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Dual functionalized task specific ionic liquid promoted in situ generation of palladium nanoparticles in water: Synergic catalytic system for Suzuki–Miyaura cross coupling

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Here in we report, a synthesis of a novel, dual functionalized task specific ionic liquid possessing cation with hydroxyl functionality which induces reaction in water and acts as a reducing agent as well as an anion with prolinate functionality serves as ligand and stabilizes and/or activates the in situ formed palladium nanoparticles (Pd-Nps) thus act as palladium (0) reservoirs. The generated palladium nanoparticles were characterized by UV–visible spectroscopy, High resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) and Energy-dispersive X-ray spectroscopy (EDX) analysis. These in situ synthesized palladium nanoparticles with particle size between 3-9 nm exhibited a high catalytic activity in the Suzuki cross-coupling of aryl halide with aryl boronic acid without using external phosphine ligand. Less activated aryl chlorides also coupled smoothly with aryl boronic acid. It is noteworthy that, isolation of the products were performed by the simple extraction in diethyl ether, and the aqueous system containing ionic liquid along with Pd-NPs was recycled for seven times, without significant loss of catalytic activity.

Introduction

In recent years, the palladium-catalyzed Suzuki-Miyaura cross-coupling has been one of the most studied catalytic reaction due to its aids of functional group compatibility.[1]In 1981, biaryls were synthesized by the Suzuki-Miyaura cross-coupling of aryl boranes with haloarenes.[2] After this discovery, traditionally phosphine ligands along with inert atmosphere and organic solvents were employed for this coupling to avoid the side products formed due to use of phosphine ligands. Pd(0) or Pd(II) derivatives associated with appropriate ligands in conventional organic or biphasic media is basic need of this coupling. In this context, significant innovations have been made through modifications of traditional phosphine ligands and the discoveries of novel phosphine systems,[3] but most of the phosphine ligands are sensitive to air and moisture, also their synthesis is laborious. These problems were overcome by exploring non-phosphine alternatives for the Suzuki-Miyauracoupling. A number of phosphine-free ligands have been developed such as palladacycles,[4] N-heterocyclic carbenes,[5] imines,[6] diazabutadienes,[7] amines,[8] pyrazoles,[9] triazoles[10] and bipyridine-based systems.[11] Although, complexes containing such ligands often show excellent activity, in the majority of cases, the principal drawback is the availability, stability, and cost of the palladium complexes as well as related ligands and in most cases reactions were performed in organic solvents.

Transition metal nanoparticles (NPs) have attracted attention and became a best choice over other alternatives in coupling chemistry due to their unique physicochemical properties.[12-19] Due to high surface-to-volume ratio of NPs it provides larger number of active sites per unit area and shows excellent catalytic activity in the cross-coupling. As they are thermodynamically unstable, stabilizers should be chosen to prevent their aggregation. Various non-phosphine stabilizers of palladium NPs, such as surfactants,[13] polymers,[14] dendrimers,[15] PEG[16] have been reported. In contrast to the heterogeneous supported metal NPs that are restricted by support surfaces, soluble metal NPs have much superiority, such as controllable size, more rotational degree of freedom and more active sites accessible to reactants. Moreover, the optimum balance between activity and stability of palladium NPs can be easily tuned through the careful choice and modification of ligands, which enhances the scope of NPs for different catalytic applications.[20]

Recently, innovations in ILhave been explored as ILs are coupled with nanotechnology to produce nano-materials with improved catalytic, optical, electrical, magnetic, biological, or biomedical properties.[21] Ionic liquids (ILs) have paved the way for alternative and new synthetic strategies, because this methodology allows not only high reaction activity but also the possibility of recycling the catalyst.[22] Regrettably, these processes suffer from some limitations *viz.* the need for the use of toxic, expensive and air-sensitive phosphine[23] and use sophisticated methodology, such as ultrasound or microwave.[24]

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These limits are of significant concern in large-scale organic syntheses. Moreover, this reaction system requires a large amount of expensive ionic liquid. It would be desirable to reduce the amount of ionic liquid phase from an economic and toxicological viewpoint.[25] As a result; the search for new readily available ILs addressing these drawbacks remains an impending goal.

