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Dioxin-Linked Covalent Organic Framework-Supported Palladium Complex for Rapid Room-Temperature Suzuki–Miyaura Coupling Reaction

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Abstract: Covalent organic framework (COF)-supported palladium catalysts have garnered enormous attention for cross-coupling reactions. However, the limited linkage types in COF hosts and their suboptimal catalytic performance have hindered their widespread implementation. Herein, we present the first study immobilizing palladium acetate onto a dioxin-linked COF (Pd/COF-318) through a facile solution impregnation approach. By virtue of its permanent porosity, accessible Pd sites arranged in periodic skeletons, and framework robustness, the resultant Pd/COF-318 exhibits exceptionally high activity and broad substrate scope for the Suzuki–Miyaura coupling reaction between aryl bromides and arylboronic acids at room temperature within an hour, rendering it among the most effective Pd/COF catalysts for Suzuki–Miyaura coupling reactions to date. Moreover, Pd/COF-318 demonstrates excellent recyclability, retaining high activity over five cycles without significant deactivation. The leaching test confirms the heterogeneity of the catalyst. This work uncovers the vast potential of dioxin-linked COFs as catalyst supports for highly active, selective, and durable organometallic catalysis.

Keywords: covalent organic framework (COF); dioxin-linked COF; Pd(II) immobilization; Suzuki–Miyaura coupling

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1. Introduction

Palladium (Pd)-catalyzed cross-coupling reactions, epitomized by Suzuki, Heck, Negishi, and Sonogashira couplings, have relentlessly been pursued in organic synthesis as they are powerful synthetic tools able to create new C–C bonds, which are pivotal in the synthesis of fine chemicals [1]. Although traditionally homogeneous Pd catalysts such as $PdCl_2$, $Pd(OAc)_2$ and $Pd[PPh_3]_4$ are frequently used, their broad application is restrained by their lack of reusability, ligand/metal contamination, thermal instability, and bimolecular deactivation during reactions. To overcome these limitations, Pd-based heterogeneous catalysts have summoned substantial attention due to their reduced cost, facile recovery, and sustainable usage, which are appealing for industry application and green chemistry. To design Pd-based heterogeneous catalysts, immobilizing molecular Pd complexes onto porous solids such as mesoporous silica [2], alumina [3], zeolites [4], porous organic polymers (POPs) [5], and metal–organic frameworks (MOFs) has been proven as a viable strategy [6]. The porous supports can enhance the dispersion of Pd and prevent its aggregation and leaching during catalysis, thereby playing a crucial role in the catalytic performance of hosted Pd catalysts. In this regard, seeking advanced porous supports to anchor organometallic Pd catalysts while retaining their high activity is much desired.

Among the heterogeneous porous supports, covalent organic frameworks (COFs) have attracted tremendous attention recently. COFs are constructed by covalently stitching organic units into extended 2D or 3D periodic networks [7]. In comparison to conventional

porous solids, COFs offer an unparalleled combination of structural merits, including ultralow density, high porosity, regular networks, tailorable structures, and diversified functionalities, which endow COFs with immense potential in a wide array of applications, such as gas separation, water harvesting, energy storage, sensing, radionuclide sequestration, and particularly heterogeneous catalysis [8–13]. Over the past decade, COFs have demonstrated tremendous potential in heterogeneous catalysis owing to their multifold advantages [14–16]: (i) the immense structural diversity of COFs underpins the design of myriad COF catalysts; (ii) the high stability of COFs ensures recyclable catalytic performance; (iii) the atomically tunable structures of COFs permit precise control over the emergent catalytic behaviors; (iv) the high surface areas of COFs promote the mass transport of substrates and accessibility to active sites; (v) the modular pore environment of COFs imparts catalytic reactions with high regio-, size-, and enantio-selectivity; (vi) the spatial arrangement of multiple catalytic sites within COFs enables cooperative catalysis; and (vii) merging COFs with other functional materials results in heterostructures with boosted catalytic efficiency.

