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CRITICAL REVIEW
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Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?

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ARTICLE

A designed bi-functional sugar-based surfactant: micellar catalysis for C-X coupling reaction in water

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A bi-functional sugar-based surfactant ALA14 was designed as the ligand and micelle constructor and demonstrated to promote the copper-catalyzed C-X coupling reaction in water. The nature of this micelle, formed by sugar-based surfactants, was investigated with CMC, DLS, and TEM, via which encapsulating and aggregation of the substrates in micelle were verified. Additionally, it was addressed by ^{1}H-NMR analysis that the enrichment position of the substrates is in the lipophilic alkyl chain. Finally, moderate to excellent yields of the aimed products were obtained in this work. This remarkably simple strategy expanded the scope of C-X coupling reaction in water; most notably, both water and ALA14 can be recycled and reused.

Introduction

Carbon-heteroatom bonds are important structural motifs[1-4] of various chemicals like natural products, clinically used drugs, pesticides, and so on. Thus, the cross-coupling reactions to construct C-X bond, in particular the green processes, continue to be in the spotlight of chemical research, as for example, Cu-catalyzed Ullmann reaction.[5] Previous studies on Ullmann C-X reaction focus mainly on ligand effects and are carried out in organic solvents (e.g., DMSO, DMF, THF, dioxane).[6-16] Although many efforts have been made to improve the C-X coupling process with optimized ligands, the use of potentially toxic organic solvents and unrecyclable ligands violates the 12 Principles of Green Chemistry.[17] In order to make organic reactions "greener", water is often employed as reaction media to reduce or eliminate the use of hazardous organic solvent, as nature has been doing for billions of years.

As the favourite solvent of nature, water is a cheap, safe, non-toxic, and clean reaction medium.[18] Quite a few reactions have been proven to proceed successfully in water, e.g. Suzuki-Miyaura reactions[19-21], Still reaction[22], Mizoroki Heck reactions[23, 24], Olefin Metathesis reactions[25], and arylation reactions[26, 27]. Moreover, the industrial process of water recovering has made a significant breakthrough by using membrane separation and phase separation technology. In spite of these efforts, the utilization of water as reaction media

for organic processes is still rather limited due to the insolubility of organic species in water. To solve this problem, alternative approaches were developed, e.g. micellar catalysis[28], *in-water* catalysis of homogeneous system[29], and *on-water* catalysis of heterogeneous system[18]. Micellar catalysis is an effective strategy to disperse water-insoluble organic compounds in aqueous system, which depends on the surfactants to form supramolecular aggregates. Similar to biological enzymes[30], the amphiphilic structure of micelle formed by self-aggregation of surfactants in water isolates species from water and improves the solubility of organic reactants. Up till now, commercially available surfactants like SDS[31, 32], CTAB[33, 34], Brij35[35-37], triton X-100[38], tween 20/40[39], and newly designed surfactants such as TPGS-750-M[40], NOK[41], PQS[42], BABTGA[43], have been developed for efficient promotion of organic reactions. Especially, the TPGS-750-M series surfactants established by Lipshutz have been well-studied and have strong universality[20, 21, 40, 44-46]. However, most of the metal-catalyzed reactions still require the addition of ligands or promoters even when using surfactants, and the recovery of surfactants remains challenging. Thus, we envisioned whether it is possible to combine the functions of surfactants and ligands. It is always urgent and interesting to explore more eco-friendly and more simple protocols.

As green and biodegradable natural compounds, sugars are frequently used as ligands in metal-catalyzed coupling reactions. In 2008, D-glucosamine was reported to efficiently promote copper-catalyzed Ullmann coupling reaction in DMSO.[47] Moreover, it was found that replacing DMSO with the mixed water solvent improves this reaction.[48] However, toxic organic solvent is still required, and the contradiction of water-soluble catalyst and water-insoluble reactant remains unsolved. Thus, following the interests in the fine-tuning and design of carbohydrate structures[49-56], we attempted to design a bi-functional sugar-based surfactant, ALA14, which acts as a

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ligand and meanwhile, provides a micellar environment for the

Scheme 1. Synthesis of N-alkyl-glucosamine (AGA12, AGA14, AGA16)

