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Synthesis of a novel 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid and its application in palladium-catalyzed Heck reaction under solvent-free conditions

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ABSTRACT

A novel 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid ([HQ-PEG_{1000}-DIL][BF_4]) was synthesized and characterized. It was applied as an efficiently recyclable ligand for Pd-catalyzed Heck reaction under solvent-free conditions. It is noteworthy that the $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4] catalytic system could be easily recovered and reused without obvious loss of catalytic activity after five recycling runs.

1. Introduction

The palladium-catalyzed Heck reaction is one of the most important and general methodologies for carbon–carbon bond formation in organic synthesis [1–4]. In general, the palladium-catalyzed Heck reaction is performed with phosphine ligands and base under an inert atmosphere. However, phosphine ligands are often toxic, expensive, unrecoverable, sensitive to air and moisture, which limited the large-scale application in the industrial chemistry. On the other hand, recovery or recycling of the expensive palladium complex is difficult or impossible. It is desirable to develop a robust, simple and cost-effective non-phosphine ligand for palladium-catalyzed Heck reaction to make the catalyst recyclable.

Ionic liquids (ILs), which are a special class of molten salts composed of organic cations and inorganic or organic anions, have attracted lots of chemists' attention in the last decades. ILs are considered as reaction media or catalysts in the organic chemistry because of their unique properties, such as undetectable vapour pressure, excellent thermal stability, remarkable solubility, and ease of recovery and reuse [5–8]. Recently, functionalized ionic liquids (FILs), so-called task-specific ionic liquids (TSILs), which incorporate a covalently linked reactive functionality, such as amine, amide, nitrile, ether, alcohol, acid, urea and thiourea, have been designed and synthesized. Such ionic liquids find application in a wide range of areas, including catalysis, synthesis, analysis, gas absorption and new materials [9–11]. Recently, ILs have been reported to be applied in the Heck reaction [12–17]. Hagiwara and co-workers prepared a novel heterogeneous catalyst by the immobilization of $Pd(OAc)_2$ on the reversed phase silica gel in low concentration with the aid of [bmim][PF_6] and used for Heck reaction in water [14]. Sawant and co-workers designed an ester appending multifunctional ionic liquid for Heck reaction [16].

Poly (ethylene glycol) (PEG) is a linear polymer formed from the polymerization of ethylene oxide. It has received rising interest as environmental friendly reaction medium for organic synthesis and catalytic process because it is cheap, thermally stable, nontoxic, recoverable, nonvolatile and easily degradable. The commercial availability of many PEGs and its derivatives with either one or two terminal hydroxyl groups make it easy to prepare a variety of PEG supported ligands and catalysts [18–22]. The PEG based functionalized ionic liquids have proved to display special chemical and physical properties. Some PEG based functionalized ionic liquids have been prepared and used as solvents and (or) catalysts in organic synthesis, such as Heck reaction [23], hydrosilylation reaction [24], synthesis of peptide [25], Suzuki reaction [26], synthesis of 2-oxazolidinones [27], cycloaddition reaction of CO_2 [28].

8-Hydroxyquinoline is a versatile ligand in coordination chemistry, which is mainly used for analytical purposes and separation

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techniques [29]. More recently, 8-hydroxyquinoline and its derivatives have been used as an efficient N,O-ligand for the transition-metal catalyzed reactions, such as Ullmann reaction [30–38], Sonogashira coupling [39], Suzuki reaction [40,41], hydroxylation [42], anti-Markovnikov intermolecular hydroalkoxylation [43]. Iyer and co-workers reported that Heck reaction could be catalyzed by Pd complex of 8-hydroxyquinoline, however, hazardous organic solvents were used and the catalyst could not be recovered [44].