Since the first report of COF-supported metal complexes for heterogeneous catalysis in 2011 [17], COFs have been widely used as supporting matrixes to anchor Pd nanoparticles/complexes [18–24], exhibiting efficient and reusable catalytic performance in various cross-coupling reactions, such as Suzuki, Stille, Heck, and Sonogashira reactions [25]. To name a few, Wang's group used the first Pd(II)-doped COF (Pd/COF-LZU1) to catalyze the Suzuki–Miyaura coupling reaction under harsh conditions (150 °C for 2–3 h) [17]. In 2020, Dong's group encapsulated Pd nanoparticles (NPs) into a paraffin-chain quaternary ammonium salt-bearing COF [26], which served as an efficient phase transfer catalyst for the aqueous Suzuki–Miyaura coupling. Very recently, in 2022, Alemán's group immobilized Pd(II) within a phenanthroline-containing COF, which exhibited ultrahigh activities with a turnover number of up to 16,000 [27]. Despite remarkable advances in Pd/COF catalysts in cross-coupling reactions, most studies have utilized imine-linked COFs as supports with inadequate chemical stability, restricting their broad utility in stringent conditions. Moreover, harsh reaction conditions, such as elevated temperatures (50–150 °C) and extended reaction times, are typically needed for satisfactory catalytic activity. To the best of our knowledge, the exploration of Pd/COF catalysts for the room-temperature Suzuki–Miyaura reaction remains elusive [27–31]. Hence, it is of substantial interest to develop novel COF-based heterogeneous catalysts showing high activity, selectivity, and recyclability for cross-coupling reactions under mild conditions.

On the other hand, the limited chemical stability of COFs has posed a considerable obstacle to their widespread application. To alleviate this shortcoming, extensive scientific efforts have been applied toward the development of robust COFs [32]. Three primary strategies have been employed to construct ultra-stable COFs: (i) de novo synthesis using reactions with low reversibility [33]; (ii) reversible–irreversible cascade reactions [34–37]; and (iii) the post-synthetic modification of imine linkages in existing COFs [38–40]. Among the stable COFs, dioxin-linked COFs, often known as polyarylether-based COFs, have gained increasing attention since seminal reports by the groups of Yaghi and Fang were published in 2018 [41,42]. By leveraging the poorly reversible nucleophilic aromatic substitution reaction, a handful of dioxin-linked 2D COFs have been synthesized and have exhibited extraordinary chemical stability in various drastic conditions. As a result, dioxin-linked COFs have been widely exploited in various fields, including electrocatalysis [43], energy storage [44], water remediation [42,45,46], and organic electrodes [47]. However, the utilization of dioxin-linked COFs in heterogeneous thermocatalysis remains uncharted. Given their exceptional chemical robustness, permanent porosity, and high crystallinity, we envisage that dioxin-linked COFs hold great promise as supports for immobilizing molecular Pd complexes toward cross-coupling reactions.

In this work, we disclose the first immobilization of palladium acetate onto a known dioxin-linked COF-318, termed Pd/COF-318, via a simple solution impregnation method. The chemical integrity, crystallinity, and permanent porosity of the resultant Pd/COF-318

were well retained upon postsynthetic metalation. Remarkably, Pd/COF-318 exhibited high activity and broad functional group tolerance for the Suzuki–Miyaura coupling reaction between aryl bromides and arylboronic acids at room temperature, outperforming commercial Pd/carbon and most prior Pd/COF catalysts. Moreover, Pd/COF-318 retained its catalytic activity over at least five consecutive cycles without obvious deactivation.

2. Materials and Methods

2.1. Reagents

2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, 95%), phenylboronic acid (99.9%), 4-hyrdoxyphenylboronic acid (99.72%), 4-nitrophenylboronic acid (97%), (4-(methoxycarbonyl) phenyl)boronic acid (98%) and pallidum (II) acetate (99.98%) were purchased from Ambeed (Arlington Hts, IL, USA). 2,3,5,6-Tetrafluoro-4-pyridinecarbonitrile (TFPC, 99%) was purchased from Combi-Blocks (San Diego, CA, USA). 1,4-Dioxane (99.8%), mesitylene (98%), bromobenzene (99.5%), potassium carbonate (99.0%), sodium carbonate (99.5%), ethanol, methanol, and cesium carbonate (99%) were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Deuterated chloroform was purchased from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). 4-Bromotoluene (99.0%), 4-bromoanisole (99.7%), and 1-bromo-4-nitrobenzene (99.0%) were purchased from TCI America (Portland, OR, USA). In addition, 5% palladium on activated carbon and 4-bromoaceptophenone (98%) were purchased from Alfa Aesar (Ward Hill, MA, USA). Tetrahydrofuran (THF), acetone (99.8%) and dichloromethane were purchased from VWR Chemicals (Radnor, PA, USA). Acetonitrile was purchased from Fisher Scientific (Waltham, MA, USA).