Scheme 2. Synthesis of *N*-alkyl-lactosamine (ALA12, ALA14, ALA16)
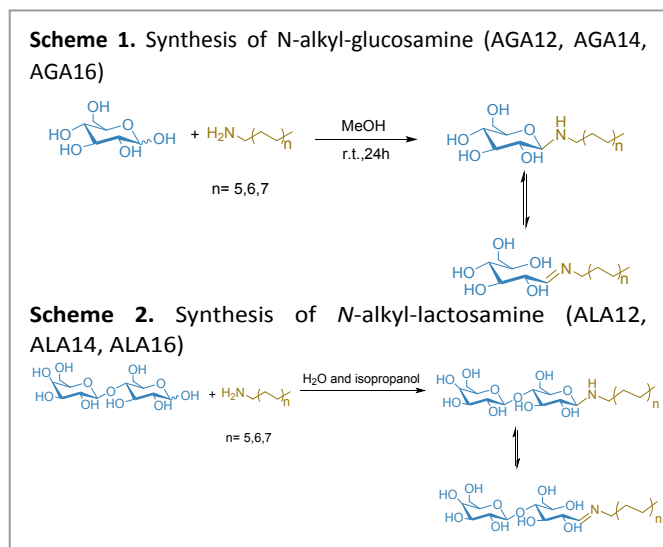
aggregation of substrates. Herein, we report a green, simple, and sustainable micellar protocol for the construction of C-S and C-N bond via Ullmann reactions.

Results and discussion

In general, the condensation of glucose or lactose with long-chain alkylamine resulted in the formation of nonionic surfactant. Pure *N*-alkyl-glucosamine (AGA12, AGA14, AGA16) and *N*-alkyl-lactosamine (ALA12, ALA14, ALA16) were obtained in good yields with recrystallization[57]. The anomeric configurations of these carbohydrate-derived alkylamines were confirmed as β-configuration by the $^1J[^{13}CH(1)]$ coupling constants[58]. Notably, the configuration of D-glucose and D-lactose is in dynamic equilibrium between open chain and ring structures. After condensation with a long-chain alkylamine, the open-chain form, in equilibrium with the ring form, is the structure of a Schiff base, which can effectively anchor the metal catalyst.

With these sugar-based nonionic surfactants in hand, the evaluation of their performances began with the Ullmann C-S coupling of iodobenzene with sodium benzenesulfinate in various aqueous micellar solution (AGA12, AGA14, AGA16, ALA12, ALA14, ALA16); copper salt was employed as the catalyst (Table 1, entries 1-6). Since the water-solubility of the glucosamine part is unsatisfactory, the performance in AGA aqueous micellar solutions is inferior to that in ALA aqueous micellar solutions. Moreover, the disaccharide part of ALA can effectively enhance its hydrophilicity, resulting in higher reactivity. Most notably, ALA14 showed the highest efficiency with a 65% yield, indicating that ALA14 aqueous solution provides the most suitable size of micelles and the best hydrophilic-lipophilic balance. Glucose, lactose and D-glucosamine were also tested (Table 1, entries 8-10). It turns out that no coupling products were obtained in the presence of glucose and lactose. When D-glucosamine was used as ligand, the yield of final product is only 20%. In addition, the control experiment exhibited the importance of sugar-based

nonionic surfactants for this reaction (Table 1, entry 7). Increasing the amount of surfactant promotes obviously the yield of desired product (Table 1, entries 11-13,5). When only a little surfactant is added, no aggregates occurred in the system and the surfactant molecules serves only as ligand. Further,

Table 1. Optimization of Ullmann C-S coupling in water

Entry	Promoter	Copper salt	Temp/°C	Yield/% [e]
1	AGA12 [a]	CuI	80	25
2	AGA14 [a]	CuI	80	50
3	AGA16 [a]	CuI	80	30
4	ALA12 [a]	CuI	80	45
5	ALA14 [a]	CuI	80	65
6	ALA16 [a]	CuI	80	58
7	-	CuI	80	0
8	Glucose	CuI	80	0
9	Lactose	CuI	80	0
10	D-Glucosamine	CuI	80	20
11	ALA14 [b]	CuI	80	0
12	ALA14 [c]	CuI	80	trace
13	ALA14 [d]	CuI	80	15
14	ALA14 [a]	CuBr	80	40
15	ALA14 [a]	CuCl	80	40
16	ALA14 [a]	Cu(CH₃COO)₂	80	40
17	ALA14 [a]	CuSO₄	80	40
18	ALA14 [a]	CuI	90	75
19	ALA14 [a]	CuI	100	90

