

Article

# Palladium Comprising Dicationic Bipyridinium Supported Periodic Mesoporous Organosilica (PMO): Pd@Bipy-PMO as an Efficient Hybrid Catalyst for Suzuki–Miyaura Cross-Coupling Reaction in Water

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**Abstract:** In this study, we developed a novel catalysts consisting of periodic mesoporous organosilica functionalized with bipyridinium ionic liquid supported palladium. The physiochemical properties of the hybrid catalyst were investigated using Fourier transform infrared spectroscopy, small angle X-ray powder diffraction, field emission scanning electron microscope, transmission electron microscope, nitrogen adsorption–desorption analyses, and atomic absorption spectroscopy. The stabilized Pd species inside the mesochannels provided good catalytic efficiency for the Suzuki–Miyaura coupling reactions in water. The activity of the designed catalysts retained for several consecutive recycle runs. The stability, recoverability, and reusability of the designed heterogeneous catalyst were also studied under various reaction conditions.

**Keywords:** ionic liquid; heterogeneous catalyst; hybrid materials; mesoporous silica; Suzuki–Miyaura reaction

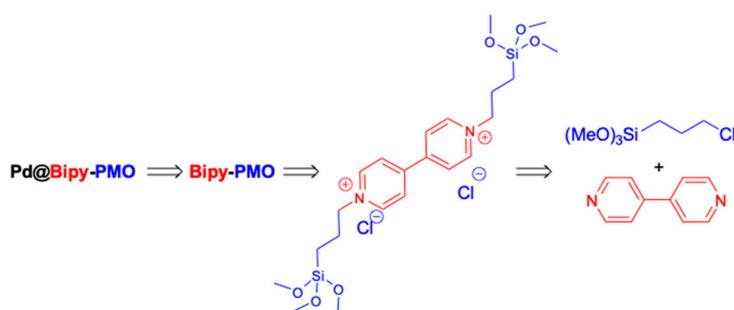
## 1. Introduction

The widespread applications of carbon–carbon bond forming reactions in synthesis of intermediate compounds, pharmaceuticals, and biologically and naturally produced products demonstrate the importance of this transformation for academia and industries [1–3]. The frequently utilized Suzuki–Miyaura, Heck, Sonogashira, Negishi, Kumada, and Stille cross-coupling reactions have become powerful procedures in organic chemistry [4–7]. Although, various transition metals have been utilized to catalyze the aforementioned cross-coupling reactions, palladium based–catalysts have been applied more extensively due to their good catalytic activities and selectivity [8]. Among these transformations, Suzuki–Miyaura reaction is one of the most effective cross-coupling yielding sp<sup>2</sup>–sp<sup>2</sup> carbon–carbon bond formation [9]. Suzuki–Miyaura reactions are traditionally achieved in homogeneous systems under basic conditions at high reaction temperatures. In addition, the homogeneous Pd catalysts generally need to be stabilized by costly phosphorus- or *N*-heterocyclic carbene-based ligands [10]. The Pd–black as a non-active particle is also predicated in these systems, contaminating the reaction medium and product [11]. Furthermore, the recovery and reuse of the

homogeneous catalysts is always challenging [12–14]. Alternatively, the heterogeneous catalysts have the advantages of easy separation and recycling after the completion of the reactions [15–17]. Exploiting the merits of a heterogeneous system, the feature of the Suzuki reaction generally appears in organic–mineral hybrid supports for Pd stabilization and recycling.

Recently, hybrid materials or organic–inorganic solid supports have attracted attention in catalysis and chemical engineering processes. One of the reasons for their fast development is the difficulties resolving for mass transfer of substrates onto the solid catalysts active sites in molecular scale and also adjusting lipophilicity of the supports [18].

After the report of periodic mesoporous organosilica structures (PMOs) as new class of hybrid mesoporous organosilica materials, a wide range of precursors have been used to synthesize new mesoporous structures [19,20]. It is noteworthy that due to the particular properties and importance of the ionic liquids (ILs), their combination with PMOs produces fabulous hybrid catalysts [21,22]. Herein, we first designed and synthesized a new ionic liquid bipyridinium linker (1,1'-Bis[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium chloride), which was used as a novel bridge for the preparation of dimeric IL-based bipyridinium skeleton PMO (Scheme 1). Then, we applied the Bipy-PMO as a support for immobilization of the Pd species envisioning its high catalytic activity for Suzuki reaction in water. The yield and selectivity of the corresponding delivered cross-coupling products were also found to be excellent.

