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Microwave-Assisted One-Step Synthesis of Palladium-Encapsulated Covalent Organic Frameworks for Heterogeneous Catalysis

Ziad Alsudairy,[a, b] Allea Campbell,[a] Qi Zheng,[c] Chelsea Harrod,[a] Normanda Brown,[a] Allison Saintilma,[a] Raghu V. Maligal-Ganesh,[d] Conrad Ingram,[a] and Xinle Li*[a]

Metal-encapsulated covalent organic frameworks (metal/COFs) represent an emerging paradigm in heterogeneous catalysis. However, the time-intensive (usually 4 or more days) and tedious multi-step synthesis of metal/COFs remains a significant stumbling block for their broad application. To address this challenge, we introduce a facile microwave-assisted *in situ* metal encapsulation strategy to cooperatively combine COF formation and *in situ* palladium(II) encapsulation in one step. With this unprecedented approach, we synthesize a diverse range of palladium(II)-encapsulated COFs (termed Mw-Pd/COF) in the air within just an hour. Notably, this strategy is scalable for large-scale production (~0.5 g). Leveraging the high crystallinity, porosity, and structural stability, one representative Mw-Pd/COF exhibits remarkable activity, functional group tolerance, and recyclability for the Suzuki-Miyaura coupling reaction at room temperature, surpassing most previously reported Pd(II)/COF catalysts with respect to catalytic performance, preparation time, and synthetic ease. This microwave-assisted *in situ* metal encapsulation strategy opens a facile and rapid avenue to construct metal/COF hybrids, which hold enormous potential in a multitude of applications including heterogeneous catalysis, sensing, and energy storage.

Introduction

Palladium (Pd)-catalyzed cross-coupling and related reactions, such as Suzuki-Miyaura, Heck, Stille, Sonogashira, Negishi, and Buchwald-Hartwig reactions, are deemed highly versatile synthetic tools in organic synthesis.[1] Homogeneous catalysts, such as Pd salts and complexes, are widely adopted due to exceptional activity and tunability in ligand environments. However, they suffer from drawbacks such as metal contamination, intramolecular deactivation, and lack of catalyst reusability.[2] To alleviate these limitations, significant research efforts have focused on the heterogenization of Pd species onto insoluble solid supports.[3] The resulting heterogeneous catalysts not only prevent the degradation and leaching of the Pd complex during catalysis but also enable catalyst recycling, which offers significant advantages for industrial-scale synthesis processes, including cost reduction, environmental sustainability, improved efficiency, and enhanced product quality. Importantly, solid supports profoundly influence the catalytic behaviors of the encapsulated Pd species through synergistic host-guest interactions, leading to equivalent or even superior catalytic performance in comparison to their homogeneous counterparts.[4] As such, the development of advanced supports to heterogenize Pd species has become a topic of intense research interest. A wide range of porous solids such as carbons,[5] mesoporous silica,[6] zeolites,[7] porous organic polymers,[8] and metal-organic frameworks (MOFs)[4b] have been employed as potential support materials.

Covalent organic frameworks (COFs) have gained escalating attention as porous supports for immobilizing Pd catalysts in the past decade.[9] COFs are a novel class of permanently porous, crystalline, two-dimensional or three-dimensional (2D or 3D) network polymers renowned for their ultralow density, ordered structures, high porosity, diverse functionalities, and tunable topology.[10] These compelling structural merits endow them with enormous potential in gas separation,[11] sensing,[12] energy storage,[13] water harvesting,[14] environmental remediation,[15] catalysis,[16] etc. Notably, the permanent porosity, accessible 1D nanochannels, and adjustable pore metrics position COFs as appealing candidates for immobilizing Pd catalysts.[9] The first successful demonstration of using COF to heterogenize Pd species was reported in 2011 when Wang's group immobilized palladium (II) acetate ($Pd(OAc)_2$) onto the first 2D imine-linked COF (COF-LZU1) for the Suzuki coupling reaction.[17] Since then, COFs have been widely employed as supporting matrixes to host Pd complexes and nanoparticles, showcasing efficient and recyclable catalytic performance in various cross-coupling reactions.[18] However, traditional methods for synthesizing Pd/COF catalysts face significant synthetic barriers. One barrier lies in the traditional solvothermal syn-

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[a] Z. Alsudairy, A. Campbell, C. Harrod, N. Brown, A. Saintilma, C. Ingram, X. Li
Department of Chemistry, Clark Atlanta University, Atlanta, Georgia 30314, United States
E-mail: xli1@cau.edu

