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Synthesis of glucoside-based imidazolium salts for Pd-catalyzed cross-coupling reaction in water

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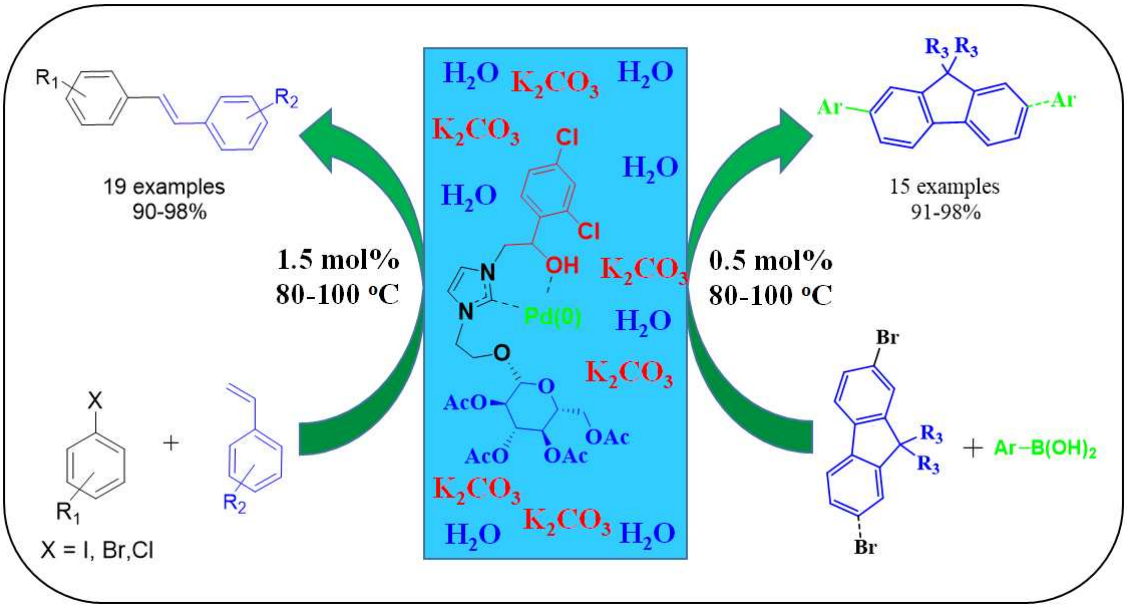
Graphical Abstract



A series of glucoside-based imidazolium salts (Glu-IMSs) combining glucoside and imidazolium head groups with different substituents were synthesized. The catalytic activities of these Glu-IMSs were evaluated in Pd-catalyzed Heck–Mizoroki (19 examples) and Suzuki–Miyaura (15 examples) reactions in water media. Glu-IMSs with -OH and NHCs two coordination sites was found to be most efficient ligand among them. HR-TEM analysis showed that in the presence of Glu-IMSs in water, palladium nanoparticles was formed with an average size of around 4.0 nm, the generation of Pd(0) nanoparticles would act as efficient real catalytic species to accelerate the cross coupling reaction in water media.

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Synthesis of glucoside-based imidazolium salts for Pd-catalyzed cross-coupling reaction in water

Zhonggao Zhou,* Qian Xie, Xin Zhou, Yangyang Yuan, Yan Pan, Dongliang Lu, Ziyi Du, Jun Xue*

Abstract

Sugar-based imidazolium salts (IMSs) represent an outstanding type of material making them eye-catching for a wide variety of applications. Herein, a series of glucoside-based IMSs (Glu-IMSs) combining glucoside and imidazolium head groups with different substituents were synthesized. The catalytic activities of these Glu-IMSs were evaluated by Pd-catalyzed Heck–Mizoroki and Suzuki–Miyaura reactions in water. Among them, the Glu-IMSs contain both -OH and NHCs coordination sites was found to be the most efficient ancillary ligand in comparison with other Glu-IMSs with just single NHCs coordination site. The HR-TEM analysis showed that the palladium nanoparticles stabilized by the Glu-IMSs with an average size of ~4.0 nm was formed in the reaction system, which may be act as an efficient real catalytic species. Under the optimized reaction conditions, a series of novel fluorine-cored organic small molecule functional materials were synthesized with favorable yields.

Keywords

Imidazolium salts; Sugar-based; Palladium catalysts; Cross-coupling reaction; Fluorine-cored functional materials

Introduction

Transition metal-catalyzed, especially, palladium-catalyzed Suzuki reaction,[1] Heck reaction,[2] and Negishi reaction[3] dominate the most important landmarks in the field of modern organic chemistry. Industrial criteria for the technologies to be identified as a reliable green method include comply with a low value for the “E-factor”, the “twelve