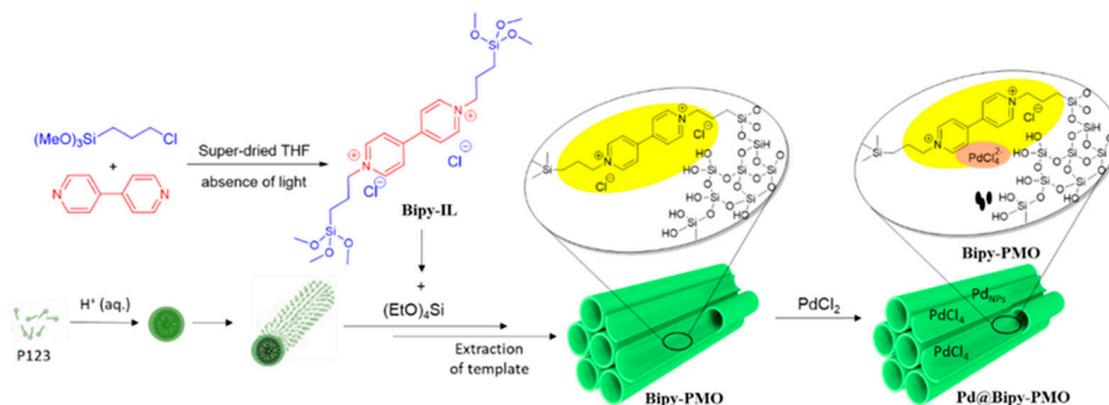


**Scheme 1.** Step-wise schematic procedure for the synthesis of Pd@Bipy-PMO (periodic mesoporous organosilica structure).

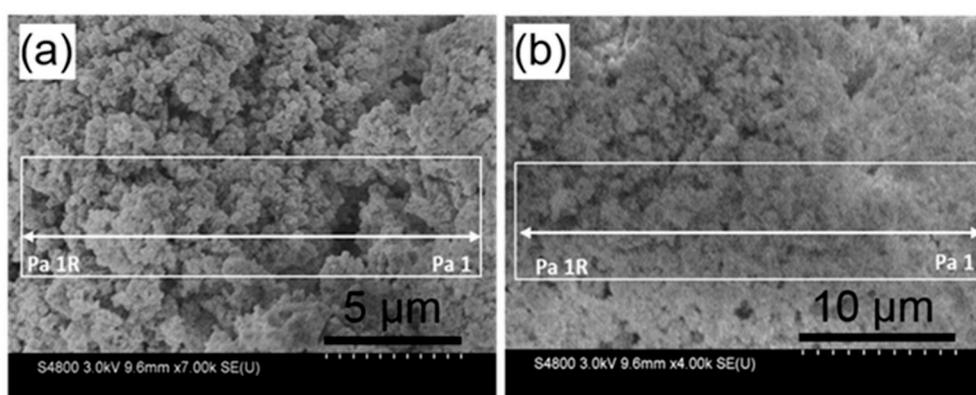
## 2. Results and Discussion

Synthesis of the palladium containing ionic liquid-based periodic mesoporous organosilica, Pd@Bipy-PMO catalyst, was prepared by hydrolysis and co-condensation of as-synthesized 1,1'-Bis[3-(trimethoxysilyl)propyl]-4,4'-bipyridinium chloride and TEOS in the presence of Pluronic P123 as a soft-template under acidic condition based on our previous PMO synthetic methods [23–25]. The dicationic bipyridinium IL-based bridge, which was used for the fabrication of PMO exhibits a better lipophilicity than pure silica phases synthesized under the same conditions. The Bipy-PMO was incorporated to immobilizing Pd ions inside the pore walls of Bipy-PMO to produce Pd@Bipy-PMO (Scheme 2). The Pd@Bipy-PMO material was applied as the catalyst to expedite Suzuki–Miyaura cross-coupling reaction which was even active in water green media.

The field emission scanning electron microscopy (FESEM) image clearly shows the surface morphology of the Bipy-PMO and Pd@Bipy-PMO (periodic mesoporous organosilica structure) hybrid catalysts. As seen in Figure 1a,b, pure PMO and Pd-PMO presented a cabbage-like smooth morphology. These were observed in the form of agglomerates formed through the stacking of porous SiO<sub>2</sub>. The incorporation of ionic liquids (ILs) onto Bipy-PMO structure, related to rod-like SBA-15 morphology, resulted in assembles of materials formed by polar bipyridinium IL distributed over the entire surface of the silicate skeletons.



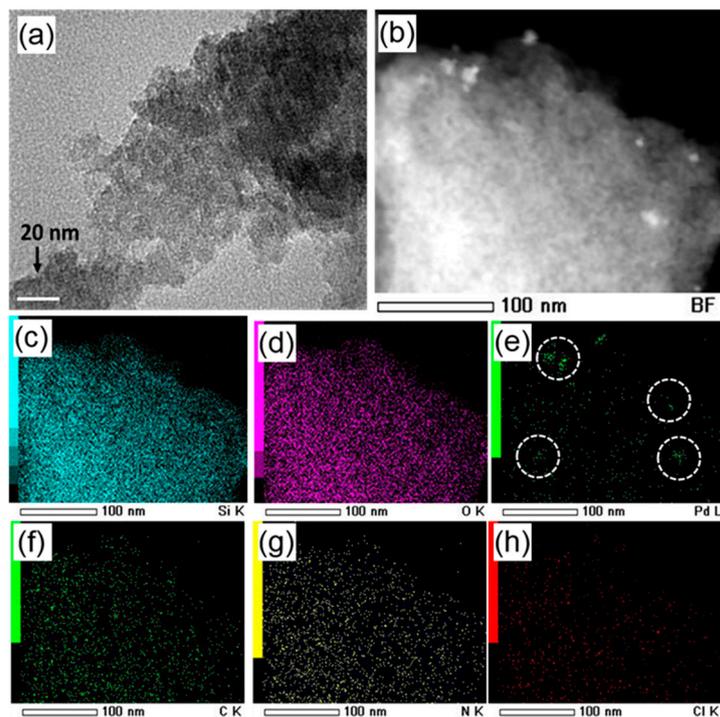
**Scheme 2.** Procedure for the preparation of the Pd@Bipy-PMO hybrid catalyst.