In our continuous research on synthesis and application of poly (ethylene glycol) bridged dicationic ionic liquid in synthetic organic chemistry [45–48], herein, we report a novel 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid ([HQ-PEG$_{1000}$-DIL][BF$_4$]) (Scheme 1) as an efficient recyclable ligand for the palladium-catalyzed Heck reaction under solvent-free conditions. In consideration of the structural feature of [HQ-PEG$_{1000}$-DIL][BF$_4$], besides the *N*-heterocyclic carbene (NHC) donor derived from the imidazolium skeleton [49], the ether of 8-hydroxyquinoline could act as an excellent bidentate chelating ligand (N,O-ligand) for the palladium.

2. Experimental

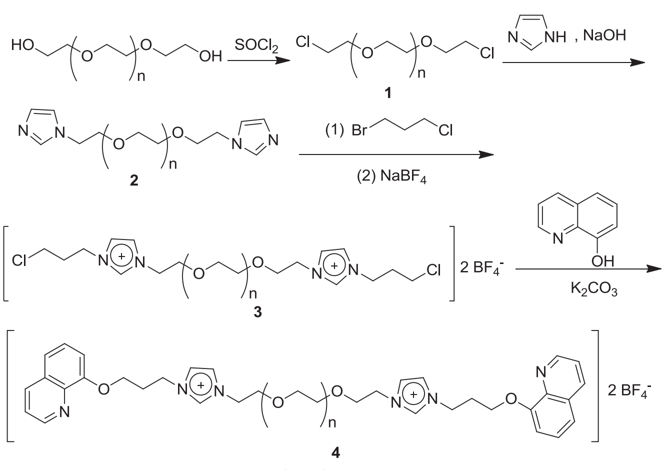
2.1. General remarks

All of the reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR were recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as internal standard. GC analyses were performed on an Agilent 7890A instrument. IR spectra were recorded in KBr disks with a SHIMADZU IRPrestige-21 FT-IR spectrometer. The thermogravimetric analysis (TGA) was performed on a TGA/SDTA851e thermal analyzer (Switzerland-Mettler Toledo). Samples were loaded into an aluminium oxide crucible and heated at a rate of 20 °C min^{-1} from 50 °C to 600 °C under N$_2$. The differential scanning calorimetry (DSC) was performed on a DSC823e (Switzerland-Mettler Toledo), and heated at a rate of 10 °C min^{-1} from −50 °C to 300 °C under N$_2$.

2.2. Synthesis of 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid

2.2.1. Synthesis of PEG$_{1000}$ dichloride (*1*)

To a solution of PEG$_{1000}$ (25 g, 0.025 mol) and pyridine (4.0 mL, 0.05 mol) in CH$_2$Cl$_2$ (150 mL) was dropped SOCl$_2$ (4.0 mL, 0.055 mol) at ambient temperature. The reaction mixture was stirred at ambient temperature for 12 h. After completion, the solvent was evaporated in vacuum. The residue was then dissolved in ethyl acetate to allow the pyridine hydrochloride to be precipitated and filtered off. After evaporating the solvent, the intermediate **1** was obtained and used directly for the next reaction. ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 3.77 (t, J = 5.9 Hz, 4H), 3.73–3.60 (m, 78H).



Scheme 1. Synthesis of 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid ([HQ-PEG$_{1000}$-DIL][BF$_4$]).

2.2.2. Synthesis of PEG$_{1000}$ bridged di-imidazolium compound (*2*)

Imidazole (8.2 g, 0.12 mol) was melted at around 100 °C and NaOH (4 g, 0.1 mol) was added. After the solid NaOH thawed, toluene (50 mL) was added and heated to remove water by azeotropy for 3 h. Then, the toluene was evaporated under reduced pressure. Subsequently, the solution of intermediate **1** obtained in CH$_3$CN (80 mL) was added. The mixture was stirred at 70 °C for another 12 h. After completion, the solvent was removed by distillation. The residue was dissolved in CH$_2$Cl$_2$ and washed with deionized water several times to remove inorganic salts and excess imidazole. After removal of solvent, 20.5 g of the desired compound **2** was obtained, yield 89%. ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 7.47 (s, 2H), 6.96 (d, J = 11.8 Hz, 4H), 4.05 (t, J = 5.2 Hz, 4H), 3.68 (t, J = 5.2 Hz, 4H), 3.65–3.48 (m, 87H).

