Table 1, entry 1). When $FeCl_3$ was used as a solid catalyst, the reaction time and the yield of product were unsatisfied (Table 1, entries 2–7). By using a typical IL such as butyl methyl imidazolium chloride [BMIm][Cl] as solvent system for $FeCl_3$ as a catalyst, 70% yields of the product was obtained after 12h, respectively (Table 1, entry 8). In comparison with [BMIm][Cl], butyl methyl imidazolium tetrachloro ferrate [BMIm]$FeCl_4$ as solvent-catalyst increased the yield up to 75% in a shorter reaction time (Table 1, entry 9). But unfortunatly, the separation and reuse of the [BMIm]$FeCl_4$ from the product wasn't so perfect. Therefore, with the new catalyst at hand, we have decided to use of chitosan supported magnetic ionic liquid (CSMIL) as a heterogeneous catalyst. The use of 8 mg of CSMIL afforded 84% of the desired nitrile. Optimization of the reaction condition was undertaken to increase the yield of the product using different amounts of CSMIL. The yield was increased to 96% using 15 mg of CSMIL under solvent-free conditions.

Morever, We screened a variety of solvents and examined their effect on reaction time and yield (Table 1). Use of DMF, DMSO, MeCN (Table 1, entries 5-7) led to moderate yields of 4-nitrobenzonitrile; whereas, the reaction proceeded in the absence of solvent and the best yields of the nitrile was attained. Therefore, solvent-free (entry 8) was found to be the most appropriate condition and was used for all subsequent reactions. Additionally, we also evaluated the effect of temperature on the progress of the model reaction (entries 8 and 9). The best result was obtained at 70 ºC. Further increases in temperature caused no distinguishable improvement in the progress of the reaction that is because of the gelification of chitosan in the structure of catalyst at high temperature.



Scheme 2. Preparation of chitosan supported magnetic ionic liquid (CSMIL); i) 1,2- dichloro ethane, acetone, 25 °C, ii) chitosan, isopropanol, 25 °C

Table 1. Effect of solvent on the conversion of 4-nitrobenzaldehyde into 4-nitrobenzonitrile [a]

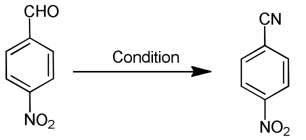


Entry	Catalyst/ mg	Solvent	Time (h)	Temp (ºC)	Yeild[b] (%)
1	No catalyst	DMF	24	120	trace
2	$FeCl_3$/15	DMF	24	120	42
3	$FeCl_3$/15	(BMIM)Cl	6	120	70
4	-	(BMIM)$FeCl_4$	4	120	73
5	Dry-CSMIL/8	EtOH	3	120	77
6	Dry-CSMIL/8	MeCN	3	120	77
7	Dry-CSMIL/8	DMSO	4	120	80
8	Dry-CSMIL/8	DMF	4	120	80
9	Dry-CSMIL/8	neat	2	120	84
10	Dry- SMIL/8	neat	2	70	87
11	Dry-SMIL/10	neat	1. 5	70	90
12	Dry-SMIL/15	neat	1. 0	70	96

[a] Reaction condition: 4-nitrobenzaldehyde (1mmol), NH_2OH. HCl (1. 2 mmol), MsCl (1. 2 mmol). [b] Isolated yield.

Many methods directed towards this goal have therefore been developed; the present methodology was compared to some reported oxidizing condition that summarized in Table 2. This method has the distinction of providing a green biopolymer-supported catalyst, and has attracted much interest in relation to the available methods catalyzed by different catalysts; because this method was undertaken at 70°C, with high yields in short reaction time. It can be seen that 90-96% yield of products is obtained at 70°C in the presence of 15 mg CSMIL after 1-2h whereas 72-98% yield is obtained at 90-120 °C in the presence of another catalysts such as DMSO,[34] $Al_2O_3/MeSO_2Cl$,[35] KF/Al_2O_3,[36] grafit/$MeSO_2Cl$,[37] and DBU/$EtOPOCl_2$.[38]

