

CONTENTS

The 5th International Symposium on Environmental Economy and Technology (ISEET-2012)

Sensitive voltammetric and amperometric responses of respiratory toxins at hemin-adsorbed carbon-felt Yasushi Hasebe, Yue Wang	1055
Destruction of 4-phenolsulfonic acid in water by anodic contact glow discharge electrolysis Haiming Yang, Baigang An, Shaoyan Wang, Lixiang Li, Wenjie Jin, Lihua Li	1063
Nitrous oxide emissions from black soils with different pH Lianfeng Wang, Huachao Du, Zuoqiang Han, Xilin Zhang	1071
Coulometric determination of dissolved hydrogen with a multielectrolytic modified carbon felt electrode-based sensor Hiroaki Matsuura, Yosuke Yamawaki, Kosuke Sasaki, Shunichi Uchiyama	1077
Palladium-phosphinous acid complexes catalyzed Suzuki cross-coupling reaction of heteroaryl bromides with phenylboronic acid in water/alcoholic solvents Ben Li, Cuiping Wang, Guang Chen, Zhiqiang Zhang	1083

Aquatic environment

Organic matter produced by algae and cyanobacteria: Quantitative and qualitative characterization Maud Leloup, Rudy Nicolau, Virginie Pallier, Claude Yéprémian, Geneviève Feuillade-Cathalifaud	1089
Effects of environmental factors on sulfamethoxazole photodegradation under simulated sunlight irradiation: Kinetics and mechanism Junfeng Niu, Lilan Zhang, Yang Li, Jinbo Zhao, Sidan Lv, Keqing Xiao	1098
Irrigation system and land use effect on surface water quality in river, at lake Dianchi, Yunnan, China Takashi Tanaka, Takahiro Sato, Kazuo Watanabe, Ying Wang, Dan Yang, Hiromo Inoue, Kunzhi Li, Tatsuya Inamura	1107
Temporal and spatial changes in nutrients and chlorophyll- <i>a</i> in a shallow lake, Lake Chaohu, China: An 11-year investigation Libiao Yang, Kun Lei, Wei Meng, Guo Fu, Weijin Yan	1117
Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and ³¹ P NMR Runyu Zhang, Liying Wang, Fengchang Wu, Baoan Song	1124
Effect of ammonium on nitrous oxide emission during denitrification with different electron donors Guangxue Wu, Xiaofeng Zhai, Chengai Jiang, Yuntao Guan	1131
Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite Ping Jing, Meifang Hou, Ping Zhao, Xiaoyan Tang, Hongfu Wan	1139
Differences in rheological and fractal properties of conditioned and raw sewage sludge Hui Jin, Yili Wang, Ting Li, Yujing Dong, Junqing Li	1145
Competitive sorption between 17 α -ethinyl estradiol and bisphenol A/ 4- <i>n</i> -nonylphenol by soils Jianzhong Li, Lu Jiang, Xi Xiang, Shuang Xu, Rou Wen, Xiang Liu	1154
Determination of estrogens and estrogenic activities in water from three rivers in Tianjin, China Kaifeng Rao, Bingli Lei, Na Li, Mei Ma, Zijian Wang	1164

Terrestrial environment

Adsorption and desorption characteristics of diphenylarsenicals in two contrasting soils Anan Wang, Shixin Li, Ying Teng, Wuxin Liu, Longhua Wu, Haibo Zhang, Yujuan Huang, Yongming Luo, Peter Christie	1172
Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from contaminated soils in Hai-Pu, Taiwan Jyoti Prakash Maity, Yuh Ming Huang, Cheng-Wei Fan, Chien-Cheng Chen, Chun-Yi Li, Chun-Mei Hsu, Young-Fo Chang, Ching-I Wu, Chen-Yen Chen, Jiin-Shuh Jean	1180

Environmental biology

Vertical diversity of sediment bacterial communities in two different trophic states of the eutrophic

Lake Taihu, China (**Cover story**)

Keqiang Shao, Guang Gao, Yongping Wang, Xiangming Tang, Boqiang Qin 1186

Abundance and diversity of ammonia-oxidizing archaea in response to various habitats

in Pearl River Delta of China, a subtropical maritime zone

Zhixin Li, Wenbiao Jin, Zhaoyun Liang, Yangyang Yue, Junhong Lv 1195

Environmental catalysis and materials

Effect of pretreatment on Pd/Al₂O₃ catalyst for catalytic oxidation of *o*-xylene at low temperature