2.2.3. Synthesis of 3-chloropropyl PEG$_{1000}$ bridged di-imidazolium tetrafluoroborate (*3*)

Compound **2** (20.5 g) was mixed with 1-bromo-3-chloropropane (6.5 g, 2.2 equiv) in CH$_3$CN and stirred at 50 °C for 48 h under nitrogen atmosphere. After completion, the solvent was removed by distillation. The residue was dissolved in deionized water and washed with ethyl ether several times to remove traces of starting materials, followed by evaporation under reduced pressure to yield the yellow oily liquid. Subsequently, NaBF$_4$ (6.7 g, 2.4 equiv) and acetone (60 mL) were added. The reaction mixture was stirred at room temperature for 48 h. After completion, the resulting mixture was filtered. With removing solvent of filtrate, the compound **3** was finally obtained (25.1 g, yield 94%). ^{1}H NMR (500 MHz, D$_2$O, ppm) δ 8.86 (d, J = 12.5 Hz, 2H), 7.54 (dd, J = 7.4, 5.5 Hz, 4H), 4.42–4.25 (m, 10H), 3.86 (dd, J = 10.3, 5.5 Hz, 6H), 3.79–3.45 (m, 105H), 2.54–2.27 (m, 4H).

2.2.4. Synthesis of [HQ-PEG$_{1000}$-DIL][BF4]

A mixture of compound **3** (25.1 g), K$_2$CO$_3$ (5.8 g, 2.4 equiv) and 8-hydroxyquinoline (6.2 g, 2.4 equiv) in acetone (80 mL) was stirred at 50 °C for 72 h. After acetone was removed in vacuum, the residue was washed repeatedly with ethyl acetate to remove excess 8-hydroxyquinoline, followed by evaporation under reduced pressure, and the 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid was finally obtained (23.5 g, yield 81%). ^{1}H NMR (500 MHz, CDCl$_3$, ppm) δ 9.32 (s, 2H), 8.84 (d, J = 3.4 Hz, 2H), 8.10 (d, J = 8.3 Hz, 2H), 7.61 (s, 2H), 7.51 (s, 2H), 7.42–7.33 (m, 6H), 7.06 (d, J = 7.3 Hz, 2H), 4.55 (t, J = 6.5 Hz, 4H), 4.38–4.29 (m, 6H), 4.22 (t, J = 5.5 Hz, 4H), 3.82–3.71 (m, 6H), 3.65–3.42 (m, 122H), 2.56–2.45 (m, 4H). ^{13}C NMR (126 MHz, CDCl$_3$, ppm) δ 153.90, 149.16, 140.04, 136.96, 136.18, 129.46, 126.90, 123.18, 122.66, 121.78, 120.41, 109.91, 70.42, 70.23, 70.14, 68.62, 65.39, 49.72, 47.18, 29.44. IR (KBr, cm^{-1}): 2868, 1568, 1502, 1468, 1375, 1349, 1318, 1257, 1052, 946, 827, 796, 761, 730, 668, 643. ESI-MS, m/z: 612.9 (M^{++}/2, n = 20), 635.0 (M^{++}/2, n = 21), 657.3 (M^{++}/2, n = 22).

2.3. General procedure for Heck reaction and recycling of catalyst

In a typical reaction, aryl halide (1.0 mmol), olefin (1.5 mmol), Et$_3$N (2 mmol), Pd(OAc)$_2$ (0.01 mmol) and [HQ-PEG$_{1000}$-DIL][BF$_4$] (0.1 mmol) were added to a tube and sealed. The reaction mixture was stirred at 100 °C for a certain time. At the end of the reaction, the final mixture was cooled to room temperature and extracted with diethyl ether. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated to give the crude product, which was purified by column chromatography on silica gel (200–300 mesh) using ethyl acetate/petroleum ether as eluent to afford the desired product in high purity. Only the *trans*-products were selectively obtained and characterized by comparison of ^1H NMR data in the literature.