Hydroxyl functionalized ILs possess higher solvent polarities, high dielectric constants which remarkably increases the hydrophilicity of these ILs.[26] Anderson group[27] suggest that IL cation appending a hydroxyl moiety greatly increases its H-bond acidity with a small increase in H-bond basicity and no change in dipolarity. The Weingartner group[28] reported that, hydroxyl-containing ILs exhibited higher dielectric constant than non-functionalized ILs. The Welton group[29] suggests that hydroxyl-containing ILs have a higher hydrogen-bond acidity (the value based on The Kamlet–Taft scale) than non-functionalized ILs. Solvatochromic study of Chiappe et al.[30] of variety of hydroxyl-functionalized ILs confirm that the introduction of –OH groups in the cation increases polarity.The Dyson group[31] reported that, hydroxyl-functionalized ILs act as reducing agent and formed highly stable, small PdNPs with a narrow size distribution. Amino acid (AA) is one of the most versatile classes of natural, bio-renewable, and non-toxic raw materials; it is easy to obtain pure AAs in low costas well as further advantages of AAs, including biodegradability[32] and biological activity[33] induce utilization of amino acids (AA) as ionic liquid precursors for designer ionic liquid synthesis. Due to these reasons, amino acid-functionalized ILs were developed as reagents and catalysts to mediate chemical transformations.[34] A variety of prolinate functionalized precursors has been used to form organometallic catalysts or in stabilizes metal catalyst in organic transformation.[35] Hence there should be an optimum combination of cations and anions for an IL with a specific function that in the case of a catalyzed reaction facilitates the solvation of the catalyst, the formation and stabilization of the active catalytic species.

Herein we report the use of easily accessible, cheap and nontoxic, hydroxyl functionalized TSIL as an excellent promoter in palladium catalyzed Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids in water.

Results and discussion

Initial attempts were focused on synthesis of novel dual functionalised task specific ionic liquid incorporated cation with hydroxyl functionality which not only induces reaction in water but also act as reducing agent while anion with prolinate functionality serves as ligand and able to stabilize and/or activate the *in situ* formed palladium nanoparticles thus act as palladium (0) reservoirs. Thus this ionic liquid can facilitate Suzuki-Miyaura coupling in water and provide an efficient, eco-friendly, recyclable system for said coupling. (Fig.1)

In this perspective, we designed 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro] as a dual functionalized task specific ionic liquid (TSIL). Synthetic route for its synthesis is outlined in Scheme 1. Initially, quaternisation of 1-methylpyrrolidine (1) was carried out with chloroethanol (2) in toluene employing reflux conditions for 24 h to form 3. 3 on metathesis reaction with potassium hydroxide in dichloromethane carried out at room temperature for 24 h furnished 4. Finally, desired TSIL 6 was achieved through acid-base reaction of 4 and L-proline 5 in water initially at 0-5 °C and then stirring at room temperature for 12 h.

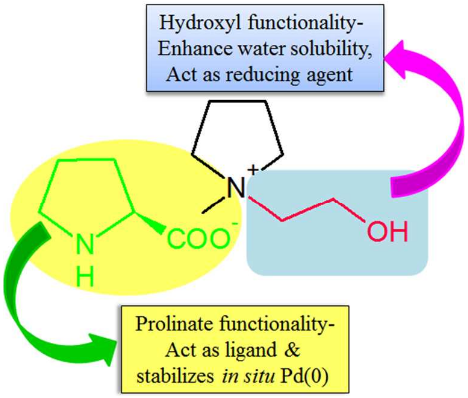
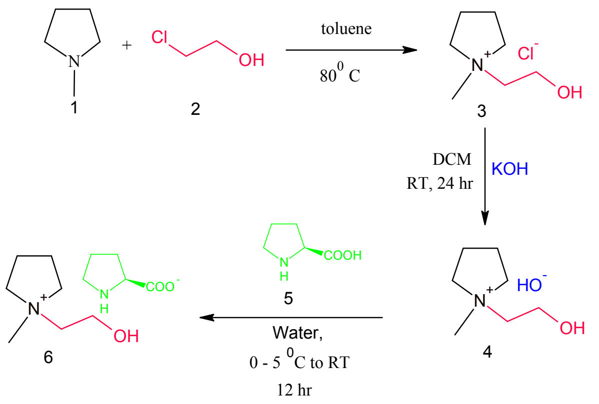


Fig. 1 Dual functionalized task specific ionic liquid (TSIL): 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy] [Pro]



Scheme 1: Synthesis of TSIL 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro]

The confinement of hydroxyl functionality and prolinate functionality in the TSIL [HEMPy][Pro] was confirmed by IR spectroscopy (Fig. 2). The IR spectrum of TSIL [HEMPy][Pro] displayed characteristic vibrational bands at 3361 and 3260 cm^{-1} due N–H and O–H stretching vibrations respectively, while bands at 1670, 1584 and 774 cm^{-1} relevant to the carboxylate functionality of prolinate anion. The thermal stability profile of the TSIL [HEMPy][Pro] was studied using TGA-DSC analysis in the temperature range of 25–400 °C. The TGA-DSC profile is shown in Fig. 3. The initial weight loss of 14.51% may be due to the elimination of water of crystallization or water associated with the ionic liquid through hydrogen bonding. The steep weight loss of 65.29% at temperature range 100-350 °C was mainly attributed to the decomposition of organic groups of TSIL.

