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A Robust and Recyclable Polyurea-Encapsulated Copper(I) Chloride for One-Pot Ring-Opening/Huisgen Cycloaddition/CO_2 Capture in Water

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The multicomponent ring-opening/Huisgen cycloaddition reactions combined with CO_2 capture with polyurea-encapsulated copper salt as catalyst that in-situ formed from simple CuCl and soluble polyurea during the reaction were carried out successfully for the synthesis of β-hydroxytriazoles under exceptionally mild conditions, in which the polyurea-encapsulated copper(I) chloride was proved to be a robust and recyclable catalyst system with high yields as well as excellent chemoselectivity in this reaction.

Introduction

In heterogeneous catalysis or heterogenization of homogeneous catalytic systems that are robust and could be readily separated from the reaction mixtures[1], reactions at the liquid-liquid or solid-liquid interface is a common phenomenon and still hold a great potential for polymerization and synthetic organic chemistry.[2,3] For example, Bergbreiter and coworkers[4] have recently reported that the enforced phase-selective solubility of polyisobutylene (PIB)-bound Rh(II) catalysts in biphasic liquid-liquid (heptane/acetonitrile mixtures) could be used not only to recycle these rhodium catalysts but also to suppress the formation of by-product in the cyclopropanation and O-H insertion reactions of ethyl diazoacetate, which might be due to increased phase segregation of the soluble polymer-bound catalyst and the reactant (ethyl diazoacetate). Thus and nowadays, reactions “in/on water”, “at the surface/interface”, or by “phase-transfer” are important platforms for modern catalysis and synthetic chemistry,[2-5] especially as in most cases solid or water can be used as the second phase, which would be useful for the isolation of catalyst and products. In addition, immiscible reaction partners react at the surface of solid or interface of two liquids, which is also a convenient and versatile route for the facile preparation of organic molecules or polymeric materials. However, heterogeneous catalysts are usually less reactive, necessitating harsher conditions, such as higher temperature and pressure, and could be less selective or substrate-selective in some cases.[6] Of course, a general drawback is that reactivity of immiscible metal catalysts that generally immobilized on solid-state supports is often decreased in comparison to that of the corresponding original catalysts in homogeneous phase. Moreover, in many cases, recovered metal catalysts have lower reactivity than that of freshly used catalysts. Therefore, on the basis of basic phenomenon with controllable reactions at the liquid-liquid or solid-liquid interface, the development of more efficient heterogeneous catalyst that has higher TON and TOF than that of original catalyst in homogeneous system is highly desirable from a viewpoint of Green Chemistry.[7] It should be noted that, considerable effort has been directed towards immobilizing metal catalyst onto immiscible supports include amorphous silica,[8] porous ordered materials,[9] and organic polymers.[10]

Notably, since the microencapsulation method was first introduced in 1998,[11] organic polymer support –based microencapsulated technology has been worked as a privileged method for immobilizing metal catalysts onto polymers in the past decades.[12] As a new strategy, microencapsulated catalysts (MC) were new type of heterogeneous catalysts, in which the microcapsules are backbones of immobilized catalysts, such as cross-linked polymers and inorganic materials, including silica gel and alumina, and thus are completely different from conventional microcapsules that are used for coating and isolating substances until their activity is needed.[13] Thus with the MC technique, the polymer incarcerate metal catalysts are generally more robust against many solvents, including water. Notably, among the polymers used in MC technique, polyureas (PUA) have been attracted increasing attractions in the past years.

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Polyureas (PUA) that are defined as ureylene containing functional –NHCONH- in the polymer backbones, are known as an interesting and high performance polymer owing to the high mechanical, thermal and chemical stability, good abrasion resistance, high rate of healing, fast curing, and viscoelastic properties.[14] Especially, PUA has been well known to have good flexibility and water repellency, which inspired chemists to expand the use of PUA as protective coating materials to new applications,[15,16] such as heterogeneous support in catalysis.[16] In this context, Ley and co-workers have ever reported the polyurea-encapsulated palladium for versatile cross-coupling reaction[16a,16b,16f,16g], reduction of ketones[16c], hydrogenolysis of epoxides[16e], in which one of the most promising features of palladium catalyst immobilization on polyurea is microencapsulation. Ley and co-workers have also used microencapsulation technique to encapsulate osmium tetroxide within a polyurea matrix that has been effectively used in the dihydroxylation of olefins[16d]. Subsequently, these commercially available polyurea-encapsulated palladium (also simplified as PdEnCat catalysts) with microencapsulation technique have been used by other groups as an attractive catalyst for tandem catalysis because of their high activity, wide substrate scope, low leaching, and strong recycling capability.[16,17] Furthermore, the polyurea microcapsules are proved to be completely insoluble in aqueous and most of organic solvents, and it was found that polyurea is extremely robust without any degradation under general reaction conditions.[16-18] Therefore, further efforts are directed in this work toward the development of polyurea-encapsulated copper catalyst with improved chemoselectivity and high performance for environmentally benign transformations. Herein we report a new reaction system for the one-pot multicomponent ring-opening/Huisgen cycloaddition that can be run with the need of green chemistry.

Results and discussion

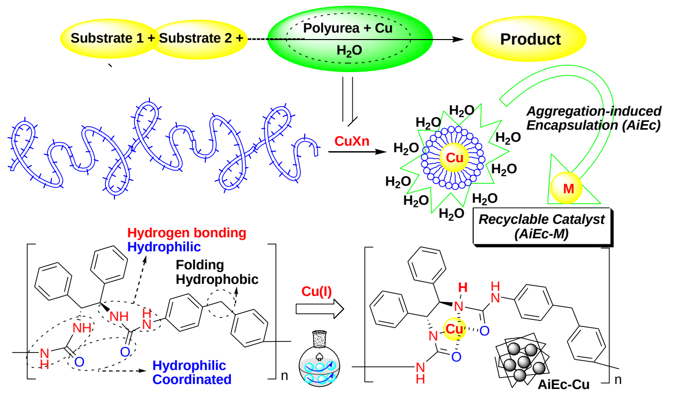
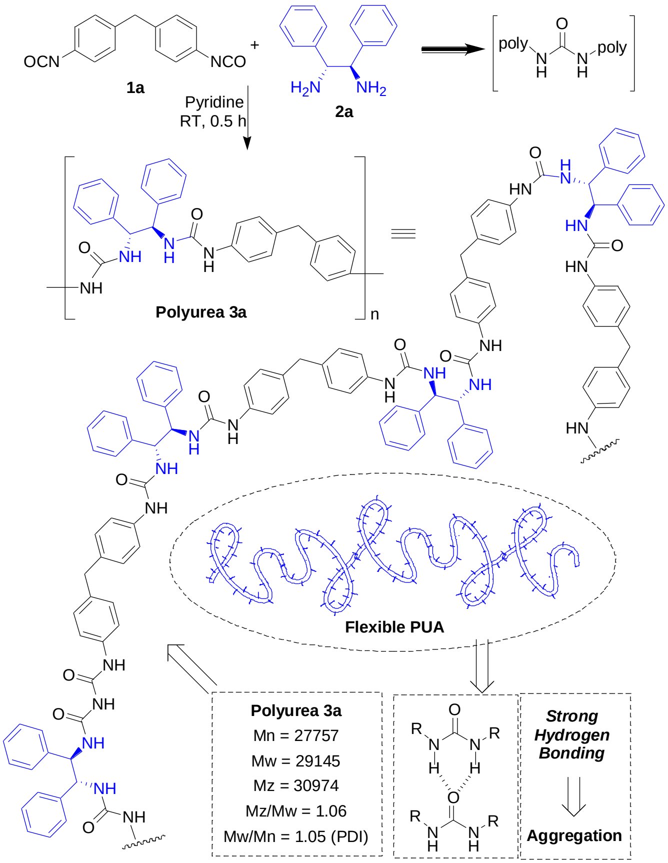


Figure 1. The development of aqueous copper-catalyzed transformations and the illustration of polyurea-encapsulated copper(I) catalyst on the basis of the hypothesis of aggregation-induced encapsulation (AiEc).