The catalyst left in the reaction vessel was dried in vacuo for 2 h. The residue was subjected to a second run by charging the reaction tube with fresh starting materials without further addition of $Pd(OAc)_2$ and [HQ-PEG_{1000}-DIL][BF_4].

2.4. Characterization data of products

2.4.1. (E)-Methyl cinnamate [50,52,54,55]

^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 16.0 Hz, 1H), 7.58–7.52 (m, 2H), 7.44–7.36 (m, 3H), 6.46 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H).

2.4.2. (E)-Ethyl cinnamate [50–52,54,55]

^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 16.0 Hz, 1H), 7.54 (dd, J = 6.7, 2.9 Hz, 2H), 7.40 (dd, J = 6.3, 3.8 Hz, 3H), 6.46 (d, J = 16.0 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

2.4.3. (E)-n-Butyl cinnamate [50,55]

^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 16.0 Hz, 1H), 7.54 (dt, J = 5.5, 3.5 Hz, 2H), 7.45–7.36 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 4.23 (t, J = 6.7 Hz, 2H), 1.71 (tt, J = 15.6, 7.9 Hz, 2H), 1.51–1.40 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

2.4.4. (E)-Stilbene [53,55]

^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.30 (s, 1H), 7.14 (s, 1H).

2.4.5. (E)-Ethyl 3-(4-acetylphenyl)acrylate [54]

^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 16.0 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 6.54 (d, J = 16.0 Hz, 1H), 4.30 (d, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H).

2.4.6. (E)-Ethyl 3-(4-bromophenyl)acrylate [51,52]

^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 16.0 Hz, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 6.43 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

2.4.7. (E)-Ethyl 3-(4-cyanophenyl)acrylate [51,52]

^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 12.1, 10.2 Hz, 3H), 7.63 (d, J = 8.3 Hz, 2H), 6.53 (d, J = 16.1 Hz, 1H), 4.30 (d, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H).

2.4.8. (E)-Ethyl 3-(4-nitrophenyl)acrylate [51,52,54,55]

^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.4 Hz, 2H), 7.71 (dd, J = 17.7, 12.3 Hz, 3H), 6.58 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H).

2.4.9. (E)-Ethyl 3-(4-methoxyphenyl)acrylate [50,51,53]

^1H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.32 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H).

2.4.10. (E)-Ethyl 3-(2-methoxyphenyl)acrylate [51]

^1H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 16.2 Hz, 1H), 7.52 (dd, J = 7.7, 1.6 Hz, 1H), 7.40–7.33 (m, 1H), 6.98 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.55 (d, J = 16.2 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).

2.4.11. (E)-Ethyl 3-(3-methoxyphenyl)acrylate [52]

^1H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 16.0 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.06 (s, 1H), 6.95 (dd, J = 8.2, 2.5 Hz, 1H), 6.44 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).

2.4.12. (E)-Ethyl 3-(p-tolyl)acrylate [50,51]

^1H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 16.0 Hz, 1H), 7.44 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 6.41 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H).

2.4.13. (E)-Ethyl 3-(4-aminophenyl)acrylate [53]

^1H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 15.9 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.25 (d, J = 15.9 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.95 (s, 2H), 1.34 (t, J = 7.1 Hz, 3H).

2.4.14. (E)-Ethyl 3-(4-hydroxyphenyl)acrylate [51,56]

^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 16.0 Hz, 1H), 7.45 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.32 (d, J = 16.0 Hz, 1H), 5.24 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H).