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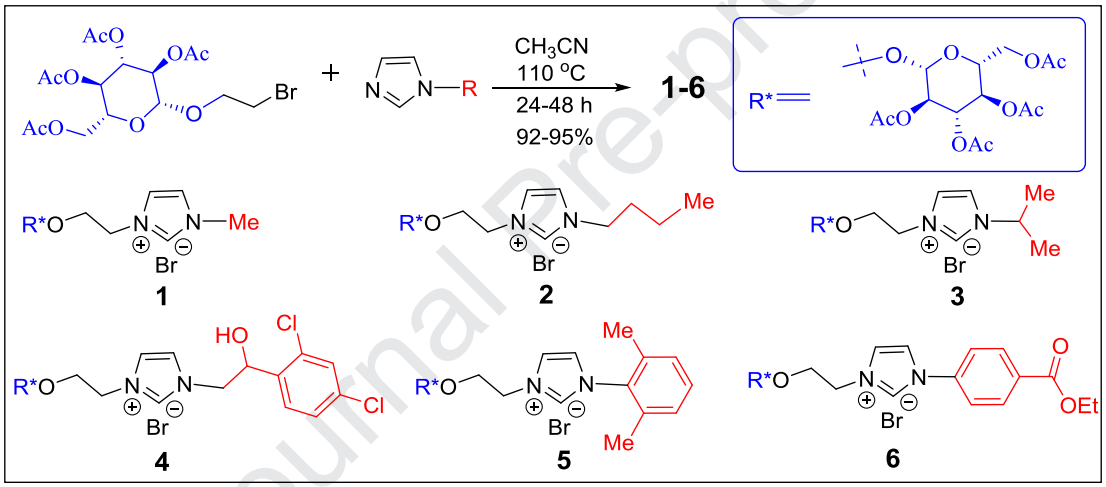
principles of green chemistry", and economically competitive production costs.[4] Since the first example of carboxylate- and sulfonate-based water-soluble N-heterocyclic carbenes (NHCs) ligands,[5] subsequently remarkable research progress has been made in Pd/NHCs-catalyzed aqueous cross coupling.[4, 6-9] Over the last decades, sugar-based various materials have attracted both economic and scientific interest because of increasing concerns in biocompatibility and recycled resources.[10-17] Related reviews also deal with the sugar-based ligands and complexes, including IMSs and NHCs-Metal complexes.[17-22] More recently, the catalytic activity of several examples about sugar-derived IMSs and NHCs-Metal complexs has been reported,[23-30] such as NHCs-Pd,[30] NHCs-Ir,[25] and NHCs-Ru etc..[26, 31] We also found that most Pd-catalyzed cross-coupling demand extra additives to enhance the dissolve and reactivity in water, including the use of biphasic organic solvent-water systems.[32] However, the catalytic activities of sugar-based IMSs have not been investigated extensively.[22, 33-35] To explore the influence of sugar-based IMSs on Pd catalyst, we turn our attention to systematically study of Pd/sugar-based IMSs-catalyzed Suzuki reaction.[36-38]

Transition metal nanoparticles (NPs) are usually functionalized with organic ligands including thiols, thioethers, amines, phosphines, and NHCs.[39] A series of literatures reported that Pd NPs were formed during the Pd/NHCs-catalyzed chemical reaction in aqueous media.[39-41] Herein, a simple strategy is the use of Glu-IMSs to establish micelles with an organic interior that can entrain Pd NPs in water, and the Pd NPs act as the efficient catalytic species for cross coupling. Firstly, a series of Glu-IMSs combining glucoside and imidazolium head groups with different substituents were synthesized with 92-95% isolated yield (Scheme 1). Secondly, the catalytic activities of these Glu-IMSs materials were evaluated in Pd-catalyzed Heck–Mizoroki and Suzuki–Miyaura reactions in water media. Tertiary, the Glu-IMSs material contained both -OH and NHCs coordination sites was found to be most efficient ancillary ligand among them. Additionally, under the optimized reaction conditions, a series of novel structure fluorine-cored organic small molecule functional materials (OFMs) were also synthesized with Suzuki–Miyaura reactions. Finally, the HR-TEM analysis showed that the Pd NPs stabilized by Glu-IMSs with an average size of around 4.0 nm

was formed, which may be act as a true catalytic species.

Results and Discussion

Glucoside-based imidazolium salts (Glu-IMSs, **1-6**) combining glucoside and imidazolium head groups with various substituents were synthesized in 92-95% isolate yields from the reaction of 2-bromoethyl glucoside with different N-substituent imidazole. It's found just β anomer-glucoside can be formed herein along with the TLC result, isolate yield, and NMR spectra, this is similar to previous results.[29, 42] The structures of these Glu-IMSs were confirmed with ^{1}H NMR, ^{13}C NMR and 2D NMR, these data combined with elemental analysis strongly verify the structure of Glu-IMSs (see SI).



Scheme 1. Synthesis of Glu-IMSs **1-6**.