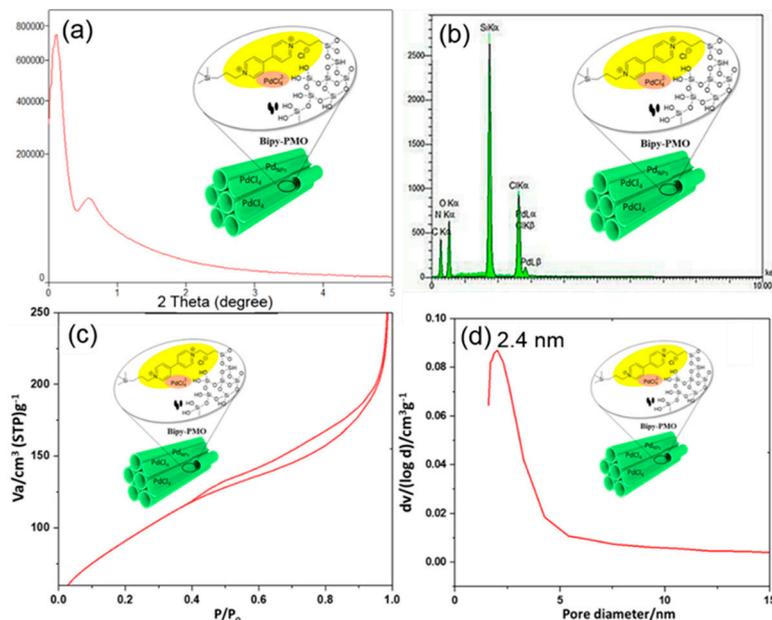
**Figure 1.** Field emission scanning electron microscopy (FESEM) images of (a) Bipy-PMO, and (b) Pd@Bipy-PMO.

Figure 2 shows the transmission electron microscopy (TEM) images obtained at high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) for Pd@Bipy-PMO, clarifying the presence of Pd nanoparticles within the PMO pores. TEM-elemental mapping images of the Pd@Bipy-PMO were clearly revealed the successful incorporation of the Si, O, C, N, Cl, and Pd species over the Bipy-PMO support (Figure 2).

Small angle X-ray diffraction (SAXRD) pattern of Pd@Bipy-PMO shows one sharp peak at  $2\theta = 0.34^\circ$  which originates from the periodicity of the mesoporous structure (Figure 3a). The existence of the related elements including Si, O, N, C, Cl, and Pd was verified by energy-dispersive X-ray spectroscopy (EDX, Figure 3b). The nitrogen adsorption-desorption isotherms (BET) of the Pd@Bipy-PMO was also performed to investigate their textural properties and pore size regularity (Figure 3c,d). BET illustrates the same type IV nitrogen adsorption-desorption isotherm with an H1 hysteresis loop for mesoporous materials according to IUPAC classification. Moreover, the Barrett-Joyner-Halenda (BJH) pore size distribution isotherms showed a singlet sharp peak for materials. The pore-size distribution has its maximum at 2.4 nm, as shown in Figure 3d.

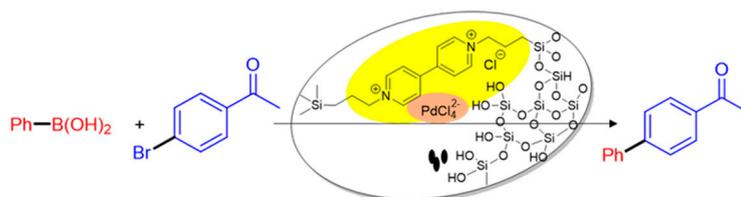


**Figure 2.** Pd@Bipy-PMO: (a) TEM, (b) high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and (c–h) energy-dispersive X-ray spectroscopy (EDX)-mapping images.



