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### A palladium complex with functionalized β-cyclodextrin: a promising catalyst featuring recognition abilities for Suzuki–Miyaura coupling reactions in water†

Guofu Zhang, Yuxin Luan, Xingwang Han, Yong Wang, Xin Wen, Chengrong Ding\* and Jianrong Gao

A water-soluble palladium complex (PdL<sub>n</sub>@ $\beta$ -CD) was designed and prepared based on functionalized  $\beta$ -cyclodextrin. It showed high turnover numbers (TONs) and turnover frequencies (TOFs) of up to 9.9 × 10<sup>8</sup> and 4.9 × 10<sup>8</sup> h<sup>-1</sup>, respectively, in aqueous Suzuki-Miyaura coupling reactions. The detailed reason for the excellent catalytic activity was studied.

The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has attracted tremendous attention in the construction of biaryl compounds due to its benefits of functional group compatibility, mild reaction conditions, and excellent yields of products.<sup>1</sup> However, drawbacks like the high cost of palladium catalysts and toxic noble metal residuals greatly hamper its large-scale practical applications, especially in the pharmaceutical industry.<sup>2</sup> To try to overcome these issues, considerable efforts have been made on the exploration of catalytic Suzuki-Miyaura coupling reactions with a low catalyst loading.<sup>3</sup> For instance, Bedford and Welch<sup>4</sup> reported that coupling reactions between aryl bromides and phenylboronic acid were catalyzed by phosphinite-based palladacycles in toluene at 130 °C, with a turnover number (TON) of up to  $9.1 \times 10^8$ . Sémeril and co-workers<sup>5</sup> synthesized several calix[4]arenebased monophosphanes and combined them with  $10^{-4}$  mol% palladium acetate for Suzuki-Miyaura reactions in dioxane/ decane at 100 °C, which provided coupling products in 3.2%-32.1% yields and exhibited a turnover frequency (TOF) of up to  $3.2 \times 10^5$  h<sup>-1</sup>. Although great progress has been made, these aforementioned catalytic procedures usually occurred in organic solvents, which from an environmental and economic perspective, were undesirable media and might induce toxicity and waste treatment issues.

Recently, interest in the exploration of catalytic reactions in neat water is increasing dramatically due to advantages such as reaction rate acceleration, work-up procedure simplification, etc. offered by this green and commercially available solvent.<sup>6</sup> Hence during the past years, many efforts have been made to design novel ligands/catalysts to promote aqueous organic transformations. A great array of endeavours mainly focus on the conjunction of efficient homogeneous ligands/catalysts with water-soluble polymers (polyethylene glycol) or salts (sulfonate salt or quaternary ammonium salt).7 In particular, cyclodextrin (CD) has also drawn much attention due to its water-solubility and special hydrophobic cavity. Indeed, CDs and their derivatives have shown excellent performances in aqueous organic reactions including oxidation, reduction, hydrolysis, hydroformylation, and so on.<sup>8</sup> However, the application of hydrophilic CD derivatives as ligands in organometallic catalysis has not been fully explored, especially for aqueous coupling reactions.9

In this context, we wish to report a triazolyl  $\beta$ -cyclodextrin supported palladium complex (PdL<sub>n</sub>@ $\beta$ -CD) and its application for Suzuki–Miyaura coupling reactions in neat water.

The detailed preparation route for  $PdL_n@\beta$ -CD is shown in Scheme 1. First, commercially available  $\beta$ -cyclodextrin was treated successively with TsCl and NaN<sub>3</sub> to afford 6-monodeoxy-6-monoazido- $\beta$ -CD, which was further reacted with



College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China.

E-mail: dingcr2004@yahoo.com.cn; Fax: (+86)-571-8832-0147;

Tel: (+86)-571-8832-0147

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2-ethynylpyridine *via* a click reaction<sup>10</sup> in DMSO-H<sub>2</sub>O at room temperature to give functionalized  $L_n$ @ $\beta$ -CD. Then the obtained ligand was stirred with Pd(OAc)<sub>2</sub> in anhydrous toluene for 12 h, and the desired complex PdL<sub>n</sub>@ $\beta$ -CD was obtained as light yellow powder. Notably, the catalyst has shown excellent solubility in the aqueous phase. The palladium content in PdL<sub>n</sub>@ $\beta$ -CD, measured using inductively coupled plasma atomic emission spectrometry (ICP-MS), was 0.1550 mmol g<sup>-1</sup>.