From the ^{1}H NMR spectrum of Glu-IMSs **1-6** (Fig. S1), we can find a characteristic peak of NC*H*N proton in imidazolium heterocycle is a single peak at relative low field (δ_H 9.27, 9.35, 9.99, 10.02 and 10.15 ppm for Glu-IMSs **1-3, 5** and **6**, respectively),[37, 43] and there is no obvious pattern of changes in chemical shifts and substituents in imidazolium heterocycle. Surprisingly, the NC*H*N proton of Glu-IMSs **4** corresponding δ_H 9.00 ppm is not a single peak, in contrast is a doublet of doublets peak. A correlation is apparently observed between this proton and the NC*H*C*H*N protons in the COSY spectrum, this is what is expected from the coupling of the NC*H*N proton with the two inequivalent NC*H*C*H*N protons (Fig. S6). Next, the chemical shift of NC*H*C*H*N proton in imidazolium heterocycle also very different (Fig. S1), there are two independent doublet peaks in δ_H 7.36 (1.5 Hz) and 7.11 (1.5

Hz) ppm for Glu-IMSs **4**, but for Glu-IMSs **5**, just one single peak in δ_H 7.46 ppm with two proton can be found. There are two independent single peaks for Glu-IMSs **1** (δ_H 7.43 and 7.39 ppm), **2** (δ_H 8.03 and 7.97 ppm), **3** (δ_H 7.56 and 7.11 ppm), and **6** (δ_H 7.92 and 7.86 ppm), these results are consistent with previously literature data.[37, 42]

We got more information from ^{13}C NMR spectrum of Glu-IMSs **1**-**6** (Fig. S2), the chemical shift of N*C*HN carbon in imidazolium heterocycle at δ_C 136.6, 135.4, 135.8, 136.3, 137.4, and 137.2 ppm, respectively, and the chemical shift of N*C*H*C*HN carbon at 118-126 ppm. Because 1-poisition carbon of glucoside connected to the imidazolium heterocycle with ethoxy bridge, the chemical environment has less affected on its chemical shift, δ_C 61.1, 60.6, 61.6, 61.0, 61.3, and 61.4 ppm correspond to Glu-IMSs **1**-**6**, respectively. The σ-donor properties of Glu-IMSs ligands are crucial in dominating their interaction with palladium, as a result, to determine the catalytic activity of Glu-IMSs ligands in Pd-catalysis.[44, 45] The σ-donor properties of NHCs ligands can be evaluated based on the NMR data of imidazolium salts,[45-47] and we can get the order of their σ-donor properties from the ^1H NMR of Glu-IMSs herein.[45] Combine with the one-bond CH J-coupling constants of N*C*HN carbon for Glu-IMSs **1**-**6** (221.6, 221.5, 220.8, 224.8, 224.0, and 214.8 Hz), the one-bond CH J-coupling constants suggest the order of their σ-donor properties as following Glu-IMSs **6** > Glu-IMSs **3** > Glu-IMSs **2** ≈ Glu-IMSs **1** > Glu-IMSs **4** > Glu-IMSs **5**.

Next, with these Glu-IMSs in hand, we investigate the catalytic activity of them in Pd-catalyzed C-C cross coupling, including Heck and Suzuki reactions in water. For this purpose, firstly, we choose Pd-catalyzed Heck–Mizoroki reaction as initial research, the coupling of 4-bromotoluene and styrene was used as standard substrates (Table 1), $PdCl_2$ was used as catalyst, Glu-IMSs **4** was used as ancillary ligand. In the presence of 1.0 mol% of $PdCl_2$/Glu-IMSs **4** (mol:mol = 1:2), 85% of the target product was obtained after 6 h (Table 1, entry 4). By increasing the loading amount of the $PdCl_2$ to 1.5 mol%, the yield was improved to 96% (Table 1, entry 6), and 1.5 mol% of $PdCl_2$ was the optimum loading of catalyst (Table 1, entries 4-6 and 8). By contrast, only 15% yield of product was obtained in the absence of Glu-IMSs (Table 1, entry 7). Other Glu-IMSs **1**-**3**, **5** and **6** were also tested (Table 1, entries 1-3 and 9-10),

and among all of them, Glu-IMSs **4** was recognized as the best ancillary ligand (Table 1, entry 6). These above experiments revealed that the type of coordination atom in the Glu-IMSs chain play important role in the stabilizing and improving catalytic activity of Pd active catalytic species formed during the reaction. The Glu-IMSs **4** with -OH groups can be regarded as having two coordination units simoultanously, and shows better catalytic activity in comparing with the other Glu-IMSs with single NHCs ones, which could maybe due to the week ligation property of the hydroxyl group.[48]

Table 1. The Heck reaction between 4-bromotoluene and styrene in the presence of Glu-surfactants[a]

Entry	Pd (mol%)	Ligand (wt.%)	Time (h)	Yield (%)[b]
1	1.0	**1** (2)	6	32
2	1.0	**2** (2)	6	40
3	1.0	**3** (2)	6	55
4	1.0	**4** (2)	6	85
5	1.2	**4** (3)	12	76
6	1.5	**4** (3)	6	96
7	1.5	No ligand	6	15
8	2.0	**4** (4)	6	93
9	1.5	**5** (3)	6	70
10	1.5	**6** (3)	6	88

[a]Reaction conditions: 4-bromotoluene (1.0 mmol), styrene (1.25 mmol), K_2CO_3 (2.0 mmol), H_2O (3.0 mL), 90 ^oC oil bath under N_2 atmosphere. [b]Determined by GC-MS with nitrobenzene as internal standard, average of two runs.