2.2. Instrumentation

The ^{1}H NMR spectra were acquired using a Bruker Avance III 500 NMR spectrometer (Bremen, Germany). Powder X-ray diffraction (PXRD) data were collected using a benchtop Rigaku MiniFlex 600 X-ray diffractometer (Akishima, Japan) with Cu Kα1 radiation (λ = 1.5406 Å) operating at 40 kV and 15 mA. Nitrogen sorption isotherms were obtained at 77 K using a Micromeritics 3Flex gas sorption analyzer (Norcross, GA, USA), with the COF samples activated under vacuum at 120 °C for 12 h before measurement. Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Spectrum One FTIR system (Waltham, MA, USA). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha XPS apparatus equipped with a monochromatic Al K(alpha) source (Waltham, MA, USA). Scanning electron microscopy (SEM) imaging was carried out using a Zeiss Gemini Ultra-55 Analytical Field Emission Scanning Electron Microscope (Oberkochen, Germany), operated at 15 kV and utilizing an in-lens detector. A Field Emission Transmission Electron Microscope (FETEM, JEOL 2100-F, Tokyo, Japan) equipped with an Oxford high solid-angle Silicon Drift Detector (SDD) X-Ray Energy Dispersive Spectrometer (EDS) system and a High-Angle Annular Dark Field (HAADF) detector was used for structural and chemical elemental analysis. The microscope was aligned for an electron beam energy of 200 keV.

2.3. Synthesis

Synthesis of COF-318: The synthesis was based on a previously reported procedure with a slight modification. 2,3,6,7,10,11-Hexahydroxytriphenylene (30 mg, 0.0928 mmol), 2,3,5,6-tetrafluoro-4-pyridinecarbonitrile (24 mg, 0.138 mmol), 1,4-dioxane (0.5 mL) and mesitylene (0.5 mL) were charged into a 5 mL Biotage Microwave vial. The reaction mixture was sonicated for 10 min, and then triethylamine was added (78 µL, 0.56 mmol). After sonication for 3 min, the vial underwent freeze–pump–thaw cycles and was evacuated to an internal pressure of 100 mTorr. After heating at 120 °C for 72 h, the obtained COF was isolated via filtration and washed with DMF. The solid was solvent exchanged with DMF and water at 50 °C for 3 days. Then, the COF was Soxhlet washed with THF for 1 day and dried at 120 °C under vacuum overnight to yield brown powder (24.1 mg, 50%).

Synthesis of Pd/COF-318: COF-318 (30 mg) was dispersed in 2 mL of acetone under sonication for 10 min. Subsequently, an acetone solution of palladium acetate (1.32 mg $Pd(OAc)_2$ in 1 mL of acetone) was added dropwise to the COF solution under vigorous stirring at 600 rpm. After stirring at room temperature for 24 h, the obtained Pd/COF was isolated via centrifugation, washed three times time with fresh acetone, and dried at 120 °C overnight in a vacuum oven.

2.4. Catalysis

Suzuki–Miyaura coupling reaction using Pd/COF-318: A 5 mL vial was charged with aryl bromides (0.113 mmol), phenylboronic acid (0.124 mmol), potassium carbonate (0.226 mmol), 2 wt.%Pd/COF-318 (3 mg, 0.05 mol% Pd), and ethanol (2 mL). The reaction mixture was stirred at 600 rpm in the air at room temperature for 1 h. Upon completion of the reaction, the catalyst was isolated via centrifugation at 10,000 rpm. After removing the solvent via evaporation, the products were analyzed using ^{1}H NMR to calculate the yield.