Reaction conditions: iodobenzene (1.0 mmol), sodium benzenesulfinate (1.2 mmol), CuI (0.1 mmol), [a] 0.1 mmol surfactant in 10 mL water, 7 h. [b] 0.003 mmol surfactant in 10 mL water, 7 h. [c] 0.005 mmol surfactant in 10 mL water, 7 h. [d] 0.01 mmol surfactant in 10 mL water, 7 h. [e] Isolated yield.

abundant phenol can be produced by hydrolysis of iodobenzene; however, when sufficient surfactant was present in the system to exhibit a micellar environment, the target product yield was significantly improved. The essential role of the micellar environment in such a C-S coupling process is thus clarified.

Next, various copper sources, *i.e.* CuI, CuBr, CuCl, Cu(CH₃COO)₂, and CuSO₄, were examined regarding this process (Table 1, entries 5, 14-17). Although all copper salts can initiate the C-S coupling, obviously CuI outperformed the others. Finally, different temperatures were examined (Table 1, entries 5, 18-19). As the reaction temperature increases, the yield is significantly improved. In summary, the optimal conditions for the C-S coupling can be concluded as: using CuI as the catalyst, the aqueous solution of surfactant ALA14 as the solvent, and controlling the temperature at 100 ℃; additional ligand or base is not needed.

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To investigate the nature of micelle upon the dissolution of sugar-based surfactants in water, the critical micelle concentration (CMC) values of employed surfactants must be clear. As shown in Figure S1, CMC values of three surfactants, AGA12, ALA12, and ALA14 were found graphically from dependence of the surface tension (γ) of their aqueous
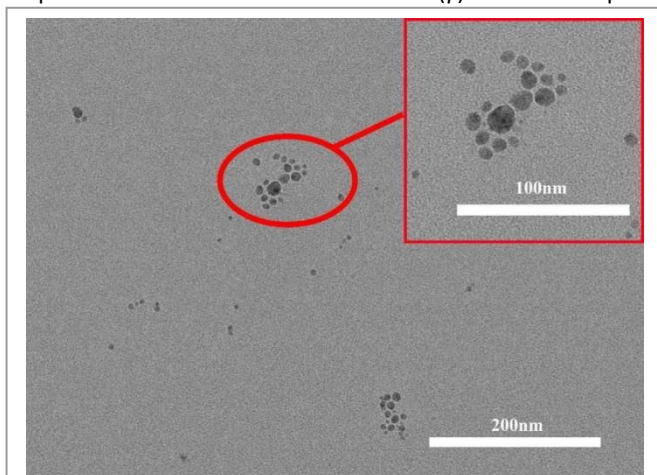

Figure 1. TEM images of 0.1 wt% ALA14 aqueous solution

solutions from their bulk molalities at 40 °C. CMC values of these surfactants were summarized in Table S1. It was exhibited that CMC values of ALA series surfactants are significantly smaller than those of AGA. Moreover, ALA14 has the minimum CMC with only 5×10^{-4} mol·L^{-1}, which leads to the highest catalytic activity in Ullmann C-S reaction. Furthermore, under TEM analysis, the nature of the micelles formed by ALA14 was found to be spherical in shape and has a tendency to aggregate (Figure 1). TEM also revealed that micelle size distribution of ALA14 aqueous solution is in range of 5-15 nm. The FTIR spectra of ALA14 and ALA14@CuI are shown in Figure S2. For ALA14, the characteristic absorption peaks appeared at 3371 cm^{-1} (O-H stretching vibration), 2917 cm^{-1} and 2849 cm^{-1} (C-H stretching vibration), 1464 cm^{-1} (C-H bending vibration of -CH$_2$-), 1375 cm^{-1} (C-H bending vibration of -CH$_3$), 1170 cm^{-1} (C-N stretching vibration), 1064 cm^{-1} (C-O-C stretching vibration), 1025 cm^{-1} (C-O stretching vibration). Compared with the FTIR spectra of ALA14, a wide and high absorption peak (1567 cm^{-1} and 1645 cm^{-1}) emerged for ALA14@CuI, which might be due to the C=N stretching vibration. The new peak implied the stability of Schiff base structure after ALA14 anchored the metal. The TG curves of ALA14 was shown in Figure S4. It was obvious that the mass loss occurred from 150 °C to 500 °C, which implied the decomposition of ALA14. Importantly, the surfactant was stable below 150 °C.

