FULL PAPER



Ultra-small sugar-substituted N-heterocyclic carbeneprotected palladium nanoparticles and catalytic activity

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Gannan Normal University; Key Laboratory of Jiangxi University for Functional Materials Chemistry, Grant/Award Number: FMC16201; National Natural Science Foundation of China, Grant/Award Number: 21562002 Ultra-small Pd nanoparticles (UNPs) represent a distinctive type of nanomaterial making them very attractive for a range of applications. Herein, chiral sugar-substituted N-heterocyclic carbenes (NHCs) with various lengths of alkyl chain (sugar-NHCs- ${}^{n}C_{n}H_{2n+1}$) were first used to prepare water-soluble Pd@NHCs-sugar UNPs via an efficient ligand-exchange strategy, which can be handled under air and are stable over 10 months. The Pd@NHCs-sugar UNPs were highly monodisperse, with tunable core diameters from 1.7 to 2.1 nm, and an effect of the particle size on the N-substituted aliphatic chains was observed. To investigate the accessibility of the surface, the Pd@NHCs-sugar UNPs were studied as catalysts for C-C coupling reaction in eco-friendly ethanol aqueous solution without any precipitation of metallic Pd. The presence of the longest aliphatic group in the Pd@NHCs-sugar UNPs imparts to them the highest catalyst activity (turnover number and turnover frequency up to 196 000 and 3 920 000 h⁻¹).

KEYWORDS

ligand exchange, palladium nanoparticle, sugar-substituted NHCs, ultra-small, water-soluble

1 | INTRODUCTION

Metal nanoparticles (NPs) have been studied extensively due to their numerous applications in green chemistry, catalysis, biology and medicine.^[1,2] Such metal NPs are usually stabilized with ligands including phosphines, amines, thiols and thioethers.^[3-7] The neutral, electronrich N-heterocyclic carbenes (NHCs) are an emerging class of protected anchor for metal NPs due to their strong σ -donation,^[2,8-12] since Arduengo *et al.* reported the isolation of free NHCs in 1991.^[13] Most recently, NHCs were used as alternative anchors for metal (including Au, Pd, Pt, Ru, Ag, etc.) surface modifications and so provided many notable properties, which might make them surpass thiol-based systems.^[2,12] Just a few examples of NHC-protected Pd NPs are reported in the literature,^[9,14–20] and the exchange strategy is an outstanding method because it employs preformed Pd NPs with

known shapes and sizes.^[17] Richter et al.^[17] and Planellas et al.^[18] have synthesized Pd NPs stabilized by NHCs with a size distribution around 4.0 nm. Glorius and coworkers^[20] have reported the preparation of NHCprotected water-stable Pd NPs with a size distribution of 4.0-4.9 nm. Jesús and co-workers have synthesized a series of water-soluble NHC-stabilized Pd NPs with different shapes and sizes, ranging from 1.3 to 7.0 nm.^[9,19] Pdbased nanocatalysts have attracted considerable attention because of their superior catalytic activity in many types of reactions. The smaller Pd NPs expose more lowcoordination sites, and ultra-small nanoparticles tend to have unexpectedly distinctive properties.^[21] The best advantage of using NHCs is the practical modification of groups in the heterocycle which can give rise to a tunable metal surface. Furthermore, specific properties of metal NPs capped with chiral compounds have attracted a great deal of attention.^[15,22]

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The biological roles of sugars as recognition markers and signaling effectors are associated with specific molecular recognition in which proteins, DNA, RNA or other sugars are involved.^[23,24] Their excellent catalytic performance is one of the important highlights of sugar-based NHCs and their metal complexes.^[23,25-28] For example, a series of sugar-based mono-NHCs-Pd complexes were used for Suzuki reactions with low Pd loading of 0.05-1.0 mol%.^[29-34] We also reported several sugar-based NHC precursors for Suzuki reactions at a Pd loading of 0.1-0.05 mol%.^[35-37] However, the catalytic activity of sugar-based Pd@NHCs NPs was not investigated. In a continuation of our previous work based on sugar-based NHCs, we were interested in synthesizing the first example of sugar-based Pd@NHCs NPs, and the catalytic activity of these Pd NPs may be very attractive.