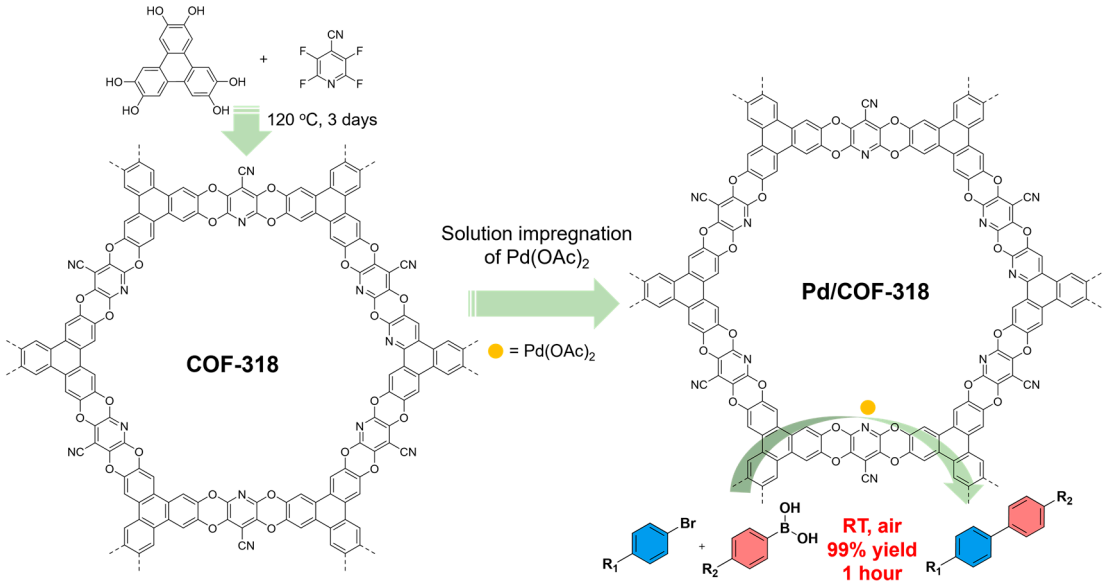
Filtration test: The reaction mixture was stirred at 600 rpm in the air at room temperature for 10 min, resulting in a yield of ~61%. Subsequently, the heterogeneous catalyst was separated via centrifugation at 10,000 rpm. The filtrate was then transferred to a new vial and stirred at room temperature for an additional 90 min, while the yield of the coupling product was monitored using ^{1}H NMR spectroscopy.

Recycling test: After the completion of the reaction, the COF catalyst was recovered via centrifugation and washed with ethanol three times. The recovered catalyst was then dried under vacuum and subsequently reused in subsequent catalytic runs.

3. Results

Among the limited number of dioxin-linked COFs that have been reported, COF-318, which comprises 2,3,5,6-tetrafluoro-4-pyridinecarbonitrile and 2,3,6,7,10,11-hexahydroxytriphenylene (Scheme 1), stands out for two primary reasons. Firstly, the intrinsic pyridine nitrogens in the skeleton are proven chelating sites for anchoring Pd(II) [27]. Secondly, the building blocks are readily available compared to synthetically arduous monomers such as phthalocyanine [44,48]. We commenced our study with the synthesis of COF-318 following a protocol previously reported by Yaghi's group [41]. To immobilize Pd(II) within the COF host (Pd/COF-318), a well-known solution impregnation strategy was employed [6]. Specifically, the COF-318 solid was submersed in acetone under sonication, followed by the addition of a palladium acetate solution under vigorous stirring at room temperature for 24 h (see Section 2.3 for detailed procedures). The resulting solid was then centrifuged and thoroughly washed multiple times with acetone to remove any uncoordinated Pd(II). The successful incorporation of the Pd complex into COF-318 was confirmed by the X-ray photoelectron spectroscopy (XPS) survey spectrum, which clearly showed the presence of Pd signals (Figure S1) (see Supplementary Materials). Furthermore, the Pd loading in COF-318 was determined to be 2.0 wt.% by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

The powder X-ray diffraction (PXRD) pattern of COF-318 revealed a prominent peak at 4.3°, accompanied by several minor peaks at 8.8°, 11.4°, and 27.0° (Figure 1a, black curve), corresponding to the (100), (200), (210), and (001) planes, respectively. This PXRD pattern matched well with the reported one of an eclipse stacking mode [41]. Upon the Pd immobilization, the long-range order of Pd/COF-318 was retained (Figure 1a, red curve). The Fourier transform infrared (FTIR) spectrum of COF-318 displayed characteristic dioxin C–O symmetric and asymmetric stretches at 1012 and 1242 cm^{-1}, respectively, indicating the successful formation of a dioxin linkage. After Pd(II) metalation, the FTIR spectrum of Pd/COF-318 remained unchanged, which underscored the retained chemical integrity of COF (Figure S2). Thermogravimetric analysis (TGA) indicated that Pd/COF-318 was thermally stable, revealing no significant weight loss up to 400 °C under N_2 (Figure S3).



Scheme 1. Synthesis of Pd/COF-318 through a solution impregnation strategy and its exceptional catalytic performance in room-temperature Suzuki–Miyaura coupling reaction. Note: the illustration does not accurately depict the actual Pd–N percentage in Pd/COF-318.