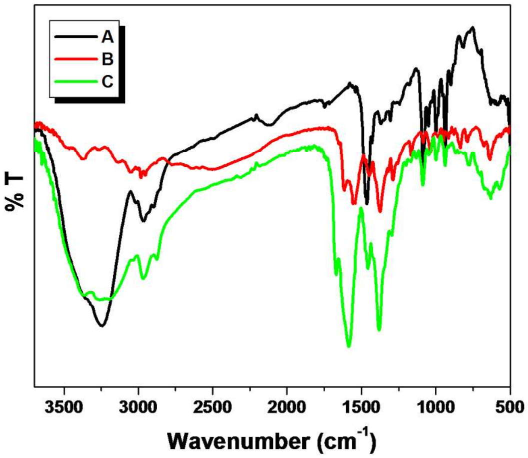


Fig. 2 IR spectra of IL [HEMPy][Cl] (A), L-proline (B) and TSIL [HEMPy][Pro] (C)

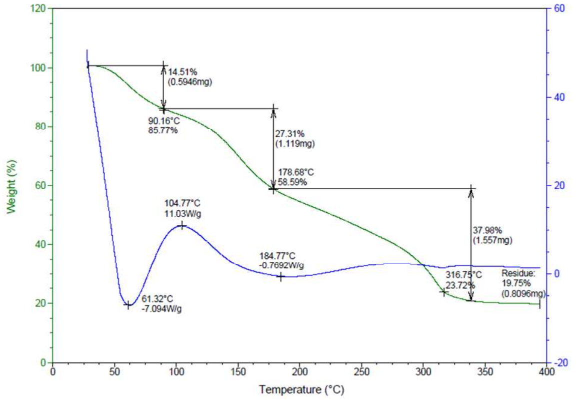
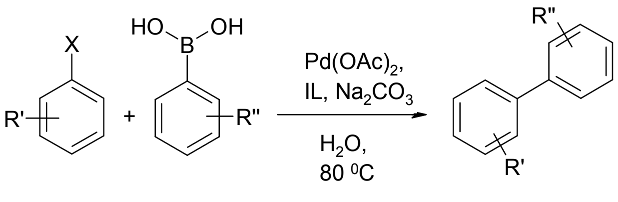


Fig. 3 TGA analysis of the TSIL 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro]

Next, we focused our attention to explore this task specific ionic liquid for Suzuki-Miyaura coupling. (Scheme 2) While optimization of reaction conditions, initially screening of ionic liquids was done for model reaction of bromobenzene (1 mmol) and phenylboronic acid (1.2 mmol), base and palladium acetate in water at 80 °C.



Scheme 2 Suzuki-Miyaura coupling in waterusing dual functionalized task specific ionic liquid

Ionic liquids with hydrophilic, hydrophobic, prolinate functionalized and hydroxyl functionalized were employed (Table 1; entries 1-7). Pleasingly, in ionic liquid *viz.*1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro] desired biaryl was obtained in high yield (98 %) within short time duration (2 h) as compared to other utilized ionic liquids (Table1, entry 7). When l-proline (20 mol%) was employed without ionic liquid under the identical conditions the desired product was obtained with 50% yield (Table 1; entry 8), While without [HEMPy][Pro] ionic liquid only 40% yield of product was obtained (Table 1; entry 9) indicating the influence of ionic liquid on the activity of the coupling reaction. After this success, attempts were then focused on effect of amount of ionic liquid on model reaction, it is found that 20 mol% of [HEMPy][Pro] provided the maximum yield. Exceeding the catalyst quantity than 20 mol% did not affect the yield of product and reaction time. (Table 1; entries 10-13)

Table 1. Screening of ionic liquids for the Suzuki-Miyauracoupling[a]

Entry	IL	Loading (mol %)	Time (h)	Isolated Yield (%)
1	[BMIM][Cl]	20	2	65
2	[BMIM][BF_4]	20	1	76
3	[BMIM][Pro]	20	1	80
4	[HEMPy][Cl]	20	2	80
5	[HEMPy][BF_4]	20	1	84
6	[HEMPy][PF_6]	20	2	84
7	[HEMPy][Pro]	20	1	98
8	l-proline	20	2	50
9	---	--	2	40
10	[HEMPy][Pro]	10	1	84
11	[HEMPy][Pro]	15	1	90
12	[HEMPy][Pro]	25	1	98
13	[HEMPy][Pro]	30	1	98

[a] Reaction conditions: Bromobenezene (1mmol), phenylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), IL (mol%), Na_2CO_3 (1 mmol), Water (5 mL), temp = 80^{0}C.
[BMIM]= 1-Butyl-3-methylimidazolium, [HEMPy]=1-(2-hydroxyethyl)-1-methylpyrrolidinium, [Cl]= Chloride, [BF_4]= Tetrafluoroborate, [PF_6]=Hexafluorophosphate, [Pro]= prolinate.