The micelle size is an important factor that provides information about the hydrodynamic radius of the self-aggregated nanoparticle. ALA14 dissolves in water to form 0.1 wt% ALA14 aqueous solution, which provides micelles with an average diameter sized of 9nm, as determined by dynamic light scattering (DLS) measurement in Figure 2. In addition, the average micelle size, after iodobenzene was dissolved into ALA14 aqueous solution, was studied by DLS. As shown in

Figure 2, it was found that the average micelle size increased from 9 nm to 15 nm, indicating that the micelles play a certain role in the encapsulating and aggregation of the substrate.
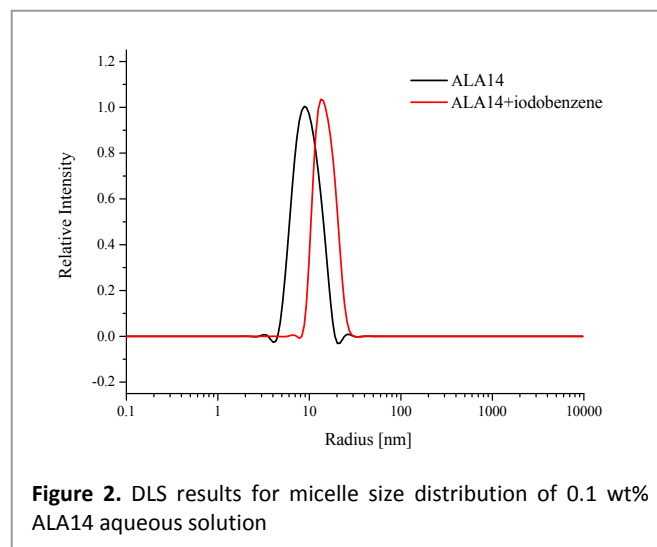

Figure 2. DLS results for micelle size distribution of 0.1 wt% ALA14 aqueous solution

In general, micelles are formed to ensure their solubility and keep the palisade area at the junction between the headgroup and the alkyl chain by a hydrophobic core and a hydrophilic surface; around the latter, the hydrophilic groups remain exposed to water. To elucidate the reaction mechanisms, we used ^{1}H NMR spectra at 40 °C to explore the enrichment position of substrate in surfactant micellar solutions. When solute molecule interacts with surfactant, the chemical shift of surfactant protons in the ^{1}H NMR spectra reveals its location. Figure 3 represents the change of chemical shifts of ALA14 due to the addition of iodobenzene. The chemical shifts in the hydrophilic lactose part of ALA14 are strictly identical. But in the lipophilic part, the upfield shifts of methylene and methyl groups on the long carbon chain were changed from 1.36ppm and 0.96ppm to 1.26ppm and 0.88ppm, respectively. It proved
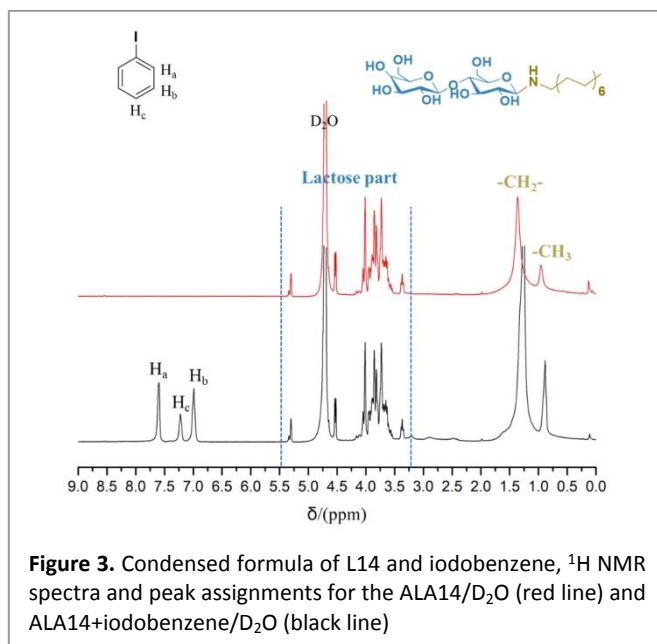