3. Results and discussion

The synthetic route of 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid is illustrated in Scheme 1. It was readily prepared through a straightforward four-step procedure from commercially available starting materials and reagents in good yields. Firstly, PEG_{1000} was chlorinated with thionyl chloride in the presence of pyridine in CH_2Cl_2 to afford PEG_{1000} dichloride **1**. Next, the solution of **1** in CH_3CN was added into sodium imidazole, which was prepared from imidazole and NaOH in toluene, to afford PEG_{1000} bridged di-imidazolium compound **2**. And then, the quaternization of **2** and 1-bromo-3-chloropropane was conducted in CH_3CN, and then bromide was exchanged with $NaBF_4$ in acetone to afford the 3-chloropropyl PEG_{1000} bridged di-imidazolium tetrafluoroborate **3**. Finally, ionic liquid **3** reacted with 8-hydroxyquinoline in the presence of K_2CO_3 in acetone to afford the target 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid [HQ-PEG_{1000}-DIL][BF_4], which was characterized by ^1H NMR, ^{13}C NMR, IR, MS. The thermal property of this dicationic ionic liquid was determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA results indicates that the [HQ-PEG_{1000}-DIL] [BF_4] have good thermal stability for the high decomposition temperature (>300 °C) (Fig. 1). As shown in Fig. 2, there was no melt point for this ionic liquid but had a glass transition temperature of −35 °C from differential scanning calorimetry (DSC). In addition, the solubility of [HQ-PEG_{1000}-DIL][BF_4] was determined at room temperature. In general, it is immiscible with heptane, cyclohexane, diethyl ether, toluene and water, but miscible with dichloromethane, acetone, methanol, ethanol, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

To optimize the reaction conditions, iodobenzene and ethyl acrylate were chosen as the substrates for model Heck reaction. Selected results from our screening experiments are summarized in Table 1. The amount of catalyst loading was firstly investigated. It was observed that 1.0 mol% loading amount of $Pd(OAc)_2$ could give ethyl cinnamate in high yields (Table 1, entries 1–3). However, Pd black precipitated and low yield was obtained if no [HQ-PEG_{1000}-DIL][BF_4] was added (Table 1, entry 4). When PEG_{1000} was added in the reaction, the yield was increased to 58% (Table 1, entry 5). Only trace of product was detected with 8-hydroxyquinoline as ligand under solvent-free conditions, but 31% of product was afforded when the NMP was added as solvent (Table 1, entry 6–7). A high yield of 72% was obtained in the presence of 3-chloropropyl

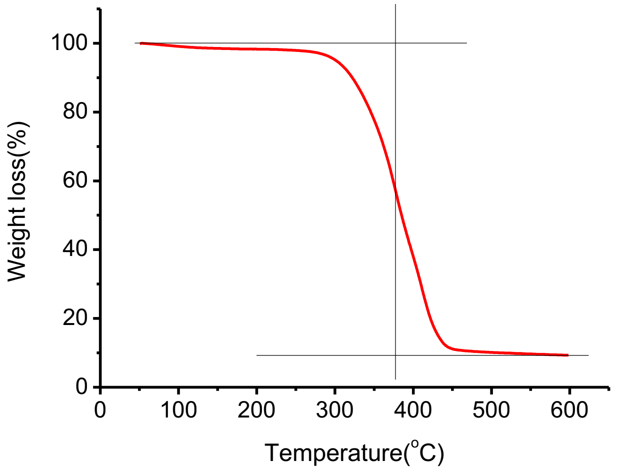
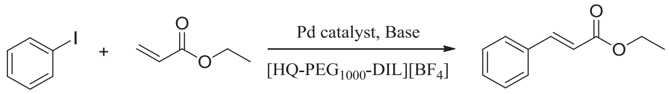


Fig. 1. The TGA spectrum of [HQ-PEG_{1000}-DIL][BF_4].