Then screening of base for Suzuki-Miyaura coupling was carried out employing Na_2CO_3, K_2CO_3, K_3PO_4, NaOH, KOH, NaOAC, and TEA (Table 2). In the course of this study, it was found that Na_2CO_3 is the most effective base in terms of the yield (98 %) as compared with studied organic and inorganic bases (Table 2, entries 1-8). From further study for effect of amount of base on model reaction revealed that 1 mmol of Na_2CO_3 was sufficient.

Table 2. Effect of different bases on the Suzuki-Miyaura coupling [a]

Entry	Base	Base (mmol)	Time (h)	Yield (%)
1	Na_2CO_3	2	1	98
2	K_2CO_3	2	1	98
3	K_3PO_4	2	1	96
4	NaOH	2	1	92
5	KOH	2	1	94
6	NaOAC	2	1	84
7	TEA	2	1	80
8	Na_2CO_3	1	1	98

[a] Reaction conditions: Bromobenezene (1mmol), phenylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), IL (20 mol%), base, Water (5 mL), temp = 80^0 C.

We next investigated suitable palladium source for model reaction by employing Pd/C, $Pd(PPh)_4$, $Pd_2(dba)_3$, $PdCl_2$, and $Pd(OAc)_2$ (Table 3, entries 1-5). We observed that simple palladium inorganic salts *viz*. $Pd(OAc)_2$ and $PdCl_2$were proved to be the best choice as desired biaryl was obtained in 98 % and 86 % yield, respectively while Pd/C, $Pd_2(dba)_3$, $Pd(PPh_3)_4$ were found to be inferior. From further study for effect of amount of $Pd(OAc)_2$ on model reaction revealed that 2 mol% of $Pd(OAc)_2$was enough.

Table 3. Effect of different palladium catalysts on the Suzuki-Miyauracoupling[a]

Entry	Palladium source	Loading (mol %)	Isolated Yield (%)
1	Pd/C	2	32
2	$Pd(PPh)_4$	2	55
3	$Pd_2(dba)_3$	2	50
4	$PdCl_2$	2	86
5	$Pd(OAc)_2$	2	98
6	$Pd(OAc)_2$	1.5	94
7	$Pd(OAc)_2$	1	82
8	$Pd(OAc)_2$	0.5	78
9	$Pd(OAc)_2$	3	98

[a]Reaction conditions: Bromobenezene (1.0 mmol), phenylboronic acid (1.2 mmol), Palladium source (mol%), IL (20 mol%), Na_2CO_3 (1 mmol), Water (5.0 mL), temp = 80 °C

From these experiments for optimization of reaction conditions, we found optimized condition as specific ionic liquid (20 mol%), base Na_2CO_3 (1mmol) and $Pd(OAc)_2$ (2 mol%), water (5 mL). After optimization of reaction conditions, we examined the scope of the substrates to illustrate generality of the method. It was found that aryl iodide, bromide as well as less activated aryl chlorides also get coupled with aryl boronic acid under optimized reaction conditions. A variety of functional groups can be tolerated for aryl halides including methyl, carbonyl, amino, phenyl, formyl and cyano group as well as for aryl boronic acids bearing methoxy, nitro or chloro groups. The results are summarized in Table 4. These results conclude that the electronic characters of aryl halides or aryl boronic acids have no obvious effect on the Suzuki-Miyaura coupling under optimized reaction conditions. It is noticeable that less activated aryl chlorides bearing either electron-donating or electron-withdrawing substituents afford the corresponding products in excellent yields (entries 9-12; Table 4). As one-pot double coupling of aryl 1,4-dihalide is highly valuable for the synthesis of functionalized terphenyls, we proceeded to investigate the double coupling of 1- bromo-4-chlorobenzene with phenyl boronic acid under the optimized reaction conditions. (Entry 12; Table 4) Gratifyingly, terphenyl was obtained in good yield illustrate generality of the method.