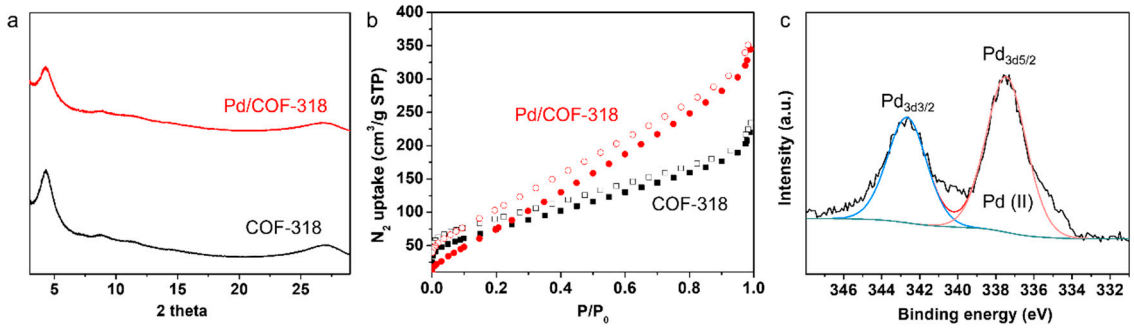


Figure 1. (**a**) PXRD patterns. (**b**) N_2 sorption isotherms of COF-318 and Pd/COF-318. (**c**) XPS Pd 3d spectrum of Pd/COF-318.

The porosity of the COF samples was evaluated by measuring the N_2 sorption isotherms at 77 K (Figure 1b). The Brunauer–Emmett–Teller (BET) surface area of Pd/COF-318 was calculated to be 190 m^2 g^{-1}, which was slightly lower than that of pristine COF-318 (236 m^2 g^{-1}). This decrease in surface area can be attributed to the immobilization of Pd species within the COF, a well-documented phenomenon in previous reports of Pd/COF systems [17,26,27]. To investigate the coordination state of the immobilized Pd in COF-318, XPS measurements were performed. The XPS Pd 3d spectrum of Pd/COF-318 showed characteristic binding energies at 337.4 eV and 342.6 eV (Figure 1c), which were assigned to the $3d_{5/2}$ and $3d_{3/2}$ orbitals of Pd(II), respectively [17,27]. We attempted to explore a potential Pd–N interaction through the N 1s XPS spectra. However, due to the overlap between pyridine N and nitrile around 399.4 eV, we failed to deconvolute the XPS spectra to determine the specific chemical state of nitrogen (Figure S4).

The morphology of the COF samples was analyzed via scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The SEM images revealed that COF-318 adopted an irregular nanoplate morphology with a lateral length of 1–2 μm, which was well retained after the Pd(II) immobilization (Figure S5). As depicted in Figure 2, the HRTEM images of Pd/COF-318 demonstrate the nanoplate morphology of COF, consistent with the findings from the SEM analysis. Additionally, the energy-

dispersive spectrometer (EDS) mapping showed the uniform distribution of Pd within the COF, suggesting the successful embedment of Pd in COF-318 without apparent aggregation.

