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#### PAPER

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#### Introduction

For the past few years, chemists have been facing many challenges in their metamorphosis to become green chemists. Today, the development of environmentally friendly processes to convert molecules into products of interest, using clean transformations and technologies in accordance with the 12 principles of green chemistry, is a major goal. Great effort was made to replace traditional organic solvents, often incriminated due to pollution problems, by environmentally benign reaction media.<sup>1–5</sup> Neat water remains a less harmful solvent for the synthesis of many target molecules.<sup>4,6</sup> With the expansion in finding new routes for reactions in water combined with the emergence of metal catalyzed reactions, there is an urge to develop mass transfer strategies<sup>7</sup> and water soluble ligands.<sup>8</sup>

In this context, 2010 Nobel Prize awarded palladium cross coupling reactions,<sup>9,10</sup> powerful tools for C–C bond formation widely used in both industry and academia,<sup>11–16</sup> are an important target for catalysis in water. Commonly, when performed in water, these reactions require the use of amphiphile phosphine ligands.<sup>9,10,14,17</sup> These ligands suffer from poor stability upon storage, require handling under nitrogen and generate hazardous byproducts. Furthermore, the lack of commercial sources for the generation of new phosphine ligands, as well as their extensive and often expensive synthetic routes, makes them not so suitable targets for green chemistry.<sup>11</sup>

In this context, water soluble N-heterocyclic carbene (NHC) ligands emerged as potential candidates for palladium cross coupling reactions in water.<sup>18,19</sup> These ligands feature good

stability toward oxygen and moisture. Their strong  $\sigma$ -donor character and robust bonds to metals make NHC metal complexes excellent catalysts for a wide range of organometallic reactions. Although several examples of NHC water soluble complexes have been reported in the literature, transformation of hydrophobic substrates into desired products without the use of toxic co-solvents and exhaustive procedures remains a challenge.<sup>20–27</sup>

Among various approaches developed to counter the poor substrate solubility, mass transfer strategies employing hydrophilic carriers such as cyclodextrins (CDs) have shown promising potential in aqueous catalysis.<sup>28–33</sup> CDs are cyclic oligosaccharides composed of 6 to 8 units of  $\alpha$ -1,4 linked p-glucopyranose in a rigid truncate conic structure, displaying a hydrophilic external rim and a hydrophobic cavity. The disparity between both rims leads to solubilization of hydrophobic molecules in aqueous media *via* reversible complexation in the hydrophobic cavity of the CD. Although the use of CDs as a mass transfer strategy was previously described in catalysis by improving the catalytic activity of the coupling reaction in water, recycling was not possible under the reaction conditions.<sup>7,34</sup>

Our strategy was the construction of a single amphiphile bimodal ligand by the combination of a mass transfer unit, covalently bound to a ligand moiety for aqueous catalysis.<sup>25,31,35</sup> A major advantage of combining both cyclodextrins and imidazolium salts, precursors of the NHC ligand, is the versatility of the hybrid properties of the resulting system, combining those of hydrophilic carriers and NHCs. To the best of our knowledge, Monflier *et al.*<sup>35</sup> were the first to report the synthesis of an NHC-appended methylated CD as a catalyst in dioxane. Nonetheless, a major drawback of their system was the inefficient catalysis in neat water and the absence of recycling possibility, due to palladium degradation.

# Imidazolium-functionalized $\beta$ -cyclodextrin as a highly recyclable multifunctional ligand in water $\dagger$

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We describe here the synthesis and the catalytic properties of a novel dodecyl-imidazolium modified  $\beta$ -cyclodextrin as a self-assembled catalytic system (Fig. 1) in neat water for an effective Suzuki–Miyaura reaction. The introduction of the dodecyl-imidazolium motif on the primary face of the  $\beta$ -cyclodextrin allowed the development of a green highly recyclable catalytic system for reactions in an aqueous environment. We present the application of this system to the Suzuki–Miyaura coupling without the use of a co-solvent or stabilizing phosphine ligands in aqueous media. The catalytic system is highly recyclable, allowing the reuse of the palladium catalyst in subsequent catalytic runs without loss of activity.



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Fig. 1 Schematic representation of the self-assembly of 4 in water.

Herein, we report the synthesis, characterization and catalytic properties of a novel alkyl imidazolium modified  $\beta$ -CD 4. We demonstrate that the introduction of a dodecyl chain on the imidazolium moiety attached to the primary face of a native  $\beta$ -CD allows the formation of a micellar self-assembled catalytic system<sup>36,37</sup> (Fig. 1) in neat water with highly recyclable properties in the Suzuki–Miyaura reaction.