As illustrated in Figure 1, we hypothesized that the 1,2-diamine-linked urea functionality on polyurea could be effective group for the adsorption of metal salts in water, such as various copper salts, including unstable CuCl, and other Cu(I) salts, in which the backbone of the polyurea would ligate and retain the metal species within the polymeric matrix. Although simple in concept of aggregation-induced encapsulation (AiEc), encapsulation of copper is synthetically challenging since the supported catalyst must be firmly trapped inside the immiscible supports (such as PUA) in order to avoid leaching of metal ion into the liquid phase. Considered the facts that ureas are geometric compatible with copper ion and the hydrogen-bond acceptor,[19] and known as excellent hydrogen-bond donors,[20] we believed the aggregation-induced encapsulation of copper catalyst could be recovered and reused in aqueous organic transformations, which would also provide a facile approach with new strategy to the green synthesis of useful compounds, such as β-hydroxytriazoles reported in this work.

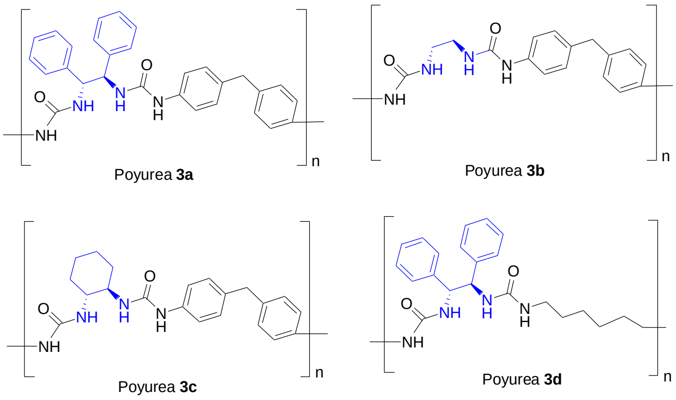


Scheme 1. The synthesis of 1,2-diamine -derived polyurea (PUA) featured with hydrogen bond network and possible folding backbone.

Initially, on the basis of previous investigation on the use of 1,2-diamine that could be an important moiety for the construction of stable copper complexes, such as salen- or salan-Cu complex,[21] we designed and prepared several 1,2-diamine-derived polyureas with possible folding backbone for encapsulated copper-catalyzed transformations reported in this work (Scheme 1). Four different polyureas were achieved in high yields. Interestingly, only the polyurea **3a** was a soluble polymer with high molecular weight (Mw = 29145 that detected by GPC) and other 1,2-diamine -derived polyureas

3b-3d exhibited poor solubility in general solvents (Scheme 2), which hindered the determination of molecular weight by GPC and the structural analysis of **3b**-**3d**. With four polyureas in hand, we evaluated the catalytic application of these structurally clear polyureas in the promotion of copper-catalyzed azide-alkyne cycloaddition reaction.

To our knowledge, one of the most powerful and widely applied copper-mediated reactions of recent times is arguably the azide-alkyne cycloaddition (Huisgen reaction).[22,23] Notably, this click-type transformation could be performed in water, which would be beneficial to numerous applications in green chemistry and biological systems. Seeking a route that did not require a preparation of organic azides that might be an explosive reagent during the purification, we reasoned that the direct use of sodium azide for multicomponent azide-alkyne addition is ideal procedure in green chemistry. Meanwhile, multicomponent cycloadditions are synthetically important transformations, both in academic laboratory and in industry. Accordingly, the need for a practical, atom-economical, and environmentally benign version of multicomponent azide-alkyne cycloaddition transformations has received considerable interest in homogeneous catalytic systems.[24] However, previous methods are mostly restricted to the use of complicated ligand, defectiveness in chemoselectivity, and the difficulty in recyclability of catalyst makes these strategies not ideal for green chemistry. Therefore, the development of new catalyst system, polyurea - encapsulated copper, that is devoid of these deficiencies in multicomponent azide-alkyne cycloaddition would be of great importance.



Solubity of polyurea in organic solvents

Polyurea	Toluene	$CHCl_3$	EtOAc	THF	MeOH	EtOH	DMSO
3a	yes	no	no	no	no	no	yes
3b	no	no	no	no	no	no	no/swelling
3c	no	no	no	no	no	no	no/swelling
3d	no	no	no	no	no	no	no/swelling

Scheme 2. Various 1,2-diamine-deirved polyureas evaluated in this work.

Therefore, the multicomponent click addition of sodium azide, epoxide **4a**, and alkyne **5a** is carried out at room temperature in water using polyurea **3a** as a capsule in the copper catalysis. Under the initial reaction conditions, the combinational use of polyurea **3a** and CuCl was proved to be an effective catalyst system in this reaction. As shown in Table 1, the desired product **7a** was obtained in excellent yield (95%) and high chemoselectivity (Entry 1, >99:1, only **7a** was achieved without isomer **6a**). However, only moderate yield (50%) and inferior chemoselectivity was achieved in the absence of polyurea **3a** (Entry 2), which supported the powerful role of polyurea in the stabilization and activation of copper catalyst for click cycloaddition. In other words, the polyurea **3a** also has a strong ability to work as polymeric ligand because of its urea moiety.

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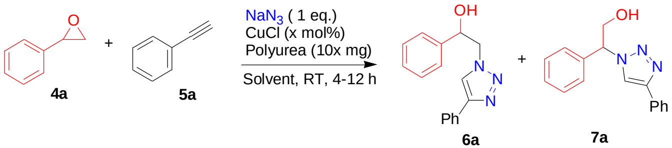
Table 1. The effect of polyurea in the copper-catalyzed multicomponent azide-alkyne cycloaddition: Domino ring-opening and Huisgen cycloaddition of sodium azide, epoxide **4a**, and alkyne **5a**.[a]



Entry	Cu	PUA	Solvent	Yield (%)[b]	6a/7a[c]
1	CuCl	**3a**	H_2O	95	<1/99
2	CuCl	-	H_2O	50	2:98
3	CuCl	**3a**	CH_2Cl_2	NR	-
4	CuCl	**3a**	CH_3CN	NR	-
5	CuCl	**3a**	THF	NR	-
6	CuCl	**3a**	Toluene	NR	-
7	CuCl	**3a**	H_2O	70[d]	2:98
8	CuCl	**3a**	H_2O	75[e]	2:98
9	CuCl	**3a**	H_2O	90[f]	<1/99
10	$CuCl_2$	**3a**	H_2O	60	2:98
11	Cu_2O	**3a**	H_2O	55	2:98
12	CuBr	**3a**	H_2O	85	2:98
13	$CuBr_2$	**3a**	H_2O	73	2:98
14	CuCl	**3b**	H_2O	70	2:98
15	CuCl	**3c**	H_2O	85	2:98
16	CuCl	**3d**	H_2O	80	2:98
17	CuCl	**3a**	H_2O	96[g]	<1/99

[a] Except the specified note, the reaction conditions as following: epoxide **4a** (1 mmol), alkyne **5a** (1 mmol), NaN_3 (1 mmol), CuCl (1 mol%), and polyurea **3a** (10 mg), in water/solvent (2 mL), at room temperature for 4-12 hours (entries 1, and 7-15, reaction time is 4-8 h; and for entries 2-6, reaction time is 12 h. [b] The isolated yield of **7a**. [c] It was determined by NMR, and confirmed by GC-MS. [d] The use of 2.5 mol% of CuCl and 25 mg of polyurea **3a** in this case. [e] The use of 5 mol% of CuCl and 50 mg of polyurea **3a** in this case. [f] The use of 0.5 mol% of CuCl and 5 mg of polyurea **3a** in this case. [g] Under the CO_2 atmosphere (balloon).

