# Macromolecules

# Novel Functional Organic Network Containing Quaternary Phosphonium and Tertiary Phosphorus

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**Supporting Information** 

**ABSTRACT:** A quaternary phosphonium and tertiary phosphorus functionalized microporous polymer was obtained via nickel(0)-catalyzed Yamamoto-type cross-coupling reaction. The integration ratio of signals (quaternary phosphonium to tertiary phosphorus atoms) was close to 3:2. The polymer networks were stable toward water, base, and acid, and indeed no change in surface area was observed even after the material was treated with 10 M HCl. The pore size distribution calculated by the Horvath–Kawazoe method indicated the presence of micropores with a mean width of about 0.7 and 1.4 nm. Their apparent BET specific surface areas can be tuned (from 650 to 980 m<sup>2</sup> g<sup>-1</sup>) by changing the counteranions (Br<sup>-</sup> to F<sup>-</sup>). It displays high intrinsic catalytic activity for the reaction between epoxide and  $CO_2$  (yield: 98%, 1 atm). Pd nanoparticles supported on the polymer networks were also prepared, which exhibits high catalytic activity for cross-coupling reaction between 1-chlorobenzene and phenylboronic acid (yield: >95.8%).



# 1. INTRODUCTION

The past decade has witnessed an immense growth in the importance of microporous organic polymers (MOPs) with pore size smaller than 2 nm.<sup>1</sup> They have broad potential applications in the area of molecular storage, separation, delivery, or catalysis.<sup>1</sup> Such applications often rely on the presence of a large permanent surface area. In the past decades, there has been an intense international effort to produce the highly porous materials with large surface areas. However, it is recognized that there is a pressing requirement for porous materials containing functional groups to fulfill a certain task.<sup>2</sup> For example, the incorporation of some functional groups will play a major role in interacting more strongly with a certain compound than others in a mixture or a solution, resulting in excellent performance in the areas of ion exchange, purification, and absorption or separation. For catalysts, catalytically active centers or binding sites have to be incorporated in a porous, heterogeneous material.<sup>2a</sup>

MOPs include polymers of intrinsic microporosity (PIMs),<sup>3</sup> hypercrosslinked polymers (HCPs),<sup>4</sup> covalent organic frameworks (COFs),<sup>5</sup> or in the case where fully aromatic compositions are used, conjugated microporous polymers (CMPs).<sup>6</sup> Because most polymer skeletons do not incorporate any functional groups or active sites, functionalization of MOPs could open up second-generation porous materials with useful combined chemical and physical properties.<sup>1c,2</sup> Functional group containing MOPs combines a robust functional frame-work together with an open porous structure. The pores provide space for the transmission of molecules, thus promoting the performance of these materials. MOPs functionalized with amines, carboxylic acids, tetrazole, triazine rings, and hydroxyl groups exhibited excellent CO<sub>2</sub> adsorption/ separation due to the microporous structures and interaction between these polar groups and CO<sub>2</sub>.<sup>3,7</sup> Noble metals have been incorporated into MOPs containing functional units such as bipyridine, metalloporphyrin, and triazine ring, which displayed high catalytic activity for a host of reactions.<sup>8</sup> For example, a recent paper reported a porphyrin-derived MOP that shows high catalytic activity for the oxidation of thiols.<sup>8b</sup> The bipyridine-functionalized precursor networks were prepared and treated with (DBPP)<sub>2</sub>Ir-( $\mu$ -Cl)<sub>2</sub>-Ir(DBPP)<sub>2</sub>, which have been studied as heterogeneous catalysts for reductive amination reaction.<sup>1c</sup>

A tetrahedral MOP based on a tetraphenylmethane unit has been synthesized recently, which exhibits high surface area and excellent stability.<sup>9</sup> The high surface area can be attributed to the default diamondoid framework topology imposed by the tetrahedral monomer, which provides wide openings and interconnected pores to eliminate efficiently "dead space".<sup>10</sup> Subsequently, the central carbon in tetrahedral networks was replaced by other quadricovalent building centers such as adamantane, silicon, and germanium atoms.<sup>11</sup> In the present work, the quaternary phosphonium cation has been selected to be the center for the tetrahedral networks (Figure 1a). To the best of our knowledge, this is the first report on ionic microporous polymer prepared by homopolymerization. In comparison with other tetrahedral MOPs containing centers such as carbon, silicon, germanium, and adamantane, it

