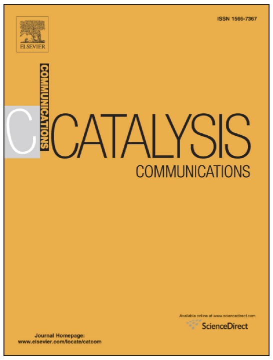

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Recyclable copper-catalyzed ambient aerobic oxidation of primary alcohols to aldehydes in water using water-soluble PEG-functionalized pyridine triazole as ligand

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ABSTRACT:

A water-soluble **PEG-PyTa** ligand, conveniently derived from commercially available reagents *via* a simple synthetic approach, could efficiently promote copper/2, 2, 6, 6-tetramethyl piperidine-1-oxyl (TEMPO)-catalyzed aerobic oxidation of primary alcohols to aldehydes in water under room temperature. A number of primary benzylic, allylic alcohols and heteroaryl methanols were selectively converted into their corresponding aldehydes with excellent yields. The oxidation products could be isolated by simple extraction, and the residual aqueous phase containing the catalyst Cu(OTf)$_2$/**PEG-PyTa** could be reused at least 7 times.

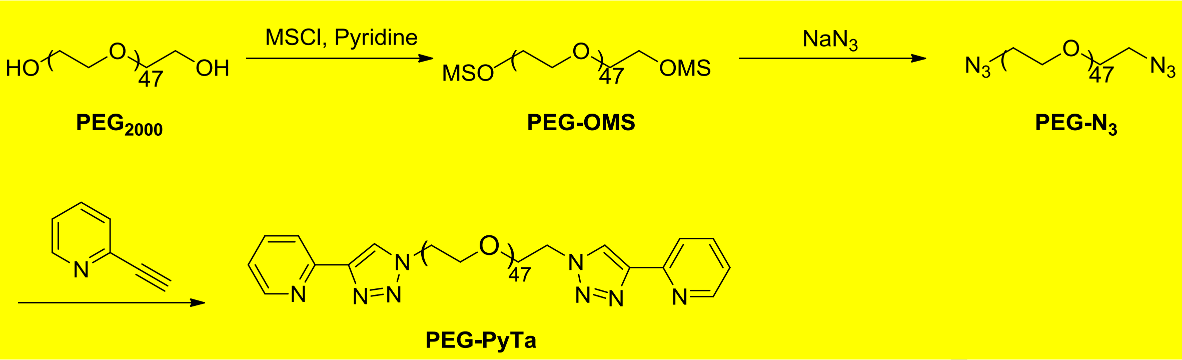
Keywords: PEG-functionalized pyridine triazole ligand (**PEG-PyTa**); copper/TEMPO-catalyzed aerobic oxidation of alcohols; Aqueous homogeneous catalysis.

1. Introduction

The selective oxidation of alcohols to their corresponding aldehydes or ketones is one of most important processes in industry and academia. [1, 2] Traditional methods to accomplish this transformation rely on the stoichiometric amount of metallic or organic oxides, which are expensive, toxic and tend to generate large amounts of hazardous waste. [3] To overcome these inherent problems, significant efforts have been devoted to developing catalytic oxidation alternatives using molecular oxygen as the terminal oxidant during the past decade. [4-8] Among them, quite a lot reports have been focusing on synergistic catalytic systems of simple copper salts and TEMPO, initially described by Semmelhack and co-workers. [9] To improve the catalytic efficiency, Sheldon, Koskinen and others introduced a variety of ligands to stabilize copper catalysts. [10-20] Recently, Stahl reported a more general and efficient Bipy-Cu(I)/TEMPO/*N*-methyl imidazole catalytic system, where a detailed mechanism was also investigated. [21, 22] Despite of a number of efficient copper/TEMPO-related catalytic systems available for aerobic alcohol oxidation, most of these reactions occurred in organic solvents for high conversion. In the view of green chemistry, in recent years, exploring of these catalytic systems in the environmentally benign solvents has been attracted increasing interests.