After the completion of reaction, we have extracted the reaction mixture by ethyl acetate to separate the synthesized biaryls. Then the aqueous phase have been analysed by recording UV–Vis spectrum in acetone medium and compared the same with that of $Pd(OAc)_2$ and ionic liquid (Fig. 4). The absorption at 405 nm due to $Pd(OAc)_2$ disappeared from the reaction mixture due to the formation of palladium nanoparticles. These obtained Pd-Nps is characterized by high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) and Energy-dispersive X-ray spectroscopy (EDX) analysis as shown in Fig 5. HR-TEM image, Fig 5b, shows Pd-Nps having *d*-spacing 0.651nm. The selected area electron diffraction (SAED) patterns of the Pd-NPs are shown in Fig 5c, exhibiting sharp diffraction rings corresponding to the specific crystalline, confirming the formation of nano-crystalline Pd-NPs. The HRTEMand SAED pattern also indicate that the Pd-NPs are mainly random orientated. A surface-averaged Pd-NPs particle size of 4.4 ± 0.20 nm was derived from the corresponding size histogram Fig 6a. The uneven distribution of the catalytic Pd-NPs particles exhibit in the range of 3nm and 9 nm, which shows in corresponding histogram (Fig 6a). These obtained Pd-Nps with variable size in the range of 3-9 nm are confirmed by High resolution transmission electron microscopy (HR-TEM) analysis Fig. 6b, c. Thus palladium nanoparticles with high catalytic activity are *in situ* synthesized and efficiently stabilized, due to the synergetic effect between hydroxyl groups containing cation and the prolinate anion of task specific ionic liquid.

Table 4. Suzuki-Miyaura coupling between different aryl halides and phenylboronic acid in water using dual functionalized task specific ionic liquid[a]

Entry	R’	X	R”	Time (h)	Yield[b] (%)
1	H	I	4-Meo	1	98
2	H	Br	H	1	98
3	4-CN	Br	H	2	94
4	H	Br	$4\text{-}NO_2$	2	96
5	$4\text{-}NH_2$	Br	4-Cl	1	95
6	4-Me	Br	H	1	94
7	4-Ph	Br	2,4-Cl	2	90
8	4-CHO	Br	H	3	92
9	H	Cl	H	2	90
10	$4\text{-}NH_2$	Cl	H	3	86
11	4-Ac	Cl	H	3	80
12	4-Br	Cl	H	3	80

[a]Reaction conditions: aryl halide (1mmol), phenylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), IL (20 mol%), Na_2CO_3 (1 mmol), Water (5 mL), temp = 80^0 C;[b]Isolated yield .

In order to ascertain reaction really catalyzed by the *in situ* formed Pd-NPs, we performed a mercury poisoning experiment using the coupling reaction of 4-bromotoluene (1 mmol) with phenylboronic acid (1.2 mmol) in the presence 1 mol% of $Pd(OAc)_2$, 20 mol% of ionic liquid, Na_2CO_3 (1mmol), one drop of mercury and 5 mL of water at 80 °C for 2h. No product was detected due to formation of Pd(0) amalgam, which exhibits no catalytic activity.

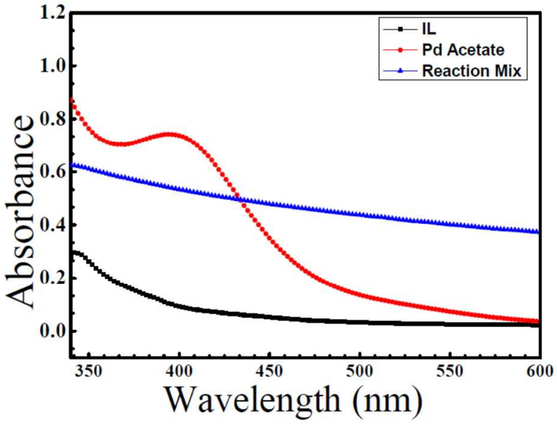


Fig 4: UV-visible spectra of reaction mixture

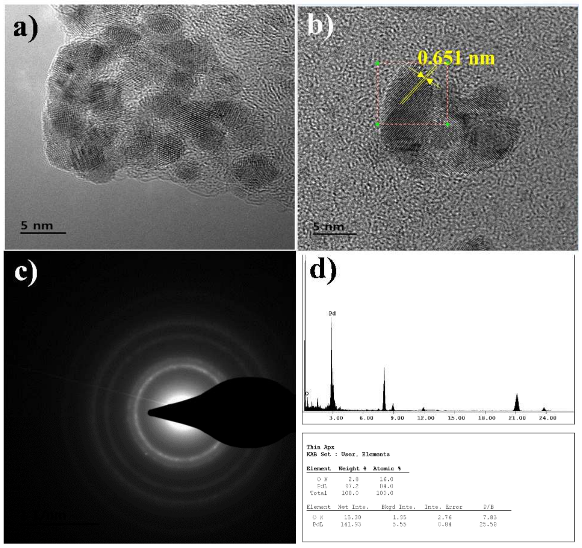


Fig 5:a) TEM images of *in situ* formed and stabilized Pd-NPs, b)HRTEM images of *in situ* formed and stabilized Pd-NPs with d-spacing 0.651 nm, c) SAED confirms that the particles are crystalline, d) EDX shows that the *in situ* formed and stabilized Pd-NPs are metal-free (Pd peaks are from the TEM grid)

Fig. 7a, shows a Fast Fourier transform images for single-Pd-NPs. From the FFT images, the measured lattice spacing of the Pd-NPs 0.672 nm, 0.464 nm, respectively and confirmed that Pd-NPs are crystalline in nature. In the inset of (Fig. 7a), the intensity pattern of the Pd-NPs layer is presented. Fig. 7b, c represents the TEM images of Pd-NPs and Energy-dispersive spectrometer (EDS) scanning transmission electron microscopy (STEM) mapping images of the same Pd-NPs.