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Figure 1. (a) Structure of PP-Br polymer and (b) SEM image of microporous polymer.

possesses many unique properties, which has been applied in conducting materials,<sup>12a,b</sup> catalyst transfer agents,<sup>12c</sup> ionic liquids,<sup>12d</sup> and flame-proofing agents.<sup>12e</sup> Some of these properties could be easily controlled by varying the counterions. Also, the cationic centers could act as a catalyst in the reaction of  $CO_2$  with epoxides yielding cyclic carbonates. Quaternary phosphonium-containing polymers have been applied as ion exchange materials, which exhibited excellent stability and remarkable ion conductivity<sup>12a,b</sup> It also has potential applications as an ion absorbent due to its high surface area and ion exchange capacity (2.75 mmol/g) or as a scaffold to immobilize noble metal nanoparticles for heterogeneous reactions.

# 2. EXPERIMENTAL SECTION

**Materials.** 1-Bromo-4-chlorobenzene,  $Pd(OAc)_2$ , 1,5-cyclooctadiene,  $Ni(cod)_2$ , and 2,2'-bipyridyl were purchased from Aldrich and used as received. Anhydrous THF was distilled from its sodium naphthalenide solution under nitrogen. DMF was dried over CaH<sub>2</sub> and distilled under reduced pressure prior to use. Other chemicals were used as received.

**Tris**(*p*-chlorophenyl)phosphine. Tris(*p*-chlorophenyl)phosphine was prepared according to the previously reported method.<sup>12f</sup> Yield: 65%; mp: 102.0–102.5 °C. <sup>1</sup>H NMR (600 MHz; DMSO)  $\delta$ : 7.23–7.25 (6 H, t, *J* = 6.1 Hz), 7.48–7.50 (6 H, d, *J* = 12.0 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 135.6 (s), 134.8 (d, *J*<sub>C-P</sub> = 21 Hz), 133.3 (s, *J*<sub>C-P</sub> = 11 Hz), 129.0 (d, *J*<sub>C-P</sub> = 7.2 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>)  $\delta$ : -7.21. Anal. Calcd for C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P: C, 59.15; H, 3.21. Found: C, 59.17; H, 3.02. MS (M+H)<sup>+</sup> C<sub>18</sub>H<sub>12</sub>Cl<sub>3</sub>P: calculated, 364.9814; observed, 364.9818.

**Tetrakis(4-chlorophenyl)phosphonium bromide.** 1-Bromo-4-chlorobenzene (1.15 g, 6 mmol),  $Pd(OAc)_2$  (0.013 g, 1 mol %) and tris(*p*-chloropheny1)phosphine (2.19 g, 6 mmol) were mixed together under an inert atmosphere of argon in a dry 50 mL tube. To this mixture was added dry *o*-xylene (2 mL, 3 M) and a magnetic stir bar. The reaction mixture was heated to reflux for 5 h under argon. The phosphonium salts precipitated as the reaction proceeded. After 5 h, the tube was cooled to room temperature, 20 mL of diethyl ether was added, and the resulting suspension was stirred at room temperature for 2 min. The precipitate was filtered and washed with 50 mL of diethyl ether. Yield: 50%. mp: above degradation temperature. <sup>1</sup>H NMR (600 MHz; DMSO)  $\delta$ : 7.71–7.78 (8 H, q, J = 5.4 Hz), 7.84–7.88 (8 H, q, J = 16.8 Hz). <sup>13</sup>C NMR (100 MHz, DMSO)  $\delta$ : 115.4–116.3 (4 C, d, J = 89.6 Hz), 130.6 (8 C, d, J = 12.6 Hz), 136.6 (8 C, d, J = 10.2 Hz), 141.2 (4 C, d, J = 2.6 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ: 23.2. Anal. Calcd for C<sub>24</sub>H<sub>16</sub>Cl<sub>4</sub>PBr: C, 51.74; H, 2.89; Found: C, 51.67; H, 2.64. MS (M+H)<sup>+</sup> C<sub>24</sub>H<sub>16</sub>Cl<sub>4</sub>PBr: 557.0728, observed 557.0734.