In the work reported herein, we designed four sugarbased chiral NHC precursors with various lengths of aliphatic chains directly attached to the N atom of imidazole heterocycle. Pd@NHCs-sugar ultra-small NPs (UNPs) stabilized by these sugar-based chiral NHC ligands were synthesized via an efficient ligand-exchange procedure, and the catalytic activity was investigated in C–C coupling reactions in eco-friendly ethanol aqueous solution (turnover number (TON) up to 196 000 and turnover frequency (TOF) up to 3 920 000 h^{-1}) without any aggregation of Pd NPs.

2 | SYNTHESIS

In order to obtain ultra-small, water-soluble Pd NPs, we synthesized a library of sugar-substituted NHC precursors, **1**-Br–**4**-Br, in a four-step sequence from D-glucose (Figure 1).^[38] The sugar-substituted NHC precursors **1**-Br–**4**-Br have never been applied in the synthesis of metal complexes and metal NPs. The NHC precursors usually start from *N*-substituted imidazole with halogenoarene or haloalkane.^[30,33,39] Herein, sugar-substituted NHCs precursors **1**-Br–**4**-Br could be obtained in high yields (above 95%) with a convenient one-step method directly from the reaction of brominated alkanes, including bromoethane, bromobutane, bromobutane, and hexadecyl bromide with 1-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyl)imidazole following a literature procedure.^[36]

We find the chemical shift of NCHN proton in imidazolium heterocycle at relatively low field (10.38, 10.83, 10.30 and 10.76 ppm) (Figure S1) after forming NHC precursors **1**-Br–**4**-Br.^[40] The substituent effect of the sugar-substituted NHC precursors can be observed from the ¹H NMR and ¹³C NMR spectra (Figure S1), especially from the ¹³C NMR signal of 1-position C



FIGURE 1 Synthesis of sugar-substituted NHC precursors

atom in the sugar ring (Figure S1). The chemical shift of 1-position C atom in precursors **1**-Br–**4**-Br corresponds to 83.77, 83.75, 83.62 and 83.56 ppm, respectively (Figure S1).

Displacement of weakly binding didodecylsulfide (DDS) ligands from the surface of DDS@Pd NPs by stronger binding NHCs is a universal procedure for attaching functional NHCs to Pd@NHCs NPs.^[20] Herein, Pd NPs stabilized by DDS were obtained according to a literature method and have a size distribution of 4.0 (+0.3) nm.^[41] Then Pd@NHCs-sugar UNPs (5-8) were synthesized by aliphatic chains and sugar-substituted chiral NHCs 1-Br-4-Br with an efficient ligand-exchange method (Figure 2). The free sugar-NHCs were generated in situ by deprotonation of the corresponding sugarbased NHCs precursors 1-Br-4-Br with KO^tBu in dimethylformamide (DMF). After the addition of DDS@Pd NPs, a phase transfer of the Pd NPs from nonpolar hexane into the more polar DMF phase could be seen with the naked eve, indicating the successful sugar-NHC exchange on the surface of Pd NPs. The unbound DDS ligand can be removed by simple extraction after the exchange process. The Pd@NHCs-sugar UNPs could be isolated as a brown solid after purification by repeated washing, precipitation and dialysis against water. To confirm the crucial role of the alkyl chains, N-substituted C₂H₅, C₄H₉, C₈H₁₇ and C₁₆H₃₃ NHCs were also investigated as stabilizer. We were able to synthesize the first example of ultra-small, watersoluble chiral Pd NPs using sugar-based NHCs with the ligand-exchange method. It should be pointed out that the Pd@NHCs-sugar UNPs can be handled in air and are stable over 10 months.