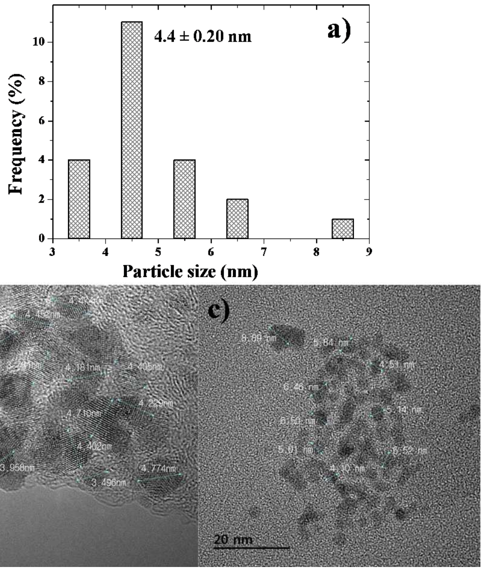


Fig 6: Histogram of the particle diameters as measured from TEM analysis (Fig. 5b,c) of ~22 particles shows that the particles are primarily between 3 to 9 nm

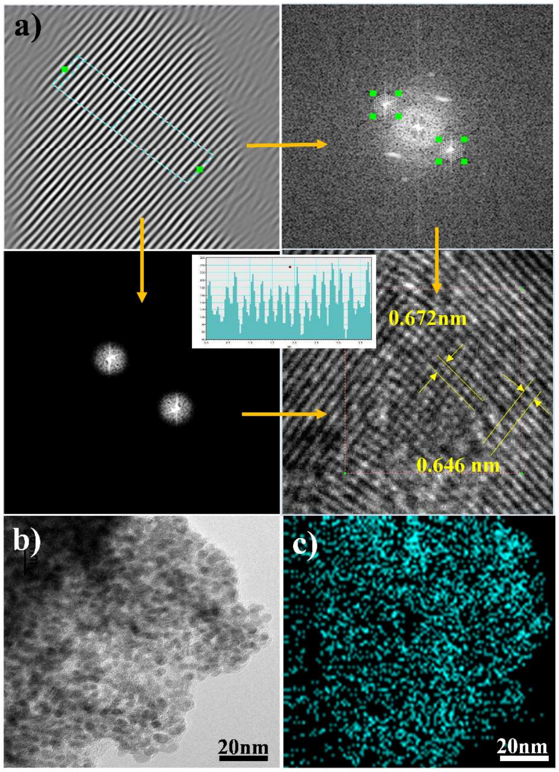


Fig 7: Single-particle analysis by FFT filtering-(a) High-resolution transmission electron microscopy images of two Pd-NPs aligned with the electron beam. Corresponding FFT images and inverse FFT images. In the inset of (a),the intensity pattern of the Pd-NPs layer is presented b)TEM images of Pd-NPs c) Energy-dispersive spectrometer (EDS) scanning transmission electron microscopy (STEM) mapping images for Pd-NPs.

Table 5. Comparison study of efficiency of IL-Pd$^-$Nps catalytic system with other reported catalysts in the Suzuki-Miyaura coupling