Figure 3. Condensed formula of L14 and iodobenzene, ^{1}H NMR spectra and peak assignments for the ALA14/D$_2$O (red line) and ALA14+iodobenzene/D$_2$O (black line)
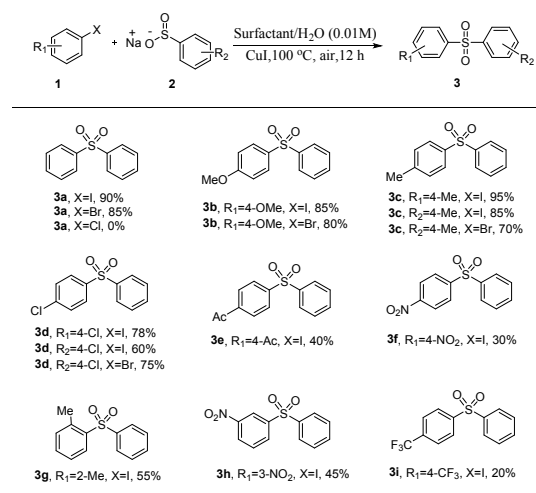
that the substrate iodobenzene is mostly wrapped in the micellar hydrophobic core.

Further, a plausible mechanism of micellar catalysis for C-S coupling reaction in water is proposed based on the change of the particle size of the micelle after iodobenzene is dissolved into ALA14 aqueous solution. As shown in Figure 4, initially ALA14 in water self-assembles to form micelle. In the hydrophilic lactose part, the Schiff base acts as a ligand to chelate the copper salts. Moreover, iodobenzene was concentrated in the lipophilic part, which is the center of the micelle. Then, the reaction occurred in the palisade area at the junction between the headgroup and the alkyl chain. **B** is formed via nucleophilic reaction of **A** with benzenesulfonate. The oxidation addition of complex **B** with iodobenzene generates complex **D**. Finally, the target product was obtained by reductive elimination and the micellar catalyst was regenerated.

Figure 4. Proposed reaction mechanism.
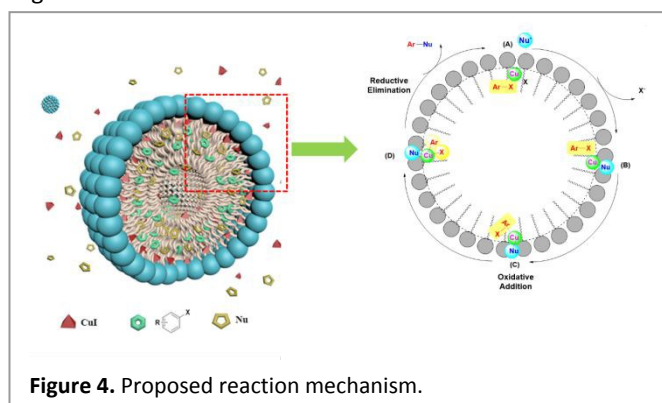
Further study focused on expanding the substrate scope to reveal the generality of this protocol. More attention was paid on different functional groups, steric and electronic effects. Associated details are summarized in Table 2. Electron