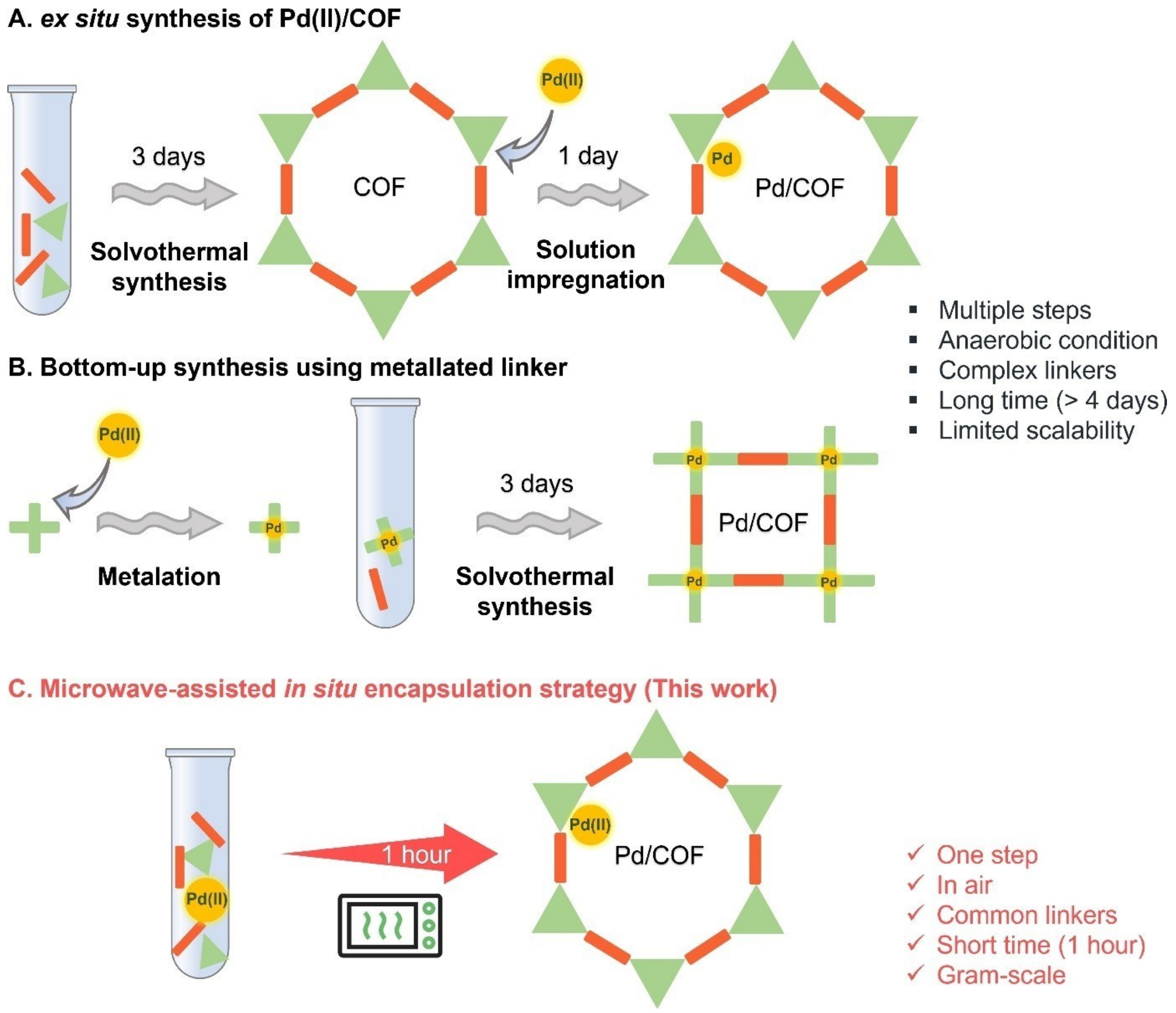
[b] Z. Alsudairy
Department of Chemistry, College of Science, Qassim University, Buraidah 51452, Saudi Arabia

[c] Q. Zheng
School of Materials Science and Engineering, Southeast University, Nanjing 211189, PR China

[d] R. V. Maligal-Ganesh
Division of Sciences, Krea University, Sri City, Andhra Pradesh 517646, India

Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202402513 thesis of COF supports, which often necessitates harsh conditions, including extended reaction times (typically 3 days), vacuum conditions, and limited scalability, impeding the accelerated discovery and practical application of these materials.[19] Another barrier is that the encapsulation of Pd within COFs predominantly relies on the *ex situ* encapsulation method, where the Pd complex is infiltrated into a pre-existing COF (Scheme 1A). This approach suffers from lengthy procedures (typically 1 day) and can potentially cause the loss of COF crystallinity during the impregnation process. While alternative strategies employ pre-synthesized Pd-containing linkers such as metallated bipyridine[20] and porphyrin[21] to construct Pd/COFs (Scheme 1B), the limited choice of such specialized linkers restricts the scope of this method. To address these challenges, *in situ* encapsulation, where the Pd complex is embedded within the framework during COF synthesis, can streamline and enhance the efficiency of the overall preparation process (Scheme 1C).[22] The effectiveness of *in situ* encapsulation has been well demonstrated in the synthesis of various COF-based composites, including those with enzymes, nanoparticles, polymer, graphene, perovskite, and MOFs.[23] For instance, in 2022, Chen's group developed a range of enzyme/COF biocatalysts via *in situ* assembly of enzymes with COFs under ambient conditions.[24] In 2024, Lou's group developed a series of inorganic 2D material/COF hybrids through *in situ* assembly of 2D inorganic materials such as hexagonal boron nitride and transition metal dichalcogenides with COFs.[25] Nonetheless, up until recently, the utilization of the *in situ* strategy in COFs still largely relies on the traditional solvothermal method.

In this regard, exploring alternative synthetic methods for COFs beyond the classical solvothermal approach has been relentlessly pursued in recent years.[26] Microwave energy, an invaluable heating technique that transforms electromagnetic radiation (0.3 to 300 GHz) into efficient internal heat, offers significant advantages over conventional heating, including higher yield, shorter reaction time, more uniform heating, and better product properties.[27] Microwave irradiation has found extensive application in the realms of organic synthesis,[28] inorganic nanomaterials,[29] polymers,[30] and MOFs.[31] The microwave-assisted synthesis of COFs was first reported in 2009 and



Scheme 1. Synthesis of Pd(II)/COF catalysts via (A) *ex situ* synthesis, (B) bottom-up synthesis using metallated linkers, and (C) the microwave-assisted *in situ* encapsulation strategy in this study.

has subsequently triggered increasing interest.[32] Since 2021, our group has actively leveraged microwave technology for the expeditious synthesis of COFs. In 2023, we reported a facile and rapid microwave-assisted synthesis of 2D imine-linked COF adsorbents for high iodine vapor capture, which exhibited superior performance compared to their solvothermal analogs.[33] Moreover, we recently pioneered the combination of microwave-assisted synthesis and mixed-linker strategy to construct multivariate COFs, which enabled the fine-tuning of adsorption properties for static iodine vapor capture.[34] Building upon our group's prior research efforts, we hypothesize that combining microwave-assisted COF synthesis with *in situ* Pd(II) impregnation could offer a novel approach to rapidly and efficiently generate diverse Pd/COF catalysts, thereby overcoming the aforementioned synthetic barriers associated with traditional methods. To the best of our knowledge, the microwave-assisted one-step synthesis of metal/COF catalysts has yet to be explored.

In this work, we report the first one-step synthesis of various Pd(II)-encapsulated COFs (Mw-Pd/COFs) via a novel microwave-assisted *in situ* encapsulation strategy. This approach integrates the microwave-assisted synthesis of imine-linked COFs with the *in situ* impregnation of the Pd(II) complex in one pot, dramatically reducing preparation time from the typical four days to a mere hour. A range of Mw-Pd/COFs were obtained in high yields, excellent scalability, and remarkable crystallinity. As a proof of concept, one representative Mw-Pd/COF was utilized to catalyze the room-temperature Suzuki-Miyaura coupling reaction between aryl bromides and arylboronic acids, exhibiting outstanding catalytic activity and broad functional group tolerance. Furthermore, the Mw-Pd/COF maintains its catalytic activity over five consecutive cycles without any noticeable deactivation. This facile and versatile strategy tackles the long-lasting challenges in the synthesis of metal/COF hybrids, opening up tremendous possibilities for various niche applications.