Shaoyong Huang, Changbin Zhang, Hong He 1206

Efficient visible light photo-Fenton-like degradation of organic pollutants using *in situ* surface-modified

BiFeO₃ as a catalyst

Junjian An, Lihua Zhu, Yingying Zhang, Heqing Tang 1213

Basic properties of sintering dust from iron and steel plant and potassium recovery

Guang Zhan, Zhancheng Guo 1226

Degradation of direct azo dye by *Cucurbita pepo* free and immobilized peroxidase

Nabila Boucherit, Mahmoud Abouseoud, Lydia Adour 1235

Environmental analytical methods

Determination of paraquat in water samples using a sensitive fluorescent probe titration method

Feihu Yao, Hailong Liu, Guangquan Wang, Liming Du, Xiaofen Yin, Yunlong Fu 1245

Chemically modified silica gel with 1-f4-[(2-hydroxy-benzylidene)amino]phenylgethanone:

Synthesis, characterization and application as an efficient and reusable solid phase extractant
for selective removal of Zn(II) from mycorrhizal treated fly-ash samples

R. K. Sharma, Aditi Puri, Anil Kumar, Alok Adholeya 1252

Serial parameter: CN 11-2629/X*1989*m*207*en*P*25*2013-6



Palladium-phosphinous acid complexes catalyzed Suzuki cross-coupling reaction of heteroaryl bromides with phenylboronic acid in water/alcoholic solvents

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Abstract

Highly active, air-stable and water-soluble palladium-phosphinous acid complexes have been applied to Suzuki cross-coupling reaction of heteroaryl bromides under mild conditions in water/alcoholic solvents. Suzuki cross-coupling reaction of heteroaryl bromides with phenylboronic acid occurred efficiently using palladium phosphinous acid complexes (POPd) and phase transfer catalyst (tetrabutylammonium bromide and polyethylene glycol) in water/ethanol mixture, water/propanol mixture and neat water respectively, the corresponding yields of cross-coupling heteroaryl-aryls were satisfied. The *tert*-butyl substituted ligand di-*tert*-butylphosphino in combination with POPd was found to be more active than the same family derived catalysts dipalladium complexes POPd1 and POPd2, and other two kinds of Pd-catalysts Pd(PPh₃)₄ and Pd₂(dba)₃. The mechanism of Suzuki cross-coupling reaction between heteroaryl bromides and phenylboronic acid in water was proposed with respect to the key role of phase transfer catalyst on the transmetallation step. Compared with other solid phase transfer catalysts, TBAB was tested as the ideal one. The alkalinity of base and the molar proportion between POPd and TBAB were investigated in water and alcoholic solvents. Notably, in the presence of TBAB adding alcoholic solvents into water enhanced the yields of target products. However in terms of the liquid phase transfer catalyst of PEGs, mixing water into PEGs could slightly decrease the yields with respect to the water free PEGs bulk phase, which was probably due to the homogenous liquid conditions in pure PEGs and weak interactions between PEGs and heteroaryl bromide molecules in water depending on their molecular chain lengths.

Key words: POPd; Suzuki cross-coupling reaction; heteroaryl bromides; phase transfer catalyst; water

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Introduction

Pd-catalyzed Suzuki cross-coupling reaction of organoboronic reagents with organic halides has been proven as a highly efficient and versatile synthetic method to afford new C–C bond between molecules (Miyaura and Suzuki, 1995; Suzuki, 1999), and awarding the laurel of the 2010 Nobel Chemistry Prize can be deemed as a milestone for the development of Suzuki cross-coupling reaction in last 20 years. Developing stable and highly active ligands for palladium catalysts have received tremendous interests for performing the Suzuki cross-coupling reaction in both organic and aqueous mixtures. Various ligands including aminophosphine- (Wolfe et al., 1999), diamine- (Zhou et al., 2009), P-O coordinated complex (Lerebours and Wolf, 2005; Ghosh et al., 2010), organic frameworks (Ding et al., 2011; Huang et al., 2011), graphite oxide (Scheuermann et al., 2009) have been widely studied. Among these ligands, phosphinous