Table 2. Substrate scope of Ullman C-S couplings in ALA14 aqueous solution ^{a}

3a, X=I, 90%
3a, X=Br, 85%
3a, X=Cl, 0%

3b, R_1=4-OMe, X=I, 85%
3b, R_1=4-OMe, X=Br, 80%

3c, R_1=4-Me, X=I, 95%
3c, R_2=4-Me, X=I, 85%
3c, R_2=4-Me, X=Br, 70%

3d, R_1=4-Cl, X=I, 78%
3d, R_2=4-Cl, X=I, 60%
3d, R_2=4-Cl, X=Br, 75%

3e, R_1=4-Ac, X=I, 40%

3f, R_1=4-NO$_2$, X=I, 30%

3g, R_1=2-Me, X=I, 55%

3h, R_1=3-NO$_2$, X=I, 45%
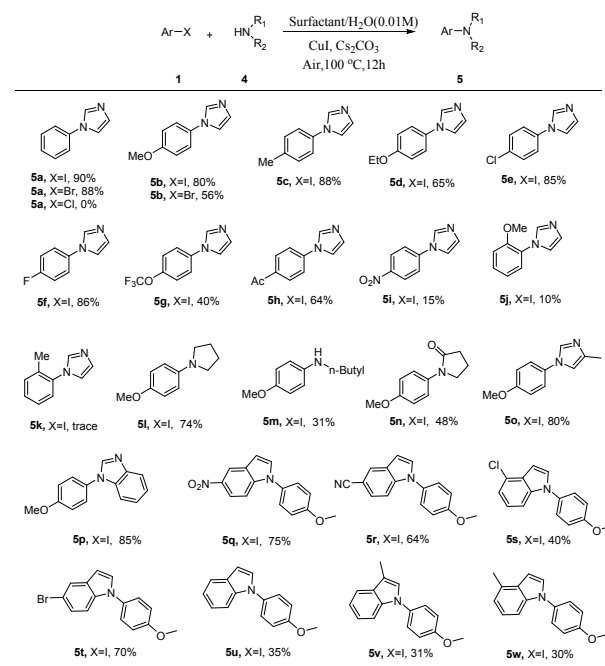
3i, R_1=4-CF$_3$, X=I, 20%

^{a} Reaction conditions: **1** (1.0mmol), **2** (1.2 mmol), CuI (0.1 mmol) and surfactant ALA14 (0.1 mmol) in water (10 ml) under air at 100 °C for 12 h.

withdrawing and donating effects of the group substituted on aryl ring have much influence on the C-S coupling reaction. When electron-withdrawing groups, *e.g.* 4-Ac (3e), 4-Cl (3d), 4-NO$_2$ (3f), 3-NO$_2$(3h), and 4-CF$_3$ (3i) were located in the aryl ring, the corresponding yields were much lower as compared to those with electron donating substituents, e.g., 4-OMe (3b) and 4-Me (3c). In addition, influences of different aryl halides were examined. As a result, the activities of different aryl halides with sodium benzenesulfinate was determined as: PhI > PhBr > PhCl. Further, the low yield of 3g revealed that the steric hindrance from the ortho-substituents significantly hindered the progress of the reaction.

The ALA14 micellar-catalyzed protocol was further expanded to the Ullmann C-N coupling reaction of aryl halides with nucleophiles, and the results are shown in Table 3. To our delight, nucleophiles coupled smoothly with aryl halides. It was shown that the electron withdrawing and donating effect of the groups substituted at the aryl halide, exerted no obvious influence on the C-N coupling with imidazole. The aryl halides with electron-donating groups, e.g., 4-OMe (5b), 4-Me (5c), 4-OEt (5d) gave the corresponding products in good yields. When electron-withdrawing groups, e.g., 4-Cl (5e), 4-F (5f), 4-Ac (5h), were located in the aryl ring, the corresponding yields did not drop significantly (64%-86%). Because of the steric hindrance, the ortho-substituents such as 2-OMe (5j), 2-Me (5k), led to poor yields. Moreover, the coupling with various nucleophiles including several heterocycles, e.g. pyrrolidine (5l), n-butylamine (5m), 2-pyrrolidinone (5n), 4-methyl-1H-imidazole (5o), and 1H-benzoimidazole (5p) proceeded successfully, with moderate to good yields. Finally, to test the

Table 3. Substrate scope of Ullman C-N couplings in ALA14 aqueous solution ^{a}

5a, X=I, 90%
5a, X=Br, 88%
5a, X=Cl, 0%

5b, X=I, 80%
5b, X=Br, 56%

5c, X=I, 88%

5d, X=I, 65%

5e, X=I, 85%

5f, X=I, 86%

5g, X=I, 40%

5h, X=I, 64%

5i, X=I, 15%

5j, X=I, 10%

5k, X=I, trace

5l, X=I, 74%

5m, X=I, 31%

5n, X=I, 48%

5o, X=I, 80%

5p, X=I, 85%

5q, X=I, 75%

5r, X=I, 64%

5s, X=I, 40%

5t, X=I, 70%

5u, X=I, 35%

5v, X=I, 31%

5w, X=I, 30%

^{a} Reaction conditions: **1** (1.0 mmol), **4** (1.2 mmol), CuI (0.1 mmol), Cs$_2$CO$_3$ (2.0 mmol), surfactant ALA14 (0.1 mmol), water (10 ml), 100 °C, 12 h.