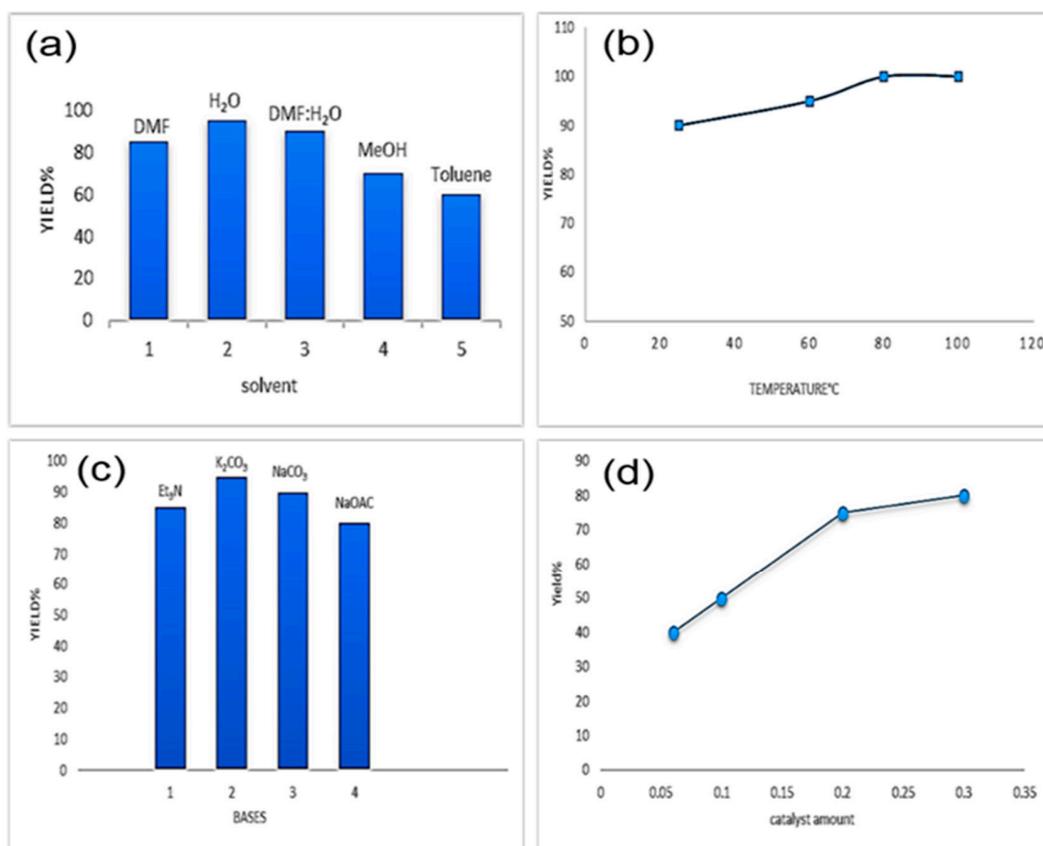
**Figure 3.** Pd@Bipy-PMO: (a) small angle X-ray diffraction (SAXRD) pattern, (b) EDX spectrum, and (c) nitrogen adsorption-desorption isotherms (BET) surface area and (d) Barrett-Joyner-Halenda (BJH) absorption.

The catalytic activity of the Pd@Bipy-PMO catalyst was investigated in the Suzuki–Miyaura cross-coupling reaction. To optimize the overall process, the reaction of 4-bromoacetophenone with phenylboronic acid was chosen as a model reaction (Scheme 3). The all effective parameters including solvent, temperature, catalyst amount, and base effect were studied, optimizing the reactions conditions.



**Scheme 3.** Model reaction for Suzuki–Miyaura coupling reaction.

Among several available solvents for the Suzuki coupling, we chose water as the green and optimum solvent for this study. The designed heterogeneous catalyst produced the coupled biaryl product typically in 98% yield (Figure 4a). Reaction set-up for bromo-substrate (1 mmol) and phenylboronic acid (1.2 eq.) in a model reaction was adjusted using  $K_2CO_3$  (2 eq.), and Pd-catalyst (0.2 mol%) in water (5 mL) for 4 h. To study the effect of the reaction conditions and figure out the temperature and reaction time interrelation, the reaction under the identical conditions were screened to achieve the acceptable product yields. Increasing the temperature to 80 °C improved the yield of the biaryl product to quantitative yield (Figure 4b). Although at a higher temperature, the reaction time becomes shorter to acquire the product, the catalyst nature may be changed. In addition, achieving the chemical processes in lower temperatures provides green and environmentally benign protocols. We also investigated the effect of bases on the proceeding model reaction. As can see in Figure 4c, among the various bases examined in water,  $K_2CO_3$  provided the highest yield in 4 h. The effect of the catalyst amount was found to be crucial on the progress of the Suzuki cross-coupling reaction. Therefore, we investigated this parameter and the results are represented in Figure 4d.



**Figure 4.** Cross-coupling of 4-bromoacetophenone and phenylboronic acid substrate as a model reaction of Suzuki–Miyaura reaction: (a) solvent effect (in DMF:H<sub>2</sub>O the ratio is 1:1), (b) effect of temperature, (c) effect of base, and (d) effect of the catalyst amount.

After optimizing the reaction conditions (water as solvent,  $K_2CO_3$  as the base,  $80\text{ }^\circ\text{C}$ ), we next examined the efficiency of the designed Pd catalyst in the cross-coupling reactions of various iodo- and bromo-aryl derivatives and different boronic acids (Table 1). All aryl iodines with boronic acid derivatives gave excellent yields in a short reaction time. There was no significant difference in the yield of products between electron deficient and electron-rich aryl iodines (Table 1, entries 9–13). Furthermore, to extend the scope and generality of this method the coupling of aryl bromides was also investigated. The results also indicated that the electron-deficient aryl bromides showed high reactivity with boronic acids (Table 1, entries 5–8).