acid complexes (*t*-Bu)₂P(OH)]₂ was reported as a highly effective and environmental friendly Pd-catalyst for Suzuki cross-coupling reaction of (hetero) aryl halides and arylboronic acids (Khanapure and Garvey, 2004; George, 2002; Wolf and Ekoue-Kovi, 2006). POPd and its family derivatives [(*t*-Bu)₂P(OH)PdCl₂]₂ (POPd1) and {[(*t*-Bu)₂PO···H···OP(*t*-Bu)₂]PdCl₂}₂ (POPd2) are typically characterized by air-stable, good water solubility, high reactivity, and easy separation from the organic mixtures, their steric molecular frameworks are depicted in **Fig. 1** (Li, 2002). The Suzuki cross-coupling reaction is often used to form the unsymmetrical biaryl compounds using arylborane reagents as partner. The development of water-based organic transformations is growing in importance in chemistry. Its low cost and lack of inflammable, explosive, mutagenic and carcinogenic properties makes water the most suitable solvent for the production of fine chemicals (Shaughnessy and Booth, 2001). In addition, several synthetic advantages are expected using water as the solvent. Among others, phase

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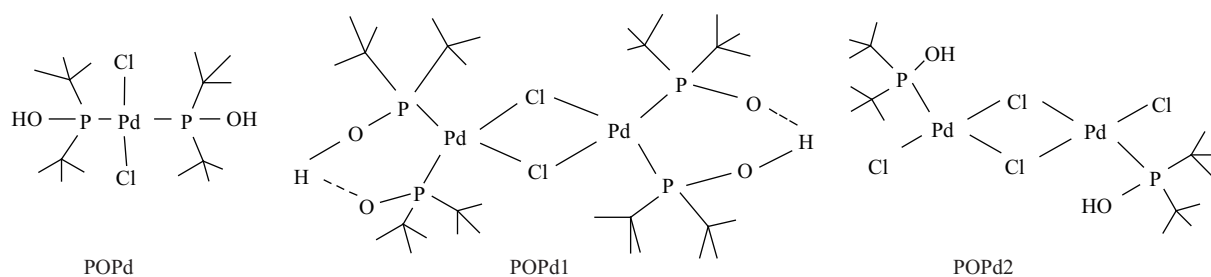


Fig. 1 Highly active and air-stable (di)palladium phosphinous acid complexes, steric framework of POPd, POPd1 and POPd2.

separation is easier because most organic compounds are lipophilic and are easily separated from the aqueous phase. Hence, Pd-catalyzed Suzuki cross-coupling reactions of (hetero-)aryl halides with arylboronic acids performed in water and water/alcoholic solvents have been intensively studied in last decade (DeVasher et al., 2004; Arcadi et al., 2003; Badone et al., 1997; Bussolari and Rehborn, 1999; Bedford et al., 2003; Wang et al., 2009; He et al., 2012; Milde et al., 2012). Moreover, water could also improve the selectivity and catalytic performance (Genet and Savignac, 1999).

In general, Suzuki cross-coupling reaction of aromatic compounds with organoboronic reagents is impossible to take place in neat water due to the immiscible properties between organic and water phase. To solve the problem of immiscible inter-phases for Suzuki cross-coupling reaction between organic and water phase, using phase transfer catalysts (PTCs) can bridge the gap between these two impossible phases. **Figure 2a, b** shows that in the absence of PTCs, Suzuki cross-coupling reaction is impossible to occur in water due to the failure of molecular interactions between two phases. However, with adding PTCs such as tetrabutylammonium bromide (TBAB) and polyethylene glycol (PEG) into the immiscible mixture, an interlayer phase boundary will be formed between these immiscible phases in liquid mixture, then PTC molecules can transport reactant molecules from the organic phase (e.g., heteroaryl bromides) to the aqueous phase (Pd-catalyst and phenylboronic acid), vice versa. Hence, direct interactions

among molecules in the mixture could be realized leading to the transmetalation between heteroaryl bromides and phenylboronic acid via transporting functions of PTC. In **Fig. 2**, TBAB used as a PTC on a model experimental, and a possible reaction mechanism using PTC (Snelders et al., 2009) between immiscible phases is proposed in **Fig. 2c**.

We have reported the environmental friendly Suzuki coupling reaction using a variety of aryl halides in water by palladium-catalyzed (Wang et al., 2009). Herein we report palladium-catalyzed heterogeneous Suzuki cross-coupling reaction in water and its mixtures (**Fig. 3**).