Water is an extremely cheap, non-toxic and non-flammable solvent. It is obviously advantageous to use water as solvent for organic reactions, which include low cost, work-up procedure simplification and minimum environmental impact. [23] More importantly, the concern about the potential explosion hazard associated with the combination of O_2 and the flammable organic solvents also could be completely eliminated when an aerobic oxidation reaction was implemented in water. [24] More recently, several water-compatible copper/TEMPO-related catalytic systems for aerobic alcohol oxidation have been reported. [25-32] However, many of them suffered from one or more limitations, such as the requirement of heating [25, 27, 28], elevated O_2 pressure [25], long reaction time [26] and the presence of special phase transfer agents [29, 31]. Poly(ethylene glycols) (PEG), a kind of less expensive, non-toxic and biocompatible polymers and also being widely used as green solvents and phase transfer regents in various organic synthesis, are well-known water-soluble supports for catalysts. [33, 34] However, the application of PEG-supported ligand for the aerobic alcohol oxidations in water was rare reported to date. Previously, Toy and co-workers reported a PEG-functionalized 2, 2’-bipyridine as water-soluble ligand for the copper/TEMPO-catalyzed aerobic oxidation of alcohols, however, CH_3CN was crucially required as co-solvent under elevated reaction temperature (80 ^{o}C). [35]

Due to our interest in developing practical and efficient aqueous catalytic systems for transition metal-catalyzed reactions, we reported herein the development of a new PEG-functionalized pyridine triazole (**PEG-PyTa**) ligand (Scheme 1) and its application as water soluble *N*, *N*-bidentate ligand for copper/TEMPO-catalyzed aqueous aerobic alcohols oxidation reactions. With a balloon of oxygen under room temperature, the *in-situ* generated catalytic species could efficiently catalyze a wide range of primary alcohols to their corresponding aldehydes in water. Moreover, after extracting the desired oxidation products, the residual aqueous phase could be reused as recovery catalyst for at least 7 times.



Scheme1. The synthetic route for **PEG-PyTa** ligand

2. Experimental

2.1. Synthesis of PEG-PyTa ligand

The **PEG-PyTa** was synthesized *via* a three-step reaction sequence as described in Scheme 1. The detailed experimental procedure was as following.

To a solution of 20.0 g of PEG_{2000} (10 mmol) and 6.8 g of methanesulfonyl chloride **MSCl** (60 mmol) in 250 mL of dry CH_2Cl_2, was dropwisely added 4.7 g of pyridine (60 mmol) at 0 ^{o}C under N_2 atmosphere. After completion of addition, the mixture was stirred at room temperature for 24 h. The reaction was quenched with 100 mL of ice-water and pH was adjusted to 7 with a 20 % aqueous NaOH solution (about 15 mL). Then the organic layer was separated, washed with brine, dried with Na_2SO_4 and filtered. After removal of solvent (CH_2Cl_2) under vacuum, the residue was precipitated with 150 mL of methyl *tert*-butyl ether (MTBE) to afford 20.7 g of **PEG-OMS** (93%) as a white solid.

A mixture of 17.8 g of **PEG-OMS** (8 mmol) and 3.1 g of NaN_3 (48 mmol) was stirred in 150 mL of DMF at 65 ^{o}C for 12 h. The resulting mixture was cooled to room temperature and most of DMF was removed under vacuum. 100 mL of CH_2Cl_2 was added to dissolve the residue, washed with brine, dried with Na_2SO_4 and followed a similar procedure as described above to afford 15.1 g of **PEG-N_3** (91%) as a white solid.

To 50 mL of 1:1 of CH_3OH/H_2O, were sequentially added 10.3 g of **PEG-N_3** (5 mmol), 1.24 g of 2-ethynylpyridine (12 mmol), 0.50 g of $CuSO_4{\cdot}5H_2O$ (2.0 mmol) and 0.40 g of sodium ascorbate (2.0 mmol). The mixture was stirred at 45 ^{o}C for 24 h. Then the solution was concentrated under vacuum and 50 mL of 10% $NH_3{\cdot}H_2O$ was added. After stirred for 12 h, the mixture was extracted twice with 50 mL of CH_2Cl_2, dried with Na_2SO_4 and followed a similar procedure as described above to afford 9.8 g of **PEG-PyTa** (87%) as a white solid. ^{1}H NMR (500 MHz, MeOD): δ=8.60 (d, *J*=4.7 Hz, 1H), 8.52 (s, 1H), 8.09 (d, *J*=8.0 Hz, 1H), 7.96-7.92 (m, 1H), 7.40-3.38 (m, 1H), 4.69 (t, *J*=5.0 Hz, 2H), 3.97 (t, *J*=5.0 Hz, 2H), 3.65-3.63 (m, 92H, CH_2 of PEG chain); ^{13}C NMR (125 MHz, MeOD): δ=151.2, 150.5, 148.5, 138.8, 125.0, 124.4, 121.3, 71.5-71.4 (C of PEG chain), 70.3, 51.6. MALDI-TOF-MS (m/z) calcd. for $C_{110}H_{203}N_8O_{47}$ $[M_{n=47}+H]^+$ 2388.37, found: 2388.48, $C_{110}H_{202}N_8O_{47}Na$ $[M_{n=47}+Na]^+$ 2410.37, found: 2410.39.