#### **Results and discussion**

The synthetic pathway to obtain the alkyl imidazolium modified  $\beta$ -CD **4** is shown in Scheme **1**. The mono-6-tosyl- $\beta$ -cyclodextrin **2** can be easily obtained *via* tosylation of the commercially available  $\beta$ -CD with the tosyl precursor **1**.<sup>38</sup> Subsequent reaction of **2** with 1-dodecyl-imidazole **3** followed by



Scheme 1 Synthesis of 4.

anion-exchange on Amberlite Cl<sup>-</sup> resin afforded the desired amphiphile imidazolium-functionalized  $\beta$ -CD **4** as a pale yellow solid, stable towards oxygen and moisture. The synthesis of this NHC-precursor was achieved in a 4 step straightforward synthesis with 12% overall yield.

To gain insights into the self-assembly properties of 4 in aqueous media, the evolution of its surface tension  $(\prod)$  versus the concentration in water is shown in Fig. 2. At 25 °C, upon increasing the concentration of 4, the curve exhibits a first inflexion point at 100 µM, suggesting the presence of a preaggregation state, followed by micelle formation at 500 µM (critical micellar concentration, CMC). These two states are also present at 75 °C, where micelle formation occurs at 250 µM. As the temperature increases, compound 4 takes more space at the air-water interface due to the fluidity and mobility of the alkyl chain, and the CMC is reached at lower concentrations. The CMC values are low, which indicates that fewer molecules are required to form a micelle and hence allows significant atom economy when micellar catalysis is performed in the presence of this compound. Furthermore, the hydrophobic core of the micelle, along with the mass transfer units ( $\beta$ -CDs), forms several hydrophobic clusters among a single micelle (Fig. 1), enhancing the solubilization of hydrophobic substrates. The formation of micelles is also supported by 2D ROESY NMR experiments where only head to head ( $\beta$ -CD/  $\beta$ -CD) and tail to tail (alkyl chain/alkyl chain) interactions of 4

were observed (see ESI<sup>†</sup>). No self-inclusion or intramolecular inclusion of the hydrophobic alkyl chain into the hydrophobic cavity of the  $\beta$ -CD was observed (see ESI<sup>†</sup>).

Having in hand a self-assembled bimodal ligand precursor, the catalytic activity of 4 was evaluated in the Suzuki-Miyaura cross coupling reaction in neat water. In all the experiments, the catalyst was formed in situ. Initial studies were carried out in water using phenyl boronic acid (1.2 equiv.) and 4-bromoacetophenone (1 equiv.) as model substrates in the presence of 1 mol% (1 mM) of 4 and 0.5 mol% of Pd(OAc)<sub>2</sub> with 2 equiv. of different bases at 100 °C. A 4: Pd 2:1 ratio was chosen as the starting point in order to obtain a better stabilization of the catalytic species, as previously proposed.<sup>35</sup> As shown in Table 1, the presence of the base is required for the reaction to occur (entry 1). All tested bases gave the desired coupling product in high yields (entries 2-8). The next step consisted of examining different Pd derivatives. Both Pd(II) and Pd(II)sources presented in Table 2 promoted the formation of the desired biaryl products in good yields. Nonetheless, only  $Pd(OAc)_2$  in the presence of  $Cs_2CO_3$  inhibits the degradation and precipitation of the palladium species in the form of black Pd. Even if good results in terms of conversion were observed in the presence of less toxic K<sub>2</sub>CO<sub>3</sub>, palladium precipitation was observed at the end of the reaction. Considering the recycling perspectives, Cs<sub>2</sub>CO<sub>3</sub> and Pd(OAc)<sub>2</sub> were used for subsequent optimizations. Afterwards, catalyst loading was investigated (Table 3). In the absence of 4, no reaction was



Fig. 2 Surface tension variation of 4 in water at (a) 25 °C and (b) 75 °C.