Impact of proportion between POPd and PTC was initially investigated in aqueous mixtures with a model reaction of 2-bromothiophene and phenylboronic acid. Effects of alkaline properties and other alcoholic solvents upon Suzuki cross-coupling reaction of 2-bromothiophene, 2-bromothiazole and 2-bromopyridine with phenylboronic acid were also performed. High yields of target products could be obtained using proper amount of POPd, TBAB and moderate bases such as K_2CO_3 . The ratio between POPd and TBAB is also a key factor for deciding the distribution between the target products and by-products in the mixture. Experimental findings showed higher reactivity of 2-bromothiazole and 2-bromopyridine in alcoholic solvents than those in neat water.

Inspired by the interesting aqueous phase Suzuki cross-coupling findings using TBAB, heterogeneous Suzuki cross-coupling reactions with another PTC, namely PEGs were performed in parallel. Because of liquid properties,

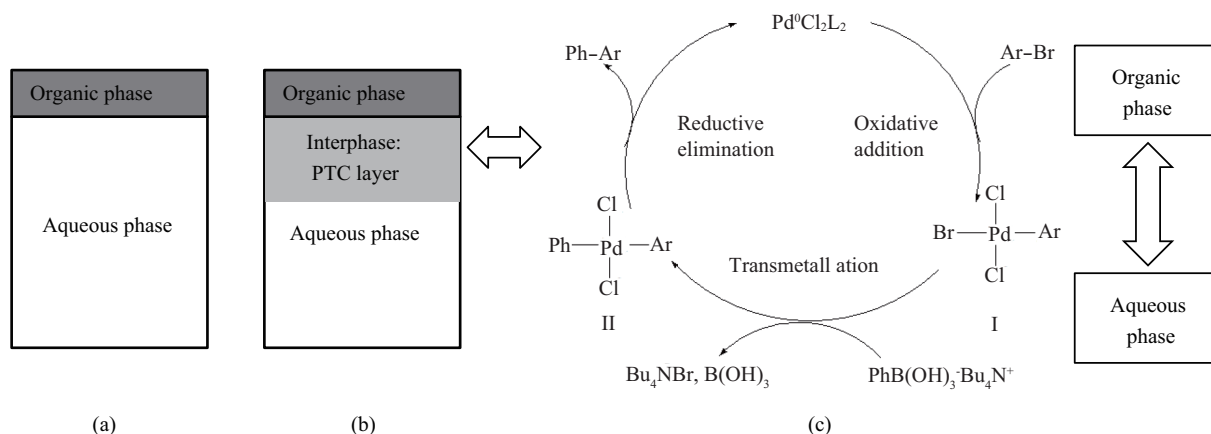


Fig. 2 A scheme of heterogeneous Suzuki cross-coupling reactions in the absence of (a) and in the presence of (b) phase transfer catalyst (PTC) in aqueous solvent, and a proposed reaction mechanism using PTC for Suzuki cross-coupling reaction (c).

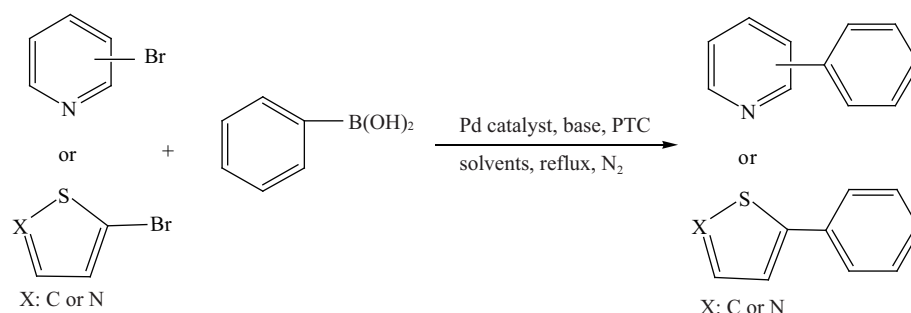


Fig. 3 A general Suzuki coupling reaction formula in aqueous medium

PEGs could be directly used as a potential solvent except for the phase transferring functions. Hence, bulk phase Suzuki cross-coupling reaction of 3-bromopyridine and phenylboronic acid in the absence of water and in water/PEGs mixtures were both experimentally investigated, and remarkably different experimental tendencies were observed.