FIGURE 2 Synthesis of Pd@NHCs-sugar UNPs with ligand-exchange procedure



FIGURE 3 (a–d) HR-TEM images and (e) XRD patterns of Pd@NHCs-sugar UNPs

TABLE 1 Selected parameters of Pd@NHCs-sugar UNPs

Entry	Pd UNPs	Water contact angle (°)	δ _{NCHN} (ppm) ^a	NHCs/Pd	Pd (%)	Size (nm)
1	5	10.4	10.38	3.02:1	60.32	2.1 ± 0.4
2	6	10.8	10.83	3.16:1	59.89	2.0 ± 0.3
3	7	11.1	10.30	3.42:1	59.00	1.8 ± 0.3
4	8	13.2	10.76	3.70:1	58.52	1.7 ± 0.4

^aThe NCHN proton signal of four sugar-based NHC precursors.

3 | RESULTS AND DISCUSSION

Purification was performed by dialysis to remove some impurities. The purified Pd@NHCs-sugar UNPs were redispersed in ethanol and examined using high-resolution transmission electron microscopy (HR-TEM). The dynamic light scattering size distribution histograms and HR-TEM images are shown in Figure 3a-d (standard deviations given in parentheses). According to the HR-TEM results, Pd@NHCs-sugar UNPs consist of monodisperse and well-distributed NPs with an ultra-small size of 1.7 (0.4), 1.8 (0.3), 2.0 (0.3) and 2.1 (0.4) nm (Table 1), respectively, indicating formation without aggregation during the thioether ligand-exchange process. The size distribution of Pd@NHCs-sugar UNPs 6-8 remained essentially unchanged over a period of 10 months under air. Some coalescence was observed over longer periods for Pd@NHCs-sugar UNPs 5 because of the shortest ethyl chain. Powder X-ray diffraction (XRD) analyses (Figure 3e) of the Pd@NHCs-sugar UNPs clearly indicated that the Pd@NPs were highly crystalline.

Thermogravimetric analysis (TGA; Figure 4b) and elemental analysis were used to determine the composition of the Pd@NHCs-sugar UNPs. The Pd content was around 60%, which is consistent with a Pd-to-NHCs-sugar ligand ratio of 3.02:1 (60.32%) for **5**, 3.16:1 (59.89%) for **6**, 3.42:1 (59.00%) for **7** and 3.70:1 (58.52%) for **8**. From the elemental analysis, C:H:N ratios were in agreement with the theoretical calculated values for these Pd@NHCssugar UNPs, confirming that the Pd NPs are stabilized by the sugar-based NHCs exclusively. It is worth mentioning that the Pd-to-NHCs-sugar ratio is in principle sufficiently high to enable the coordination of all sugarbased NHC molecules, except for steric factors, since the calculated number of Pd surface atoms exceeds the estimated number of ligands (up to around 3 times for Pd@NHCs-sugar UNPs).

The ¹H NMR spectra of the Pd@NHCs-sugar UNPs clearly showed that all four acetyl groups remained. The lack of observation of the NCHN proton signal in the ¹H NMR spectrum may be because of the formation of Pd–NHC bond (Figure S6); moreover it can also be due to the widening of the resonance due to the interaction with the Pd NP surface.

Recent research results suggested that hydrophilic Pd@NHCs NPs containing water-soluble functional groups show efficient catalytic activity in neat water.^[19] Incorporation of sugar groups into Pd@NHCs NPs not only introduces chirality but also improves water solubility. Herein, as-cast films of Pd@NHCs-sugar UNPs **5–7** exhibit contact angles of 10.4°, 10.8° and 11.1°, respectively (Figure 4a(a–c)). Pd@NHCs-sugar UNPs **8** exhibits a relatively large contact angle of 13.2° (Figure 4a(d), which may be attributed to the longer aliphatic chain. The water contact angles of these Pd@NHCs-sugar UNPs films are lower than 15°, indicating that all of them are fairly hydrophilic.^[42]

Water-soluble Pd NPs can catalyze chemical reactions in aqueous solution.^[19] After the successful synthesis and characterization of Pd@NHCs-sugar UNPs, we were interested in investigating in detail whether these Pd@NHCs-sugar UNPs systems are catalytically active or whether the aliphatic chains shield the active sites. With high hole mobility, fluorene, triphenylamine, carbazole and fluorine moieties have been identified as



FIGURE 4 (a) Water contact angles and (b) TGA curves of of Pd@NHCs-sugar UNPs

TABLE 2 Pd@NHCs-sugar UNPs-catalyzed reaction of 2-bromofluorene and phenylboronic acida