**Synthesis of PP-Br.** The polymer networks are denoted as PP–X, where X represents the counterions. Ni $(cod)_2$  (2.25 g, 8.18 mmol) was added to a solution of 1,5-cyclooctadiene (1.05 mL, 8.32 mmol) and 2,2'-bipyridyl (1.28 g, 8.18 mmol) in anhydrous DMF (100 mL), and the mixture was heated to 80 °C for 30 min. To the resulting solution was added tetrakis(4-chlorophenyl)phosphonium bromide (0.874 g, 1.57 mmol) at 80 °C, and the mixture was stirred at that temperature for 10 h. After cooling to room temperature, concentrated HCl (5 M, 20 mL) was added to the solution. The solid obtained was filtered, and the residue was successively washed with DMF (5 × 30 mL), THF (5 × 30 mL), H<sub>2</sub>O (5 × 30 mL), and propan-2-one (5 × 30 mL). The polymer was then dried in a vacuum oven at 120 °C (Yield: 83%).

Gel fractions (GF = weight of insoluble dried sample/initial sample weight) were determined gravimetrically from samples. The GF content was estimated by weighing the insoluble portion obtained after Soxhlet extraction in tetrahydrofuran (THF) for 24 h.

**Reaction of 2-Phenoxymethyloxirane with CO<sub>2</sub>.** The PP-Br (0.042 g) was added to a solution of 2-phenoxymethyloxirane (1.5 g, 10 mmol) in DMF (10 mL), and the mixture was stirred at the given temperature under a slow stream (40 mL/min) of carbon dioxide gas. The catalyst was filtered, and the filtrate was analyzed by GC–MS.

**Preparation of PP–Pd<sup>0</sup>.** The PP-Br polymer (0.1 g) was soaked in aqueous  $H_2PdCl_4$  (20 mL, 5.0 mmol L<sup>-1</sup>) for 24 h to convert the Br<sup>-</sup> form into the  $PdCl_4^-$  form and finally washed thoroughly with water (200 mL) to remove any excess  $H_2PdCl_4$ . A 10-fold excess of aqueous NaBH<sub>4</sub> was added with vigorous stirring; then, the mixture was kept at RT for 12 h. The resultant PP–Pd<sup>0</sup> particles were collected by filtration, washed with water several times, and dried under vacuum at 80 °C for 12 h.

**Typical Procedure for the Suzuki Reaction.** Phenylboronic acid (1.2 mmol),  $K_2CO_3$  (2.5 mmol), Pd catalyst (1 mol %), aryl halide (1.0 mmol), and  $H_2O/EtOH$  (10 mL; 3:1 v/v) were added to a screw-capped vial with a side tube under argon. The mixture was stirred at 80 °C for 6 h and then

#### Scheme 1. Synthesis of Polymer Networks



cooled. The product was extracted from the reaction mixture with diethyl ether, and the organic phase was analyzed by GC–MS.

**lonic Exchange.** The PP-Br polymer (0.1 g) was converted to the PP-Cl or PP-F form by immersing the polymer in 1 M NaCl (20 mL) or NaF (20 mL) at 80 °C for 12 h, followed by immersion in deionized water for 24 h. This route was also applied for the preparation of ionic exchange membranes.<sup>13</sup>

## 3. RESULTS AND DISCUSSION

**Synthesis and Characterization.** We selected tetrakis(4chlorophenyl)phosphonium bromide as the building unit. The monomer was obtained through the reaction of tris(pchlorophenyl)phosphine and 1-bromo-4-chlorobenzene in the presence of Pd(OAc)<sub>2</sub> as catalyst, and the synthetic route was illustrated in Scheme 1. The yield of the reaction was 50%, and the proposed structure was confirmed by <sup>1</sup>H NMR (Figure S1 of the Supporting Information). The signals at 7.86 and 7.74 ppm were assigned to the hydrogen atom in ortho and meta position to quaternary phosphonium atom, respectively. The integration ratio of the two signals is very close to 1:1, as expected for the composition of tetrakis(4-chlorophenyl)phosphonium bromide. The <sup>13</sup>C NMR spectrum also verified the structure of tetrakis(4-chlorophenyl)phosphonium bromide (Figure S2 of the Supporting Information).