1 Experimental

All chemicals including $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}_2(\text{dba})_3$ were purchased from Aldrich and Acros, and used without any further treatment. A series of palladium-phosphinous catalysts were kindly supported by Combiphos Catalysts, USA. ^1H and ^{13}C NMR spectra were recorded on a 500 MHz Bruker nuclear magnetic resonance (NMR) using CDCl_3 as solvent and tetramethylsilane (TMS) as the internal standard substance. High-resolution mass spectra were analyzed by Agilent 1100 LC-MS equipped with electrospray and atmospheric pressure chemical ionization source. Melting points were measured on an X-6 melting point apparatus (Beijing Tech Instrument Co., Ltd., China). The separation of the target product from the organic residue was accomplished with flash chromatography (200–300 mesh silica gel) using the binary mixture of petroleum ether and ethyl acetate as the eluting solvent. Thin layer chromatography (TLC, silica gel 60 F_{254}) was used to trace the elution of target products with UV detector.

1.1 Typical procedure for heterogeneous Suzuki coupling reaction

A mixture of 2-bromothiophene (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (3.0 mmol), $(n\text{-Bu})_4\text{BrN}$ (0.3 mmol), POPd (0.002 mmol) and 3 mL water was magnetically stirred and heated to reflux in a Schlenk bottle under nitrogen for 2 hr. The organic layer was firstly extracted with ethyl acetate (5 mL \times 3), each collected organic part was dried with anhydrous magnesium sulfate, and then the solvent was removed from the mixture by rotating evaporation. Then, the concentrated crude product was selectively separated by flash chromatography (silica gel packed column, eluting solvent: a mixture of petroleum ether and ethyl acetate) and the target products dissolved in

the elution mixtures were collected.

1.2 NMR and MS analysis of heteroaryl-aryl products

2-Phenylthiophene: ^1H NMR (TMS, CDCl_3) δ : 7.13 (m, 1H), 7.32 (hm, 1H), 7.37 (t, $J = 0.67$ Hz, 1H), 7.42 (t, $J = 7.79$ Hz, 2H), 7.67 (t, $J = 7.34$ Hz, 2H); ^{13}C NMR (TMS, CDCl_3) δ : 123.16, 124.88, 126.03, 127.54, 128.08, 128.96, 134.48, 144.50; $[\text{M}]^+ = 160.9$ m/z .

2-Phenylpyridine: ^1H NMR (TMS, CDCl_3) δ : 7.12 (m, 1H), 7.36 (t, $J = 7.00$ Hz, 3H), 7.42 (t, $J = 7.50$ Hz, 2H), 7.62 (t, $J = 8.00$ Hz, 2H), 7.67 (d, $J = 7.00$ Hz, 1H); ^{13}C NMR (TMS, CDCl_3) δ : 120.56, 122.13, 126.96, 128.79, 129.01, 136.77, 139.42, 149.68, 157.44; $[\text{M}]^+ = 156.0$ m/z .

3-Phenylpyridine: ^1H NMR (TMS, CDCl_3) δ : 7.25 (m, 1H), 7.32 (t, $J = 7.32$ Hz, 1H), 7.39 (t, $J = 7.67$ Hz, 2H), 7.49 (d, $J = 7.35$ Hz, 2H), 7.76 (d, $J = 7.85$ Hz, 1H), 8.56 (d, $J = 4.21$ Hz, 1H), 8.84 (d, $J = 1.09$ Hz, 1H); ^{13}C NMR (TMS, CDCl_3) δ : 123.61, 127.11, 128.15, 129.09, 134.43, 136.65, 137.66, 148.06, 148.22; $[\text{M}]^+ = 156.0$ m/z .

2-Phenylthiazole: ^1H NMR (TMS, CDCl_3) δ : 7.28 (d, 3.00 Hz, 1H), 7.39 (t, $J = 7.50$ Hz, 3H), 7.85 (d, $J = 3.00$ Hz, 1H), 7.62 (d, $J = 7.00$ Hz, 2H); ^{13}C NMR (TMS, CDCl_3) δ : 118.86, 126.62, 129.00, 130.04, 133.61, 143.70, 168.44; $[\text{M}]^+ = 161.9$ m/z .