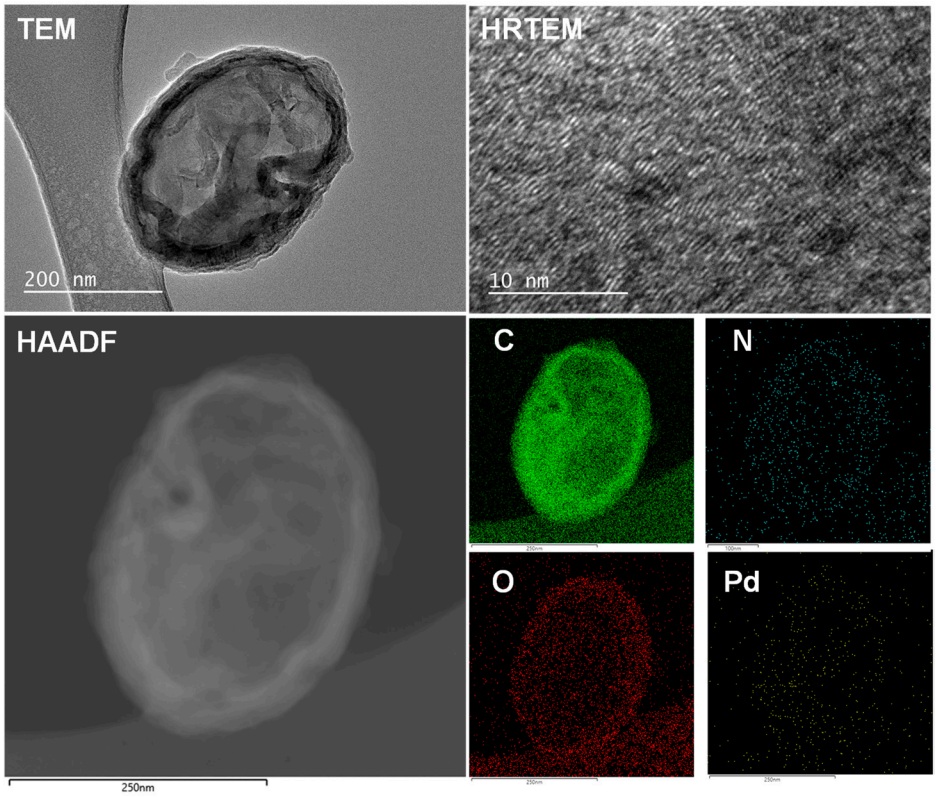
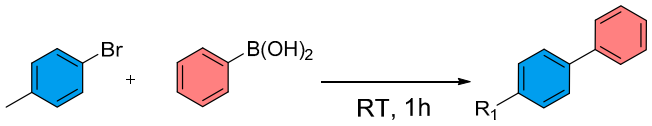


Figure 2. HRTEM images and corresponding EDS mapping images of Pd/COF-318.

4. Discussion

With the COF samples characterized, we proceeded to investigate the catalytic performance of Pd/COF-318 in the Suzuki–Miyaura coupling reaction using a model reaction of 4-bromotoluene and phenylboronic acid. To achieve the optimal reaction condition, a series of experiments were conducted with respect to the base choice (Na_2CO_3, K_2CO_3, Cs_2CO_3) and solvents (MeOH, EtOH, acetonitrile, THF, CH_2Cl_2) (entries 1–7, Table 1). The optimal condition was obtained in ethanol at room temperature, with K_2CO_3 as a base and 3 mg of Pd/COF-318 (0.05 mol% Pd). Under this condition, a high yield of 99% was observed in 1 h at room temperature in the air. Notably, Pd/COF-318 can achieve a high turnover frequency (TOF) of 199.6 h^{-1}, far superior to previously reported Pd/COF catalysts [26]. As expected, bare COF-318 showed no activity, indicating the indispensable role of the Pd species (entry 8, Table 1). In comparison, the use of a commercial 5%Pd/carbon catalyst resulted in inferior yields under identical conditions (entries 9, Table 1). To further assess the catalytic efficiency and highlight the merit of Pd/COF-318, we compiled a summary of reported COF catalysts for the Suzuki–Miyaura coupling reaction. As shown in Table 2, Pd/COF-318 not only enriches the diversity of COF supports, diverging from the predominant imine COF supports, but also stands out as one of the most effective COF catalysts for the Suzuki–Miyaura coupling reaction reported thus far. This underlines the tremendous potential of dioxin-linked COFs as catalyst supports for heterogenous cross-coupling reactions.

Table 1. Optimization of reaction conditions and control experiments for room-temperature Suzuki–Miyaura coupling reaction [a].



Entry	Catalyst	Base	Solvent	Yield [b]
1	Pd/COF-318	Na_2CO_3	EtOH	87%
2	Pd/COF-318	K_2CO_3	EtOH	>99%
3	Pd/COF-318	Cs_2CO_3	EtOH	82%
4	Pd/COF-318	K_2CO_3	MeOH	94%
5	Pd/COF-318	K_2CO_3	Acetonitrile	90%
6	Pd/COF-318	K_2CO_3	CH_2Cl_2	4%
7	Pd/COF-318	K_2CO_3	THF	53%
8	COF-318	K_2CO_3	EtOH	/
9	5% Pd/carbon	K_2CO_3	EtOH	90%

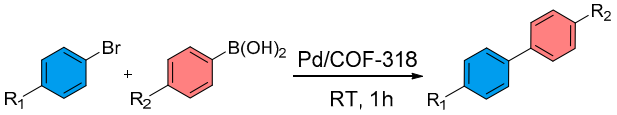
[a] Reaction conditions: 4-bromotoluene (0.113 mmol), phenylboronic acid (0.124 mmol), base (0.226 mmol), catalyst (0.05 mol% Pd), solvent (2 mL), air, room temperature, stirring at 600 rpm for 1 h. [b] Determined via ^{1}H NMR.