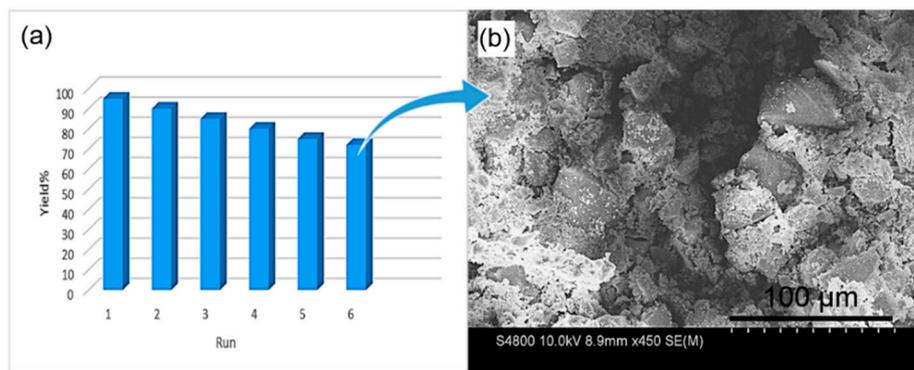
**Table 1.** Suzuki cross-coupling reactions of various aryl halides and boronic acid substrates catalyzed by Pd@Bipy-PMO<sup>1</sup>.

[Pd] = Pd@Bipy-PMO-IL

Entry	Halide	R <sup>1</sup>	R <sup>2</sup>	Time (h)	Yield (%) <sup>2</sup>
1	Br	H	H	4	98
2	Br	4-t-Bu	H	4	98
3	Br	H	4-Me	3	95
4	Br	H	4-OMe	3	90
5	Br	H	2-NO <sub>2</sub>	4	93
6	Br	H	4-COMe	4	98
7	Br	3-Me	4-COMe	4	95
8	Br	H	3-NO <sub>2</sub>	4	96
9	Br	H	2-CHO	4	83
10	Br	3-Me	2-CHO	4	86
11	I	H	H	0.5	quant.
12	I	H	4-COMe	0.5	quant.
13	I	4-t-Bu	H	1.5	96
14	I	H	2-OMe	2	97
15	I	3-Me	2-OMe	1	96
16	I	3-Me	2-NH <sub>2</sub>	1	91
17	Cl	H	4-COMe	6	18 <sup>3</sup>
18	Cl	H	4-Me	6	12 <sup>3</sup>
19	Cl	H	4-COMe	12	34 <sup>3</sup>
20	Cl	H	2- <i>i</i> -Pr	6	8 <sup>3</sup>
21	Cl	3-Me	2- <i>i</i> -Pr	6	6 <sup>3</sup>
22	I	H	2-t-Bu	6	12
23	F	H	4-COMe	72	trace

<sup>1</sup> Reaction conditions: aryl halide (1 mmol), boronic acid (1.2 eq.), 0.2 mol % of Pd, and  $K_2CO_3$  (2 eq.) at  $80\text{ }^\circ\text{C}$  in 5 mL  $H_2O$ . <sup>2</sup> Isolated yields. <sup>3</sup> Contain 0.5 mmol TBAB.

In the next step, we tested the recyclability of Pd@Bipy-PMO catalyst in the model reaction of Suzuki–Miyaura cross-coupling reaction in Figure 5. The reusability of the catalysts is very important from the industrial point of view [26–33]. The heterogeneous catalyst preserved 6 recycle runs. After the 6th run Pd leaching was detected by the Hot Filtration Test (HFT). FESEM image of the recovered Pd@Bipy-PMO catalyst after the last reaction cycle shows that the catalyst stayed intact after the reuse (Figure 5b).



**Figure 5.** (a) Recyclability study of Pd@Bipy-PMO catalyst in Suzuki reaction, and (b) the corresponding FESEM image after 6th run.

### 3. Experimental

#### 3.1. Synthesis of Bridged Bipyridinium Chloride Ionic Liquid

The bipyridinium chloride-based ionic liquid was synthesized according to the procedure in literature with slight modifications [23]. In a typical synthesis, 4,4'-bipyridin (3.2 mmol, Maragheh, Iran) and 3-chloropropyl-trimethoxysilane CPTMS (10 mmol, Maragheh, Iran) were added to a well-dried flask containing super-dry tetrahydrofuran (10 mL, Maragheh, Iran) and stirred under the reflux conditions in the absence of light for 24 h under a pure nitrogen atmosphere. The obtained viscous yellow ILs product was washed with pure *n*-hexane several times and dried in vacuum, leading to the bipyridinium bridge.

#### 3.2. Synthesis of Bipy-PMO

Bipy-PMO-IL was synthesized by a modification of our previous procedure in PMO synthesis [24–26]. Pluronic P123 (4 g, Maragheh, Iran) was added in HCl (2 M, 150 mL, Maragheh, Iran) and fully stirred for 24 h at 40 °C in a beaker. In another reaction vial, 1,1'-Bis[3-(trimethoxysilyl) propyl]-4,4'-bipyridinium chloride ionic liquid (IL, 3 mmol) and tetraethyl orthosilicate (TEOS, 9 mmol) were mixed and then added to the P123 mixture and stirred for 24 h at 40 °C. The formed white gel was transferred to a stainless steel autoclave and kept at 100 °C in an oven. Finally, the mixture was purified using a Soxhlet extractor with 200 mL of ethanol and 0.5 mL of HCl to remove the Bipy-PMOs surfactant producing the porous PMO after ~40 h.