2.2. General procedure for aerobic oxidation of alcohols in water

To a 48 mL tube, were added Cu(II) or Cu(I) salt (0.05 mmol), **PEG-PyTa** (0.025 mmol) and H_2O (3.0 mL). The mixture was stirred for 30 min at room temperature and a clear dark-blue solution was observed. Then alcohols (1.0 mmol), TEMPO (0.05 mmol), and K_2CO_3 (0.2 mmol) were sequentially added, followed by connecting a balloon of oxygen. The reaction mixture was stirred at room temperature until the reaction completed based on GC analysis. After that, the reaction mixture was extracted with MTBE (3 mL × 3) and the extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under vacuum. Finally, the residue was purified by flash chromatography on silica to afford the desired aldehydes.

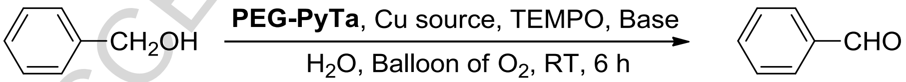
3. Results and discussion

3.1. Optimization of the reaction conditions

The performance of **PEG-PyTa** on the copper/TEMPO-catalyzed aerobic alcohol oxidation in water was investigated with benzyl alcohol as a model substrate (Table 1). As previous reports, base is essential for the reaction. Therefore, we started our aerobic oxidation reaction in water with 5 mol% $CuCl_2$, together with 5 mol% TEMPO and 20 mol% K_2CO_3 as catalyst system under a balloon of O_2. After stirred at room temperature for 6 h, only 27% of benzaldehyde was observed according to GC analysis (entry 1, Table 1). However, the conversion could be significantly improved when adding **PEG-PyTa** as ligand. In the presence of 2.5 mol% **PEG-PyTa**, the conversion was increased to 83% under the same reaction conditions (entry 2, Table 1). This positive result promoted us for further optimizations. With **PEG-PyTa** as ligand, copper sources, including Cu(II) salts ($CuBr_2$, $CuSO_4$, $Cu(NO_3)_2$, $Cu(OTf)_2$, $Cu(TFA)_2$ and $Cu(OAc)_2$) and Cu(I) salts (CuBr and CuCl), were first screened. It was found that Cu source has an obvious effect on the reaction conversion and Cu(II) salts generally exhibited better catalytic activity than Cu(I) salts (entries 3-10, Table 1). To our delight, quantitative conversion was achieved when $Cu(OTf)_2$ was employed (entries 6, Table 1). Next, the effect of base was also investigated. Na_2CO_3 afforded a similar result as K_2CO_3 (entry 11, Table 1). However, either stronger base (KOH and K_3PO_4) or weaker base ($NaHCO_3$) dramatically decreased the conversion (entries 12-14, Table 1). We also attempted to lower down the amount of $Cu(OTf)_2$, TEMPO and K_2CO_3. Unfortunately, decreasing each of them resulted in lower conversions (entries 15-19, Table 1).

Noteworthy, increasing **PEG-PyTa** could not improve the reaction, which hinted that Cu(II) and **PyTa** formed a 1 : 1 complex (entries 18 and 19, Table 1). In addition, we also tested air to replace O_2. Under the same reaction conditions, only a 39% conversion was observed. However this lower conversion could be compensated by elongating the reaction time (99% conversion after 18 h, entry 20, Table 1). The different reaction rates with balloons of air and O_2 were contributed to their different oxygen concentrations in water (10.6 mg/L under a balloon of air *vs* 29.4 mg/L under a balloon of O_2, determined by Dissolved Oxygen Meter). Noteworthy, we found that increasing the reaction temperature to 40 °C remarkably decreased the reaction rate (entry 21, Table 1). Such negative effect might also be ascribed to the relative lower oxygen concentration in water at higher temperature. As expected, no reaction occurred without TEMPO (entry 22, Table 1). Furthermore, kinetic study revealed that 6 h was necessary for the complete reaction (See Figure 2S). Finally, the optimal conditions were concluded as: $Cu(OTf)_2$ (5 mol%), **PEG-PyTa** (2.5 mol%), TEMPO (5 mol%) and K_2CO_3 (20 mol%) in water with a balloon of O_2 under room temperature.

