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Mechanochemical *in situ* Encapsulation of Palladium in Covalent Organic Frameworks

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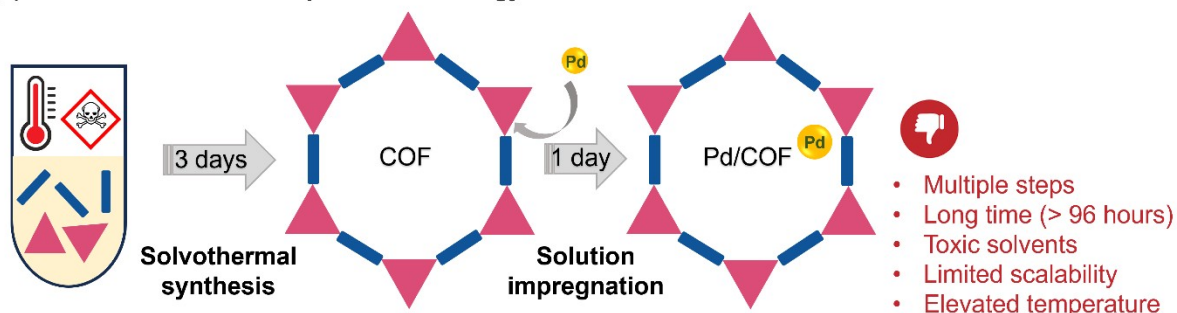
ABSTRACT. Palladium-encapsulated covalent organic frameworks (Pd/COFs) have garnered enormous attention in heterogeneous catalysis. However, the dominant *ex situ* encapsulation synthesis is tedious (multistep), time-consuming (typically 4 days or more), and involves the use of noxious solvents. Here we develop a mechanochemical *in situ* encapsulation strategy that enables the one-step, time-efficient, and environmentally benign synthesis of Pd/COFs. By ball milling COF precursors along with palladium acetate (Pd(OAc)₂) in one pot under air at room

temperature, Pd/COF hybrids were readily synthesized within an hour, exhibiting high crystallinity, uniform Pd dispersion, and superb scalability up to gram scale. Moreover, this versatile strategy can be extended to the synthesis of three Pd/COFs. Remarkably, the resulting Pd/DMTP-TPB showcases extraordinary activity (96-99% yield in 1 hour at room temperature) and broad substrate scope (> 10 functionalized biaryls) for the Suzuki-Miyaura coupling reaction of aryl bromides and arylboronic acids. Furthermore, the heterogeneity of Pd/DMTP-TPB is verified by recycling and leaching tests. The mechanochemical *in situ* encapsulation strategy disclosed herein paves a facile, rapid, scalable, and environmentally benign avenue to access metal/COF catalysts for efficient heterogeneous catalysis.

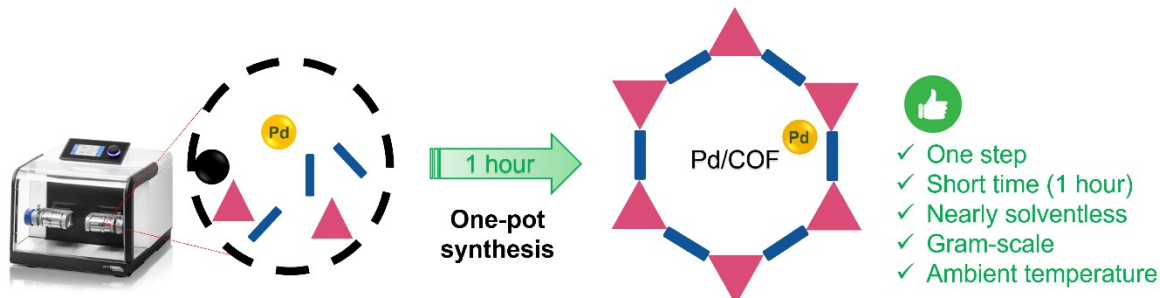
Covalent organic frameworks (COFs) are crystalline porous solids that permit the precise integration of organic subunits into extended two-dimensional or three-dimensional (2D or 3D) networks.¹ Compared to conventional porous materials, COFs possess a set of salient structural merits, including ultralow density, ordered networks, high porosity, customizable skeletons, and versatile synthesis, which are promising for widespread applications, such as gas separation, sensing, energy storage, water harvesting, environmental remediation, heterogeneous catalysis and so on.²⁻⁸ Of particular interest, COFs have emerged as promising porous scaffolds to anchor homogenous metal catalysts over the past decade. Compared to traditional solid supports such as carbons, mesoporous silica, and zeolite, COF features exceptional structural tunability, high porosity, and ordered nanochannels, which promote the mass diffusion of substrates and their ready access to active sites. Moreover, the atomically precise structure of COFs enables the establishment of clear structure-catalysis relationships, thereby facilitating the rational design and optimization of catalysts; In comparison to crystalline supports such as metal-organic