#### 3.3. Synthesis of Pd@Bipy-PMO

Na<sub>2</sub>PdCl<sub>4</sub> (0.015 g, Tehran, Iran) was added to a well-dispersed suspension of periodic mesoporous organosilica based on bipyridinium ionic liquid (Bipy-PMO, 1 g) in MeOH (14.5 mL, Maragheh, Iran). The mixture was stirred for 5 h at room temperature and then at 60 °C for 0.5 h. After cooling the reaction solution to room temperature, the resulting mixture was washed thrice with MeOH and dried at 60 °C in a vacuum oven. A 1.2% Pd content (w/w) was determined for this material by atomic absorption spectrometry (AAS).

#### 3.4. Heterogeneous Suzuki–Miyaura cross-coupling reaction

General procedure for the Suzuki coupling reaction by using Pd@Bipy-PMO as the catalyst is as follows. The Suzuki reactions were performed by using aryl boronic acid (1.2 eq.), aryl halide (1 eq.), K<sub>2</sub>CO<sub>3</sub> (2 eq.), and the hybrid catalyst (0.2 mol %) at 80 °C in 5 mL H<sub>2</sub>O. The reaction progress was monitored by gas chromatography. After the reaction completion, the mixture was allowed to cool down to room temperature and was then filtered and washed with water and diethyl acetate.

### 3.5. NMR Data for Selected Compounds

**Biphenyl:** White solid, mp: 71–72 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.62–7.65 (m, 4 H), 7.46–7.50 (m, 4 H), 7.38–7.40 (m, 2 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 141.25, 128.77, 127.27, 127.19.

**1-Biphenyl-4-yl-ethanone:** White solid, mp: 121–123 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.03–8.06 (m, 2 H), 7.63–7.78 (m, 4 H), 7.41–7.50 (m, 3 H), 2.65 (s, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 197.83, 145.80, 139.87, 135.85, 128.95, 128.92, 128.23, 127.27, 127.23, 26.65.

**4-Methoxybiphenyl:** White solid, mp: 89–91 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.57–7.61 (m, 4 H), 7.44–7.48 (m, 2 H), 7.32–7.37 (m, 1 H), 7.01–7.04 (m, 2 H), 3.88 (s, 3 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 159.19, 140.86, 133.80, 128.75, 128.18, 126.76, 126.69, 114.24, 55.35.

**2-Methoxybiphenyl:** Colorless viscous liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.62 (m, 2 H), 7.50 (m, 2 H), 7.41–7.43 (m, 3 H), 7.05–7.14 (m, 2 H), 3.88 (s, 3 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 156.54, 138.63, 130.96, 130.79, 129.63, 128.83, 128.05, 126.98, 120.91, 111.31, 55.59.

**3-Methyl-2'-methoxy-biphenyl:** Colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.00–7.36 (m, 8 H), 3.84 (s, 3 H), 2.44 (s, 3 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 156.46, 139.50, 138.49, 137.52, 130.91, 130.24, 128.52, 127.87, 127.73, 126.68, 120.76, 111.13, 55.54, 21.57.

## 4. Conclusions

We have developed a protocol for the preparation of novel palladium-supported periodic mesoporous organosilica based on bipyridinium ionic liquid (Pd@Bipy-PMO) and studied its catalytic efficiency in the Suzuki–Miyaura coupling reaction. We have demonstrated an active palladium catalyst immobilized onto the dimeric ionic liquid scaffold hybrid PMO. The Pd@Bipy-PMO catalyst having structural porosity and high excellent catalytic efficiency was used as a powerful catalyst to expedite the Suzuki–Miyaura coupling of aryl halides in water. The catalyst was successfully recovered and reused for 6 cycles with stable activity.