To gain insight into the coordinative conformation of palladium in the PdL<sub>n</sub> $(a)\beta$ -CD complex, <sup>1</sup>H NMR spectra were obtained and the results are displayed in Fig. 1. It was gratifying to find that all the proton signals on both the triazole- and pyridine-rings of  $PdL_n$   $\[Begin{subarray}{c} \beta \] CD$  shifted over a certain scale when compared with its uncoordinated ligand  $L_n$   $\beta$ -CD (Fig. 1a and b). In addition, the above proton signal differentiation was further confirmed by comparison of the corresponding ligand (1-methyl-4-(2'-pyridyl)-1,2,3-triazole, Fig. 1c) and palladium complex (PdL'<sub>n</sub>, Fig. 1d). Hence the <sup>1</sup>H NMR data indicates that the palladium was coordinated with the nitrogen atoms in the triazole- and pyridine-rings. Then a two-dimensional ROESY NMR experiment was conducted, with the aim of examining the potential spatial proximities among the different protons of PdL<sub>n</sub> $(\mathfrak{B}\beta$ -CD (Fig. 2). From the spectrum, it turned out that no contacts were observed among the aromatic protons of triazole-pyridine and the cyclodextrin protons, implying that the functional group was not embraced in the hydrophobic cavity of the  $\beta$ -CD-fragment.

With water soluble  $PdL_n(\mathfrak{A}\beta)$ -CD in hand, we next evaluated its catalytic activity in Suzuki–Miyaura coupling reactions. Initially, *p*-bromobenzaldehyde and phenylboronic acid were selected as the model substrates to probe the optimal reaction conditions, and the results are shown in Table 1. A 41% yield of the desired product was obtained when the reaction was carried out with  $10^{-2}$  mol% PdL<sub>n</sub>(\mathfrak{A}\beta)-CD in water at 50 °C for



**Fig. 1** Partial <sup>1</sup>H NMR spectra (500 MHz, DMSO-d<sub>6</sub>, 298 K) of (a) the ligand  $L_n@\beta$ -CD, (b) the palladium complex PdL<sub>n</sub>@\beta-CD, (c) the ligand L'<sub>n</sub> and (d) the palladium complex PdL'<sub>n</sub>.



Fig. 2 2D ROESY NMR spectrum of saturated PdL<sub>n</sub>@β-CD in D<sub>2</sub>O (25 °C)

Table 1 Optimization of the reaction conditions<sup>a</sup>

	Br + B(OH) <sub>2</sub>		
Entry	$PdL_n$ @ $\beta$ -CD (mol%)	Base	$\operatorname{Yield}^{b}(\%)$
1 <sup><i>c</i></sup>	$10^{-2}$	Na <sub>2</sub> CO <sub>3</sub>	41
$2^d$	$10^{-2}$	$Na_2CO_3$	98
3	10 <sup>-7</sup>	Na <sub>2</sub> CO <sub>3</sub>	98
4	$10^{-7}$	$K_2CO_3$	95
5	$10^{-7}$	$K_3PO_4$	96
6	$10^{-7}$	$NaHCO_3$	90

<sup>*a*</sup> All the reactions were carried out under reflux in the presence of *p*-bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.5 mmol), PdL<sub>n</sub>@ $\beta$ -CD, base (1.5 mmol), and H<sub>2</sub>O (2.0 mL), for 4 h, unless otherwise stated. <sup>*b*</sup> Isolated yields based on the amount of *p*-bromobenzaldehyde used. <sup>*c*</sup> The reaction was performed at 50 °C. <sup>*d*</sup> The reaction was carried out for 1 h.