The polymer networks were synthesized by the nickel(0)catalyzed Yamamoto-type cross-coupling reaction. This reaction produced an off-white powdery compound, which had a low density (0.0546 cm<sup>3</sup> g<sup>-1</sup>) and was not soluble in any common organic solvents. PP-Br was characterized by FT-IR spectroscopy. The spectra clearly indicated the disappearance of the C–Cl stretching resonance around 763  $\text{cm}^{-1}$  (Figure S3 of the Supporting Information),<sup>14</sup> thus indicating the completion of the phenyl-phenyl coupling. To confirm further the structure of the polymeric networks, the polymer was characterized at the molecular level by solid-state <sup>31</sup>P NMR (Figure 2). Two signals at approximately 23 and -8.8 ppm were observed, corresponding to quaternary phosphonium and tertiary phosphine atoms, respectively. The resonance at -8.8ppm corresponds to the tertiary phosphine atoms, resulting from P-C-bond cleavage during Yamamoto polymerization. The integration ratio of signals (quaternary phosphonium to



Figure 2. Solid-state <sup>31</sup>P NMR spectrum of PP-Br polymer.

phosphine atoms) was close to 3:2. Figure S4 of the Supporting Information gives the assignment of each carbon in polymer networks. X-ray diffraction measurement of the material indicated an amorphous structure (Figure S5 of the Supporting Information), and scanning electron micrograph showed that PP-Br consisted of relatively uniform spheres with a diameter of 100–200 nm (Figure 1b). The gel fraction of PP-Br was examined by Soxhlet extraction in THF for 24 h. The weight loss of PP-Br was negligible after Soxhlet extraction, indicating that the gel fraction was 100%.

The polymer was also stable toward water, base (NaOH 10 M, 1 h), and acid, and indeed no change in surface area was observed even after the material was treated with 10 M HCl for 1 h. As shown in Figure S6 of the Supporting Information, PP-Br displayed 5% weight loss at temperature of 360 °C. The result reveals that it possesses a high thermal stability.

Micropore Size and Surface Area. The porosity parameters of the polymer were studied by sorption analysis using nitrogen as the sorbate molecule. Nitrogen adsorptiondesorption isotherms measured at 77 K are shown in Figure 3. The nitrogen isotherm for PP-Br exhibited a combination of type I and II nitrogen sorption isotherms according to the IUPAC classification.<sup>15</sup> Applying the Brunauer–Emmett– Teller (BET) model within the pressure range of  $P/P_0$  = 0.05 to 0.3 resulted in an apparent surface area of 650 m<sup>2</sup> g<sup>-1</sup>, which makes PP-Br the first microporous polymer based on an quaternary phosphonium salt. The high uptake at very low pressures indicates a high microporosity. With increasing pressure, the nitrogen uptake increases too. This indicates a high external surface area due to the presence of very small particles.<sup>16</sup> The isotherm shows a hysteresis extending to low relative pressure. The effect was interpreted as a result of swelling in polymer framework. A further hint in this interpretation is the high loss of volume of the sample, when it is dried after synthesis. The pore size distribution calculated by the Horvath-Kawazoe method indicated the presence of micropores with a mean width of  $\sim 0.7$  and 1.4 nm (Figure 3b). As the Br<sup>-</sup> anion is located inside the micropores, the surface area can be fine-tuned by changing the anion size. For example, their apparent BET specific surface areas increased from 650 to 750 and 980 m<sup>2</sup> g<sup>-1</sup>, respectively, as the Br<sup>-</sup> anion was changed to Cl<sup>-</sup> or F<sup>-</sup> by ionic exchange due to the decreasing ionic radius of Cl<sup>-</sup> and F<sup>-</sup>. The amount of counterions was measured by elemental analysis (Table S1 of the Supporting Information), indicating that the Br<sup>-</sup> was completely replaced by other counterions. In general, the surface area can only be controlled on varying the monomer structure.<sup>17</sup> We have thus developed a novel approach for the variation of surface area that is more facile than the traditional methods.

**Catalytic Performances.** Microporous polymers used in heterogeneous catalysis systems usually contain various noble metal complexes.<sup>1c,8a,18,19</sup> However, microporous polymers rarely possess intrinsic catalytic activity due to lack of active sites.<sup>20</sup> It is well known that the addition reaction of oxiranes

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**Figure 3.** (a) Nitrogen adsorption—desorption isotherms measured at 77 K (the adsorption and desorption branches are labeled with solid and open symbols, respectively) and (b) pore size distribution of the polymer with different anions.