Entry	Catalyst	Time (h)	Conversion (%) ^b	TON
1	5	1.0	88	44 000
2	6	1.0	92	46 000
3	7	0.3	93	46 500
4	8	0.2	94	47 000
5	Pd (OAc) ₂ / 4 -Br	2.0	86 ^c	4 300

^aReaction conditions: 2-bromofluorene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst Pd@NHCs-sugar UNPs (0.02 mg, 0.005 mol% from TGA), KOH (2.0 mmol), H_2O (3.0 ml), TBAB (2.0 mmol), reflux in air.

 $^{b}Average$ of two runs, measured by GC-MS. $^{c}Pd(OAc)_{2}/4\text{-}Br$ in situ (1:1, 0.05 mol%).

effective π -conjugated hole transporting materials and are widely used in organic light-emitting devices, thin-film transistors, polymer light-emitting devices and solar cells.^[43-47] Especially, π -conjugated fluorene-based polymers and small molecules are suitable candidates for serving as hole transporting materials of perovskite solar cells.^[48–51] Therefore, we chose the template coupling between 2-bromofluorene with phenylboronic acid as a model reaction to investigate whether the Pd@NHCssugar UNPs with *N*-sugar group and different *N*-aliphatic substituents have unique catalytic activity.

As evident from Table 2, the conversion of 2bromofluorene is significantly affected by the size of Pd@NHCs-sugar UNPs with different lengths of aliphatic chain. Pd@NHCs-sugar UNPs **5** afforded the lowest conversion of 88% after 1.0 h (Table 2, entry 1), and **8** with the smallest Pd NP size afforded the highest conversion of 94% in just 0.2 h (Table 2, entry 4). The smallest, most rigid and sterically demanding sample **8** afforded higher conversion (Table 2, entries 1–4). We briefly compared Pd@NHCs-sugar UNPs with a homogeneous catalyst, combining Pd(OAc)₂ directly with **4**-Br as catalyst, which generates active species Pd/NHCs-sugar- $C_{16}H_{33}$ with the aid of KOH *in situ* and afforded 86% conversion in 2 h, exhibiting a moderate TON value of 4300 (Table 2, entry 5). The catalytic activity of catalyst **8** is about 450 times that of catalyst Pd(OAc)₂/**4**-Br. This shows that ultra-small nanometric size of the Pd@NHCs-sugar UNPs catalyst greatly improves the catalytic activity.

Next, we investigated the coupling of 2-bromofluorene and phenylboronic acid with different bases, solvents and Pd loadings, confirming the best catalytic activity of Pd@NHCs-sugar UNPs 8 (Table 3). TON and TOF of catalvst 8 reached 96 000 and 960 000 h^{-1} (Table 3, entry 9), respectively. The presence of a small amount of ethanol improves the solubility of the reaction system, enhancing the catalytic activity of NHCs-sugar UNPs. TON and TOF reached 164 000 and 3 280 000 h^{-1} (Table 3, entry 14). The catalytic activity of these complexes is far higher than that reported for a sugar-incorporated NHC pincer Pd complex (TON, 800 000; TOF, 50 000 h⁻¹)^[52] and sugarincorporated bis-NHC Pd complex (TON, 85 000; TOF, 170 000 h⁻¹).^[53] This result suggested that stabilization of the Pd UNPs by sugar-based NHCs is enough to prevent decomposition under the reaction conditions.

Additionally, we investigated the catalytic activity of Pd@NHCs-sugar UNPs **8** for a range of π -conjugated fluorene-based small-molecule substrates with the best conditions in hand (Figure 5). In general, all these reactions proceeded to complete conversion to the desired products in good to excellent isolated yields. The results indicate that the catalytic activity of Pd@NHCs-sugar UNPs **8** is related to the ultra-small size of the Pd NPs,

TABLE 3 Effect of conditions on coupling of 2-bromofluorene and phenylboronic acid^a