4 h (entry 1). We were pleased to obtain 4-formylbiphenyl with 98% yield when the reaction was conducted under reflux for only 1 h (entry 2). Notably, the amount of palladium catalyst in the reaction can be further reduced to  $10^{-7}$  mol% while maintaining 98% yield of the reaction outcome (entry 3). Later on, different bases were also screened and Na<sub>2</sub>CO<sub>3</sub> turned out to be the optimal base when compared with other bases like K<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub> and NaHCO<sub>3</sub> (entries 3–6). Thus, we gained the optimal conditions: 1.0 mmol aryl halide, 1.5 mmol phenylboronic acid,  $10^{-7}$  mol% catalyst PdL<sub>n</sub>@ $\beta$ -CD, 1.5 mmol Na<sub>2</sub>CO<sub>3</sub>, 2.0 mL H<sub>2</sub>O under reflux.

Having determined the optimal conditions, we proceeded to investigate the substrate scope of the catalytic system. Representative results are summarized in Table 2. Generally, different aryl halides underwent coupling reactions with

phenylboronic acid to give the corresponding biaryl products in good to excellent yields (entries 1-8, 9c, 10b, 11b, 12, 13, 14b). Remarkably, the catalyst  $PdL_n$   $\beta$ -CD has shown extremely high catalytic efficiency during the coupling transformation, whose TONs and TOFs could reach up to  $9.9 \times 10^8$  and  $4.9 \times 10^8 \text{ h}^{-1}$ , respectively. It was also worth noting that the hydrophilic/hydrophobic property of the substituents on aromatic ring had a profound influence on the products' yields. Specifically, for substrates with hydrophilic functional groups, such as formoxyl, acetyl, hydroxyl, hydroxymethyl, carboxyl etc., biaryl compounds were obtained in 93-99% yields under standard conditions (entries 1-8). For the coupling reactions of some other substrates, like m-bromonitrobenzene, p-chlorobromobenzene and p-bromotoluene, the catalytic activity of PdL<sub>n</sub>@ $\beta$ -CD at  $10^{-7}$  mol% loading was not satisfactory (entries 9a, 10a, 11a), which might be caused by the poor water-solubility of tested substrates and limited β-CD cavities in the system. Fortunately, when we increased the amount of  $PdL_n$   $\beta$ -CD, the coupling reactions of these substrates were greatly improved, yielding the desired products in good yields (Table 2, entries 9b, 9c, 10b, 11b, 12, 13). As demonstrated by entry 14, this catalytic method was also suitable for sterically hindered materials such as 2-iodoanisole.

Gratifyingly, substituted arylboronic acids also proved to be good coupling partners in this system, providing the desired biaryl products with good to excellent yields in neat water (entries 15–20). Functional groups including methoxyl, methyl and chlorine were all well tolerated.

Prompted by the aforementioned interesting observations like the high catalytic efficiency and the catalytic activity differentiation among different substrates, we set out to further clarify the advantage of  $PdL_n$   $\beta$ -CD, especially the role of the β-CD-fragment, in promoting aqueous Suzuki-Miyaura reactions. Control experiments were carried out with  $Pd(OAc)_2$ or  $PdL'_n$  as the catalyst and the results are shown in Table 3. From the table, it was obvious that when the coupling reactions of hydrophilic aryl halides like p-bromobenzaldehyde were catalyzed by  $Pd(OAc)_2$  or  $PdL'_n$  instead of  $PdL_n@\beta-CD$ , the yields of the coupling products decreased dramatically even with a prolonged reaction time (entries 1-3). Interestingly, although substrates bearing hydrophobic functional groups performed poorly (less than 20% yields) with  $10^{-7}$  mol% PdL<sub>n</sub> $(@\beta-CD)$ , their coupling reactions catalyzed by Pd(OAc)<sub>2</sub> or  $PdL'_n$  barely proceeded in the aqueous phase, and no coupling products were detected during the reactions (entries 4-6). We believe that the differences in catalytic efficiency among unsupported palladiums and  $PdL_n$   $\beta$ -CD may be partially ascribed to the employment of  $\beta$ -CD into the catalytic system, which was regarded as an excellent phase-transfer-catalyst to accelerate aqueous organic transformation.