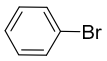
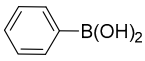
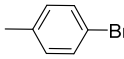
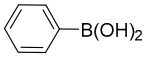
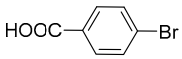
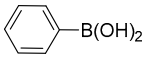
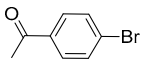
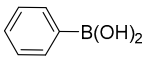
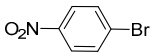
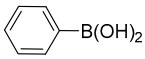
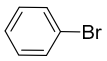
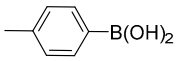
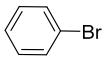
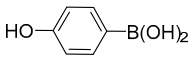
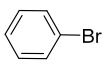
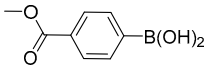
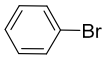
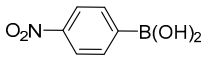
Table 2. Comparison with previously reported Pd/COFs catalysts in the Suzuki–Miyaura cross-coupling of bromobenzene and phenylboronic acid.

Entry	COF Catalyst	Linkage	Pd Valence	T	Time	Yield	Stability (Runs)	Ref.
1	Pd/COF-318	Dioxin	Pd^{2+}	RT	1 h	99%	5	This work
2	Pd@COF-NHC	Imine	Pd^0	RT	1 h	99%	8	[28]
3	Pd/TATAE	Imine	Pd^{2+}	RT	2 h	98%	4	[29]
4	Pd@OC-MA	Imine	Pd^{2+}	RT	5 h	99%	4	[30]
5	Pd@COF-TM	Amide	Pd^{2+}	RT	6 h	99%	9	[31]
6	Pd/Phen-COF	Imine	Pd^{2+}	RT	16 h	99%	5	[27]
7	PdNPs@Thio-COF	Imine	Pd^0	50 °C	3 h	85%	5	[18]
8	Pd@COF-QA	Imine	Pd^0	50 °C	6 h	99%	10	[26]
9	$Pd(OAc)_2$@COF-300	Imine	Pd^{2+}	70 °C	0.3 h	100%	5	[20]
10	Pd(II)@SP-3D-COF-Bpy	Imine	Pd^{2+}	70 °C	2 h	98%	5	[49]
11	Pd@TPM-3D-COF-Bpy	Imine	Pd^0	70 °C	5 h	98%	5	[50]
12	Pd/COF-SMC2	Imine	Pd^0, Pd^{2+}	80 °C	1 h	96%	4	[22]
13	Pd/H_2P-Bph-COF	Imine	Pd^{2+}	110 °C	1.5 h	98%	5	[19]
14	Pd^{II}/TAT–DHBD	Imine	Pd^{2+}	120 °C	24 h	56%	/	[51]

Encouraged by the exceptional catalytic activity, we investigated the substrate scope of Pd/COF-318 under optimal conditions. Notably, Pd/COF-318 exhibited excellent catalytic activity (>99% yield) in the coupling reactions of different aryl bromides and arylboronic acids, encompassing both electron-withdrawing and -donating groups (Table 3). For instance, high yields were observed for electron-donating substituted aryl bromides with methyl (entry 2, Table 3), as well as substituted aryl bromides with electron-withdrawing groups such as carboxylic acid (entry 3), ketone (entry 4), and nitro (entry 5). In addition, Pd/COF-318 effectively catalyzed the coupling reactions of bromobenzene with a range of phenylboronic acids, including those with electron-donating groups like methyl (entry 6) and hydroxy (entry 7), as well as withdrawing groups like ester (entry 8) and nitro (entry 9). These results convincingly demonstrate the high generality of Pd/COF-318 in the Suzuki–Miyaura coupling reaction.

Table 3. The substrate scope of Pd/COF-318 for Suzuki–Miyaura coupling reaction [a].



Entry	R_1-Ar-Br	R_2-Ar-$B(OH)_2$	Yield [b]
1			>99%
2			>99%
3			>99%
4			>99%
5			>99%
6			>99%
7			>99%
8			>99%
9			>99%

[a] Reaction conditions: bromoarene (0.113 mmol), arylboronic acid (0.124 mmol), K_2CO_3 (0.226 mmol), Pd/COF-318 (0.05 mol% Pd equiv.), EtOH (2 mL), air, stirring at 600 rpm at room temperature. [b] Isolated yield was determined via ^{1}H NMR.