Br	+ B(OH)2 + -B(OH)2 + -B(OH	l %) bquiv.) .5 mol %) ≿, 30 min
Entry	Base	Isolated yield (%)
1	_	7
2	$Cs_2CO_3$	95
3	CsF	93
4	$K_2CO_3$	87
5	NaOH	83
6	KOH	85
7	$K_3PO_4$	93
8	Et <sub>3</sub> N	84

Table 2 Optimisation of the nature of the Pd source

4 (1 mol %) Cs <sub>2</sub> CO <sub>3</sub> (2 equiv.) Pd (0.5 mol %)	
H <sub>2</sub> O, 100 °C, 30 min	

Entry	Pd	Isolated yield (%)	
1	$Pd(OAc)_2$	95	
2	PdCl <sub>2</sub>	90	
3	$Pd(ACN)_2Cl_2$	92	
4	$Pd_2(dba)_3$	84	

	0 + -B(OH)2 -	4 (a mol %) Cs <sub>2</sub> CO <sub>3</sub> (2 equiv.) Pd(OAc) <sub>2</sub> (b mol %)	
Br		H <sub>2</sub> O, 100 °C, 30 min	-
Entry	а	b	Isolated yield (%)
1	0	0.5	0
2	1	0.5	95
3	1	0.3	95
4	1	0.1	95
5	0.5	0.5	95
6	0.2	0.1	95
7	0.1	0.05	95

observed (entry 1). In contrast, C-C bond formation leading to the desired product is efficient at a loading as low as 0.05 mol% of Pd(OAc)<sub>2</sub> and 0.1 mol% of 4 (entry 6). In accordance with the surface tension curve (Fig. 2), a loading of 1 mol% of 4 (entries 2 and 3) correlates to the presence of micelles in the reaction media, while a loading of 0.1 to 0.5 mol% of 4 (entries 4-6) corresponds respectively to a transitory state between the monomer, the pre-aggregate and the micelles. The efficient catalysis at low catalyst loading suggests that the monomeric complex formed by 4 and  $Pd(OAc)_2$  is the active catalytic species. However, a slight palladium leak was observed at lower catalyst loadings (entries 5 and 6), indicating that the self-assembly of 4 plays a major role in terms of stability of this catalytic system in water. Again, with recycling goals in mind, 1 mol% of 4 and 0.5 mol% of Pd(OAc)2 (entry 2, 2:1 ratio) were retained for further optimizations.

In order to gain a better understanding of the interactions between 4 and  $Pd(OAc)_2$ , <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy experiments were conducted in deuterium oxide (Fig. 3). The <sup>1</sup>H NMR spectrum shows quantitative disappearance of the H-2 resonance at 8.8 ppm jointly with a slight shielding of the H-4 and H-5 protons (Fig. 3) after addition of  $Pd(OAc)_2$ . The for-

mation of a metal-ligand (M-L) complex is also supported by the <sup>13</sup>C NMR spectrum, where an upfield shift of the C-2 from 134.8 ppm for 4 to 138.2 and 147 ppm for the M-L complex (Fig. 4) can be observed. The existence of two different signals for C-2 of the M-L complex could be related to the presence of two catalytic species in solution: 4-Pd-4 (bis-(imidazol-2ylidene) Pd) at 138.2 ppm and Pd-4 (mono imidazol-2-ylidene Pd) at 147 ppm.<sup>35,39,40</sup> Since the Suzuki–Miyaura cross coupling reactions are performed in a micellar state, the formation of both mono- and bis-imidazol-2-vlidene Pd structures is possible (Fig. 5). Also, the C-4 and C-5 upfield shifts respectively from 123.1 and 125.1 ppm (Fig. 4a) to 126.0 and 128.6 ppm (Fig. 4b) are consistent with the formation of an M-L complex.<sup>35,39,40</sup> Unfortunately, further attempts to confirm the exact structure of the complex were unsuccessful due to the poor stability of the complex under ESI<sup>†</sup> conditions and the difficulty to obtain suitable crystals for X-ray analysis. An experiment conducted with the C-2 methylated dodecyl imidazolium-β-CD 5, which inhibits the formation of an NHC and prevents the formation of an M-L complex, afforded the desired biaryl in comparable yields to those obtained in the presence of 4. However, major palladium degradation in the form of black Pd was observed and efficient recycling was not possible in this case. These results suggest that the hydrophobic clusters (Fig. 1) contribute to the formation of the coupling product via a ligandless catalytic process but are enable to anchor the metal to the micelle in order to allow recycling of the catalyst.<sup>8,34</sup> Highly efficient recycling was observed in the presence of 4 (Table 5, entry 1), suggesting that, along with the cooperative catalytic processes combining the hydrophobic clusters and NHC formation, the Pd adhere to the self-assembled system via the formation of an M-L complex.