We also checked other parameters such as different type of base and temperature on the Heck reaction (Table 2). Among the studied base, commonly used strong organic base $NaOBu^t$, and $KOBu^t$ were found not to be the most efficient for the Heck reaction (Table 2, entries 3 and 4). The widely used weak base K_2CO_3 was chosen as the most suitable base since 97% yield was obtained in the model reaction (Table 2, entry 9). We found that using other base including NaOH, KOH, NaOAc, K_3PO_4 and

Cs_2CO_3 can't get ideal yield (Table 2, entries 1, 2 and 5-7). Under the base-free conditions, also 23% of the target product was detected, demonstrating that the Glu-IMSs **4** can be ionized into anions and cations, performing certain weak base property in this study. Varies oil bath temperatures were also investigated and 90 °C was selected as the suitable temperature in following experiments (Table 2, entries 9-12).

Table 2. The effect of different type of base and temperature on the Heck reaction[a]

Entry	Base	T (^{o}C)	Time (h)	Yield (%)[b]
1	NaOH	90	6	72
2	KOH	90	6	76
3	$NaOBu^t$	90	6	82
4	$KOBu^t$	90	6	85
5	K_3PO_4	90	6	89
6	NaOAc	90	6	60
7	Cs_2CO_3	90	6	91
8	No base	90	6	15
9	K_2CO_3	100	6	97
10	K_2CO_3	80	12	93
11	K_2CO_3	60	12	78
12	K_2CO_3	rt	24	23

[a]Reaction conditions: 4-bromotoluene (1.0 mmol), styrene (1.25 mmol), base (2.0 mmol), H_2O (3.0 mL), oil bath under N_2 atmosphere. [b]Determined by GC-MS with nitrobenzene as internal standard, average of two runs.

The optimized reaction conditions of Heck reaction obtained from above reactions are shown as following, 2.0 equivalent mol K_2CO_3 as base, H_2O as solvent, $PdCl_2$/Glu-IMSs **4** (1:2) as catalyst with 1.5 mol% loading, and all of the substrates were maintained in 90 ^{o}C oil bath with stirred for 6.0 or 12 h. The results mentioned above promoted us to investigate the scope and limitations of the Heck-Mizoroki reaction. A range of aryl halides with both electron-donating and electron-withdrawing groups coupled with olefin, and the results were summarized in

Fig. 3. Iodobenzene, 4-methoxy-iodobenzene, 4-methyl-iodobenzene could react smoothly with styrene derivatives to afford corresponding products above 96% yield (Fig. 1. **8a**, **9a**, **10a**, and **11a**). Aryl bromides was the most common substrate of the Pd-catalyzed cross coupling reaction, herein, we found that a range of aryl bromides with varying electronic and steric properties selected herein could couple smoothly with styrene derivatives and gave the desired products in yields between 90% and 98% (Fig. 1. **8-11b** and **12-19a**). With a non-activating and steric hindrance group such as a 2-methyl group, the desired product was obtained in good yield (Fig. 1. **15a**, 90%). On the other hand, in the case of cheaper aryl chlorides, the reaction of styrene with less efficient, electron-rich 4-methoxychlorobenzene affording the products in relatively low yields even consumed a longer reaction time (Fig. 1. **8c**, 46%). Fortunately, the activated aryl chlorides coupled very well with styrene and afford quite well yields (Fig. 1. **12b**, 86% and **13b**, 90%). So, our catalytic system more suitable for the coupling between activated aryl chlorides and styrene.

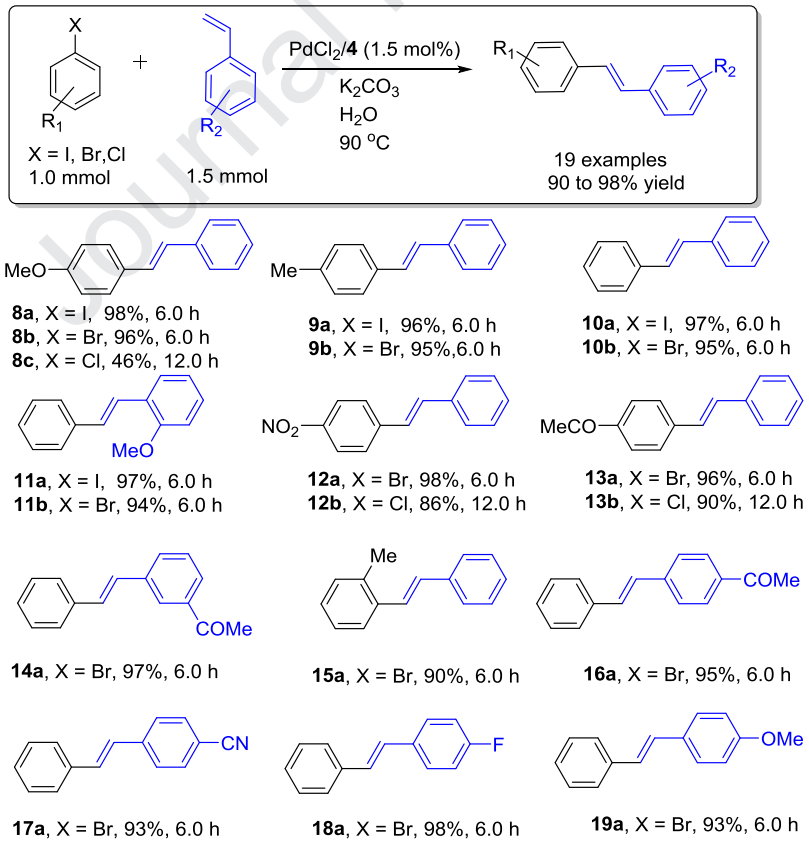


Figure 1. Heck reaction of different aryl halides and styrene under the optimized conditions.