The heterogeneity of Pd/COF-318 was confirmed through a leaching test (Figure 3a), in which the Pd/COF-318 catalyst was removed from the reaction mixture at partial conversion (~61%). The isolated filtrate was subjected to further reaction, but no further conversion was observed, suggesting the negligible or no leaching of homogeneous Pd species from the COF support. In addition, Pd/COF-318 could be easily recovered via centrifugation and displayed a high yield of >99% even after the 5th cycle (Figure 3b). Moreover, XPS analysis of the recovered catalyst revealed the presence of Pd(0) with an atomic Pd(0)/Pd(II) ratio of 0.52/1.0 (Figure S6), demonstrating that the partial reduction of Pd(II) occurs during the coupling reaction.

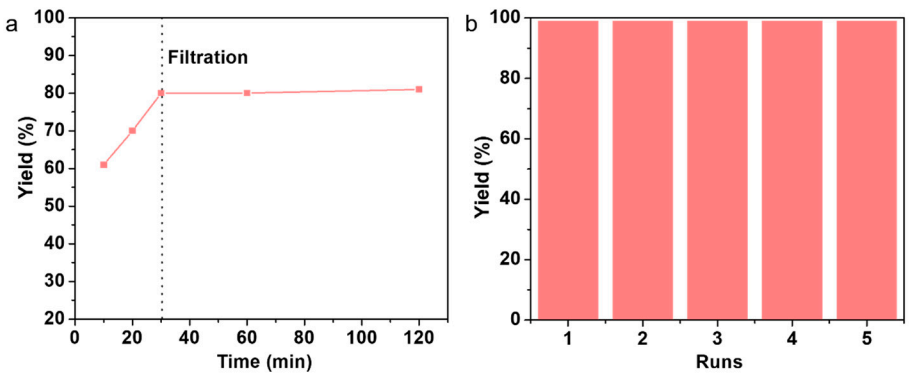


Figure 3. Leaching (**a**) and recycle test (**b**) of Pd/COF-318 in the Suzuki–Miyaura cross-coupling reaction.

We outline the plausible catalytic mechanism of Pd/COF-318 in Scheme S1. Initially, the Pd(II) complex within COF-318 facilitates the generation of catalytically active Pd(0)

species in situ [21]. The resultant Pd(0) species undergo oxidative addition with aryl bromides (R^1-Br), leading to the formation of R^1-Pd(II)-Br intermediate. Through transmetalation with aryl boronic acid (R^2-$B(OH)_2$), a biaryl palladium complex (R^1-Pd(II)-R^2) is generated. Finally, the biaryl product (R^1-R^2) is formed, concomitantly regenerating Pd(0) by reducing Pd(II) during the reductive elimination step.

5. Conclusions

In summary, we have developed the first dioxin-linked COF-supported Pd complex that can be used as an exceptionally active heterogeneous catalyst for the Suzuki–Miyaura coupling reaction at room temperature. Thanks to its permanent porosity, abundant Pd sites anchored in periodic skeletons, and robust frameworks, Pd/COF-318 demonstrated remarkable activity and broad substrate scope for the Suzuki–Miyaura coupling reaction of various substituted aryl bromides and arylboronic acids within an hour, outperforming commercial Pd/carbon and most previously reported Pd/COF catalysts. Moreover, Pd/COF-318 could be recycled well at least five times without an obvious decay in the catalytic activity, and the leaching test verified the heterogeneity of the catalyst. This work introduces a valuable addition to the toolbox of COF supports for metal immobilization and highlights the immense potential of dioxin-linked COF-supported metal complexes for heterogeneous catalysis. Further work on exploring new organic transformations using these catalytic systems is currently under investigation in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst13081268/s1, Figure S1: XPS survey spectra of COF-318 and Pd/COF-318; Figure S2: FTIR spectra of COF-318 and Pd/COF-318; Figure S3: TGA trace of Pd/COF-318; Figure S4: XPS N 1s spectra of COF-318 and Pd/COF-318; Figure S5: SEM images of COF-318 and Pd/COF-318; Figure S6: XPS Pd 3d spectrum of used Pd/COF-318. Scheme S1. The catalytic mechanism for Pd/COF-catalyzed Suzuki–Miyaura cross-coupling reaction.

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

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