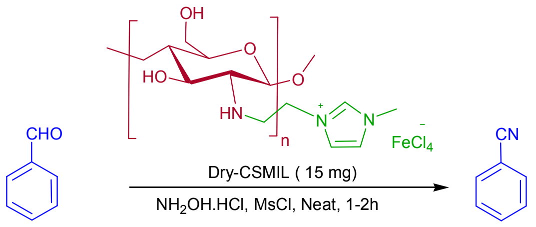
Table 2. Comparison of various catalysts with CSMIL in the synthesis of nitriles from aldehydes



Entry	Condition	Solvent	Time (h)	Temp (ºC)	Yield[a] (%)
1	NH_2OH. HCl, DMSO	DMSO	2	90	97
2	NH_2OH. HCl,dry-$Al_2O_3/MeSO_2Cl$	neat	0. 5	100	95
3	NH_2OH. HCl, KF/Al_2O_3	DMF	4. 5	100	82
4	NH_2OH. HCl,DBU, $EtOPOCl_2$	CH_2Cl_2	15	25	90
5	NH_2OH. HCl,MsCl, grafite	neat	1	100	91
6	NH_2OH. HCl, MsCl, dry-CSMIL	neat	2	70	96

[a] Isolated yield

This heterogeneous system offers an easy work-up that includes only a mixing with a suitable solvent, using simple magnet to remove the magnetic catalyst, extraction with water and evaporation of the solvent. Therefore, we report here a very simple procedure for the transformation of a wide range of aldehydes into nitriles by their treatment with NH_2OH. HCl and MsCl in solvent free condition at 70 ºC (Scheme 3)



Scheme 3.

The present system was further examined for the direct conversion of aldehydes into nitriles, and the results are summarized in Table 3. The results showed that an electron donating group or an electron withdrawing group on benzaldehyde does not have an outstanding effect and gives good yield irrespective of the electronic nature of the aldehyde.

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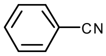
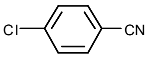
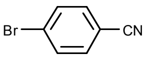
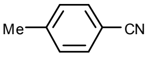
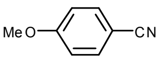
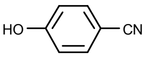
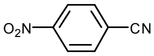
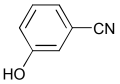
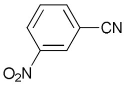
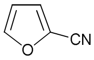
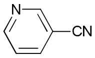
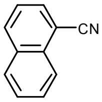
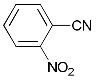
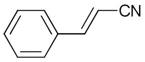
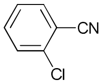
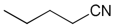
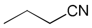
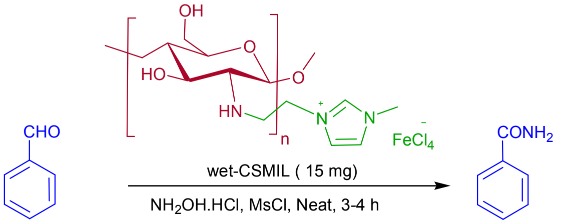
Table 3. Synthesis of nitriles from aldehydes in the presence of dry-CSMIL.[a]

Entry ref	product	Time (h)	Yeild [b] (%)	IR (cm^{-1})
3a [39]		1. 5	93	2218
3b [40]		1. 0	96	2223
3c [41]		1. 0	96	2224
3d [39]		2	92	2227
3e [40]		2	92	2224
3f [40]		2	90	2223
3g [39]		0. 75	97	2230
3h [40]		1. 5	91	2237
3i [40]		1	95	2235
3j [42]		1	95	2228
3k [40]		1	91	2233
3l [43]		1. 5	90	2213
3m [40]		0. 75	93	2233
3n [40]		2	91	2218
3o [44]		1. 5	93	2214
3p [40]		2	90	2232
3q [40]		2	91	2227

[a] Reaction conditions: Aldehyde (1 mmol), hydroxylamine hydrochloride (1. 2 mmol), mesyl chloride (1. 2 mmol), dry chitosan supported (EMIm)$FeCl_4$ (15 mg). [b] Isolated yield.