Table 1
Optimization of the reaction conditions.[a]



Entry	$Pd(OAc)_2$ (mol%)	Base	Temperature (°C)	Time (h)	Yield (%)[b]
1	2.0	Et_3N	100	2	98
2	1.0	Et_3N	100	2	98
3	0.5	Et_3N	100	2	53
4[c]	1.0	Et_3N	100	2	27
5[d]	1.0	Et_3N	100	2	58
6[e]	1.0	Et_3N	100	2	Trace
7[f]	1.0	Et_3N	100	2	31
8[g]	1.0	Et_3N	100	2	72
9	1.0	–	100	2	Trace
10	1.0	(n-Bu)$_3$N	100	2	48
11	1.0	(i-Pr)$_2$EtN	100	2	93
12	1.0	Pyridine	100	2	16
13	1.0	K_2CO_3	100	2	0
14	1.0	Et_3N	90	2	64
15	1.0	Et_3N	80	2	56
15	1.0	Et_3N	100	1	72

[a] Reagents: iodobenzene (1.0 mmol), ethyl acrylate (1.5 mmol), base (2.0 mmol), [HQ-PEG_{1000}-DIL][BF_4] (0.1 mmol).
[b] GC yield.
[c] Without [HQ-PEG_{1000}-DIL][BF_4].
[d] With PEG_{1000} (0.1 mmol).
[e] With 8-hydroxyquinoline (0.1 mmol).
[f] With 8-hydroxyquinoline (0.1 mmol), NMP (2.0 mL).
[g] With 3-chloropropyl PEG_{1000} bridged di-imidazolium tetrafluoroborate **3** (0.1 mmol).

PEG_{1000} bridged di-imidazolium tetrafluoroborate **3** (Table 1, entry 8). Base is an important factor to affect the reaction. Only a trace amount of product was detected in the absence of base (Table 1, entry 9). Lower yields were obtained when other organic bases such as (n-Bu)$_3$N, (i-Pr)$_2$EtN or pyridine was used (Table 1, entries 10–12). No desired product was detected when inorganic base K_2CO_3 was utilized (Table 1, entry 13). In addition, low temperature or short time led to lower yields (Table 1, entries 14–15).

To investigate the recyclability of this catalytic system, the recycle experiments were conducted by model Heck reaction catalyzed by $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4]. After completion of the reaction, the final mixture was cooled to room temperature and the product was extracted with diethyl ether. The catalyst left in the reaction vessel was dried under vacuum for 2 h. The resultant residues were used directly without further treatment for the next run after being charged with fresh starting materials (iodobenzene, ethyl acrylate and triethylamine). The results indicated that $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4] system could be reused for five times without apparent loss of catalytic activity (Fig. 3).

In order to extend the scope of this catalytic system, a variety of substituted aryl iodides were used to couple with olefins under the optimized conditions, and the results are presented in Table 2. In general, all the aryl iodides afforded the corresponding products in good to excellent yields ranging from 81% to 98%. The scope of this catalytic system with different vinyl substrates, such as methyl acrylate, ethyl acrylate, n-butyl acrylate and styrene, was firstly examined to result in high yields (Table 2, entries 1–4). Aryl iodides with electron-withdrawing groups afforded the corresponding products in excellent yields (Table 2, entries 5–8). Meanwhile, aryl iodides with electron-donating groups required prolonged reaction time to obtain good yields (Table 2, entries 9–14). The aryl iodides with substituted groups in *ortho* and *meta* positions gave lower yields in comparison with *para*-isomers due to steric hindrance (Table 2, entries 9–11). However, the coupling of aryl bromide bearing strong electron-withdrawing groups, such as 4-bromonitrobenzene, resulted in lower yield even reacting at elevated temperature (120 °C) for manifold reaction time (24 h) with double loading of $Pd(OAc)_2$ (Table 2, entry 15). Unfortunately,

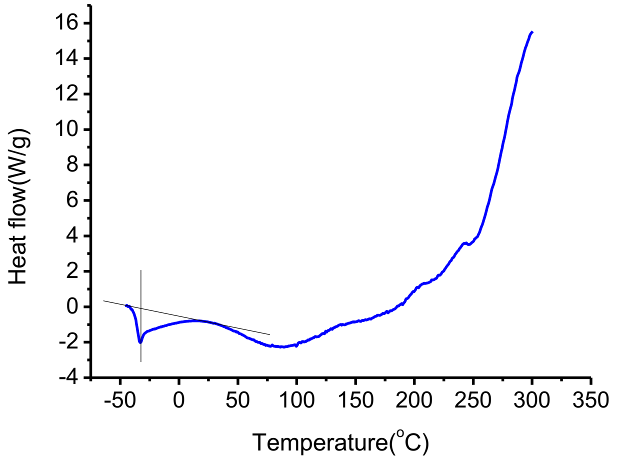


Fig. 2. The DSC spectrum of [HQ-PEG_{1000}-DIL][BF_4].