Table 1. PP-Br Catalyzed Conversion of 2-(Phenoxymethyl)oxirane to Cyclic Carbonate in the Presence of CO<sub>2</sub> at 1 atm

		+ co <sub>2</sub> PP	<u> </u>	
entry	catalyst amount (%)	temperature (°C)	time (h)	yield $(\%)^a$
1	1	90	30	29.5
2	2	90	30	41.3
3	3	90	30	46.2
4	4	90	30	50.0
5	2	90	70	80.4
6	2	100	50	75.3
7	2	110	40	78.7
8	2	120	24	76.9
9	2	130	19	84.2
10	2	140	20	98.5
<sup><i>a</i></sup> Yield was dete	ermined by GC analysis (internal standard	: dodecane).		

with CO<sub>2</sub> catalyzed by quaternary phosphonium salts gives the corresponding cyclic carbonates in high yield.<sup>21</sup> Recently, polymeric nanoparticles supported by phosphonium salt were prepared and applied as catalysts for cycloaddition of CO<sub>2</sub> to epoxides.<sup>21d</sup> An 83.7% yield for the cycloaddition reaction of CO<sub>2</sub> to styrene oxide was achieved when the reaction was conducted at 160 °C and 3 MPa for 48 h. The reaction mechanism was reported by Nishikubo and coworkers.<sup>21c</sup> In this work, the PP-Br polymer was applied as a catalyst in the conversion of CO<sub>2</sub> to cyclic carbonates via reaction with epoxides. Table 1 summarizes the catalytic activity of PP-Br in the formation of cyclic carbonate from the reaction between 2-(phenoxymethyl) oxirane and  $CO_2$  in DMF at 1 atm. The yield of 4-(phenoxymethyl)-1,3-dioxolan-2-one increased gradually with reaction time, temperature, and catalyst concentration, and a yield of 98% was obtained at 140 °C after 20 h. According to entries 1-10, it can be concluded that the reaction temperature seems to be a relatively more critical factor than others. Under these reaction conditions, no cyclic carbonate was formed in the absence of PP-Br. Compared with the polymeric nanoparticles system, the high yield (98% within 24 h) of PP-Br system resulted from the large surface area and porosity.<sup>21d</sup>

These studies demonstrate that PP-Br was active only during the reaction and that the reaction proceeded on the heterogeneous surface. The recovered PP-Br showed nearly the same reactivity as the original (Table 2).

Table 2. Activity and Recycling of the PP-Br Catalyst in the Reaction between 2-(Phenoxymethyl) oxirane and  $CO_2^a$ 

run	yield (%)
1	98.5
2	94.6
3	93.5
4	91.8
5	92.7

<sup>*a*</sup>Reaction was carried out with 2 mol % PP-Br at 140 °C for 20 h. The yield was determined by GC analysis (internal standard: dodecane).

Much interest has been directed toward noble-metal nanoparticles captured in microporous materials for use in heterogeneous catalytic systems.<sup>22</sup> Budd and McKeown have reported that microporous polymers act as scaffolds for incorporating various metal nanoparticles such as Cu, Zn, Pd, and Co.<sup>22d-f</sup> For modification with noble metals, several methods have been developed, such as chemical vapor deposition,<sup>23</sup> ionic exchange,<sup>24</sup> in situ generation,<sup>25</sup> and so on. In the present work, PP-Br has been used as a scaffold for



(b)



Figure 4. (a) Schematic diagram of Pd<sup>0</sup> nanoparticles immobilization inside PP-Br. TEM images of PP-Br (b) and PP-Pd<sup>0</sup> (c).



Figure 5. (a) Nitrogen adsorption-desorption isotherms of PP-Pd measured at 77 K. (b) Pore size distribution of PP-Pd.