Then the effect of solvent on the one-pot multicomponent ring-opening/Huisgen cycloaddition reaction was evaluated at room temperature. When the multicomponent reaction was carried out in CH_2Cl_2, CH_3CN, THF, or toluene, no desired product was obtained (Entries 3-6). Therefore water (H_2O) was proved to be an integral part of such multicomponent addition reaction. And interestingly, we found that the reaction with larger amount of catalyst and polyurea (above 2.5 mol% CuCl) gave decreased yield (Entries 7 and 8), thus the use of 1 mol% CuCl was enough good in this reaction. It should be noted that 0.5 mol% CuCl and 5 mg of polyurea was enough good to promote the one-pot multicomponent ring-opening/Huisgen

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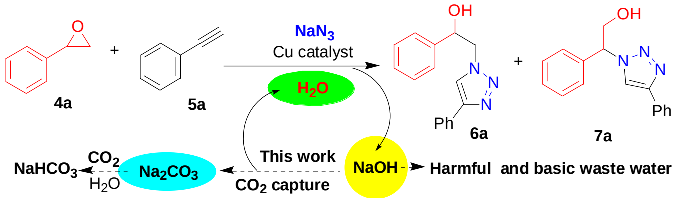
cycloaddition reaction (Entry 9, 90% yield). Interestingly, other copper sources, such as $CuCl_2$, Cu_2O, CuBr, or $CuBr_2$, only gave moderate yield in this reaction (Entries 10-13, 55-85% yield). These experimental results showed that Cu(I)Cl catalyst would be better in the polyurea-encapsulated Huisgen cycloaddition, which is different from our previous work on the enantioselective Huisgen cycloaddition[24]. The matching of polyurea **3a** and Cu(I)Cl could be supported by fluorescent analysis (See Supporting Information, Figure S1), which revealed the quenching of polyurea **3a** with CuCl is the less pronounced of the tested metal ions (chloride anion) in solution. Although the physical and chemical properties of **3b-3d** (Scheme 2, with different structure and solubility) were different from that of polyurea **3a**, the activity of these insoluble polyureas **3b-3d** was evaluated in this aqueous multicomponent transformation. As shown in Table 1 (Entries 14-16), these polyurea material exhibited inferior ability to promote this reaction because of its only moderate yields (70-85%) and slightly inferior chemoselectivity (98:2), which might be arisen from comparably weaker encapsulated ability of these insoluble polyurea in water in comparison to that of polyurea **3a**. Thus accordingly, polyurea **3a** was suitable for the multicomponent ring-opening/Huisgen cycloaddition.



Scheme 3. An overlooked product (NaOH) in the multicomponent ring-opening/Huisgen cycloaddition of sodium azide, epoxide, and alkyne in the previous reports: The environmentally benign process combined with CO_2 capture.

Interestingly, previous reports on the copper-catalyzed multicomponent ring-opening/Huisgen cycloaddition[25] neglected the formation of NaOH, which resulted into harmful sodium hydroxide-containing basic waste water that opposed to the exact demands of green chemistry. To the best of our knowledge, there are no reports on the multicomponent transformation combined with CO_2 capture to date. Therefore, we hypothesized that the sodium hydroxide could be neutralized by CO_2 in this reaction, which would be also an environmentally benign process combined with CO_2 capture (Scheme 3). Notably, carbon dioxide (CO_2) capture is recognized as a necessary and important technology related to energy security and environmental sustain ability, in which the capture and separation of CO_2 has been extensively investigated for energy-saving process, conversion applications of CO_2, and meeting green-house gas emissions reduction targets.[26] As expected, the multicomponent ring-opening/Huisgen cycloaddition under the CO_2 atmosphere gave slightly increased yield and good selectivity in term of the ring-opening reaction with epoxide **4a** (Table 1, entry 17). In this case, the addition of CO_2 balloon did not affect the catalytic performance of polyurea-encapsulated copper catalyst. And the basic aqueous solution was neutralized completely by CO_2 capture, which is not only beneficial to the stability of polyurea-encapsulated copper catalyst but also minimizes the waste-water discharges.

Notably, the reaction progress of polyurea **3a** in the encapsulation of copper catalyst in this aqueous multicomponent ring-opening/Huisgen cycloaddition under the optimized reaction conditions is visually shown in Figure 2. The desired products assembled in or around the polyurea-encapsulated catalyst system in/on water, indicating the co-precipitation of the polymer-supported copper catalyst and the water-insoluble triazoles during the one-pot ring opening and Huisgen cycloaddition of sodium azide, epoxide **4a**, and alkyne **5a**. In fact, the click multicomponent reaction –initiated co-precipitation of the polymer-supported copper catalyst and the water-insoluble triazoles was similarly to that of our previously reported strategy on the reactive PMHS-SIPNs (polymethylhydrosiloxane (PMHS)-derived semi-interpenetrating networks)-involved hydrogenation reaction –initiated preparation of organosilicon-supported palladium or TiO_2/nanosilver catalyst.[27] In this regard, recyclable polyurea-encapsulated copper catalyst (AiEc-Cu) was successfully formed after the multicomponent ring-opening/Huisgen cycloaddition was completed, which would be an ideal heterogeneous isolation for green synthetic chemistry without extraction by organic solvent.

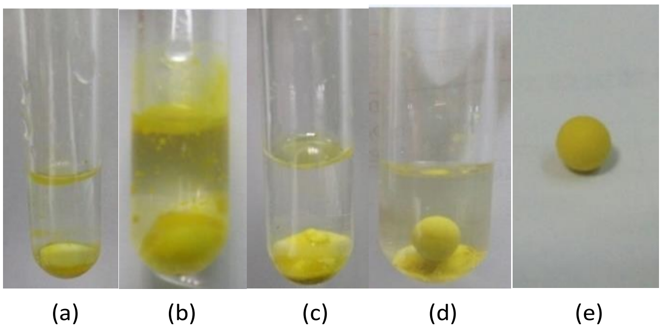


Figure 2. The image of desired polyurea-encapsulated copper catalyst (AiEc-Cu) formed in the multicomponent ring-opening/Huisgen cycloaddition: (a) initial stage (1 min); (a) initial stage (10 min); (c) when the reaction was carried out for 2 h; (d) the last stage after reaction (4 h); (e) the recovered polyurea-encapsulated copper catalyst mixed with product: The co-precipitation of the polymer-supported copper catalyst and the water-insoluble triazoles.

To further investigate the recyclability of the recovered polyurea-encapsulated copper catalyst, the catalyst recycle experiments were carried out to investigate the activity of the AiEc-Cu catalyst in the catalytic multicomponent ring-opening/Huisgen cycloaddition of sodium azide, epoxide **4a**, and alkyne **5a**. As a heterogeneous catalyst, the reusability of polyurea-encapsulated copper catalyst was easily recovered after filtration from the aqueous solution and washed with EtOAc (The reaction product was soluble in EtOAc and the polyurea-encapsulated copper catalyst was not soluble in this solvent). The resulted solid was dried overnight and was used without addition of CuCl and any further treatment. As shown in Figure 3, a comparable catalytic activity with almost same

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good selectivity was observed when repeated use of 1 mol% of CuCl catalyst combined with small amount of polyurea **3a** was carried out under the optimized reaction conditions (Figure 3).[28] Thus the recovered AiEc-Cu catalyst could be reused at least six runs and always yielded the desired product with almost the same level of activity (>90% yield), which demonstrated the advantage of polyurea-encapsulated copper catalyst (AiEc-Cu) in this multicomponent ring-opening/Huisgen cycloaddition reaction.