Results and Discussion

At the outset of our study, we conducted the *in situ* Pd(II) encapsulation during the microwave-assisted synthesis of the 2D imine-linked COF, DMTP-TPB (denoted as Mw-Pd/DMTP-TPB, Figure 1A).[35] The microwave-assisted one-step synthesis was carried out by microwave heating of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTP, 23.2 mg, 0.12 mmol), 1,3,5-tris(4-aminophenyl)benzene (TPB, 28.1 mg, 0.08 mmol), and controlled amounts of $Pd(OAc)_2$ in acetonitrile (1 mL) for one hour at 120 °C under air, giving rise to Mw-Pd/DMTP-TPB in a high yield of 96 % (refer to Scheme S1 for detailed procedure). $Pd(OAc)_2$ was selected as the Pd source due to its good solubility in acetonitrile, a solvent recognized for producing high-quality imine-linked COFs.[36] It was found that increasing the $Pd(OAc)_2$ loading resulted in COFs with darker coloration and compromised crystallinity (Figure S1). Therefore, an optimal loading of 2 mg $Pd(OAc)_2$ was selected for this study. The obtained Mw-Pd/DMTP-TPB displayed a greenish color (inset of Figure 1A), contrasting markedly with the bright yellow color of the pristine DMTP-TPB COF (inset of Scheme S1). This color difference suggested the successful encapsulation of Pd complex within the COF. X-ray photoelectron spectroscopy (XPS) survey spectrum futher corroborated this observation by

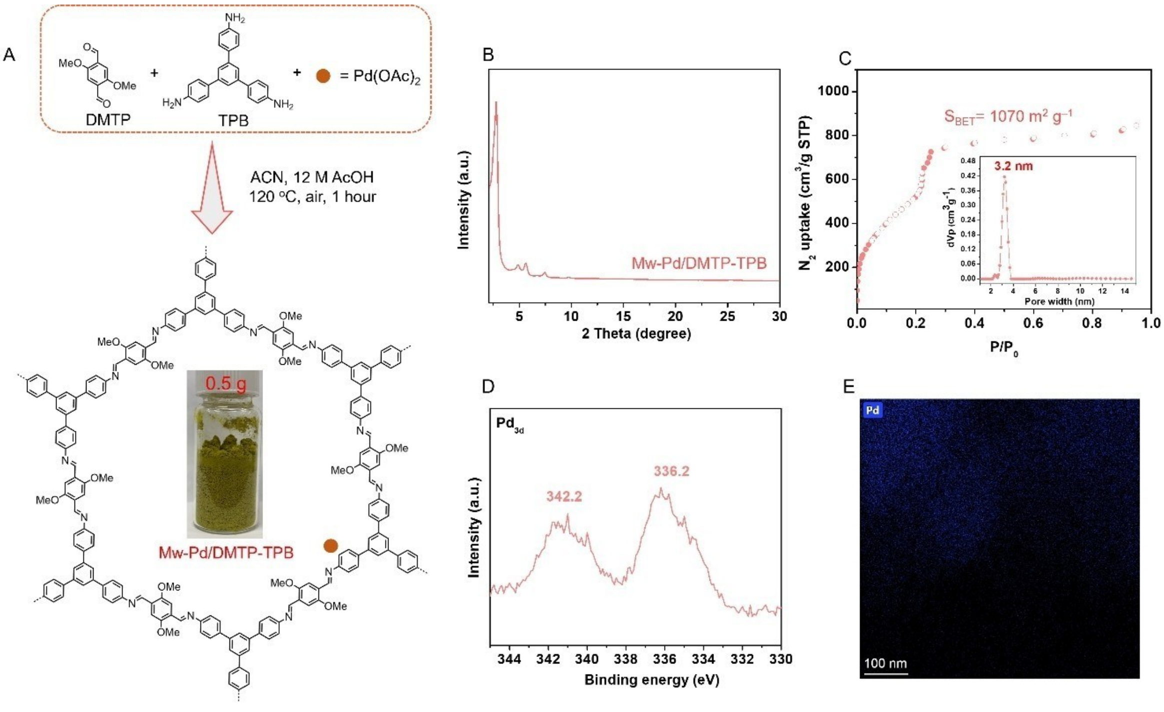
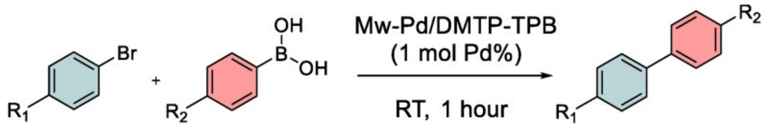