Table 2 Suzuki–Miyaura coupling reactions between aryl halides and arylboronic acid using PdL <sub>n</sub> @β-CD <sup>a</sup>									
		   	$R^2$	$\sim B(OH)_{2}$ $\frac{PdL_{n}@}{}$	β -CD (n mol%), Na <sub>2</sub> C		$=$ $\mathbb{R}^2$		
	R <sup>1</sup>			5(011)2	H <sub>2</sub> O, reflux, Time	R <sup>1</sup>	R <sup>1</sup>		
Entry	$R^1$	Х	$R^2$	n	Time (h)	$\operatorname{Yield}^{b}(\%)$	TON	TOF $(h^{-1})$	
1	Н	Ι	Н	$1 \times 10^{-7}$	2	99	$9.9 \times 10^{8}$	$4.9  imes 10^8$	
2	COCH <sub>3</sub>	Ι	Н	$1 \times 10^{-7}$	4	95	$9.5  imes 10^8$	$2.3  imes 10^8$	
3	OH	Ι	Н	$1 \times 10^{-7}$	3	94	$9.4  imes 10^8$	$3.1  imes 10^8$	
4	Н	Br	Н	$1 \times 10^{-7}$	2	98	$9.8  imes 10^8$	$4.9 \times 10^{8}$	
5	CHO	Br	Н	$1 \times 10^{-7}$	4	98	$9.8  imes 10^8$	$2.4  imes 10^8$	
6	$COCH_3$	Br	Н	$1 \times 10^{-7}$	6	94	$9.4  imes 10^8$	$1.5 imes 10^8$	
7	COOH	Br	Н	$1 \times 10^{-7}$	8	93	$9.3 \times 10^{8}$	$1.1 imes 10^8$	
8	$CH_2OH$	Br	Н	$1 \times 10^{-7}$	6	94	$9.4  imes 10^8$	$1.5  imes 10^8$	
9a	3-NO <sub>2</sub>	Br	Н	$1 \times 10^{-7}$	12	18	$1.8  imes 10^8$	$1.5  imes 10^7$	
9b	3-NO <sub>2</sub>	Br	Н	$1 \times 10^{-5}$	12	54	$5.4  imes 10^6$	$4.5  imes 10^5$	
9c	$3-NO_2$	Br	Н	$1 \times 10^{-3}$	12	90	$9.0  imes 10^4$	$7.5 \times 10^{3}$	
$10a^c$	Cl	Br	Н	$1 \times 10^{-7}$	12	19	$1.9  imes 10^8$	$1.5  imes 10^7$	
$10b^c$	Cl	Br	Н	$1 \times 10^{-3}$	12	96	$9.6  imes 10^4$	$8.0  imes 10^3$	
11a	$CH_3$	Br	Н	$1 \times 10^{-7}$	12	8	$8.0  imes 10^7$	$6.6 \times 10^{6}$	
11b	$CH_3$	Br	Н	$1 \times 10^{-3}$	24	85	$8.5 imes10^4$	$3.5 \times 10^{3}$	
12	$3-NO_2$	Ι	Н	$1 \times 10^{-3}$	15	92	$9.2  imes 10^4$	$6.1 \times 10^{3}$	
13	3-OCH <sub>3</sub>	Br	Н	$1 \times 10^{-3}$	20	93	$9.3  imes 10^4$	$4.6 \times 10^{3}$	
14a	$2-OCH_3$	Ι	Н	$1 \times 10^{-5}$	20	45	$4.5  imes 10^6$	$2.2  imes 10^5$	
14b	$2-OCH_3$	Ι	Н	$1 \times 10^{-3}$	15	94	$9.4  imes 10^4$	$6.2 \times 10^{3}$	
15	Н	Ι	$OCH_3$	$1 \times 10^{-5}$	10	95	$9.5 \times 10^{6}$	$9.5 \times 10^{5}$	
16a	$COCH_3$	Br	$OCH_3$	$1 \times 10^{-5}$	15	35	$3.5  imes 10^6$	$2.3 \times 10^{5}$	
16b	$COCH_3$	Br	$OCH_3$	$1 \times 10^{-3}$	12	94	$9.4  imes 10^4$	$7.8 \times 10^{3}$	
17	F	Ι	$OCH_3$	$1 \times 10^{-3}$	6	93	$9.3  imes 10^4$	$1.5  imes 10^4$	
18	$COCH_3$	Ι	$OCH_3$	$1 \times 10^{-3}$	10	90	$9.0  imes 10^4$	$9.0 \times 10^{3}$	
19	$3-NO_2$	Ι	$CH_3$	$1 \times 10^{-3}$	24	93	$9.3  imes 10^4$	$3.8 \times 10^{3}$	
20	$COCH_3$	Br	Cl	$1 \times 10^{-3}$	24	82	$8.2  imes 10^4$	$3.4  imes 10^3$	