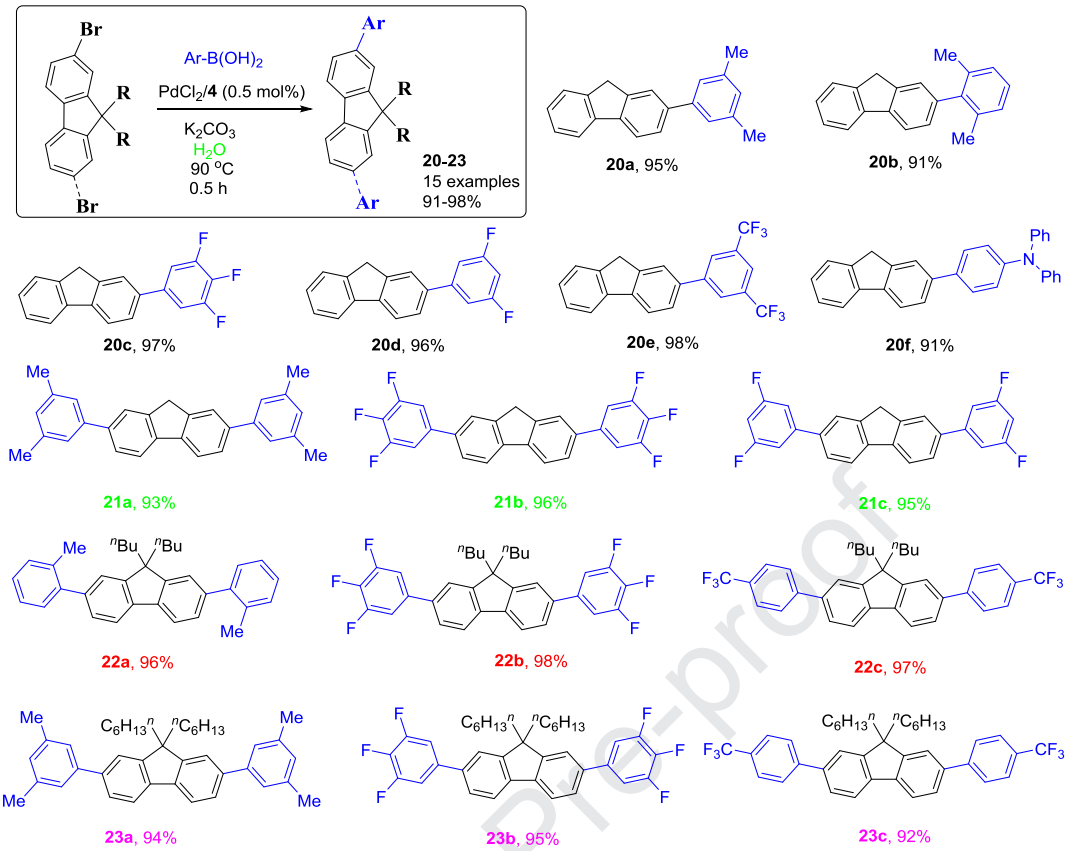


Figure 2. The fluorine-cored OFMs prepared by Suzuki reaction (15 examples). (Reaction condition, 2.0 equivalent mol K_2CO_3 as base, H_2O as solvent, $PdCl_2$/Glu-IMSs **4** (mol/mol = 1:2) as catalyst with 1.5 mol% loading, and all of the substrates were maintained in 90 °C oil bath with stirred for 0.5 h.)

In another part of this study we investigated the catalytic activity of $PdCl_2$/Glu-IMSs **4** in Suzuki reaction. Conjugate materials containing fluorine unit, fluorine element, triphenylamine, and carbazole groups have obviously attracted attention as popular OFMs including OPV, OLED, and PVSCs devices.[49-53] Based on our previously results about Glu-Ims for Pd-catalyzed Suzuki coupling.[38] The substrate range of Suzuki coupling is still limited, but conceptionally, our catalytic system represents an interesting synthetic alternative expanding Glu-IMSs applications in Pd-catalyzed reaction. Herein, we used $PdCl_2$/Glu-IMSs **4** catalytic system synthesized a series fluorine-cored OFMs (15 examples) with optimized reaction conditions mentioned above by the Suzuki reaction between 2-bromofluorene, 2,7-dibromofluorene, 2,7-dibromo-9,9-dibutyl-9H-fluorene, 2,7-dibromo-9,9-dihexyl-9H-fluorene and aryl boronic acids containing trifluoromethyl group, fluorine, and triphenylamine moieties (Fig. 2). Studies on different aryl boronic acids with electron-deficient and

electron-rich substituents were carried out. As shown in Fig. 2, the electron-rich aryl boronic acids were very suitable in this protocol with excellent yield (above 95%). The electron-deficient aryl boronic acids were also suitable in this catalytic system and obtained the desirable product in good yield (**20a**, 95%; **20b**, 91%, and **21-23a**, 93%, 96%, and 94% respectively).