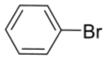
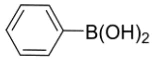
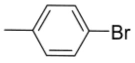
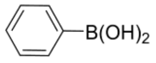
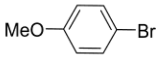
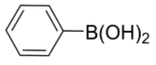
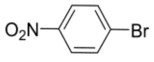
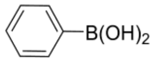
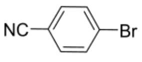
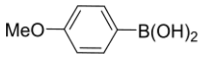
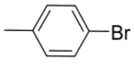
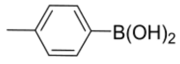
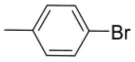
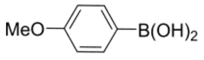
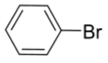
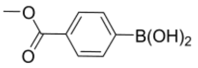
Figure 1. (A) One-step synthesis of Mw-Pd/DMTP-TPB catalyst via microwave-assisted *in situ* encapsulation strategy. (B) PXRD pattern. (C) N_2 sorption isotherm. Inset: pore size distribution from QSDFT calculations. (D) XPS Pd3d spectra of Mw-Pd/DMTP-TPB. (E) EDS Pd elemental mapping of Mw-Pd/DMTP-TPB.

revealing prominent Pd signals (Figure S2). Inductively coupled plasma-mass spectrometry (ICP-MS) analysis indicated the Pd content in Mw-Pd/DMTP-TPB was 2.1 wt.%. Notably, this approach enabled the gram-scale synthesis of Mw-Pd/DMTP-TPB, affording ~0.5 g of highly crystalline products (inset of Figures 1A and S3). These findings underscore the potential of microwave-assisted synthesis for the large-scale production of COF-based composite.

The *in situ* encapsulation of Pd during COF formation preserved the overall crystallinity and structural integrity of obtained Pd/COFs. The powder X-ray diffraction (PXRD) pattern of Mw-Pd/DMTP-TPB showed an intense characteristic reflection at 2.79°, followed by five minor peaks at 4.87°, 5.67°, 7.51°, 9.71°, and 25.4° (Figure 1B), corresponding to the (100), (110), (200), (210), (220), and (001) planes, respectively. This experimental PXRD pattern closely matched the reported one for DMTP-TPB,[37] indicating the Pd incorporation did not compromise the long-range order of the COF. The permanent porosity and surface area of Mw-Pd/DMTP-TPB were evaluated by N_2 sorption analysis at 77 K (Figure 1C). Mw-Pd/DMTP-TPB displayed a type IV isotherm, indicating the presence of mesopores. The calculated Brunauer–Emmett–Teller (BET) surface area of Mw-Pd/DMTP-TPB was 1070 $m^2\,g^{-1}$. Pore size analysis, using quenched solid functional theory (QSDFT), revealed the narrow pore size distribution centered at 3.2 nm (Inset, Figure 1C), which closely aligned with the previous report.[38] The chemical structure of Mw-Pd/DMTP-TPB was analyzed by Fourier transform infrared (FTIR) spectroscopy. The characteristic imine (C=N) band at 1612 cm^{-1} confirmed the anticipated aldehyde-amine condensation. Moreover, the FTIR spectrum of Mw-Pd/DMTP-TPB is similar to that of pristine DMTP-TPB, suggesting the retained chemical integrity of COF after Pd encapsulation (Figure S4). Thermogravimetric analysis (TGA) demonstrated the high thermal stability of Mw-Pd/DMTP-TPB, showing no significant decomposition up to 300 °C under nitrogen (Figure S5). To confirm the valence state of the encapsulated Pd, XPS analysis was performed for Mw-Pd/DMTP-TPB. The XPS Pd 3d spectrum showed characteristic binding energies at 336.2 eV and 342.2 eV of Pd $3d_{5/2}$ and $3d_{3/2}$, respectively (Figure 1D), corresponding to Pd(II) species.[17,39] In addition, the absence of diffraction peaks attributed to metallic Pd nanoparticles in the PXRD pattern of Mw-Pd/DMTP-TPB (Figure S6) further supports the successful dispersion of Pd(II) within the COF. Energy-dispersive X-ray spectroscopy (EDX) elemental mapping of Mw-Pd/DMTP-TPB displays a uniform distribution of the Pd throughout the COF particles (Figures 1E and S7). Scanning electron microscopy (SEM) images demonstrated that the morphology of COF was retained after introducing Pd during COF synthesis (Figure S8). However, a notable decrease in crystallite size was observed in Pd/COF compared to the parent COF. This reduction in crystallite size is further supported by PXRD analysis. The broader peak widths in the PXRD pattern of Mw-Pd/DMTP-TPB in comparison to bare