Entry	Catalyst	Conditions	Time (h)	Yield (%)^a	Ref.
1	Pd-NPs	$Pd(OAc)_2$ (2 mol %), TSIL (20 mol%), Na_2CO_3 (1 mmol), Water (5 mL), 80 ºC	1-3	98	This work
2	$Pd(OAc)_2$ (1-3 mol%)	Na_2CO_3 (1-3 mmol), 80 °C. H_2O:[bmim]PF_6= (3:3 g)	2-6	99	36a
3	$PdCl_2$ (2 mol%)	[C_4-DABCO] [dca] (7.4 mol), 5 M LiCl (0.4 mL), 110 ºC.	3-6	90	36b
4	$Pd(OAc)_2$ (5 mol%)	Cs_2CO_3 (2.0 mmol) PEG1000-[BMIm]PF_6 (2.0 g), 80 ºC	2-8	95	36c
5	Mag-IL-Pd (0.25-0.50 mol%)	K_2CO_3 (0.75 mmol), H_2O (3 mL), 80 °C, argon atmosphere	6-12	95^b	36d
6	Pd-NPs	$PdCl_2$ (0.015 mmol) TBAF (1.5 mmol) at 40-100 ℃, argon atmosphere	0.5-12	90	36e
7	Pd-NPs	$Pd(OAc)_2$ (2 mol %) K_2CO_3 (1 mmol), PEG (4 g), 45 °C	1-5	92	36f
8	$PdCl_2$ (0.05- 0.5mol%)	Ligand NaL_2 (0.05- 0.5 mol %), K_3PO_4 (2 mmol), H_2O (3ml), 100 ℃	6	96	36g
9	Pd-NPs	$PdCl_2$ (1.2 mol%), IL (1.0 ml), Na_2CO_3 (1.05 mmol), water (0.5 ml), 110 ºC	4	96^b	36h
10	Zwitterionic Palladium Complexes (2.0 mol%)	KOH (2.0 equiv), 1,4-dixoxane/H_2O (4/1, 2.0 mL), RT	2-12	88^b	36i
11	Pd(NHC) complexes (1 mol%)	K_2CO_3 (1.5 mmol), H_2O (5 mL), 100 °C	4-12	99^b	36j
12	palladium nanocomposite xerogel (0.15 mol% Pd)	K_2CO_3 (0.98 mmol), H_2O (1.0 mL), 90 °C	12	90	36k
13	Pd-NPs	NaOAc (2 mmol), DMF/H_2O (5:1, *V*/*V*, 6 mL), 80 ℃	1-3	95	36l
14	$Pd(acac)_2$ (2–3 mg)	KOH (2 mmol), ethanol (2 mL), 70 °C, nitrogen atmosphere	0.5-4	99^b	36m

^{a}Isolated yield, ^{b}GC yield

Comparison of catalytic system was carried out in Table 5. Table 5 highlights merits as well as demerits of the literature methods. It is noteworthy that the *in situ* generated Pd-NPs using TSIL in present method has a comparatively similar / excellent activity as compared to other known Pd catalytic systems. However, from view point of use of water as a universal solvent, cost, easy isolation of product from the reaction mixture, operational simplicity, and reusability reveal that developed protocol is superior and easily adaptable.

In coupling chemistry, the recycle or reusability of the catalytic system is an important aspect from economical point of view. Hence last attempt was focused on reusability of the catalytic system. As the products are soluble in ethyl acetate, and can be readily separated by extraction from the aqueous catalytic system, the remaining catalytic system can be recycled for fresh cross-coupling of aryl boronic acid with aryl halide. The reusability study of the catalytic system was carried out with the model cross-coupling of 4-bromotoluene (1 mmol), phenyl boronic acid (1.2 mmol), Na_2CO_3 (1mmol), $Pd(OAc)_2$ (2 mol%), and IL (20 mol%) in water (5 mL) at 80 °C for 2 h. After completion of reaction, the mixture was cooled to room temperature and extracted by ethyl acetate (2×10 mL) upper organic phase containing the product was easily separated using simple liquid–liquid extraction. The residual aqueous catalytic phase containing the IL-Pd-NPs was reused for the next run under the same reaction conditions and found reusable for 7 subsequent runs without any loss of catalytic activity. (Fig. 8) Thus illustrate that the use of this catalytic system meets the trend of green chemistry.HR-TEM analysis of Pd-Nps after seven recycles study is as shown in Fig. 9.

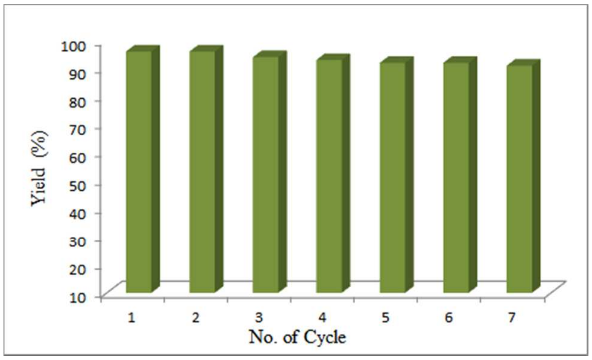


Fig 8: Reusability of aqueous catalytic system containing IL-Pd-NPs in the Suzuki–Miyaura Coupling