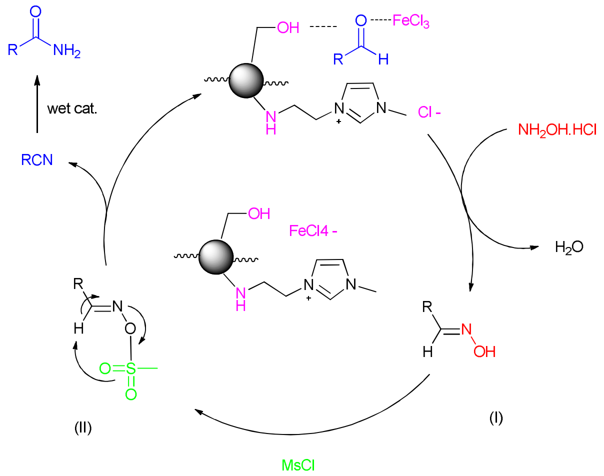
We found that, under the same reaction conditions, by using wet-CSMIL, instead of nitriles, amides were obtained in high yields. Therefore, we report a very efficient method to preparation of amides from aldehydes in wet conditions (Scheme 4). The results demonstrated that this methodology gives good yields of aryl, alkyl and heterocyclic amides from aldehydes when reacted with a mixture of $NH_2OH·HCl$/wet-CSMIL/ $MeSO_2Cl$ at 70 ºC without use of any solvents. The work-up of the reaction mixture was so simple with a quick process, and the yields of the products were high.



Scheme 4.

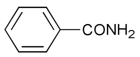
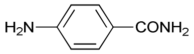
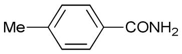
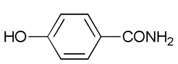
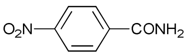
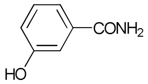
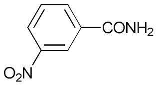
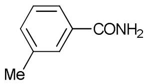
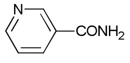
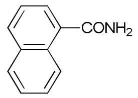
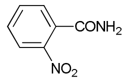
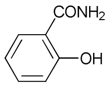
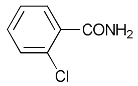
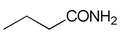
We next examined a wide variety of aldehydes to establish the scope of this transformation. Aldehydes with electron-withdrawing groups as well as electron-donating substituents underwent this one-pot conversion to give the corresponding amides in good yield (Table 4).

A plausible reaction pathway for the conversion of aldehydes to the corresponding nitriles is shown in Scheme 5. At first, aldehyde reacts with hydroxylamine hydrochloride to form an aldoxime I. Then, the aldoxime reacts with mesyl chloride in the presence of CSMIL to form an *O*-mesyloaldoxime II, followed by elimination of MsOH to generate the corresponding nitrile (Scheme 5). On the other hand, when wet-CSMIL was used, the nitrile underwent rapid hydration to produce amide.



Scheme 5. A plausible reaction pathway for the conversion of aldehydes to the corresponding nitriles and amides

Table 4. Synthesized amides from aldehydes in the presence of wet-CSMIL.[a]