Table 1. The substrate scope of Mw-Pd/DMTP-TPB for Suzuki-Miyaura coupling reaction.[a]



Entry	R_1—Ar—Br	R_2-Ar—$B(OH)_2$	Yield (%)[b]
1			99
2			96
3			88
4			97
5			98
6			99
7			97
8			99

[a] Reaction conditions: aryl bromide (0.061 mmol), arylboronic acid (0.0732 mmol), Na_2CO_3 (0.122 mmol), Mw-Pd/DMTP-TPB (3 mg, 1 mol% Pd equiv.), methanol (2 mL), air, stirring at 600 rpm at room temperature. [b] Isolated yield was determined by ^1H NMR.

Mw-DMTP-TPB suggest smaller crystallite sizes, consistent with the Debye-Scherrer equation.

The observed high crystallinity, large surface area, and uniform Pd distribution render Mw-Pd/DMTP-TPB a promising candidate for heterogeneous catalysis. As a proof of concept, Mw-Pd/DMTP-TPB was employed to catalyze the Suzuki-Miyaura coupling reaction, a cornerstone method for C—C bond formation. To achieve the optimized reaction condition, 4-bromotoluene and phenylboronic acid served as model substrates. A variety of bases (Na_2CO_3, K_2CO_3, and triethylamine) and solvents (methanol, acetonitrile, dichloromethane, and tetrahydrofuran) were tested (entries 1–7, Table S1). Under optimized conditions (1 mol % Mw-Pd/DMTP-TPB catalyst loading, methanol solvent, and Na_2CO_3 base), the reaction achieved an exceptional 99 % yield of the desired biaryl product within an hour at room temperature. In addition, the pristine DMTP-TPB did not yield any product, signifying that the Pd severed as the active site in the Suzuki-Miyaura coupling reaction (entry 8, Table S1). The superiority of Mw-Pd/DMTP-TPB was further validated by control reactions using a commercially available 5 %Pd/carbon catalyst, which provided inferior yields under the optimized condition (entry 9, Table S1). Additionally, we synthesized Pd/DMTP-TPB through a conventional *ex situ* encapsulation method, wherein $Pd(OAc)_2$ was encapsulated into a preformed COF using a solution infiltration approach (denoted as traditional-Pd/DMTP-TPB). The obtained traditional-Pd/DMTP-TPB exhibits high crystallinity and possesses a high BET surface area of 940 $m^2\ g^{-1}$ (Figure S9). When used as a catalyst in the Suzuki-Miyaura reaction, traditional-Pd/DMTP-TPB achieved a 99 % yield in an hour at room temperature. Although it showed similar catalytic performance, traditional-Pd/DMTP-TPB required a more tedious protocol and considerably longer preparation time (> 5 days), further underscoring the advantage of microwave *in situ* encapsulation strategy. Comparative analysis with existing literature (Table S2) demonstrates that Mw-Pd/DMTP-TPB is a highly effective Pd/COF catalyst reported for the Suzuki-Miyaura coupling reaction. Notably, the preparation time (1 hour) of Mw-Pd/DMTP-TPB is considerably faster than previously reported Pd/COF systems (73–144 hours). The exceptional catalytic performance, combined with the facile synthesis and significantly reduced preparation time, highlights the substantial potential of the microwave-assisted *in situ* encapsulation strategy for the rapid generation of advanced Pd/COF catalysts applicable to a broad spectrum of organic transformations.

With optimized conditions in hand, we sought to investigate the versatility of Mw-Pd/DMTP-TPB in the coupling reactions of various aryl bromides and arylboronic acids. As shown in Table 1, Mw-Pd/DMTP-TPB exhibited high functional group tolerance on both coupling partners. In the case of aryl