immobilizing palladium nanoparticles by ionic exchange. As shown in Figure 4, tetrachloropalladate  $(PdCl_4^{2-})$  was exchanged with bromide ion, followed by NaBH<sub>4</sub> reduction to obtain black PP–Pd<sup>0</sup>. Inductively coupled plasma (ICP) analysis confirmed the loading of Pd on polymer networks to be 0.96 mmol g<sup>-1</sup>; that is, the Pd/P molar ratio was found to be 1:2.2. The nitrogen-adsorption isotherms of PP-Pd<sup>0</sup> were collected at 77 K, and the results are shown in Figure 5. The

effect of the Pd on the surface area and pore size distribution was investigated. As expected, the BET surface area decreases from 650 m<sup>2</sup> g<sup>-1</sup> (PP-Br) to 114 m<sup>2</sup> g<sup>-1</sup> (PP-Pd). The decrease in specific surface area can be ascribed both to partial pore filling and to simple increase in mass. Also, no significant change in the pore size was observed and the density of micropores decreases before and after the loading of Pd (Figure Sb), which is similar to other works.<sup>18a</sup> Because the Pd<sup>0</sup> was

Table 3. PP–Pd <sup>0</sup> -Catalyzed Suzuki Cross-Co	upling Reactions of Ary	yl Halides with Phenylboronic Acid <sup>a</sup>
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	Y	Y-	
entry	Х	Y	yield (%)
1	Br	СНО	97.4
2	Br	COCH <sub>3</sub>	98.2
3	Br	Н	96.8
4	Br	Me	97.9
5	Br	OMe	96.5
6	Ι	Н	99.8
7	Cl	Н	95.8
8	F	Н	87.2

<sup>a</sup>Solution of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), Pd<sup>0</sup> (0.01 mmol), and  $K_2CO_3$  (2.5 mmol) in  $H_2O/EtOH$  (10 mL; 3:1 v/v) was heated at 80 °C under  $N_2$  for 6 h. The yield was determined by GC analysis (internal standard: dodecane).

immobilized in polymeric networks by ionic exchange, it is reasonable to assume that this synthesis route can be applied for loading other classes of transition-metal nanoparticles (e.g., Au, Rh, Ru, and Ir). X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of Pd<sup>0</sup> nanoparticles within polymer networks (Figure S7 of the Supporting Information). The diffractogram of PP-Pd<sup>0</sup> (Figure S5 of the Supporting Information) showed a signal at  $2\theta = 39.0^{\circ}$  confirming the presence of Pd (1 1 1). The Pd (1 1 1) facets are generally acknowledged to be the best surface for catalytic usage.<sup>2</sup> Transmission electron microscopy (TEM) images were obtained to check the morphology and measure the particle size of Pd<sup>0</sup> nanoparticles. The results presented in Figure 4c show that the Pd<sup>0</sup> particles are uniformly dispersed in the polymer networks, and the average particle size was found to be 2.5 nm. No free Pd<sup>0</sup> aggregates were observed in the PP-Pd<sup>0</sup> even when the weight ratio of Pd to the polymeric scaffold was increased to as high as 10%.

We carried out Suzuki cross-coupling reactions as a model reaction to evaluate the catalytic ability and recyclability of the PP-Pd<sup>0</sup> catalyst. Because of environmental, economic, and safety concerns, the Suzuki reactions were performed in water.<sup>26</sup> A suitable amount of EtOH was used as a cosolvent to increase the solubility of the substrates. The cross-coupling reactions were carried out with 1 mol % Pd catalyst in  $H_2O/$ EtOH (3:1 v/v) at 80 °C. After the reaction was complete, the mass was extracted with diethyl ether (10 mL), and the yield of the product was determined by performing GC-MS analysis of the diethyl ether phase with dodecane as the internal standard. Table 3 shows the catalytic activity of PP-Pd<sup>0</sup> for the Suzuki-Miyaura reaction with a range of aryl halides and phenylboronic acid. The reactions proceeded efficiently and gave the desired product in >95% conversion with aryl bromides or aryl chlorides after 6 h. In general, relatively lower yields have been reported for electron-rich aryl bromides. For example, Kato and coworkers have recently shown that palladium nanoparticles captured in polymeric networks gave an 82% conversion yield for the reaction between 1-bromo-4-methoxybenzene and phenylboronic acid.<sup>22a</sup> Using both electron-rich and electrondeficient aryl bromides with the PP-Pd<sup>0</sup> system, the desired coupling products were obtained in high yield (>95%). More importantly, a high yield of 95.8% for the reaction between chlorobenzene and phenylboronic acid was obtained, which is much higher than the 36% yield reported by our group with another catalytic system.<sup>27</sup> It is well known that catalytic C-C cross-coupling reactions of fluoroderivatives are rare because of the strong C–F bond.<sup>28</sup> We obtained a yield of 87% in the reaction between fluorobenzene and phenylboronic acid using this PP–Pd<sup>0</sup> catalyst. For comparison, the coupling of 1-fluoro-4-methylbenzene with phenyl boronic acid was conducted in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, and no product was obtained.