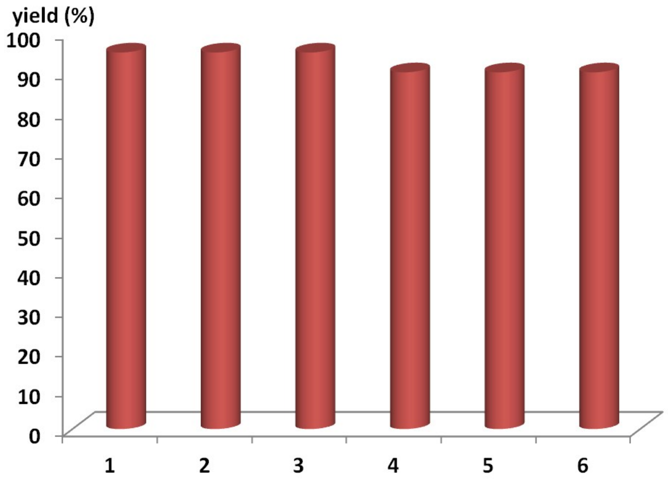


Figure 3. Recyclability of polyurea-encapsulated copper catalyst (AiEc-Cu) in the catalytic multicomponent ring-opening/Huisgen cycloaddition of sodium azide, epoxide **4a**, and alkyne **5a**: All reactions were performed with 5 mmol of sodium azide, 5 mmol of epoxide **4a**, 5 mmol of alkyne **5a**, and water (5 mL), with the recovered polyurea-encapsulated copper catalyst (50 mg polyurea **3a** and 5 mg CuCl at the initial run)[28].

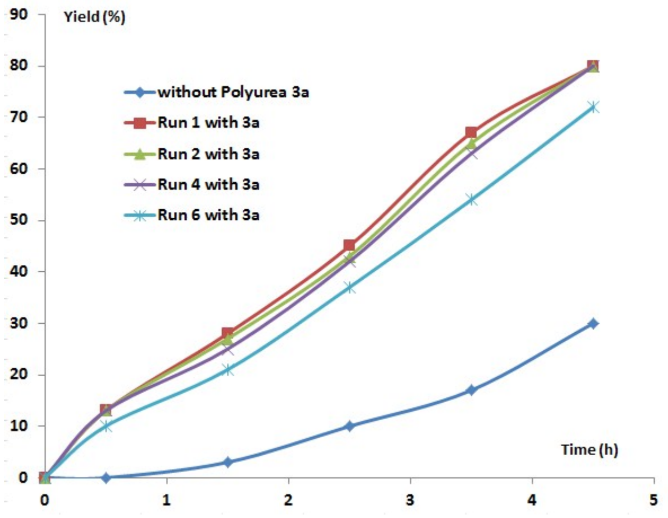
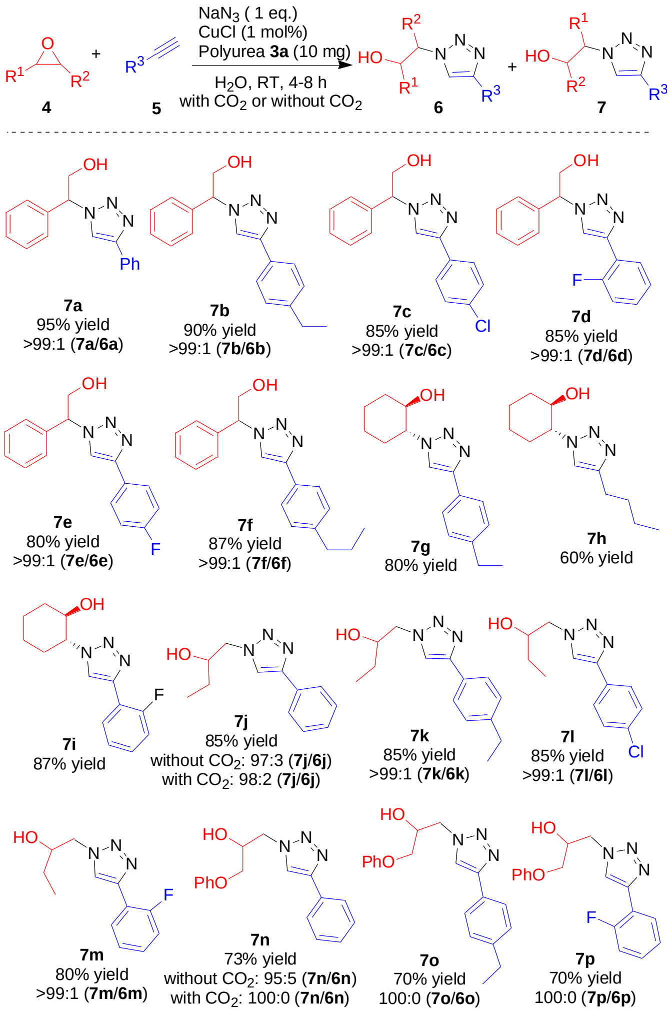


Figure 4. Plot of yield versus time (h) showing the different reaction rate in the polyurea-activated multicomponent ring-opening/Huisgen cycloaddition reaction of epoxide **4a** with alkyne **5a** in/on water.

This reaction kinetics showed in Figure 4 also visually reflects the recyclability of in-situ formed polyurea-encapsulated copper catalyst (AiEc-Cu) from the aqueous phase. Notably, the importance of polyurea **3a** was supported by the kinetic study, in which the use of polyurea **3a** as macromolecular ligand or support resulted in fast and good conversion and the reaction rate revealed the acceleration effect of polyurea (Figure 4, run 1 with **3a**). However, the multicomponent ring-opening/Huisgen cycloaddition occurred slowly in the absence of polyurea **3a** (without polyurea **3a**), which supported the crucial role of polyurea in the initial step of ring-opening of sodium azide to epoxide. In addition, the kinetics for a comparison of the first, 4th, and 6th run provided in Figure 4 showed the slight inactivation/loss of the catalyst was occurring during reaction and/or the recovery process by filtration.



Scheme 4. Substrate scope of polyurea-encapsulated copper-catalyzed multicomponent azide-alkyne cycloaddition of sodium azide, epoxides, and alkynes.

Under the optimized reaction conditions, the reaction scope for the evaluation of combinational use of polyurea **3a** and CuCl in the catalytic multicomponent azide-alkyne cycloaddition of sodium azide, epoxides, and alkynes is then investigated carefully. As shown in Scheme 4, this catalyst system (AiEc-Cu) could efficiently promote sodium azide (NaN_3) to various epoxides, and subsequent Huisgen cycloaddition and CO_2 capture, affording the corresponding triazoles with

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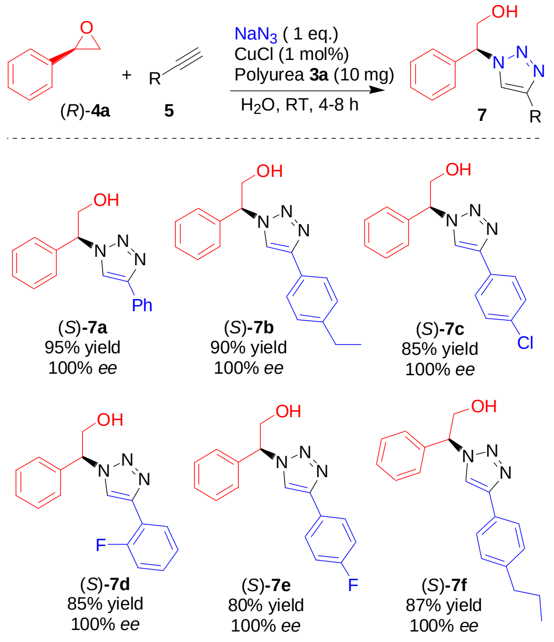
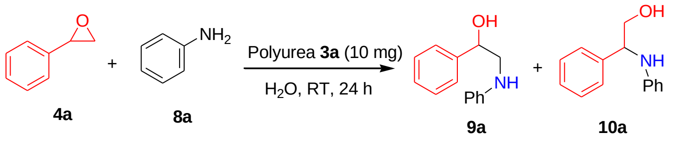
alcoholic moiety in excellent isolated yields (16 examples, up to 95% yield). For example, both aromatic epoxides and alkyl epoxides were suitable substrates for the one-pot multicomponent ring-opening/Huisgen cycloaddition, and aromatic or alkyl terminal alkynes bearing chloride, fluoride, ethyl, and other groups on aromatic rings were successfully employed in this reaction, and almost all the multicomponent transformations were completed in good yields (Scheme 4). As described above, the multicomponent ring-opening/Huisgen cycloaddition combined with CO_2 capture gave the same level of yield and chemoselectivity. Interestingly, different from that the multicomponent ring-opening/Huisgen cycloaddition of most of epoxides with alkynes, the addition of CO_2 balloon was beneficial to the enhancement of chemoselectivity for the synthesis of **7j** and **7n**. For example, the inferior ratio of 97:3 was achieved for the case of **7j** without CO_2, while better chemoselectivity (98:2) was obtained in the presence of CO_2 atmosphere. Similarly, only **7n** was obtained under the CO_2 atmosphere, which is better than that without in-situ neutralization by CO_2. Therefore, the disadvantageous effect of in-situ formed NaOH could be avoided by the process of CO_2 capture. All these results showed the efficiency of the polyurea-encapsulated copper catalyst in the multicomponent ring-opening/Huisgen cycloaddition reaction was quite good and suitable for the practical synthesis of primary or secondary alcohol-containing β-hydroxytriazoles.