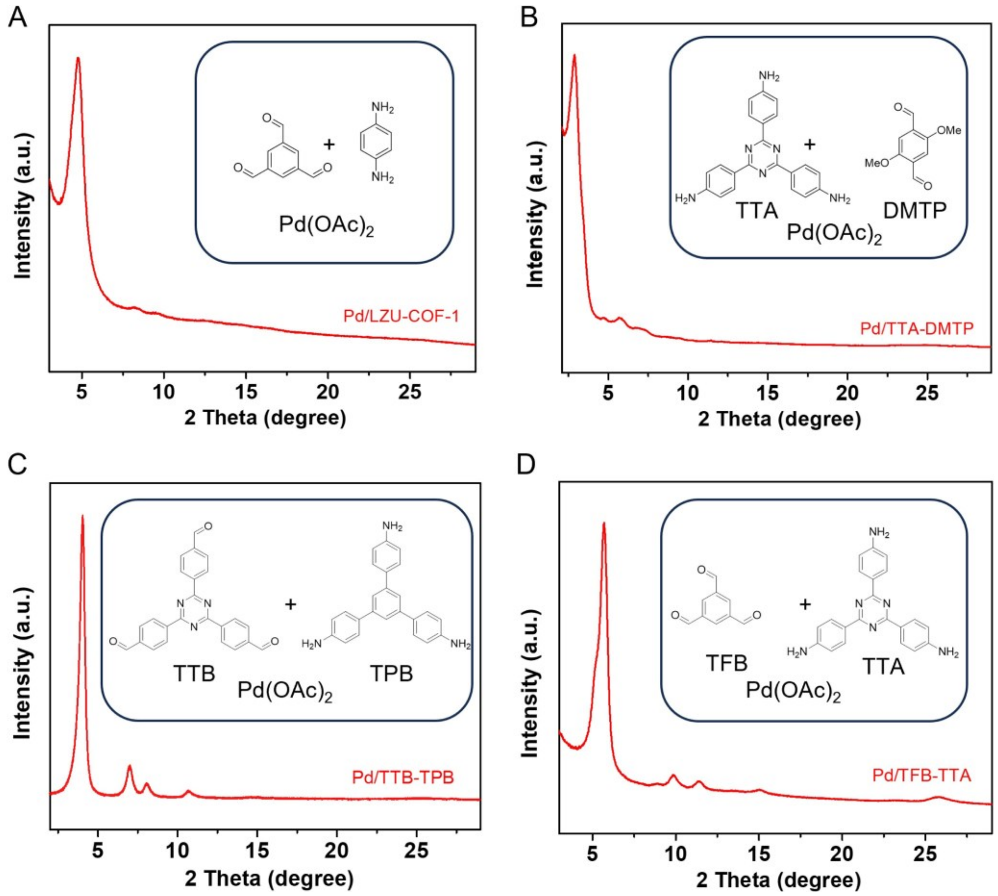


Figure 2. PXRD patterns of (A) Mw-Pd/LZU-COF-1, (B) Mw-Pd/TTA-DMTP, (C) Mw-Pd/TTB-TPB, (D) Mw-Pd/TFB-TTA. TFB = 1,3,5-triformyl benzene; TTA: 4,4',4''-(1,3,5-triazine-2,4,6-triyl) trianiline; TTB: 4,4',4''-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde; TPB = 1,3,5-tris(4-aminophenyl) benzene.

bromides, the electron-donating groups such as methyl (entry 2, Table 1) and methoxyl (entry 3), as well as electron-withdrawing groups such as nitro (entry 4), and cyano (entry 5) provided high yields (88–99 %) toward the desired products. Next, the substrate scope of the coupling partner, phenylboronic acids was evaluated. Electron-donating groups such as methyl (entry 6) and methoxyl (entry 7) and withdrawing group such as ester (entry 8), all gave the corresponding biaryls with high yields (97–99 %). These results demonstrate the high functional group tolerance of Mw-Pd/DMTP-TPB in the Suzuki-Miyaura coupling reaction.

To verify the heterogeneous nature of Mw-Pd/DMTP-TPB, typical leaching and recycling tests were performed. To assess the potential leaching of Pd species, Mw-Pd/DMTP-TPB was isolated from the reaction solution after achieving a partial conversion (60 %). The isolated reaction filtrate exhibited no further conversion even after several hours, signifying negligible leaching of homogeneous Pd species. The reusability of Mw-Pd/DMTP-TPB was subsequently investigated. Following each reaction cycle, the Pd/COF catalyst was recovered by centrifugation, washed thoroughly with methanol, and reused in a consecutive run. Notably, even after five cycles, the recovered Mw-Pd/DMTP-TPB still displayed similarly high activity with a yield of $>98\%$ (Figure S10). Moreover, the unchanged FTIR profile (Figure S11), PXRD pattern (Figure S12), and XPS spectrum (Figure S13) of the recovered Mw-Pd/DMTP-TPB confirmed the preservation of its chemical integrity, crystallinity, and Pd valence state, suggesting the high structural stability of the Mw-Pd/ DMTP-TPB catalyst under reaction conditions.