The electron-rich superb NHCs are an emerging class of stabled anchor for Pd NPs due to its strong σ-donation.[54-61] Herein, the catalytic activity of Pd/Glu-IMSs increase with the lengths of alkyl chain and steric hindrance, because this is the main difference between these ligands, and may cause best dispersed Pd NPs with the NHCs ligand.[62] Herein, the presence of the Glu-IMSs dominated the interactions of the transition metal Pd-Pd, leading to form small size IMSs functionalized Pd NPs and enlarge the surface areas of Pd catalyst species, the carbohydrate, on the other hand, increased water solubility of Pd catalyst species, slightly reduced the surface tension of IMSs solutions and stabilized molecular assemblies considerably.

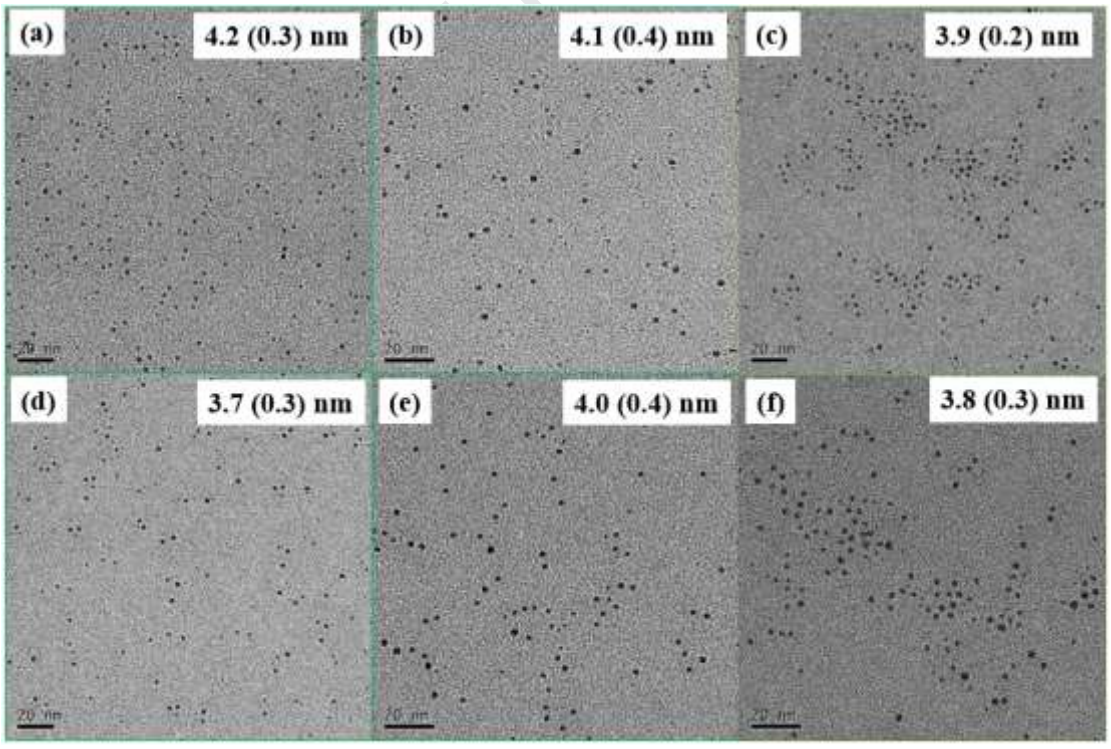


Figure 3. The HR-TEM images taken from $PdCl_2$/Glu-IMSs/H_2O.

In order to better understanding of real catalytic species, $PdCl_2$/Glu-IMSs in water was warm to refluxed, then examined by high-resolution transmission electron microscopy (HR-TEM), the results are shown in Fig. 3, standard deviations given in

brackets. According to the HR-TEM, IMSs functionalized Pd NPs have a revealed monodisperse and well-distributed nanoparticles with a relatively small size distribution of 4.2 (0.3), 4.1 (0.4), 3.9 (0.2), 3.7 (0.3), 4.0 (0.4), and 3.8 (0.3) nm with Glu-IMSs **2-7**, respectively (Fig. 3). Unfortunately, Pd NPs functionalized with Glu-IMSs **1** have not suitable for testing samples, because $PdCl_2$/Glu-IMSs **1** formed unstable Pd NPs, maybe due to least hindered methyl in imidazolinium heterocycle.[40] We believed that the IMSs functionalized Pd NPs act as an efficient real catalytic species in the Pd-catalyzed cross coupling reaction in water media.[41, 63-65] From the ^{1}H NMR spectrum of Glu-IMSs **4** functionalized Pd NPs (Fig. S4), the lack of observation of the NC*H*N proton in the imidazole ring maybe means the formation of Pd-NHCs bond, moreover can also be due to the widening of the resonance due to the interaction with the Pd NP surface, and we also found four acetyl groups still retained. We also characterized Glu-IMSs **4** with DEPT135, DEPT90 (Fig. S5), and COSY (Fig. S6), HSQC (Fig. S7), HMBC (Fig. S8) NMR spectroscopy, most of the ^{1}H NMR and ^{13}C NMR chemical shift were assigned with the help of 2D NMR and the results were listed in Table S1.