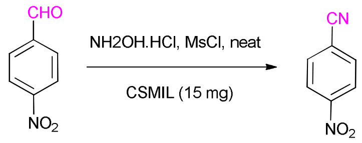
Entry [ref]	product	Time (h)	Yeild [b] (%)	MP (ºC, lit)
4a [45]		4	87	129 (127)
4b [40]		3	88	183 (183)
4d [45]		4	90	161 (163)
4f [40]		3. 5	91	161 (162)
4g [40]		3	92	199 (201)
4h [40]		3. 5	88	171 (170. 5)
4i [40]		3	90	141 (141)
4j [45]		4	89	94 (95)
4k [40]		3. 5	90	125 (125)
4l [40]		3	90	203 (204)
4m [40]		3	91	176 (176. 6)
4n [40]		3. 5	91	141 (142)
4o [40]		3	93	142 (142. 4)
4p [40]	MeCONH$_2$	4	88	80 (81)
4q [40]		4	87	114 (114. 8)

[a] Reaction conditions: Aldehyde (1 mmol), hydroxylamine hydrochloride (1. 2 mmol), mesyl chloride (1. 2 mmol), wet-CSMIL (15 mg). [b] Isolated yield.

The CSMIL catalyst was characterized using some different microscopic and spectroscopic techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), FT-IR and Raman spectroscopies (see the *supporting information*, Figure 1-5). [33]

The possibility of recycling the catalyst was tested by use of the reaction of 4-nitrobenzaldehyde, hydroxylamin hydrochloride and mesyl chloride under optimized conditions. This catalyst can be successfully recycled by different methods such as adsorption by using strong magnetic field (1T), centrifuge method, and filtration. Therefore, the use of a magnet to recover catalyst from reaction mixtures will be very useful and have great potential. Therefore, when the reaction was completed, reaction mixture was cooled to room temperature and diluted with ethyl acetate; the CSMIL was separated from the reaction mixture by use of a magnet during 5-6 minutes. The recycled catalyst was washed with ether for three times and can be used for another cycle. This catalyst was recycled and reused fifth times which was accompanied by the loss of its catalytic activity. The results are shown in Table 5.

Table 5. Recycling of CSMIL



Run	1	2	3	4	5
Time for completion of the reaction/h	0. 75	0. 75	1. 0	1. 5	1. 5

Experimental:

General Considerations:

Chitosan was purchased from Zhejiang Jinke (Golden Shell). The degree of deacetylation was 90% and average molecular weight was 5×10^4. Other chemicals were purchased from Fluka, Merck and Aldrich chemical companies. For recorded ^{1}H NMR spectra we used a Brucker (250MHZ) Avanc DRX in pure deuterated DMSO-d$_6$ and CDCl$_3$ solvents with tetramethyl silane (TMS) as the internal standard. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at 70 eV. FT-IR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer), was employed for characterization of the compounds. The scanning electron micrograph for CSMIL catalyst was obtained by SEM instrumentation (SEM, XL-30 FEG SEM, Philips, at 20 kV). Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reaction monitoring was accomplished via TLC on silica gel PolyGram SILG/UV254 plates.

General procedure for the synthesis of nitriles or amides

A mixture of aldehyde (1 mmol), hydroxyl amin hydrochloride

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(1. 2 mmol), and mesyl chloride (1.2 mmol) in the presence of 15 mg of CSMIL, was stirred at 70 °C; when TLC monitoring indicated no further improvement in the reaction, the reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (3×20 ml). The catalyst was removed by using magnetic feild or filteration and then, the resulting solution was washed with H_2O and the combined CH_2Cl_2 fractions were evaporated. The crude products thus obtained were purified by column chromatography (silica gel, 200–300 mesh; ethyl acetate/petroleum ether). All products were characterized by ^{1}H, ^{13}C NMR, FT-IR, and melting point which were in agreement with literature.

Conclusions

In summary, a convenient and facile method has been established for the conversion of aldehydes into nitriles and amides using a recyclable wet and dry biopolymer-supported ionic liquid as an efficient, inexpensive and non-corrosive catalyst under solvent-free condition. The operationally simple procedure, mild reaction conditions, short reaction time, and versatility are advantages of the current method.

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Notes and references

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† Electronic Supplementary Information (ESI) available: The ^{1}H NMR and ^{13}C NMR for some synthesized compounds and preparation and characterization of catalyst.

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