We next assessed the generality of this microwave-assisted *in situ* encapsulation strategy by extending this method to the synthesis of various Mw-Pd/COF hybrids (Figure 2). Through the microwave heating of different imine-linked COF monomers and $Pd(OAc)_2$ in acetonitrile at 120 °C for one hour, four crystalline Pd/COFs bearing different pore sizes and functionalities were obtained in high yields (88 %–94 %), underscoring the remarkable applicability of the microwave-assisted *in situ* encapsulation strategy. Imine-linked COFs based on the $[C_2+C_3]$ monomer combination, such as LZU-COF-1,[17] and DMTP-TTA,[40] demonstrated suitability for *in situ* Pd(II) encapsulation and exhibited high crystallinity consistent with previously reported PXRD patterns (Figure 2A and B). In addition, imine COFs using $[C_3+C_3]$ monomer combinations, such as TTB-TPB,[41] and TFB-TTA,[42] were also applicable in the synthesis of Pd/COF hybrids, exhibiting sharp and similar PXRD patterns to the reported ones (Figure 2C and D). The diversified COF supports encompass micro-to-meso pores ranging from 1.5 nm for TFB-TTA[42] to 3.2 nm for DMTP-TPB,[37] and exhibit varying nitrogen content. The success of our microwave-assisted *in situ* encapsulation strategy can be attributed to the synthetic versatility of imine-linked COFs, the compatibility of the acetonitrile solvent with both Pd precursors and COF monomers, and the enhanced reaction efficiency of microwave-assisted synthesis. Considering the enormous diversity of both COFs and metal species, this strategy provides a facile and expeditious approach for creating a wealth of metal/COF hybrids with task-specific properties tailored for diverse applications.

Conclusions

In summary, we have developed the first one-step synthesis of Pd(II)-encapsulated COF hybrids via a versatile microwave-assisted *in situ* encapsulation strategy. This approach effectively overcomes long-lasting limitations associated with the traditional synthesis of Pd/COF catalysts, such as tedious procedure, lengthy preparation time, anaerobic conditions, and excessive energy consumption. In addition, this strategy is highly generalizable to five Pd/COF hybrids and scalable to a half-gram scale. Thanks to the high crystallinity, permanent porosity, uniform Pd distribution, and robust frameworks, Mw-Pd/DMTP-TPB demonstrated remarkable activity and broad substrate scope for the Suzuki-Miyaura coupling reaction of various substituted aryl bromides and arylboronic acids at ambient conditions. Moreover, the heterogeneity of Mw-Pd/DMTP-TPB was confirmed by its high recyclability (reused 5 times) and the leaching test. This work not only establishes an expeditious, efficient, generalizable, and scalable approach for Pd(II)/COFs but also unveils enormous opportunities in developing metal/COF hybrids for various sought-after applications.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Covalent organic frameworks · Microwave-assisted synthesis · *In situ* metal complex encapsulation · Suzuki-Miyaura coupling

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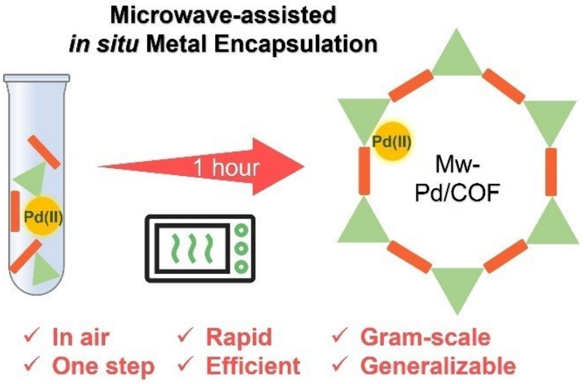

A rapid and efficient one-step synthesis of Pd(II)-encapsulated covalent organic framework (COF) composites has been developed via a versatile microwave-assisted *in situ* encapsulation strategy. Unlike the traditional multi-step synthesis, this approach establishes a succinct, expeditious, generalizable, and scalable route to access various Pd(II)/COFs.

*Z. Alsudairy, A. Campbell, Q. Zheng, C. Harrod, N. Brown, A. Saintilma, R. V. Maligal-Ganesh, C. Ingram, X. Li**

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Microwave-Assisted One-Step Synthesis of Palladium-Encapsulated Covalent Organic Frameworks for Heterogeneous Catalysis