2 Results and discussion

Due to the enhancement of steric electron atmosphere density around phosphinous ligands under proper alkaline conditions, POPd has high catalytic activity compared with other Pd-catalysts such as $\text{Pd}(\text{PPh}_3)_4$. Under alkaline conditions, the -OH group on the ligands is subject to lose H^+ ion and form hydroxyl ion *in situ*, the hydroxyl ion could strengthen the electron atmosphere density around Pd atom and eventually enhance the Pd catalytic activity (Fig. 4).

Table 1 shows that the Suzuki cross-coupling yields are moderate in neat water using TBAB at refluxing conditions. Suzuki cross-coupling reaction of 2-phenylthiophene with phenylboronic acid was initially performed as a model reaction in neat water with various bases and Pd-catalysts to investigate the effect of alkalinity upon the heterogeneous Suzuki cross-coupling reaction and the reactivity of Pd-catalysts. Among these

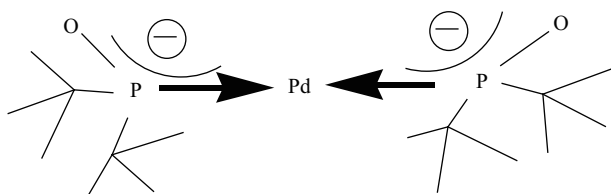


Fig. 4 POPd activity enhancement via the interaction of electron-donating hydroxyl ions under alkaline conditions (Li, 2002).

Table 1 Suzuki cross-coupling reaction of 2-bromothiophene with phenylboronic acid in water-TBAB mixtures using different bases and Pd-catalysts

Base	Pd catalyst	Yield (%)
K ₂ CO ₃	POPd	82.4
Na ₂ CO ₃	POPd	81.0
NaHCO ₃	POPd	76.0
K ₃ PO ₄	POPd	75.4
CH ₃ COOK	POPd	54.5
N(C ₂ H ₅) ₃	POPd	47.5
KOH	POPd	45.2
NaOH	POPd	44.0
K ₂ CO ₃	POPd1	75.9
K ₂ CO ₃	POPd2	74.0
K ₂ CO ₃	Pd(PPh ₃) ₄	73.1
K ₂ CO ₃	Pd ₂ (dba) ₃	55.7

bases, K₂CO₃ and Na₂CO₃ show the highest activities and yields up to 82.4%; NaHCO₃ and K₃PO₄ present moderate yields up to 76.0%; however, the other two organic bases (CH₃COOK and N(C₂H₅)₃) and inorganic bases (KOH and NaOH) give poor activities and yields. The reactivity of heteroaryl bromides in water with phenylboronic acid was in the order: K₂CO₃ > Na₂CO₃ > NaHCO₃ > CH₃COOK > N(C₂H₅)₃ > KOH > NaOH. This could be caused by the high alkalinity excessively triggering the undesired homo-coupling of phenylboronic acid in aqueous mixtures (DeVasher et al., 2004; Arcadi et al., 2003).

With the efficient catalyst systems in hand, the scope of the Suzuki cross-coupling in neat water was explored. (Table 1, K₂CO₃). The yields of synthesized products demonstrated that POPd gave the highest yield of 82.4% and Pd₂(dba)₃ gave the lowest yield of 55.7%. Hence, moderate base such as K₂CO₃ and POPd were selected for the subsequent Suzuki cross-coupling experiments.

As reported in literature (Leadbeater and Marco, 2003), the specific role of PTC such as TBAB in heterogeneous Suzuki cross-coupling reaction are generally twofold. On one hand, it facilitates the solvation of organic substrates in water, but on the other hand it could enhance the rate of the coupling reaction by activating the arylboronic acid via the transition formation of [ArB(OH)₃]⁻ [Bu₄N]⁺ (Fig. 2c). The concentration of PTC in water also played a pivotal role for the coupling product distribution. A higher TBAB concentration could accelerate the coupling reactions. In addition, TBAB molecules can co-exist in both organic and water phase, continuously transfer between phases and facilitate coupling reaction. As expected, Suzuki cross-

coupling reaction of 2-bromothiophene and phenylboronic acid completely failed to occur in neat water in the absence of TBAB. Gradual increase of TBAB concentration could significantly increase the yield, indicating TBAB could accelerate the cross-coupling reaction of 2-bromothiophene with phenylboronic acid rather than the homo-coupling of phenylboronic acid molecules. In Fig. 5a, the yield of 2-phenylthiophene pronouncedly decreases with reducing the amount of TBAB using the same amount of POPd. Alternately, in Fig. 5b, the amount of TBAB set as constant, higher yields of 2-phenylthiophene were obtained by moderate molar concentration of POPd compared to the high molar concentration. Such effect was not pronounced when POPd performed at extremely low molar concentration of 0.001 mmol.