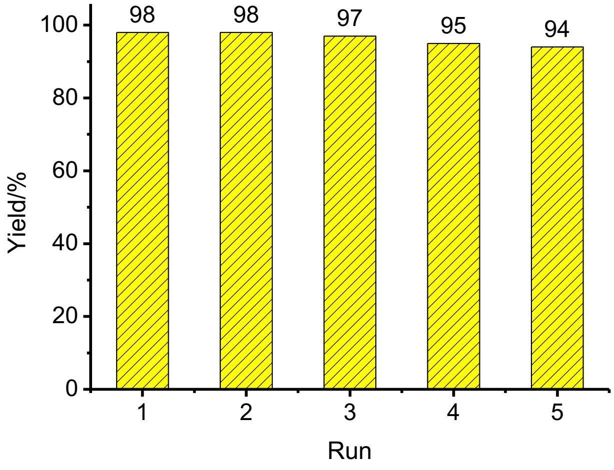
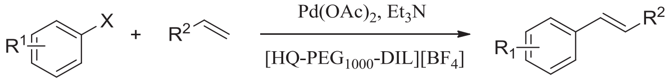


Fig. 3. Recycling results of model Heck reaction catalyzed by $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4].

Table 2
Heck reaction of aryl halide with olefin catalyzed by $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4].[a]



Entry	X	R^1	R^2	Time (h)	Yield (%)[b]
1	I	H	Me	2	96
2	I	H	Et	2	94
3	I	H	*t*-Bu	2	93
4[c]	I	H	Ph	4	86
5	I	*p*-CH_3CO	Et	2	93
6	I	*p*-Br	Et	2	95
7	I	*p*-CN	Et	2	96
8	I	*p*-NO_2	Et	2	98
9	I	*p*-CH_3O	Et	4	89
10	I	*o*-CH_3O	Et	4	81
11	I	*m*-CH_3O	Et	4	83
12	I	*p*-CH_3	Et	4	86
13	I	*p*-NH_2	Et	4	89
14	I	*p*-OH	Et	4	84
15[d]	Br	*p*-NO_2	Et	24	48
16[d]	Cl	*p*-NO_2	Et	24	Trace

[a] Reaction conditions: aryl halide (1.0 mmol), olefin (1.5 mmol), $Pd(OAc)_2$ (0.01 mmol), Et_3N (2 mmol), [HQ-PEG_{1000}-DIL][BF_4] (0.1 mmol), 100 °C.
[b] Isolated yield, all of the products were isolated as *trans*-isomers.
[c] $E/Z = 87:13$, the ratio of E/Z was determined by GC of the crude reaction mixture.
[d] $Pd(OAc)_2$ (0.02 mmol), 120 °C.

as for the aryl chloride, even bearing strong electron-withdrawing group such as 4-chloronitrobenzene, only a trace amount of product could be detected (Table 2, entry 16).

4. Conclusions

In summary, a novel 8-hydroxyquinoline functionalized poly (ethylene glycol) bridged dicationic ionic liquid was synthesized and applied to Pd-catalyzed Heck reaction as an efficient ligand under solvent-free conditions. Using the $Pd(OAc)_2$/[HQ-PEG_{1000}-DIL][BF_4] system, a series of substituted aryl iodides coupled with olefins to afford the corresponding products in good to excellent yields. Furthermore, this catalytic system could be easily recycled for five times without obvious deactivation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.04.006.

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