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scope of this procedure, this in-water catalytic system was applied to various indole derivatives. Interestingly, the C-N reaction of 4-methoxyiodobenzene with unsubstituted indole only gave 35% yield. Notably, when indoles possess electron-withdrawing groups including NO_2 (5q), CN (5r), Cl (5s) and Br (5t), the yields were obviously higher than the unsubstituted indoles. In contrast, indoles with electron-donating substituents 3-methylindole (5v) and 4-methylindole (5w) afforded the coupling products in low yields.

Finally, as a further advantage of ALA14 micellar catalysis, ALA/water system can be easily reused. Thus, during the reaction, the mixtures in ALA14/water formed a stable and slight yellow dispersion (Figure 5a). Once the reaction was finished and cooled down, the ALA began to precipitate as

Figure 5. Appearance of C-S coupling reaction in ALA14/water (a) during the reaction and (b) after cooling and extracting with ethyl acetate, (c) Recycling and reuse of ALA14/water.

white solid. Therefore, the final product was obtained by extracting with ethyl acetate. The separated ALA/water system can be reused again directly. In addition, the reusability of ALA/water was studied in the above Ullmann C-S reaction. The results about the reuse test of ALA14/water are exhibited in Figure 5c. It was obvious that the ALA/water still had excellent performance for C-S coupling reaction after being reused for five times.

Conclusions

In summary, a newly bi-functional sugar-based surfactant, ALA14, was designed to act as a ligand and provide a micellar environment for aggregation of substrates. The alkyl lactosamine ALA14 is easily synthesized and naturally degradable, which is made up of the hydrophobic part of the molecule based on long-chain alkyl and the hydrophilic portion based on lactose. The nonionic surfactant ALA14 self-

assembles to form a micellar nanoreactor with different binding sites, *i.e.*, (i) hydrophilic lactose part is responsible for chelating the copper catalyst, acting as a ligand, (ii) the lipophilic part traps the oil-soluble substrate to concentrate it in the center of the micelle. It can successfully promote the Ullmann C-X coupling reaction in water. The substrate applicability of the micellar catalysis in water is expanded and a moderate to excellent yields of C-X coupling reaction were obtained. The nature of micelle formed by sugar-based surfactant was investigated by CMC, DLS, and TEM. The encapsulating and aggregation of the substrate in micelle were clarified and the enrichment position of the substrate was revealed by ^1HNMR to be in the lipophilic alkyl chain. The possible micellar catalytic reaction mechanism was deduced. Most notably, the water and ALA14 are able to be recycled. This strategy is proven to be green, simple, and sustainable.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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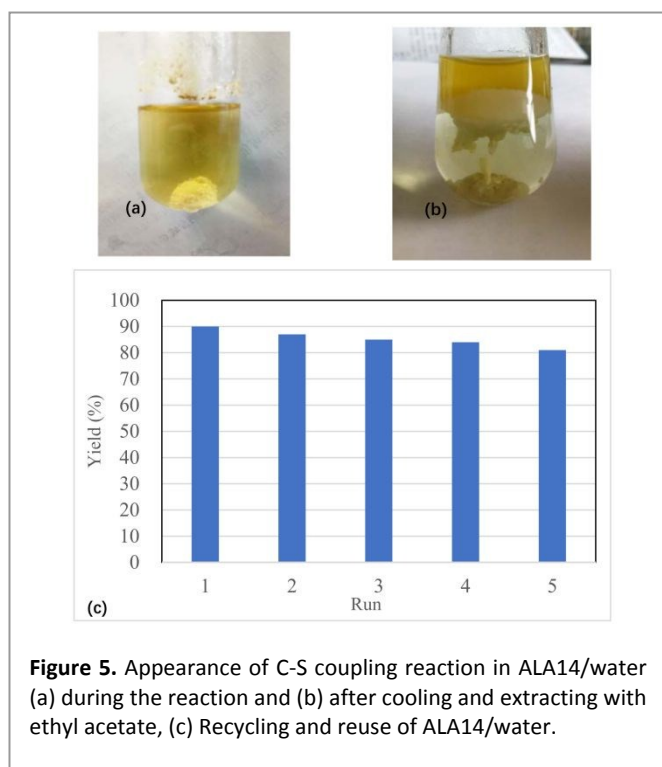16. F. Monnier, M. Taillefer, *Angew. Chem. Int. Ed.*, 2008, **47**, 3096-3099.

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Graphical Abstract