As discussed aforementioned, the aqueous PTC system is promised to be an effective media for carrying out Suzuki cross-coupling reactions of heteroaryl bromides with phenylboronic acid. Coupling findings in Table 2 shows that the highest yield of 82.4% obtained in the presence of TBAB. However, the yield drastically decreasing to 15.4% in the presence of cetyltrimethyl ammonium bromide (CTAB), and 8.0% in the presence of tetramethylammonium bromide (TMAB), it was also observed that in the absence of any PTCs into the aqueous system, no cross-coupling product was observed except for homo-coupling biphenyls, which proved the transporting role of PTC in the proposed aqueous Suzuki coupling reaction mechanism (Fig. 2). The huge difference for the coupling reaction yields of 2-phenylthiophene in the presences of TBAB, CTAB and TMAB could attribute to the lipophilic properties corresponding to their chain structures, the longer chain length it contains, the higher lipophilicity it has. Hence, the molecular interactions between heteroaryl molecules and PTC molecules were strengthened with longer chain length. Although CTAB has a chain with 16 carbon atoms and other three chains with single carbon atom, Suzuki cross-coupling reaction yield is the lowest compared to the other two kinds of PTCs. This situation was probably due to its structural steric hindrance in liquid mixture imposed by the 16 carbon atom chain.

According to the above findings, we further studied the heterogeneous cross-coupling reactions of 2-bromothiazole and 2-bromopyridine with phenylboronic acid in water, alcohols and water/alcohol mixtures, respectively (Table 3). Both components showed quite poor activities in water, the coupling yield of 2-phenylpyridine

Table 2 Aqueous Suzuki coupling reaction of 2-bromothiophene and phenylboronic acid in the presence of PTCs

PTC	Time (hr)	Catalyst	Yield (%)
TBAB	3.5	POPd	82.4
TMAB	3.5	POPd	15.4
CTAB	3.5	POPd	8.0
Without PTC	3.5	POPd	0

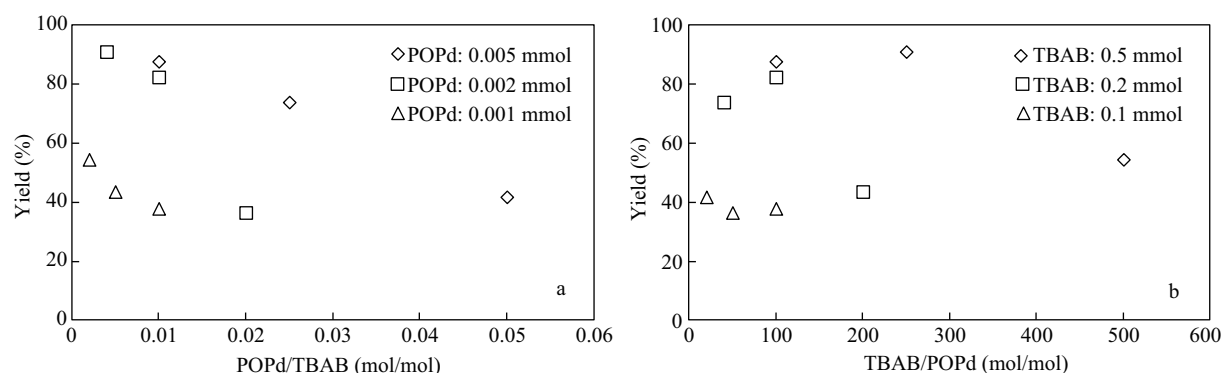


Fig. 5 Effect of the proportion between POPd (a) and TBAB (b) upon the yield of 2-phenylthiophene.

was only 32.0% and none of 2-phenylthiazole was obtained, but the amount of homo-coupling by-product biphenyl substantially increased. However, both of their yields were significantly increased to 60.8% and 69.3% in ethanol respectively, the yield of biphenyl sharply decreased in the mixture. Moderate yields of 2-phenylpyridine and poor yields of 2-phenylthiazole were obtained in *iso*-propanol, water/ethanol mixture and water/ethylene glycol mixture.