Table 1 Optimizing the reaction conditions of the oxidation of benzyl alcohol [a]



Entry	Cu source (mol%)	Base (mol%)	**PEG-PyTa** (mol%)	TEMPO (mol%)	Conv. [b] (%)
1	$CuCl_2$ (5)	K_2CO_3 (20)	--	5	27
2	$CuCl_2$ (5)	K_2CO_3 (20)	2.5	5	83
3	$CuBr_2$ (5)	K_2CO_3 (20)	2.5	5	86

4	$CuSO_4$ (5)	K_2CO_3 (20)	2.5	5	84
5	$Cu(NO_3)_2$ (5)	K_2CO_3 (20)	2.5	5	90
6	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	2.5	5	100
7	$Cu(TFA)_2$ (5)	K_2CO_3 (20)	2.5	5	79
8	$Cu(OAc)_2$ (5)	K_2CO_3 (20)	2.5	5	60
9	CuCl (5)	K_2CO_3 (20)	2.5	5	56
10	CuBr (5)	K_2CO_3 (20)	2.5	5	66
11	$Cu(OTf)_2$ (5)	Na_2CO_3 (20)	2.5	5	99
12	$Cu(OTf)_2$ (5)	KOH (20)	2.5	5	10
13	$Cu(OTf)_2$ (5)	K_3PO_4 (20)	2.5	5	49
14	$Cu(OTf)_2$ (5)	$KHCO_3$(20)	2.5	5	57
15	$Cu(OTf)_2$ (5)	K_2CO_3 (10)	2.5	5	54
16	$Cu(OTf)_2$ (5)	K_2CO_3 (5)	2.5	5	43
17	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	2.5	3	93
18	$Cu(OTf)_2$ (3)	K_2CO_3 (20)	2.5	5	86
19	$Cu(OTf)_2$ (3)	K_2CO_3 (20)	1.5	5	86
20 [c]	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	2.5	5	39 (99)
21 [d]	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	2.5	5	46
22 [e]	$Cu(OTf)_2$ (5)	K_2CO_3 (20)	2.5	5	trace

[a] Reaction conditions: Benzyl alcohol (1 mmol), H_2O (3 mL), a balloon of O_2, room temperature.

[b] GC conversions. Selectivities to benzaldehyde in all cases were 100% and no benzoic acid was

observed.

[c] Under a balloon of air, the conversion in parentheses was obtained after 18 h.

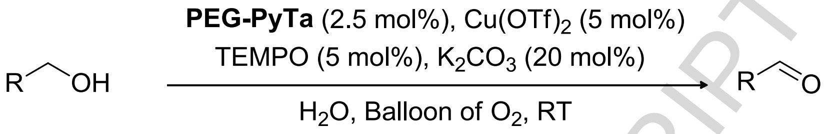
[d] Reaction at 40 °C.

[e] Without TEMPO.

3.2. Substrate scope

With the optimal conditions in hands, we then explored the substrate scope of the newly developed $Cu(OTf)_2$/**PEG-PyTa**/TEMPO/K_2CO_3 catalytic system for the aerobic oxidation of primary alcohols and the results were summarized in Table 2. To our delight, most of the tested substrates, including substituted benzyl alcohols, 1-naphthalenemethanol, heteroaryl methanols (2-thiophenemethanol and 3-pyridinemethanol) and cinnamyl alcohol, could be smoothly transformed into their corresponding aldehydes with high yields by adjusting the reaction time, no acids and esters were observed during the reaction. A wide range of functional groups such as OMe, SMe, F, Cl, Br, OH and NO_2 could be well-tolerated, some of which could be utilized for further derivation. For substituted benzyl alcohols, there appeared to be no obvious relationship between the yields and the position or electronic property of the substituents on the phenyl ring, just the oxidation time varied with different substrates. For example, much longer reaction time (24 h) was needed for complete reaction of 2-methylbenzyl alcohol than that for 4-methylbenzyl alcohol (entry 2 *vs* entry 4, Table 2). However, no obviously different reaction activity was observed between 2- and 4-bromobenzyl alcohols (entry 11 *vs* entry 12, Table 2). Generally, for an aqueous organic reaction, water-solubility of substrates plays an important role on the reaction rate. Therefore, we speculated that such irregular results might be caused by their different solubility in water. Unfortunately, 4-cyanobenzyl alcohol and 2-pyridinemethanol could not transform to their corresponding aldehydes which could be ascribed to their strong coordination ability and thus deactivating the catalyst. Furthermore, the newly developed catalytic system failed to the oxidation of aliphatic primary alcohol (entry 21, Table 2).