**Author Contributions:** Conceptualization, S.R. and A.A.; methodology, A.A.; software, P.P.; formal analysis, M.S, Z.A and Q.K.; writing—original draft preparation, A.A.; writing—review and editing, L.D.W.; supervision, S.R.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Phan, M.T.; Sluys, M.V.D.; Jones, C.W. On the nature of the active species in palladium catalyzed Mizoroki–Heck and Suzuki–Miyaura couplings—Homogeneous or heterogeneous catalysis, a critical review. *Adv. Synth. Catal.* **2006**, *348*, 609–679. [[CrossRef](#)]
2. Rostamnia, S.; Kholdi, S. Synthesis of hybrid interfacial silica-based nanospheres composite as a support for ultra-small palladium nanoparticle and application of Pd<sub>NPs</sub>/HSN in Mizoroki–Heck reaction. *J. Phys. Chem. Solids* **2017**, *111*, 47–53. [[CrossRef](#)]
3. Rostamnia, S.; Doustkhah, E.; Golchin Hossieni, H.; Luque, R. Covalently bonded PIDA on SBA-15 as robust Pd support: Water tolerant designed catalysts for aqueous Suzuki couplings. *ChemistrySelect* **2017**, *2*, 329–334.
4. Rostamnia, S.; Rahmani, T. Ordered mesoporous SBA-15/PrSO<sub>3</sub>Pd and SBA-15/PrSO<sub>3</sub>Pd<sub>NP</sub> as active, reusable and selective phosphine-free catalysts in C–X activation Heck coupling process. *Appl. Organomet. Chem.* **2015**, *29*, 471–474. [[CrossRef](#)]
5. Piao, Y.; Jang, Y.; Shokouhimehr, M.; Lee, I.S.; Hyeon, T. Facile aqueous-phase synthesis of uniform palladium nanoparticles of various shapes and sizes. *Small* **2007**, *3*, 255–260. [[CrossRef](#)] [[PubMed](#)]
6. Sydnes, M.O. The Use of Palladium on Magnetic Support as Catalyst for Suzuki–Miyaura Cross-coupling Reactions. *Catalysts* **2017**, *7*, 35. [[CrossRef](#)]
7. Kim, J.H.; Kim, J.W.; Shokouhimehr, M.; Lee, Y.S. Polymer-supported N-heterocyclic carbene–palladium complex for heterogeneous Suzuki cross-coupling reaction. *J. Org. Chem.* **2005**, *70*, 6714–6720. [[CrossRef](#)] [[PubMed](#)]

8. Shokouhimehr, M.; Lee, J.E.; Han, S.I.; Hyeon, T. Magnetically recyclable hollow nanocomposite catalysts for heterogeneous reduction of nitroarenes and Suzuki reactions. *Chem. Commun.* **2013**, *49*, 4779–4781. [[CrossRef](#)]
9. Rostamnia, S.; Lamei, K.; Pourhassan, F. Generation uniform and small particle size of palladium onto the SH-decorated SBA-15 pore-walls: SBA-15/(SH)<sub>x</sub>Pd-NP<sub>y</sub> as a recoverable nanocatalyst for Suzuki–Miyaura coupling reaction in air and water. *RSC Adv.* **2014**, *4*, 59626–59631. [[CrossRef](#)]
10. Zhong, R.; Lindhorst, A.C.; Groche, F.J.; Kühn, F.E. Immobilization of N-heterocyclic carbene compounds: A synthetic perspective. *Chem. Rev.* **2017**, *117*, 1970–2058. [[CrossRef](#)]
11. Roy, D.; Uozumi, Y. Recent advances in palladium-catalyzed cross-coupling reactions at ppm to ppb molar catalyst loadings. *Adv. Synth. Catal.* **2018**, *360*, 602–625. [[CrossRef](#)]
12. Shokouhimehr, M. Magnetically separable and sustainable nanostructured catalysts for heterogeneous reduction of nitroaromatics. *Catalysts* **2015**, *5*, 534–560. [[CrossRef](#)]
13. Pagliaro, M.; Pandarus, V.; Ciriminna, R.; Beland, F.; Cara, P.D. Heterogeneous versus homogeneous palladium catalysts for cross-coupling reactions. *ChemCatChem* **2012**, *4*, 432–445. [[CrossRef](#)]
14. Shokouhimehr, M.; Kim, J.H.; Lee, Y.S. Heterogeneous Heck reaction catalyzed by recyclable polymer-supported N-heterocyclic carbene–palladium complex. *Synlett* **2006**, 618–620. [[CrossRef](#)]
15. Kim, A.; Rafiaei, S.M.; Abolhosseini, S.; Shokouhimehr, M. Palladium nanocatalysts confined in mesoporous silica for heterogeneous reduction of nitroaromatics. *Energy Environ. Focus* **2015**, *4*, 18–23. [[CrossRef](#)]
16. Molnar, A. Efficient, selective, and recyclable palladium catalysts in carbon–carbon coupling reactions. *Chem. Rev.* **2011**, *111*, 2251–2320. [[CrossRef](#)] [[PubMed](#)]
17. Mizuno, N.; Misono, M. Heterogeneous catalysis. *Chem. Rev.* **1998**, *98*, 199–218. [[CrossRef](#)]
18. Sanchez, C.; Julián, B.; Belleville, P.; Popall, M. Applications of hybrid organic–inorganic nanocomposites. *J. Mater. Chem.* **2005**, *15*, 3559–3592. [[CrossRef](#)]
19. Yaghoubi, A.; Dekamin, M.G. Green and facile synthesis of 4H-pyran scaffold catalyzed by pure nano-ordered periodic mesoporous organosilica with isocyanurate framework (PMO-ICS). *ChemistrySelect* **2017**, *2*, 9236–9243. [[CrossRef](#)]
20. Yaghoubi, A.; Dekamin, M.G.; Arefi, E.; Karimi, B. Propylsulfonic acid-anchored isocyanurate-based periodic mesoporous organosilica (PMO-ICS-Pr-SO<sub>3</sub>H): A new and highly efficient recoverable nanoporous catalyst for the one-pot synthesis of bis(indolyl) methane derivatives. *J. Colloid Interface Sci.* **2017**, *505*, 956–963. [[CrossRef](#)]
21. Karimi, B.; Gholinejad, M.; Khorasani, M. Highly efficient three-component coupling reaction catalyzed by gold nanoparticles supported on periodic mesoporous organosilica with ionic liquid framework. *Chem. Commun.* **2012**, *48*, 8961–8963. [[CrossRef](#)]
22. Karimi, B.; Naderi, Z.; Khorasani, M.; Mirzaei, H.M.; Vali, H. Ultrasmall platinum nanoparticles supported inside the nanospaces of periodic mesoporous organosilica with an imidazolium network: An efficient catalyst for the aerobic oxidation of unactivated alcohols in water. *ChemCatChem* **2016**, *8*, 906–910. [[CrossRef](#)]
23. Doustkhah, E.; Rostamnia, S.; Zeynizadeh, B.; Kim, J.; Yamauchi, Y.; Ide, Y. Efficient H<sub>2</sub> generation using thiourea-based periodic mesoporous organosilica with Pd nanoparticles. *Chem. Lett.* **2018**, *47*, 1243–1245. [[CrossRef](#)]
24. Rostamnia, S.; Doustkhah, E.; Bulgar, R.; Zeynizadeh, B. Supported palladium ions inside periodic mesoporous organosilica with ionic liquid framework (Pd@ IL-PMO) as an efficient green catalyst for S-arylation coupling. *Microporous Mesoporous Mater.* **2016**, *225*, 272–279. [[CrossRef](#)]
25. Doustkhah, E.; Rostamnia, S.; Imura, M.; Ide, Y.; Mohammadi, S.; Hyland, C.J.T.; You, J.; Tsunoji, N.; Zeynizadeh, B.; Yamauchi, Y. Thiourea bridged periodic mesoporous organosilica with ultra-small Pd nanoparticles for coupling reactions. *RSC Adv.* **2017**, *7*, 56306–56310. [[CrossRef](#)]
26. Shokouhimehr, M.; Hong, K.; Lee, T.H.; Moon, C.W.; Hong, S.P.; Zhang, K.; Suh, J.M.; Choi, K.S.; Varma, R.S.; Jang, H.W. Magnetically retrievable nanocomposite adorned with Pd nanocatalysts: Efficient reduction of nitroaromatics in aqueous media. *Green Chem.* **2018**, *20*, 3809–3817. [[CrossRef](#)]
27. Doustkhah, E.; Rostamnia, S. Covalently bonded sulfonic acid magnetic graphene oxide: Fe<sub>3</sub>O<sub>4</sub>@GO-Pr-SO<sub>3</sub>H as a powerful hybrid catalyst for synthesis of indazolophthalazinetriones. *J. Colloid Interface Sci.* **2016**, *478*, 280–287. [[CrossRef](#)] [[PubMed](#)]
28. Sun, J.; Liu, X.; Zhu, X.; Wang, H.; Rostamnia, S.; Han, J. Well-shaped sulfonic organosilica nanotubes with high activity for hydrolysis of cellobiose. *Catalysis* **2017**, *7*, 127. [[CrossRef](#)]