Intrigued by these aforementioned findings using TBAB in aqueous solvents, PEGs were used as a liquid PTC to perform heterogeneous Suzuki cross-coupling reaction. PEGs ranged from 400 to 4000 were performed to test their phase transfer performances, the subscript number value means the value of the polymerization degree. Two different trends of the yields of 3-phenylpyridine were observed (Fig. 6). In PEGs water free bulk phase, a M-shape decreasing tendency of 3-phenylpyridine was observed, and some yields (PEG 400, PEG 600 and PEG 2000) are apparently higher than those in PEGs/water mixtures, but not including PEG 1000 and PEG 4000. When PEGs mixed with water, the yields of 3-phenylpyridine was obviously decreased to 40.0% and varied slightly from PEG 400 to PEG 4000. To our knowledge, two factors caused this situation, weak interactions of molecules in the water/PEGs mixtures with respect to the bulk PEGs solvents and irregular spacing distribution in the liquid PEGs mixture. The decrease of the yield of 3-phenylpyridine after adding water to PEGs was also considered as an evidence to Fig. 2a. For the time being, we observed using short chain length PEGs could afford relatively high yield

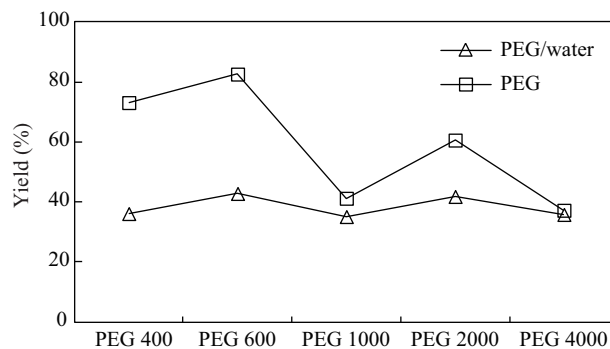


Fig. 6 Investigation of water/PEG solvents on Suzuki cross-coupling reaction of 3-bromopyridine with phenylboronic acid.

of 3-phenylpyridine with respect to using long ones, this can be explained by steric hindrance imposed on the POPd, more experimental studies will be performed to further confirm this irregular phenomenon.

3 Conclusions

Suzuki cross-coupling reaction of 2-bromothiophene, 2-bromothiazole, 2-bromopyridine and 3-bromopyridine with phenylboronic acid using palladium-phosphinous acid complexes and other Pd-catalysts in water/alcoholic solvents was reported. The proportion between POPd and PTC imposes as a key factor for controlling the product distribution in heterogeneous Suzuki cross-coupling reaction. The target product yield could be enhanced with the increase of PTC concentration, and decreased with the increase of POPd amount due to the high reactivity of POPd triggering potential homo-coupling reaction of phenyl boronic acid molecules. Moderate alkalinity and POPd were tested as the ideal components for aqueous Suzuki cross-coupling reaction. Higher yields of both 2-phenylthiazole and 2-phenyl pyridine were obtained in ethanol than those in water. In PEG/water mixture, the target product yields are higher in PEG bulk phase conditions than that in PEG/water mixed conditions, which could be attributed to the dilution of PEG concentration in presence of water and consequently decrease the reaction rate. M-shape decreasing trend in PEGs could be explained by

Table 3 Suzuki cross-coupling reaction of 2-bromothiazole and 2-bromopyridine with phenylboronic acid in water/alcoholic solvents and TBAB mixtures

Solvent	Product yield (%)	
	2-Phenylpyridine	2-Phenylthiazole
H ₂ O	32.0	0
Ethanol	60.8	69.3
H ₂ O/Ethanol (2/1, V/V)	47.8	11.0
H ₂ O/Ethylene glycol (2/1, V/V)	57.4	11.3
<i>iso</i> -Propanol	56.3	9.0

irregular spacing distribution in the liquid PEGs mixture and steric hindrance of chain length, and more experimental studies will be performed to further confirm it.

In summary, we have demonstrated that the water-surfactant palladium-phosphinous acid complexes can accomplish the Suzuki cross-coupling in milder and more environmentally friendly conditions. Further experimental Suzuki cross-coupling reaction of heteroaryl bromides containing either electron-withdrawing or electron-donating groups using short and long chain structural phase transfer catalyst will also be reported in due course.

Acknowledgments

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