Table 2 Aerobic oxidation of primary alcohols to aldehydes [a]



Entry	R	Time (h)	Conv. (%) [b]	Yield (%) [c]
1	C_6H_5	6	100	87 (99) [d]
2	4-$CH_3C_6H_4$	6	>99	93
3	3-$CH_3C_6H_4$	6	97	95
4	2-$CH_3C_6H_4$	24	>99	94
5	4-$CH_3OC_6H_4$	6	>99	96
6	3-$CH_3OC_6H_4$	6	>99	94
7	3,4-$(CH_3O)_2C_6H_3$	6	94	93
8	4-$CH_3SC_6H_4$	12	100	95
9	4-FC_6H_4	18	100	91
10	4-ClC_6H_4	6	95	95
11	4-BrC_6H_4	12	>99	96
12	2-BrC_6H_4	12	100	91

13	4-(OH)C_6H_4	18	100	92
14	4-CNC_6H_4	12	--	--
15	4-(NO_2)C_6H_4	18	100	95
16	1-naphthyl	24	94	93
17	2-thienyl	12	100	92
18	3-pyridyl	12	100	93
19	2-pyridyl	12	trace	--
20	$C_6H_5CH=CH$	6	100	99
21	*n*-butyl	12	N.R.	--

[a] Reaction conditions: Substrate (1 mmol), $Cu(OTf)_2$ (5 mol%), **PEG-PyTa** (2.5 mol%), TEMPO (5 mol%), K_2CO_3 (20 mol%), H_2O (3 mL), a balloon of O_2, room temperature.

[b] Determined by GC.

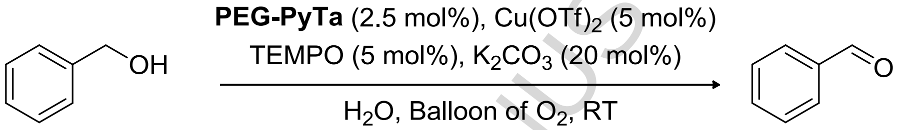
[c] Isolated yields.

[d] Benzaldehyde was volatile and some of them were lost during work-up. The yield in parentheses was determined by GC with naphthalene as internal standard.

3.3. Recycling study

As mentioned previous, one of the important advantages of using water-soluble catalyst for aqueous organic reactions is the simple product isolation by convenient solvent extraction, while leaving the catalyst in aqueous phase for potential reuse. Therefore, the recyclability of catalyst ($Cu(OTf)_2$/**PEG-PyTA**) for aqueous oxidation reaction was examined using benzyl alcohol as the tested substrate under the optimal conditions. After the reaction completed, TEMPO and the resulted benzaldehyde were extracted with MTBE. To the residual aqueous phase, was added fresh benzyl alcohol, TEMPO and K_2CO_3. To our delight, as the results illustrated in Table 3, the catalyst did not lose any activity for four cycles. Despite that reduced catalytic activity was observed in subsequent cycles, complete conversion still could be achieved at the fifth and sixth cycles and 96% conversion for the seventh cycle after prolonging the reaction time to 12 h. In this regard, the catalyst $Cu(OTf)_2$/**PEG-PyTa** could be reused for at least 7 times.

Table 3 Reusability of $Cu(OTf)_2$/**PEG-PyTa** catalyst for the oxidation of benzyl alcohol [a]



Cycle(n)	Time	Conv. (%) [b]
Fresh	6	100
1	6	100
2	6	100
3	6	97
4	6	100
5	6 (12)	87 (100)
6	6 (12)	76 (100)
7	6 (12)	56 (96)

[a] Reaction conditions: Benzyl alcohol (1 mmol), $Cu(OTf)_2$ (5 mol%), **PEG-PyTa** (2.5 mol%), TEMPO (5 mol%), K_2CO_3 (20 mol%), H_2O (3 mL), a balloon of O_2, room temperature.

[b] Conversions of benzyl alcohol were determined by GC.

4. Conclusion

In summary, we have successfully developed a novel PEG-functionalized pyridine triazole ligand from commercially available PEG_{2000} and 2-ethynyl pyridine *via* a simple synthetic approach. It was shown that **PEG-PyTa** could be utilized as water-soluble bidentate *N*, *N*-ligand to promote the aqueous aerobic $Cu(OTf)_2$/TEMPO-catalyzed oxidation of primary alcohols under room temperature in water without any organic co-solvent or phase transfer reagent. Under optimal conditions, a wide range of functionalized aldehydes could be achieved from their corresponding primary alcohols in excellent yields. The catalytic system could be reused at least 7 times. This newly developed protocol provided an efficient, practical and environmental benign method for the synthesis of various aldehydes.

Acknowledgements

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Highlights

An efficient and recyclable catalytic system for the aerobic alcohol oxidation was developed.

A variety of aldehydes were synthesized from primary alcohols in neat water under room temperature.

A novel PEG-functionalized pyridine triazole was designed and synthesized.