Entry	Base	Time (h)	Conversion (%) ^b	Entry	Base	Time (h)	Conversion (%) ^b
1	NaOH	1.0	88	8	KOBu ^t	0.2	97
2	Na ₂ CO ₃	1.5	85	9	KOBu ^t	0.1	99 ^c
3	K ₂ CO ₃	1.5	86	10	KOBu ^t	0.1	95 ^d
4	K_3PO_4	1.5	80	11	KOBu ^t	0.1	98 ^{c,e}
5	Cs_2CO_3	1.5	86	12	KOBu ^t	0.05	92 ^{c,e}
6	Et ₃ N	3.0	66	13	KOBu ^t	0.1	91 ^{c,f}
7	КОН	0.2	94	14	KOBu ^t	0.05	82 ^{c,f}

^aReaction conditions: 2-bromofluorene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst **8** (0.02 mg, 0.005 mol%), base (2.0 mmol), H₂O (3.0 ml), TBAB (2.0 mmol), reflux in air.

^bAverage of two runs, measured by GC-MS.

 $^{c}EtOH-H_{2}O = 1:1 (v/v).$

 d EtOH-H₂O = 1:2 (v/v).

^e**8** (0.004 mg, 0.001 mol%). ^f**8** (0.002 mg, 0.0005 mol%).



FIGURE 5 Reactions of fluorene-based small-molecule substrates (24 examples) catalyzed by Pd@NHCs-sugar 8 (0.0001 mol%; KOBu^t; EtOH-H₂O (1:1 v/v); reflux in air)

the rigid, steric demand of the sugar group and longest aliphatic chain.^[39] Compared with the other Pd UNPs catalysts, the difference is the length of the aliphatic chain, the relatively long aliphatic chain length perhaps enhancing the steric bulk of the Pd UNPs.

TABLE 4 Pd@NHCs-sugar 8-catalyzed coupling of 2-iodofluorene and phenylboronic acida

Run	Time (min)	Conversion (%) ^b	Yield (%) ^c	TON	TOF (h ⁻¹)
1	3	99	98	196 000	3 920 000
2	3	99	97	194 000	3 880 000
3	5	96	95	190 000	2 280 000
4	5	93	92	184 000	2 208 000
5	10	91	90	180 000	1 080 000

^aReaction conditions: 2-iodofluorene (3.0 mmol), phenylboronic acid (4.5 mmol), catalyst **8** (0.0005 mol%), KOBu^t (6.0 mmol), H₂O-EtOH (1:1 v/v) (9.0 ml), reflux in air.

^bAverage of two runs, measured by GC-MS.

^cIsolated yield, purified by column chromatography.

The recyclability of catalyst system 8 (0.005 mol%) was investigated in the coupling of phenylboronic acid and 2iodofluorene using KOBu^t as base in H₂O-EtOH (1:1 v/v). The product 2-phenyl-9H-fluorene was easily purified using ethyl acetate, petroleum ether and hexane with simple extraction. The H_2O -EtOH (1:1 v/v) polar solvent phase, which contained the catalyst 8, was easily separated. The catalyst was retained in the water layer, which could be reused directly, as presented in Table 4. However, the catalytic activity of 8 started to decline after the fifth run. The best TON was up to 196 000 and TOF up to $3\,920\,000\,h^{-1}$ (Table 4, entry 1). Inductively coupled plasma mass spectrometry analysis of the EtOH (50%) layer indicated that there was no leaching of Pd after the fifth run. The main reason may be associated with the strong donor ability of NHC ligands stabilizing the catalyst.

4 | CONCLUSIONS

In summary, an efficient ligand-exchange procedure has been established for the synthesis of ultra-small, watersoluble, stable chiral sugar-based NHC-protected Pd NPs with sizes ranging from 1.7 to 2.1 nm. The ultra-small size, rigid, sterically demanding sugar group and long aliphatic chain of Pd@NHCs-sugar UNPs catalyst greatly improves the catalytic activity, the best TON and TOF being up to 196 000 and 3 920 000 h^{-1} . In addition, the catalytic activity was not significantly decreased after being reused five times. Using this protocol we intend to synthesize and research novel chiral metal@NHCs-sugar NPs with different transition metals.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

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