We have also examined the recyclability and reusability of the  $PP-Pd^0$  catalyst. The catalyst was recycled in the reaction between 4-bromobenzaldehyde and phenylboronic acid, and the catalytic activity of the preformed  $PP-Pd^0$  catalyst proved to be almost constant with the initial yield of 97.4%, decreasing to 93% after five runs (Table 4). The catalyst was separated

Table 4. Activity and Recycling of the PP-Pd <sup>0</sup> Catalyst in
the Suzuki Coupling of 4-Bromobenzaldehyde and
Phenylboronic Acid <sup>a</sup>

run	yield (%)
1	97.4
2	97.6
3	96.5
4	96.4
5	95.2

<sup>a</sup>Solution of 4-bromobenzaldehyde (1.0 mmol), phenylboronic acid (1.2 mmol), Pd<sup>0</sup> (0.01 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.5 mmol) in H<sub>2</sub>O/EtOH (10 mL; 3:1 v/v) was heated to 80 °C under N<sub>2</sub> for 6 h. The yield was determined by GC analysis (internal standard: dodecane).

from the solution by a simple filtration, and the resultant filtrate was tested for palladium by ICP–MS. The result showed that  $\sim$ 17 ppb of palladium leached into the solution, which corresponds to an original metal loss of 0.00256% and was thus found to be one hundred times lower than the corresponding value (0.27%) reported for Kato's system.<sup>22a</sup> Therefore, PP–Pd<sup>0</sup> was demonstrated to be a durable catalyst.

A possible explanation for the superior catalytic performance of  $PP-Pd^0$  can be due to the structural features of the composite system. The  $PP-Pd^0$  polymer can draw the reactants into its pore channels by capillary condensation of the micropores, where the catalyst particles are located. The concentration of reagents around the Pd nanoparticles is relatively higher than that in the bulk solution.

The micropores within the PP–Pd<sup>0</sup> polymer can be considered to act as nanoreactors, where they pose a space confinement effect on the reactants, leading to a high catalytic activity.<sup>22c</sup> Furthermore, the highly polar ionic environment allows the electrostatic stabilization of preformed nanoparticles (as for  $Bu_4N^+$  ions in tetrabutylammonium bromide<sup>29</sup>) and

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could endow  $Pd^0$  with its high activity in the Suzuki crosscoupling reactions. The  $Pd^0$  nanoparticles inside the networks are very small, which can be another reason for the high activity of the catalyst.

# 4. CONCLUSIONS

A guaternary phosphonium and tertiary phosphorus functionalized microporous polymer was prepared by Yamamoto coupling reaction. The content ratio of quaternary phosphonium to phosphine atoms was close to 3:2, determined by <sup>31</sup>P solid-state NMR. It was also stable toward water, base (1 M NaOH, 24 h), and acid (1 M HCl, 24 h). The polymeric networks display high surface area, and the surface area can be tuned by changing the counteranions. Their apparent BET specific surface areas increased from 650 to 750 and 980  $m^2 g^{-1}$ respectively, as the Br<sup>-</sup> anion was changed to Cl<sup>-</sup> or F<sup>-</sup> by ionic exchange, due to the decreasing ionic radius of Cl<sup>-</sup> and F<sup>-</sup>. It displays high intrinsic catalytic activity for the reaction between epoxide and CO2. An 98% yield of the reaction between epoxide and CO<sub>2</sub> was obtained at 140 °C and 1 atom for 20 h. Pd nanoparticles supported on PP were also prepared, which are uniformly dispersed in the polymeric networks and exhibit high catalytic activity for Suzuki reactions. The coupling reactions between aryl chlorides and phenylboronic acid gave the desired product in >95% conversion in the presence of PP-Pd. More importantly, a yield of 87% was obtained when fluorobenzene was used as reactant. In general, catalytic C-C cross-coupling reactions of fluoroderivatives are rare.

# ASSOCIATED CONTENT

#### **S** Supporting Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra, TGA curves, IR, XPS, and WAXD spectra for polymers and monomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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