With the optimized conditions in hand, the scope of the Suzuki–Miyaura cross coupling reaction with aryl halides and boronic acid derivatives catalyzed by the self-assembled bimodal ligand precursor 4 and  $Pd(OAc)_2$  in water was investi-



Fig. 3 Partial <sup>1</sup>H NMR spectra (25 °C, 700 MHz, D<sub>2</sub>O) of (a) 4 and (b) 2 : 1 ratio of 4 : Pd in the presence of Cs<sub>2</sub>CO<sub>3</sub>



![](_page_4_Figure_4.jpeg)

Fig. 5 Simplified representation of the proposed mono- and bis-4-Pd structures in water.

gated. A first set of aryl halides with the phenylboronic acid was used in order to test the activity and tolerance of the catalytic system to various functional groups. As shown in Table 4, all reactions gave the corresponding hetero coupling products in moderate to high yields despite the nature of the halide or the presence of electron donating groups and electron withdrawing groups as substrates (Table 4, entries 1–8). Moreover, traditionally challenging reactions in neat water involving naphthalene substrates which have increased hydrophobicity and potential steric hindrance were achieved in good yields (Table 4, entries 9–11). To the best of our knowledge, this is the first example reporting a Suzuki–Miyaura cross coupling reaction in neat water with sterically hindered and strong hydrophobic character substrates without the use of degassed water, nor a co-solvent or a  $N_2$  atmosphere.

From the green chemistry point of view, recycling is a major concern, especially in metal catalysis. In contrast to traditional water soluble M–L complexes, recycling of the alkyl imidazolium- $\beta$ -cyclodextrin 4:Pd catalytic species is possible. Herein we developed a simple procedure to recycle the phase containing catalyst (Fig. 6). The recyclability of the catalytic system is directly related to the self-assembled state of 4 (Fig. 2). As shown in Table 5, more than 10 catalytic cycles (entry 1) were performed without significant loss of activity in the micellar state. The number of possible catalytic cycles decreases to 6 (entry 2) when 4 was used at a concentration corresponding to the pre-aggregation state and to 2 (entry 3) when used at a monomeric concentration. The presence of the same size of aggregates was confirmed by DLS measurements of the 4: Pd micellar solution before the reaction and in the recycled aqueous solution (see ESI<sup>†</sup>). In fact, the self-assembly, resulting from the combination of the  $\beta$ -CD covalently bound to the dodecyl imidazolium moiety, adds robustness to the catalytic system and enhances its recyclability.

To further investigate the importance of the combination of the mass transfer unit covalently bound to a ligand moiety, the

 Table 4
 Scope of the alkyl imidazolium β-CD (4)-Pd catalysed Suzuki–

 Miyaura cross coupling reactions in neat water

Entry	Reactant	Product	Isolated yield (%)
1	Br	-OMe	83
2	Br - H		91
3	Br		76
4	Br		60
5			79
6	Br-CN	CN CN	87
7 <sup><i>a</i></sup>	Br		75
8			59
9 <sup><i>a</i></sup>	Br		66
10 <sup><i>a</i></sup>	Br		79
11	Br		69

 $^{a}t = 2$  h.

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Table 5 Recyclability of the 4 : Pd catalyst

			$4(a \mod \%)$	
Br			Cs <sub>2</sub> CO <sub>3</sub> (2 equiv.) Pd(OAc) <sub>2</sub> (b mo l%)	
		H <sub>2</sub> O, 100 °C, 30 min		
Entry	а	b	Isolated yields (%)	No. of cycles
1	1	0.5	95-80	10
2	0.2	0.1	90-77	6
3	0.1	0.05	95–79	2

catalytic activity in neat water of the self-assembled ligand precursor 6 in the presence and absence of free native  $\beta$ -CD was investigated in the Suzuki-Miyaura cross coupling reaction (Table 6). As expected, the presence of 6 at a concentration above its CMC, with or without the unbound  $\beta$ -CD, allowed the solubilisation of the substrates and the Pd species, as well as the formation of the desired coupling products with comparable yields to the 4:Pd catalytic system. However, in this system, a poor recyclability was observed (entries 1 and 4). Yet, adding free  $\beta$ -CD does not improve the catalytic activity of this system and completely inhibits the recycling of the catalyst (entries 2 and 5). These results are consistent with similar micellar systems reported in the literature.<sup>8,30,37</sup> Therefore, the use of β-CD covalently bound to the dodecyl chain imidazolium salt greatly enhances the stability of the catalytic system, allowing both efficient catalysis and recycling in neat water. This result supports the hypothesis of protection of the NHC moiety by the hydrophilic CD close to the metal centre. The presence of the covalent CD may also modify the shape and the space around the metal, resulting in a stable micellar complex.