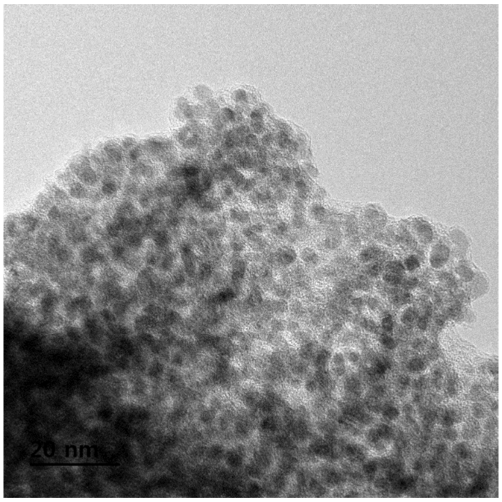


Fig 9 : HR-TEM images of Pd-NPs after seventh recycle

Conclusions

A dual functionalized task specific ionic liquid, 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate was designed and synthesized from inexpensive and commercially available precursors. Palladium nanoparticles were in situ formed and synergistically stabilized, due to the hydroxyl functionality in cation and the prolinate anion of task specific ionic liquid. 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate provided excellent catalytic activity towards the Suzuki-Miyaura cross-coupling of arylboronic acid with aryl halide in water. Noticeably, less activated aryl chlorides also get coupled. TEM analysis, mercury drop test showed Pd-Nps were involved in catalysis. The ionic ligand served as an efficient protective agent for the stabilization of palladium NPs in water. The catalytic system can also be reused several times and has potential for industrial applications.

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Experimental

General Information

Phenylboronic acids (Spectrochem, Mumbai) aryl halides (Sigma Aldrich, india) and palladium sources (Sigma Aldrich, India) were used as received. All reactions were carried out in air atmosphere in predried glassware. Infrared spectra were measured with an Agilent Cary (IR-630) spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AC spectrometer (300MHz for ^{1}H NMR and 75MHz for ^{13}C NMR), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. HR-TEM, FFT were taken on TEM 2100F, JEOL. Elemental analyses were performed on a EURO EA3000 vectro model. The thermal gravimetric analysis (TGA) curves were obtained using the instrument TA SDT Q600 in the presence of static air at a linear heating rate of 10 °C min^{-1} from 25 °C to 400 °C.

Typical procedure for the preparation of 1-(2-hydroxyethyl)-1-methylpyrrolidinium prolinate [HEMPy][Pro] ionic liquid:

To a vigorously stirred solution of 1-methylpyrrolidine (10 mmol) in toluene (25 mL), 2-chloroethanol (12 mmol) was slowly added at room temperature and quaternisation was carried out at 80 ^{o}C for 24 h, after which it was placed in a freezer at 0 ^{o}C for 4 h. Toluene was decanted and the remaining viscous oil was repeatedly washed with diethyl ether to yield white viscous ionic liquid, which was dried in vacuum furnished 1-(2-hydroxylethyl)-1-methylpyrrolidinium chloride [HEMPy][Cl]. 1-(2-hydroxylethyl)-1-methylpyrrolidinium chloride (10 mmol) was then dissolved in dichloromethane followed by addition of potassium hydroxide (12 mmol) and stirred it for 24 h at room temperature. The suspension was filtered to remove the precipitated potassium chloride salt and the solvent was evaporated under reduced pressure furnished 1-(2-hydroxylethyl)-1-methylpyrrolidine hydroxide [HEMPy][OH]. Finally, 1-(2-hydroxylethyl)-1-methylpyrrolidine hydroxide (5 mmol) was dissolved in water and l-proline (5 mmol) was added slowly at 0-5 ^{o}C after addition it was stirred at room temperature for 12 h. The solvent was removed in vacuum to furnish desire ionic liquid *viz.* 1-hydroxylethyl-1-methylpyrrolidine prolinate [HEMPy][Pro].

General procedure for the Suzuki–Miyaura Coupling:

To a mixture of aryl halide (1mmol), arylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), IL (20 mol%) and Na_2CO_3 (1 mmol), water (5 mL) was added and stirred at 80 ^{o}C under aerobic conditions. After completion of reaction monitored by TLC, the reaction mixture was cooled. The product was extracted with ethyl acetate (2×10 mL) while the IL-Pd-Nps were remaining in aqueous phase. The aqueous phase containing IL-Pd-NPs washed with ethyl acetate. The organic layer was dried with $MgSO_4$ and concentrated on a rotary evaporator to afford the desired biaryl in excellent yield. The crude products were then purified by column chromatography (5% ethyl acetate). Synthesized products were confirmed from physical constant,[37] IR, ^1H, ^{13}C NMR and Mass analysis.

General procedure for the reusability of catalytic system in the Suzuki–Miyaura Coupling

A mixture of 4-bromotoluene (1 mmol), phenylboronic acid (1.2 mmol), Na_2CO_3 (1mmol), $Pd(OAc)_2$ (2 mol%), and IL (20 mol%) in water (5 mL) was stirred at 80 °C under aerobic condition. After completion of reaction, reaction mixture was cooled to room temperature and extracted by ethyl acetate (2×10 mL). The combined organic layer was concentrated under reduced pressure, and the residue was isolated by chromatography on a silica gel (300−400 mesh) column using petroleum and ethyl acetate to afford the product. The aqueous phase containing the IL-Pd-Nps were loaded with the fresh reactants and base, for the next run under the same reaction conditions. The aqueous catalytic system was reused for 7 subsequent runs without any loss of catalytic activity.

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