29. Golchin Hossieni, H.; Rostamnia, S. Postsynthetic modified SBA-15 with  $\text{NH}_2$ -coordinately immobilized iron-oxine: SBA-15/ $\text{NH}_2$ - $\text{FeQ}_3$  as a Fenton-like hybrid catalyst for selective oxidation of organic sulfides. *New J. Chem.* **2018**, *42*, 619–627. [[CrossRef](#)]
30. Doustkhah, E.; Heidarizadeh, M.; Rostamnia, S.; Hassankhani, A.; Kazemi, B.; Liu, X. Copper (II) immobilization on carboxylic acid-rich  $\text{Fe}_3\text{O}_4$ -Pectin:  $\text{Cu}^{2+}$ @ $\text{Fe}_3\text{O}_4$ -Pectin a superparamagnetic carbohydrate source for click reaction. *Mater. Lett.* **2018**, *216*, 139–143. [[CrossRef](#)]
31. Rostamnia, S.; Gholipour, B. Immobilization of the iron (III) tris(8-quinolinolato-*N,O*) onto the silica coted Magnetite:  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\text{FeQ}_3$  as a nanomagnetically interfacial catalyst for waste-free green oxidation of sulfides. *J. Colloid Interface Sci.* **2018**, *511*, 447–455. [[CrossRef](#)] [[PubMed](#)]
32. Rostamnia, S.; Mohsenzad, F. Nanoarchitecturing of open metal site Cr-MOFs for oxodiperoxo molybdenum complexes [ $\text{MoO}(\text{O}_2)_2$ @En/MIL-100(Cr)] as a promising and bifunctional catalyst for selective thioether oxidation. *Mol. Catal.* **2018**, *445*, 12–20. [[CrossRef](#)]
33. Rostamnia, S.; Xin, H. Simultaneously application of ultrasonic irradiation and immobilized ionic liquid onto the SBA-15 nanoreactor (US/[MPIm]Cl@SBA-15): A robust, recyclable and useful combined catalytic system for selective and waste-free Kabachnik-Fields reaction. *J. Mol. Liq.* **2014**, *195*, 30–34. [[CrossRef](#)]



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