Conclusion

In summary, a series of Glu-IMSs combining glucoside and imidazolium head groups with different substituents were synthesized with 92-95% isolate yield. The method for the synthetic Glu-IMSs is simple and they can be obtained from cheap and commercial starting materials. $PdCl_2$ combined directly with Glu-IMSs (mol:mol = 1:2) represents an efficient catalyst for Heck-Mizoroki reactions of aryl iodides, bromides and activated aryl chlorides (19 examples). At the same time, the best $PdCl_2$/Glu-IMSs **4** catalytic system was used for Suzuki reactions. A series fluorine-cored OFMs (15 examples) were synthesized with the Suzuki coupling between 2-bromofluorene, 2,7-dibromofluorene, 2,7-dibromo-9,9-dibutyl-9H-fluorene, 2,7-dibromo-9,9-dihexyl-9H-fluorene and aryl boronic acids. We found Glu-IMSs **4** having the coordinating oxygen functional group was found to be most efficient among them. HR-TEM analysis showed that IMSs functionalized Pd NPs was formed with an average size of around 4.0 nm and act as an efficient catalyst to accelerate the

cross coupling in water media. The Glu-IMSs **4** contain -OH and NHCs two coordination sites show best catalytic activity. Further studies of the developed catalyst system to asymmetric catalysis were currently carried on in our laboratory.

Synthesis of Glu-IMSs 1-6

Glu-IMSs **1-6** was obtained according to previous method,[29, 42] the product was purification by chromatography (DCM/methanol, 20/1 to 3/1). A solution of 2-bromoethyl glucoside (1.0 mmol), and the N-substituent imidazole (2.0 mmol) and 10.0 mL of dry acetonitrile were sequentially added, refluxed and stirred for 24 h. The product Glu-IMSs **1-6** was purification by chromatography (DCM/methanol, 10/1 to 3/1) in around 95% yield.

1-(2-β-D-Glucopyranosyloxyethyl)-3-methyl-imidazolium bromide (1)

Viscous liquid, 97%, ^{1}H NMR (400 MHz, $CDCl_3$): 1.78 (s), 1.80 (s), 1.81 (s), 1.87 (s), 3.15 (s), 3.67 (m), 3.85 (s), 4.46 (m), 3.89 (m), 3.96 (m), 4.05 (m), 4.41 (m), 4.46 (m), 4.52 (d, J = 8.0 Hz), 4.71 (d, J = 8.0 Hz), 4.82 (t, J = 10.0 Hz), 4.99 (t, J = 8.0 Hz), 7.39 (s), 7.43 (s), 9.27 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 20.0, 20.2, 20.3, 36.1, 49.2, 53.2, 61.1, 67.3, 67.6, 70.6, 67.6, 70.6, 71.2, 71.8, 99.7, 122.6, 122.8, 136.6, 168.9, 169.2, 169.4, 170.2; Elemental analysis calcd (%) for $C_{20}H_{29}BrN_2O_{10}$: C, 44.70; H, 5.44; found C, 44.72, H, 5.43.

1-(2-β-D-Glucopyranosyloxyethyl)-3-butyl-imidazolium bromide (2)

Viscous liquid, 96%, ^{1}H NMR (400 MHz, $CDCl_3$): 1.34 (t, J = 8.0 Hz), 1.741 (m), 2.25 (m), 2.31 (s), 2.34 (s), 2.35 (s), 2.40 (s), 4.27 (m), 4.37 (m), 4.51 (m), 4.62 (m), 4.84 (s), 5.12 (d, J = 8.0 Hz), 5.21 (t, J = 8.0 Hz), 5.33 (t, J = 9.6 Hz), 5.59 (t, J = 9.6 Hz), 7.97 (s), 8.02 (s), 9.35 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.7, 18.2, 18.5, 18.6, 18.8, 30.8, 48.5, 60.6, 66.2, 67.3, 70.2, 70.6, 71.5, 99.1, 121.2, 122.0, 135.4, 168.9, 168.9, 169.2, 169.9; Elemental analysis calcd (%) for $C_{23}H_{35}BrN_2O_{10}$: C, 47.68; H, 6.09; found C, 47.69, H, 6.07.