![](_page_5_Figure_7.jpeg)

**Fig. 6** Recycling procedure of the 4: Pd catalytic solution: (1) *in situ* formation of the catalytic species. (2) Addition of boronic acid and aryl bromide. (3) Stirring for 30 min at 100 °C. (4) Cooling down to 23 °C. (5) Extraction with Et<sub>2</sub>O. (6) Evaporation of the solvent. (7) Reuse of the aqueous phase containing 4: Pd in subsequent catalytic runs.

 Table 6
 Contribution of each component to the recyclability of the catalytic system

![](_page_6_Figure_4.jpeg)

Having shown the higher recyclability of our catalytic process in water, we were interested in positioning our system in the context of already described green processes for the Suzuki-Miyaura coupling. Among already described similar processes, in terms of efficiency, are the ones recently described by Zhang<sup>41</sup> and Liu.<sup>42</sup> Zhang's water-soluble cyclodextrin-palladium complex is similar to ours in terms of synthetic chemistry employed for the synthesis of the catalyst and the use of small amounts of organic solvents and reactants. However, in our case, the recyclability of the system increases the mass intensity, and the synthetic steps can be neglected compared to the benefits of the recycling. In the case of Liu's ligand free protocol, 6 grams of polyethylene glycol (PEG) are required as a co-solvent for the synthesis of 1 mmol of coupling product while using 2 mol% of Pd(OAc)<sub>2</sub> and 2 mmol of K<sub>2</sub>CO<sub>3</sub> (mass intensity of the process was estimated to be  $30.74 \text{ kg kg}^{-1}$ ). Compared to this process, our system is more efficient, as 1.36 kg kg<sup>-1</sup> mass intensity was calculated for the synthesis of 4:Pd and 2.61 kg kg<sup>-1</sup> for the synthesis of 1 mmol of the coupling product.

#### Conclusion

As a contribution towards a greener chemistry, we characterized and studied the catalytic properties of a novel dodecyl imidazolium modified  $\beta$ -CD 4 in neat water as a catalyst for the Suzuki–Miyaura coupling reaction. The introduction of a dodecyl chain on the imidazolium moiety attached to the primary face of a native  $\beta$ -cyclodextrin allows the formation of a highly stable self-assembled catalytic reactor for the Suzuki– Miyaura cross coupling reaction in neat water. High catalytic activity and multiple time recyclability were achieved as a result of the cooperative catalytic processes combining hydrophilic carriers and NHCs. Under the optimal reaction conditions, the self-assembled bimodal system tolerated various electronics and bulky substrates. Hence, the combination of the  $\beta$ -CD with the dodecyl chain imidazolium motif, a mass transfer unit with a self-assembled ligand precursor, cherishes the hybrid properties of green catalysis along with the robustness of a self-assembled system. Future work is devoted to determine the precise structure of the M–L complex and to the study of the versatility of this self-assembled bimodal system toward other important C–C bond forming reactions as novel greener alternatives.

#### General procedure for the Suzuki– Miyaura cross coupling reaction

In a typical experiment,  $Pd(OAc)_2$  (0.005 mmol) and  $Cs_2CO_3$  (2 mmol) were added to a 1 mM solution of 4 (0.01 mmol) in 10 mL of water. The catalytic solution is stirred at 100 °C for 2 h. Phenylboronic acid (1.2 mmol) and arylhalide (1 mmol) were then added to the catalytic solution. The reaction medium was stirred at 100 °C for 30 min. Afterwards, the reaction mixture was cooled to room temperature and the coupling product was extracted with 3 × 5 mL of Et<sub>2</sub>O. After drying over MgSO<sub>4</sub>, the solvent was evaporated *in vacuo* and the desired product was purified by flash column chromatography on silica gel to obtain the pure product.

## General procedure for the recycling process

After performing a typical Suzuki–Miyaura cross coupling reaction (Fig. 6, 1–6) as described in the previous section,  $Cs_2CO_3$ (1 mmol), boronic acid (1.2 mmol) and aryl halide (1 mmol) were added to the remaining aqueous phase (Fig. 6, 7). The reaction medium was then stirred for 30 min at 100 °C (Fig. 6, 2–3). After cooling to room temperature, the coupling product was extracted with 3 × 5 mL of Et<sub>2</sub>O (Fig. 6, 4–5). The organic phase was then dried over MgSO<sub>4</sub>, the solvent was evaporated *in vacuo* and the desired product was purified by flash column chromatography on silica gel to obtain the pure product (Fig. 6, 6). The aqueous phase is once again available for subsequent cycles (Fig. 6, 7).

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