Scheme 5. Enantioselective multicomponent ring-opening/Huisgen cycloaddition promoted by polyurea-encapsulated copper catalyst.

Moreover, the enantioselective multicomponent ring-opening/Huisgen cycloaddition catalyzed by polyurea-encapsulated copper catalyst was examined to demonstrate the advantage of the catalyst system. As shown in Scheme 5, excellent results with key S_N2-type nucleophilic addition were obtained by performing the stereoselective version of multicomponent ring-opening/cycloaddition under the optimized reaction conditions. In particular, we performed the multicomponent ring-opening/Huisgen cycloaddition reaction of (*R*)-styrene oxide with various terminal alkynes examined to reveal the enantioselective transformation. As reported in Scheme 5, perfect enantioselectivities were detected by chiral HPLC with all the multicomponent ring-opening/Huisgen cycloaddition reactions (100% *ee* for six examples in Scheme 5). The absolute configuration was deduced by comparison with previously reported method for the preparation of enantiopure β-hydroxytriazoles.[25d] It is reasonable to assume that nucleophilic addition of basic azide to epoxide via S_N2-type pathway lead to the formation of β-alcoholic azide that quickly reacts with the terminal alkynes to give the desired alcohol-functionalized β-hydroxytriazoles without involvement in the competitive racemization process.

Table 2. Catalytic ring opening of styrene oxide with aniline: Additional evidence for the powerful potential of polyurea-encapsulated copper catalyst system in aqueous transformations.[a]



Entry	Catalyst	Yield (%)[b]	10a/9a[c]
1	none	60	80:20
2	Et_3N	70	90:10
3	DABCO	75	90:10
4	Polyurea **3a**	75	98:2
5	Cu@Polyurea	85	>99:1

[a] Reaction conditions: cyclohexene oxide (1 mmol), aniline (1 mmol), Et_3N or DABCO (10 mol%, entry 2 or entry 3) or polyurea (10 mg, entry 4) or Cu@Polyurea (10 mg of polyurea **3a** and 1 mg CuCl, containing 1 mo% of CuCl, entry 5); [b] Yields refer to those of the isolated pure products. [c] The ratio of **10a/9a** is determined by NMR.

Although ring-opening reaction of epoxides with amines has been performed in water in the presence of trimethylamine (Et_3N), 1,4-diazabicycl-[2.2.2]octane (DABCO), and with or without other catalysts,[29] the chemoselectivity in these aminolysis of 1,2-epoxies with arylamines is not satisfied. Thus the starting point for our investigations was the above observation that the polyurea-encapsulated copper catalyst system is effective for the ring-opening reaction of 1,2-epoxides. Preliminary experiments with the aniline as nucleophilic reagent revealed that polyurea **3a** and CuCl (1 mol%) in particular, is a highly active catalyst with excellent chemoselectivity (>99:1 **10a/9a**) for the aminolysis of styrene oxide. Notably, previous methods with Et_3N or DABCO were not good in regioselectivity (Entries 1-3, **10a/9a** < 90:10), which supported powerful potential of polyurea-encapsulated copper catalyst in ring-opening reaction of epoxide with arylamine in/on water.

Having achieved very good results with polyurea-encapsulated copper catalyst under the eco-friendly solvent (water), the scope of the catalyst has also been further extended for the

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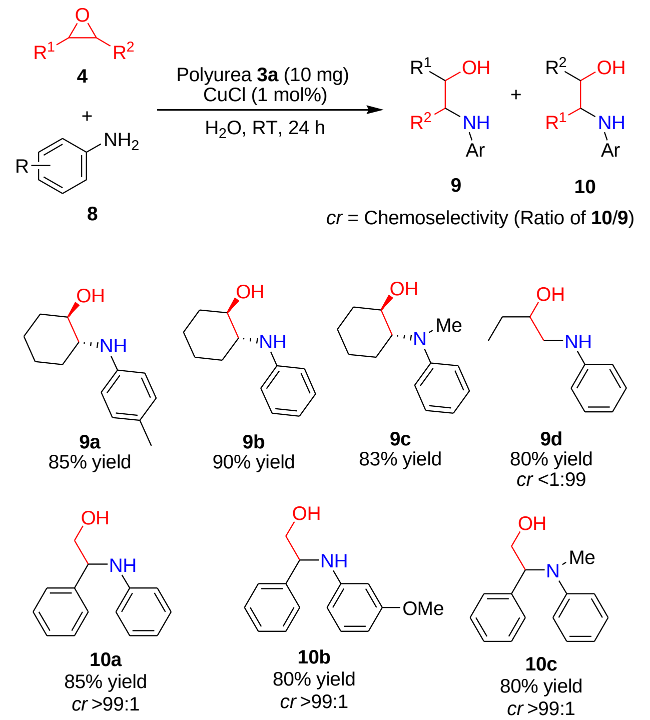
ring-opening aminolysis reaction of various epoxides like styrene oxide, and 2-ethyloxirane. As shown in Scheme 6, in each case the polyurea-encapsulated copper catalyst showed good to excellent results in terms of yields (80-90% isolated yields) and regioselectivity (>99:1 for 1,2-epoxides).



Scheme 6. Ring-opening reaction of epoxide with aromatic amines promoted by polyurea-encapsulated copper catalyst.

Experimental

General Procedure for the polyurea (3a)/CuCl -catalyzed one-pot multicomponent ring-opening/Huisgen cycloaddition for the synthesis of *β*-hydroxytriazoles combined CO_2 capture: NaN_3 (65 mg, 1.0 mmol), the epoxide (1 mmol), and the alkyne (1 mmol) were added to a suspension of CuCl (1 mg, 1 mol % Cu) and Polyurea (10 mg) in H_2O (2 mL) under the carbon dioxide atmosphere (balloon). The reaction mixture was stirred at room temperature and monitored by TLC until total conversion of the starting materials. The solid was obtained by filtration and washed by EtOAc (3 ×10 mL). The extraction of aqueous phase with EtOAc was also performed without loss of product, and collected organic phase were dried with anhydrous Na_2SO_4, and concentrated in vacuo. The product was isolated through a silica gel flash column as corresponding *β*-hydroxytriazoles. All the products are confirmed by MS, and usual spectral methods (^{1}H-NMR, ^{13}C-NMR) (*see* Supporting Information). For example, **2-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethanol (7a):** 95% yield; White solid, melt Point:153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H), 7.69 (s, 1H), 7.43 – 7.36 (m, 5H), 7.35 – 7.29 (m, 1H), 7.29 – 7.25 (m, 2H), 5.68 (dd, *J* = 8.2, 3.7 Hz, 1H), 4.63 (dd, *J* = 12.4, 8.2 Hz, 1H), 4.23 (dd, *J* = 12.4, 3.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 135.7, 130.2, 129.2, 129.0, 128.8, 128.3, 127.1, 125.7, 120.3, 67.1, 65.1. HR-MS calculated for $C_{16}H_{15}N_3O[M+H]^+$: 266.1288, found: 266.1287.