1-(2-β-D-Glucopyranosyloxyethyl)-3-isopropyl -imidazolium bromide (3)

Viscous liquid, 96%, ^{1}H NMR (400 MHz, $CDCl_3$): 1.59 (d, J = 8.0 Hz), 1.95 (s), 1.97 (s), 1.98 (s), 2.04 (s), 3.78 (m), 4.07 (m), 4.11 (d, J = 2.0 Hz), 4.20 (d, J = 6.0 Hz), 4.23 (d, J = 8.0 Hz), 4.62 (d, J = 8.0 Hz), 4.67 (m), 4.73 (m), 4.90 (dd, J = 9.6 Hz, J =

8.0 Hz), 4.99 (t, *J* = 9.6 Hz), 5.16 (t, *J* = 9.6 Hz), 7.33 (s), 7.55 (s), 9.99 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.3, 20.4, 20.67, 20.7; 22.9, 49.8, 53.2, 61.6, 67.9, 68.1, 71.1, 71.8, 72.2, 100.4, 118.9, 123.7, 135.8, 169.4, 169.6, 169.8, 170.5; Elemental analysis calcd (%) for $C_{22}H_{33}BrN_2O_{10}$: C, 46.73; H, 5.88; found C, 46.75, H, 5.86.

1-(2-β-D-Glucopyranosyloxyethyl)-3-(2-(2,4-dichlorophenyl)-2-hydroxyethyl)-imidazolium bromide (4)

White solid, 96%, ^{1}H NMR (400 MHz, $CDCl_3$): 1.74 (s), 1.76 (s), 1.79 (s), 1.82 (s), 3.62 (m), 3.83 (m), 3.96 (m), 4.12 (m), 4.35 (t, *J* = 10.8 Hz), 4.48 (t, *J* = 6.4 Hz), 4.69 (d, *J* = 16.0 Hz), 4.81 (m), 5.13 (d, *J* = 8.0 Hz), 5.16 (m), 7.05 (m), 7.11 (m), 7.26 (m), 7.35 (d, *J* = 8.4 Hz), 9.00 (q, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 19.9, 20.1, 20.2, 49.2, 53.2, 54.0, 61.0, 66.9, 67.1, 67.2, 67.3, 67.5, 70.4, 71.1, 71.6, 99.5, 99.7, 121.9, 122.0, 122.3, 127.0, 128.4, 131.2, 133.6, 135.2, 135.3, 136.3, 168.8, 169.1, 169.3, 170.0; Elemental analysis calcd (%) for $C_{27}H_{33}BrCl_2N_2O_{11}$: C, 45.52; H, 4.67; found C, 45.53, H, 4.66.

1-(2-β-D-Glucopyranosyloxyethyl)-3-(2,6-dimethylphenyl)-imidazolium bromide (5)

White solid, 96%, ^{1}H NMR (400 MHz, $CDCl_3$): 2.23 (s), 2.24 (s), 2.26 (s), 2.27 (s), 2.37 (s), 2.39 (s), 4.13 (m), 4.46 (m), 4.51 (m), 4.61 (m), 5.02 (d, *J* = 8.0 Hz), 5.16 (dd, *J* = 9.6 Hz, *J* = 8.0 Hz), 5.26 (t, *J* = 9.6 Hz), 5.28 (m), 5.46 (t, *J* = 9.6 Hz), 7.47 (m), 7.47 (m), 7.48 (s), 7.62 (m), 8.39 (t, *J* = 4.0 Hz), 10.02 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.4, 22.3, 22.3, 22.4, 22.6, 50.2, 61.4, 67.9, 68.3, 71.0, 71.8, 72.2, 100.5, 122.1, 124.4, 129.0, 130.8, 132.8, 134.4, 137.4, 169.3, 169.4, 169.6, 170.3; Elemental analysis calcd (%) for $C_{27}H_{35}BrN_2O_{10}$: C, 51.68; H, 5.62; found C, 51.69, H, 5.58.

1-(2-β-D-Glucopyranosyloxyethyl)-3-(4-ethyl benzoaty)-imidazolium bromide (6)

White solid, 92%, ^{1}H NMR (400 MHz, $CDCl_3$): 1.27 (t, *J* = 8.0 Hz), 1.85 (s), 1.86 (s), 1.88 (s), 1.91 (s), 3.74 (m), 4.01 (m), 4.12 (m), 4.26 (m), 4.52 (d, *J* = 8.0 Hz), 4.73 (s), 4.81 (t, *J* = 8.0 Hz), 4.90 (t, *J* = 8.0 Hz), 5.10 (t, *J* = 12.0 Hz), 7.82 (d, *J* = 8.0 Hz), 7.86 (s), 7.92 (s), 8.10 (d, *J* = 8.0 Hz), 10.15 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 20.1, 20.2, 20.3, 20.5, 22.3, 50.0, 61.3, 67.2, 67.7, 70.8, 71.5, 71.9, 100.0, 120.0, 121.4, 124.5, 131.4, 131.6, 135.5, 137.2, 164.5, 169.1, 169.5, 169.6, 170.3, 173.1;

Elemental analysis calcd (%) for $C_{28}H_{35}BrN_2O_{12}$: C, 50.08; H, 5.25; found C, 50.09, H, 5.23.

Conflicts of interest

There are no conflicts of interest to declare.

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Highlights

·Preparation of Glu-IMSs from commercial N-substituent imidazole.

·The catalytic activities of Pd/Glu-IMSs were evaluated with Heck–Mizoroki and Suzuki–Miyaura reactions in water.

·Glu-IMSs with -OH and NHCs two coordination sites was the most efficient ligand.

·The Glu-IMSs stabilized Pd NPs with an average size of ~4.0 nm.

·A series novel fluorine-cored OFMs were synthesized.

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