<sup>*a*</sup> The reactions were carried out in refluxing water (2.0 mL) in the presence of aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), catalyst PdL<sub>n</sub>@ $\beta$ -CD (1 × 10<sup>-7</sup>-1 × 10<sup>-3</sup> mol%), and Na<sub>2</sub>CO<sub>3</sub> (1.5 mmol), unless otherwise stated. <sup>*b*</sup> Isolated yields based on the amount of aryl halide used. <sup>*c*</sup> Only 4-chlorobiphenyl was obtained.

Table 3 The effect of the palladium complex on Suzuki–Miyaura coupling reactions<sup>a</sup>

		R	$R \longrightarrow X + A \longrightarrow B(OH)_2 \longrightarrow B(OH)_2 + R \longrightarrow B(OH)_$							
			$Pd(OAc)_2$		PdL' <sub>n</sub>		PdL <sub>n</sub> @β-CD			
Entry	R	Х	Time (h)	$\operatorname{Yield}^{b}(\%)$	Time (h)	$\operatorname{Yield}^{b}(\%)$	Time (h)	Yield <sup>b</sup> (%)		
1	OH	Ι	12	28	12	10	3	94		
2	CHO	Br	12	12	12	10	4	98		
3	$CH_2OH$	Br	12	30	12	40	6	94		
4	3-NO <sub>2</sub>	Br	12	NR	12	NR	12	18		
5 <sup>c</sup>	Cl	Br	12	NR	12	NR	12	19		
6	$CH_3$	Br	12	NR	12	NR	12	8		

<sup>&</sup>lt;sup>*a*</sup> The reactions were carried out in refluxing water (2.0 mL) in the presence of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (1 ×  $10^{-7}$  mol%), and Na<sub>2</sub>CO<sub>3</sub> (1.5 mmol), unless otherwise stated. <sup>*b*</sup> Isolated yields based on the amount of aryl halide used. <sup>*c*</sup> Only 4-chlorobiphenyl was obtained.

 $OH_6$ Hacetvl H<sub>Ar</sub> H<sub>2-6</sub> Hformy H. ppm 1 2 ô' 11 4 5 6 Br 0= H<sub>Ar</sub> H<sub>formyl</sub> 10 H<sub>formyl</sub> 11 10 3

Fig. 3 2D ROESY NMR spectrum of a mixture of *p*-bromobenzaldehyde and  $PdL_n@\beta$ -CD in  $D_2O$  (25 °C).

To further demonstrate the role of the  $\beta$ -CD-fragment in the reaction, the inclusion capacity of PdL<sub>n</sub>@ $\beta$ -CD was evaluated. A 2D ROESY NMR measurement of the PdL<sub>n</sub>@ $\beta$ -CD and *p*-bromobenzaldehyde mixture was performed (Fig. 3). Interestingly, the spectrum shows new correlation peaks between the aromatic protons of *p*-bromobenzaldehyde and internal  $\beta$ -CD protons, which implies that the catalyst PdL<sub>n</sub>@ $\beta$ -CD is able to recognise the substrate and insert it into the cavity of  $\beta$ -CD.<sup>11</sup> Thus, the role of the  $\beta$ -CD-fragment of PdL<sub>n</sub>@ $\beta$ -CD was clear: it enhances the water-solubility of the catalyst as well as accommodates the substrate through a recognition process.

In conclusion, we have successfully designed and prepared a novel water-soluble palladium catalyst based on click-triazolefunctionalized  $\beta$ -CD. The catalyst exhibited extremely high TONs and TOFs for Suzuki–Miyaura coupling reactions in neat water. Meanwhile the catalytic activity of the newly developed system was sensitive to the hydrophilicity of the examined substrates. Further study verified that the recognition ability of the catalyst partially contributed to the significant enhancement in the conversions of the tested substrates. This newly developed system represents an efficient and environmentally benign coupling protocol, and could provide a valuable approach for the design of water-soluble catalysts to mediate aqueous organic reactions.

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