Conclusions

In summary, we have successfully developed a sustainable and efficient approach that focused on the development of polyurea-encapsulated copper catalyst for multicomponent ring-opening/Huisgen cycloaddition reactions and CO_2 capture in water. Especially, it was shown that the polyurea-encapsulated CuCl was proved to be a robust and recyclable catalyst system in this reaction, in which all the multicomponent ring-opening/Huisgen cycloaddition reactions resulted into *β*-hydroxytriazoles with high yields as well as excellent chemoselectivity under exceptionally mild conditions. Except the advantages of multicomponent transformation carried out in environmentally friendly water, the corresponding new reaction systems provide the following merits: (i) Simple and high-yield method with high chemoselectivity for the synthesis of *β*-hydroxytriazoles in one-pot operation; (ii) Asymmetric synthesis of *β*-hydroxytriazoles from chiral epoxides with perfect enantioselectivity (100% *ee*); (iii) The recyclability of polyurea-encapsulated copper catalyst was determined to be carried out by six runs; and (v) it is an good example for the environmentally benign multicomponent transformation combined with CO_2 capture, which minimizes the waste-water discharge in this work. In view of the established utility of recovered copper catalyst encapsulated on polyurea with good recyclability and high level of catalytic performance in this work, we anticipate that the method by in-situ reaction-initiated polymer-encapsulated transition metal catalyst will find wide applicability and offer the possibility for the development of green synthetic transformations, such as the regioselective aminolysis of epoxides that described in this work. Further investigations to encapsulate other catalytic metal species, including new encapsulated- palladium or osmium system are underway in our laboratory.

Acknowledgements

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 About heterogenization of homogeneous catalytic systems, see: A. E. C. Collis and I. T. Horváth, *Catal. Sci. Tech.*, 2011, **1**, 912-919.

2 For recent reviews, see: (a) K. Piradashbili, E. M. Alexandrino, F. R. Wurm and K. Landfester, *Chem. Rev.,* 2016, **116**, 2141-2169; (b) M. Ding, X. Jiang, L. Zhang, Z. Cheng and X. Zhu, *Macromol. Rapid Commun.,* 2015, **36**, 1702-1721; (c) V. Divya and M. V. Sangaranarayanan, *J. Nanosci. Nanotech.,* 2015, **15**, 6863-6882; (d) C. Liu, X. Li and Z. Jin, *Catal. Today*, 2015, **247**, 82-89; (e) M. Pera-Titus, L. Leclercq, J. M. Clacens, F. D. Campo and V. Nardello-Rataj, *Angew. Chem., Int. Ed.,* 2015, **54**, 2006-2021.

3 For recent examples, see: (a) Z. Xi, H. S. Bazzi and J. A. Gladysz, *J. Am. Chem. Soc.,* 2015, **137**, 10930-10933; (b) G. C. Phan-Quang, H. K. Lee and X. Y. Ling, *Angew. Chem., Int. Ed.,* 2016, **55**, 8304-8308; (c) E. Aslan, I. Akin and H. Imren, *ChemCatChem,* 2016, **8**, 719-723; (d) B. Sandig, L. Michalek, S. Vlahovic, M. Antonovici, B. Hauer and M. R. Buchmeiser, *Chem. Eur. J.,* 2015, **21**, 15835-15842; (e) R. Pruvost, J. Boulanger, B. Léger, A. Ponchel, E. Monflier, M. Ibert, A. Mortreux and M. Sauthier, *ChemSusChem,* 2015, **8**, 2133-2137; (f) L. Feng, J. Wang, L. Chen, M. Lu, Z. Zheng, R. Jing, H. Chen and X. Shen, *ChemCatChem,* 2015, **7**, 616-624.

4 Y. Liang, M. L. Harrell and D. E. Bergbreiter, *Angew. Chem., Int. Ed.,* 2014, **53**, 8084-8087.

5 (a) M. B. Gawande, V. D. B. Bonifácio, R. Luque, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.,* 2013, **42**, 5522-5551; (b) M. E. Buck and D. M. Lynn, *Polym. Chem.,* 2012, **3**, 66-80; (c) S. Liu, Y. Kumatabara and S. Shirakawa, *Green Chem.,* 2016, **18**, 331-341; (d) Y. Zhou, Z. Guo, W. Hou, Q. Wang and J. Wang, *Catal. Sci. Technol.,* 2015, **5**, 4324-4335.

6 For recent reviews, see: (a) J. D. A. Pelletier and J. M. Basset, *Acc. Chem. Res.,* 2016, **49**, 664-677; (b) R. K. Sharma, S. Sharma, S. Dutta, R. Zboril and M. B. Gawande, *Green Chem.,* 2015, **17**, 3207-3230; (c) J. Pritchard, G. A. Filonenko, R. van Putten, E. J. M. Hensen and E. A. Pidko, *Chem. Soc. Rev.,* 2014, **44**, 3808-3833; (d) R. Dalpozzo, *Green Chem.,* 2015, **17**, 3671-3686; (e) E. Lindback, S. Dawaigher and K. Warnmark, *Chem. Eur. J.,* 2014, **20**, 13432-13481.

7 (a) R. A. Sheldon, I. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, Germany, 2007; (b) M. Lancaster, *Green Chemistry An Introductory*, The Royal Society of Chemistry, Cambridge, UK, 2010; (c) Green chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner, see: P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*. Oxford University Press, Oxford 1998.

8 (a) U. Diaz, D. Brunel and A. Corma, *Chem. Soc. Rev.,* 2013, **42**, 4083-4097; (b) A. P. Wight and M. E. Davis, *Chem. Rev.,* 2002, **102**, 3589-3614.

9 (a) C. E. Song and S. G. Lee, *Chem. Rev.,* 2002, **102**, 3495-3524; (b) D. E. de Vos, M. Dams, B. F. Sels and P. A. Jacobs, *Chem. Rev.,* 2002, **102**, 3615-3640; (c) A. Corma and H. García, *Chem. Rev.,* 2002, **102**, 3837-3892.

10 (a) C. A. McNamara, M. J. Dixon and M. Bradley, *Chem. Rev.,* 2002, **102**, 3275-3300; (b) N. E. Leadbeater and M. Marco, *Chem. Rev.,* 2002, **102**, 3217-3274; (c) P. Barbaro and F. Liguori, *Chem. Rev.,* 2009, **109**, 515-529.

11 S. Kobayashi and S. Nagayama, *J. Am. Chem. Soc.,* 1998, **120**, 2985-2986.

12 R. Akiyama and S. Kobayashi, *Chem. Rev.,* 2009, **109**, 594-642.

13 M. Donbrow, *Microcapsules and Nanoparticles in Medicine and Pharmacy*; CRC Press: Boca Raton, FL, 1992.

14 (a) H. Han, S. Li, X. Zhu, X. Jiang and X. Z. Kong, *RSC Adv.*, 2014, **4**, 33520-33529; (b) S. Das, I. Yilgor, E. Yilgor, B. Inci, O. Tezgel, F. L. Beyer and G. L. Wilkes, *Polymer*, 2007, **48**, 290-301; (c) R. Dsouza, D. Sriramulu and S. Valiyaveettil, *RSC Adv.*, 2016, **6**, 24508-24517.

15 (a) J. S. Davidson, J. W. Fisher, M. I. Hammons, J. R. Porter and R. J. Dinan, *J. Struct. Eng.*, 2005, **131**, 1194–1205; (b) M. S. Hoo-Fat, X. Ouyang and R. J. Dinan, *Mater. Struct.*, 2004, **15**, 129–138. (c) D. Koyama and K. Nakamura, *Appl. Acoust.*, 2010, **71**, 439–445; (d) Z. Cao and U. Ziener, *Nanoscale*, 2013, **5**, 10093-10107; (e) V. V. Gite, T. D. Tatiya, R. J. Marathe, P. P. Mahulikar and D. G. Hundiwale, *Prog Org. Coat.,* 2015, **83**, 11-18.

16 (a) C. Ramarao, S. V. Ley, S. C. Smith, I. M. Shirley and N. DeAlmeida, *Chem. Commun.,* 2002, **39**, 1132-1133; (b) S. V. Ley, C. Ramarao, R. S. Gordon, A. B. Holmes, A. J. Morrison, I. F. McConvey, I. M. Shirley, S. C. Smith and M. D. Smith, *Chem. Commun.,* 2002, **39**, 1134-1135; (c) J. Q. Yu, H. C. Wu, C. Ramarao, J. B. Spencer and S. V. Ley, *Chem. Commun.,* 2003, **40**, 678-679; (d) S. V. Ley, C. Ramarao, A. L. Lee, N. Østergaard, S. C. Smith and I. M. Shirley, *Org. Lett.,* 2003, **5**, 185-187; (e) S. V. Ley, C. Mitchell, D. Pears, C. Ramarao, J. Q. Yu and W. Zhou, *Org. Lett.,* 2003, **5**, 4665-4668; (f) C. K. Y. Lee, A. B. Holmes, S. L. Ley, I. F. McConvey, B. Al-Duri, G. A. Leeke, R. C. D. Santos and J. P. K. Seville, *Chem. Commun.,* 2005, **42**, 2175-2177; (g) I. R. Baxendale, C. M. Griffiths-Jones, S. V. Ley and G. K. Tranmer, *Chem. Eur. J.,* 2006, **12**, 4407-4416; (h) A. K. Sharma, K. Gowdahalli, J. Krzeminski and S. Amin, *J. Org. Chem.,* 2007, **72**, 8987-8989; (i) J. Toubiana, M. Chidambaram, A. Santo and Y. Sasson, *Adv. Synth. Catal.,* 2008, **350**, 1230-1234; (j) P. Centomo, M. Zecca, A. Zoleo, A. L. Maniero, P. Canton, K. Jeřábek and B. Corain, *Phys. Chem. Chem. Phys.,* 2009, **11**, 4068-4076; (k) J. F. M. da Silva, A. F. Y. Perez and N. P, de Almeida, *RSC Adv.,* 2014, **4**, 28148-28155; (l) S. Natour and R. Abu-Reziq, *RSC Adv.,* 2014, **4**, 48299-48309; (m) E. Weiss, B. Dutta, Y. Schnell and R. Abu-Reziq, *J. Mater. Chem. A*, 2014, **2**, 3971-3977.

17 S. J. Broadwater and D. T. McQuade, *J. Org. Chem.,* 2006, **71**, 2131-2134.

18 (a) T. Takahashi, Y. Taguchi and M. Tanaka, *J. Appl. Polym. Sci.,* 2008, **107**, 2000-2006; (b) J. Hickey, N. A. D. Burke and H. D. H. Stover, *J. Membrane Sci.,* 2011, **369**, 68-76; (c) J. Li, M. A. J. Mazumder, H. D. H. Stover, A. P. Hitchcock and I. M. Shirley, *J. Polym. Sci. A -Polym. Chem.,* 2011, **49**, 3038-3047; (d) T. Dispinar, C. A. L. Colard and F. E. Du Prez, *Polym. Chem.,* 2013, **4**, 763-772; (e) I. Polenz, S. S. Datta and D. A. Weitz, *Langmuir*, 2014, **30**, 13405-13410; (f) F. Maia, K. A. Yasakau, J. Carneiro, S. Kallip, J. Tedim, T. Henriques, A. Cabral, J. Venancio, M. L. Zheludkevich and M. G. S. Ferreira, *Chem. Eng. J.,* 2016, **283**, 1108-1117.

19 (a) A. Tarai and J. B. Baruah, *J. Mol. Struct.,* 2015, **1091**, 147-151; (b) I. Carreira-Barral, T. Rodríhuez-Blas, C. Platas-Iglesias, A. Blas and D. Esteban-Gómez, *Inorg. Chem.,* 2014, **53**, 2554-2568; (c) M. Boiocchi, L. Fabbrizzi, M. Garolfi, M. Licchelli, L. Mosca and C. Zanini, *Chem. Eur. J.,* 2009, **15**, 11288-11297; (d) C. Trujillo, A. M. Lamsabhi, O. Mó and M. Yáñez, *Phys. Chem. Chem. Phys.,* 2008, **10**, 3229-3235.

20 For representative review, see: (a) A. G. Doyle and E. N. Jacobsen, *Chem. Rev.,* 2007, **107**, 5713-5743; For representative examples, see: (b) N. Volz and J. Clayden, *Angew. Chem., Int. Ed.,* 2011, **50**, 12148-12155; (c) K. A. Haushalter, J. Lau and J. D. Roberts, *J. Am. Chem. Soc.,* 1996, **118**, 8891-8896; (d) E. Fan, S. A. Van Arman, S. Kincaid and A. D. Hamilton, *J. Am. Chem. Soc.,* 1993, **115**, 369-370.

21 Z. Xu and L. W. Xu, *Chem. Rec.,* 2015, **15**, 925-948. And references cited therein.

22 The concept of “click” addition or click chemistry was first introduced by the groups of Sharpless and Meldal, see: (a) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2001, **40**, 2004-2021; (b) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2002, **41**, 2596-2599; (c) C. W. Tornøe, C. Christensen and M. Meldal, *J. Org. Chem.,* 2002, **67**, 3057-3064.

23 For recent examples, see: (a) I. Glassford, C. N. Teijaro, S. S. Daher, A. Weil, M. C. Small, S. K. Redhu, D. J. Colussi, M. A. Jacobsen, W. E. Childers, B. Buttaro, A. W. Nicholson, A. D.

MacKerell, B. S. Cooperman and R. B. Andrade, *J. Am. Chem. Soc.,* 2016, **138**, 3136-3144; (b) S. H. Etschel, L. Portilla, J. Kirschner, M. Drost, F. Tan, H. Marbach, R. R. Tykwinski and M. Halik, *Angew. Chem., Int. Ed.,* 2015, **54**, 9235-9238; (c) R. Wirth, J. D. White, A. D. Moghaddam, A. L. Ginzburg, L. N. Zakharov, M. M. Haley and V. J. DeRose, *J. Am. Chem. Soc.,* 2015, **137**, 15169-15175; (d) Y. Shi, R. W. Graff, X. Cao, X. Wang and H. Gao, *Angew. Chem., Int. Ed.,* 2015, **54**, 7631-7635; (e) P. Michael and W. H. Binder, *Angew. Chem., Int. Ed.,* 2015, **54**, 13918-13922; (f) A. Makarem, R. Berg, F. Rominger and B. F. Straub, *Angew. Chem., Int. Ed.,* 2015, **54**, 7431-7435; and references cited therein.

24 (a) T. Song, L. Li, W. Zhou, Z. J. Zheng, Y. Deng, Z. Xu and L. W. Xu, *Chem. Eur. J.,* 2015, **21**, 554-558; (b) M. Y. Chen, T. Song, Z. J. Zheng, Z. Xu, Y. M. Cui and L. W. Xu, *RSC Adv.,* 2016, **6**, 58698-58708.

25 (a) L. S. Campbell, W. Szymański, C. P. Postema, R. A. Dierckx, P. H. Elsinga, D. B. Janssen and B. L. Feringa, *Chem. Commun.,* 2009, **46**, 898-900; (b) H. Sharghi, M. H. Beyzavi, A. Safavi, M. M. Doroodmand and R. Khalifeh, *Adv. Synth. Catal.,* 2009, **351**, 2391-2410; (c) T. Boningari, A. Olmos, B. M. Reddy, J. Sommer and P. Pale, *Eur. J. Org. Chem.,* 2010, 6338-6347; (d) F. Alonso, Y. Moglie, G. Radivoy and M. Yus, *J. Org. Chem.,* 2011, **76**, 8394-8405; (e) A. N. Prasad, B. Thirupathi, G. Raju, R. Srinivas and B. M. Reddy, *Catal. Sci. Tecnol.,* 2012, **2**, 1264-1268; (f) K. B. Mishra and V. K. Tiwari, *J. Org. Chem.,* 2014, **79**, 5752-5762; (g) H. Naeimi and V. Nejadshafiee, *New J. Chem.,* 2014, **38**, 5429-5435; (h) A. A. Jafari, H. Mahmoudi and H. Firouzabadi, *RSC Adv.,* 2015, **5**, 107474-107481; (i) A. Kamal, B. Sridhar and N. Shankaraiah, *New. J. Chem.,* 2015, **39**, 3973-3981; (j) E. Tasca, G. L. Sorella, L. Sperni, G. Strukul, A. Scarso, *Green Chem.,* 2015, **17**, 1414-1422.

26 For recent reviews, see: (a) S. B. Wang and X. C. Wang, *Angew. Chem., Int. Ed.,* 2016, **55**, 2308-2320; (b) A. Perejón, L. M. Romeo, Y. Lara, P. Lisbona, A. Martínez and J. M. Valverde, *Appl. Energy,* 2016, **162**, 787-807; (c) S. A. Didas, S. Choi, W. Chaikittisilp and C. W. Jones, *Acc. Chem. Res.,* 2015, **48**, 2680-2687; (d) B. Seoane, J. Coronas, I. Gascon, M. E. Benavides, O. Karvan, J. Caro, F. Kapteijn and J. Gascon, *Chem. Soc. Rev.,* 2015, **44**, 2421-2454; (e) M. Pera-Titus, *Chem. Rev.,* 2014, **114**, 1413-1492; (f) N. von der Assen, P. Voll, M. Peters and A. Bardow, *Chem. Soc. Rev.,* 2014, **43**, 7982-7994.

27 For the use of reactive polymethylhydrosiloxane (PMHS)-derived semi-interpenetrating networks (PMHS-SIPNs) as support for the hydrogenation reaction –initiated multi-task and maximum reuse of supported palladium catalyst in one-by-one downstream reactions, see: (a) H. Wang, L. Li, X. F. Bai, W. H. Deng, Z. J. Zheng, K. F. Yang and L. W. Xu, *Green Chem.,* 2013, **15**, 2349-2355; (b) X. Y. Dong, Y. Lin, Y. M. Cui, K. F. Yang, Z. J. Zheng and L. W. Xu, *ChemistrySelect,* 2016, **1**, 2400-2404; For the preparation of organosilicon-supported mono-dispersed hybrid Ag@TiO$_2$ nanocomposites initiated by titanium-promoted cross-linking reduction of polymethylhydrosiloxane (PMHS)-based semi-interpenetrating networks (PMHS-SIPNs), see: (c) H. Wang, K. F. Yang, L. Li, Y. Bai, Z. J. Zheng, W. Q. Zhang, Z. W. Gao and L. W. Xu, *ChemCatChem,* 2014, **6**, 580-591; (d) H. Wang, J. Zhang, Y. M. Cui, K. F. Yang, Z. J. Zheng and L. W. Xu, *RSC Adv.,* 2014, **4**, 34681-34686.

28 Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis of recycled polyurea-encapsulated copper catalyst showed that the slight loss of the copper catalyst was occurring during reaction and/or the recovery process by filtration. The ICP analysis was done on the recovered polymer after the first run, the third run, and after the fifth run, and the corresponding results of copper amount were 3.89mg/g, 3.72 mg/g, and 3.35 mg/g (average 5% leaching for every run). In fact, the partial adsorption of copper with polyurea **3a** in water was confirmed by ICP-OES analysis, in which the amount of copper was detected as 28.16 mg/g before reaction (Run 1). Fortunately, the loss of small amount of copper did not affect the catalytic performance of polyurea-encapsulated copper catalyst before 6th run of recyclability. And notably, and the catalytic turnover number were up to 173000. The detailed investigation of such highly active catalyst in click chemistry will be carried out and reported elsewhere in the near future. To detect the oxidation states of various reused polyurea-encapsulated copper catalysts, X-ray photoelectron spectroscopy (XPS) analysis was performed. Although the oxidation states of reused polyuria-encapsulated copper catalysts was difficultly confirmed by the XPS analysis (Figure S4, see Supporting Information), these Cu species mainly existed in the same form of Cu(II) or Cu(I). For the polyuria-encapsulated copper catalyst, the Cu species mainly existed in the form of Cu(II). For related references on the XPS analysis of copper, see: (a) S. Chen, H. Zhang, L. Wu, Y. Zhao, C. Huang, M. Ge and Z. Liu, *J. Mater. Chem.*, 2012, **22**, 9117-9122; (b) M. Zhang, C. Shao, Z. Guo, Z. Zhang, J. Mu, T. Cao and Y. Liu, *ACS Appl. Mater. Interfaces,* 2011, **3**, 369-377; (c) J. Yu and J. Ran, *Energy Environ. Sci.*, 2011, **4**, 1364-1371; (d) G. Mele, R. D. Sole, G. Vasapollo, G. Marcì, E. Garcìa-Lòpez, L. Palmisano, J. M. Coronado, M. D. Hernández-Alonso, C. Malitesta and M. R. Guascito, *J. Phys. Chem. B*, 2005, **109**, 12347-12352.

29 (a) M. Azizi and M. R. Saidi, *Org. Lett.*, 2005, **7**, 3649-3651; (b) J. Wu and H. G. Xia, *Green Chem.*, 2005, **7**, 708-710; (c) K. Surendra, N. S. Krishnaveni and K. R. Rao, *Synlett*, 2005, 506-510; (d) S. Bonnollo, F. Fringuelli, F. Pizzo and L. Vaccaro, *Green Chem.*, 2006, **8**, 960-964; (e) A. Procopio, M. Gaspari, M. Nardi, M. Oliverio and O. Rosati, *Tetrahedron Lett.*, 2008, **49**, 2289-2293; (f) M. Kokubo, T. Naito and S. Kobayashi, *Tetrahedron*, 2010, **66**, 1111-1118.

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Graphic Abstract

A Robust and Recyclable Polyurea-Encapsulated Copper(I) Chloride for One-Pot Ring-Opening/Huisgen Cycloaddition/CO_2 Capture in Water

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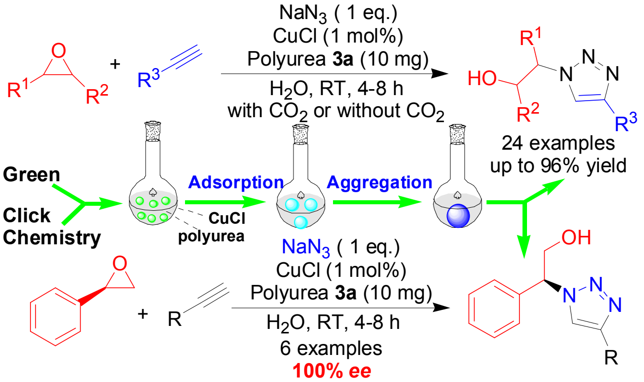

The one-pot ring-opening/Huisgen cycloaddition reactions combined with CO_2 capture were carried out successfully in the presence of polyurea-encapsulated CuCl.