frameworks (MOFs), COFs possess superior chemical stability, which ensures their durable catalytic performance and catalyst recovery even under rigorous conditions. In addition, the lightweight nature of COFs contributes significantly to their high gravimetric performance in catalysis.⁹ The encapsulation of metal species in COFs not only overcomes the limitations of homogenous molecular catalysts (e.g., product contamination, lack of reusability) but also provides a modular platform to steer the catalytic behaviors of heterogeneous catalysis.¹⁰ Among the numerous metal catalysts, palladium (Pd) has gained substantial interest due to its pivotal role in modern organic synthesis.¹¹ Since the first report of Pd/COF catalyst for heterogeneous catalysis in 2011,¹² COFs have been widely deployed as supporting matrixes for Pd nanoparticles/complexes, exhibiting high heterogeneous catalytic performance in a broad array of organic transformations such as cross-coupling reactions,¹³⁻¹⁵ conjugate addition,¹⁶ silane oxidation,¹⁷ oxidation of aryl alcohol,¹⁸ chlorobenzenes dichlorination,¹⁹ semihydrogenation of alkynes,²⁰ and reduction of nitroarenes.²¹

(a) Traditional *ex situ* Encapsulation Strategy



(b) Mechanochemical *in situ* Encapsulation Strategy (This work)



Scheme 1. (a) Traditional *ex situ* encapsulation and (b) the mechanochemical *in situ* encapsulation strategy for the synthesis of Pd/COF catalysts.

The synthesis of Pd/COF catalysts has predominantly relied on the multistep *ex situ* encapsulation strategy, by which Pd species are embedded into the pre-synthesized COF supports through solution impregnation (Scheme 1a). While widely adopted, this approach is plagued by significant drawbacks in terms of time, energy, and carbon footprint. Firstly, the prevalent solvothermal synthesis of COF host requires vigorous synthetic conditions, including long reaction times (usually 3 days), anaerobic conditions, elevated temperatures, the usage of toxic solvents, and inferior scalability.²² Secondly, the dominant solution impregnation strategy to encapsulate Pd species into the COF host is also time-consuming (1-3 days) and may erode the crystallinity of COFs during the impregnation process.²³⁻²⁵ These dual drawbacks have led to a lengthy preparation time of Pd/COF catalysts (96-144 hrs, see Table S2 for more details), adverse environmental impact, tedious procedures, and limited scalability, which posed a considerable roadblock in the broad application of Pd/COF catalysts.

To address the shortcomings associated with the conventional solvothermal synthesis of COFs, the utilization of alternative energy sources such as microwave,^{26, 27} ultrasound,²⁸ mechanical force,²⁹ and electron beam,³⁰ has been a subject of immense interest in the past few years.³¹ Among them, mechanochemistry, which induces chemical reactions by mechanical energy,³² has recently gained resurging interest due to its unique advantages, including high efficiency, low eco-footprint, reduced reaction time, mild condition, etc. Identified by the International Union of Pure and Applied Chemistry (IUPAC) as one of ten world-changing technologies, mechanochemistry offers a powerful and environmentally benign approach to the

synthesis of diverse materials, including pharmaceuticals, inorganic nanoparticles, porous carbons, polymers, and MOFs.³³⁻³⁵ The first mechanochemical synthesis of COFs began in 2013 and has attracted escalating attention in the past decade.³⁶⁻⁴⁰ This approach enabled the rapid and environmentally benign synthesis of COFs. More importantly, the obtained COFs exhibited equivalent or superior properties to their solvothermal analogs.⁴¹ To overcome the drawback associated with the multistep synthesis of metal/COF hybrids, encapsulating metal species during the porous materials synthesis provides a viable solution. For instance, previous studies demonstrate that metal-encapsulated MOF hybrids can be readily synthesized via a facile *in situ* solvothermal approach,⁴²⁻⁴⁶ whereby MOF formation and *in situ* metal encapsulation were simultaneously combined in a single pot. Nonetheless, the application of such *in situ* encapsulation strategy in COFs remains largely underexplored.^{47, 48} Given the synthetic versatility of COFs and the ease of hybridizing COF with functional materials,⁴⁹⁻⁵¹ we anticipate that combining mechanochemical synthesis of COFs and *in situ* metal impregnation in one pot will confer numerous advantages, including streamlining the preparation process for Pd/COF catalysts, minimizing environmental impact, enhancing the scalability, and thereby offering a viable solution to the aforementioned drawbacks associated with multistep synthetic procedures for Pd/COFs.

In this study, we develop a facile, rapid, and environmentally benign one-step synthesis of Pd/COF catalysts via a mechanochemical *in situ* encapsulation strategy. This strategy merges the mechanochemical synthesis of COF and *in situ* Pd encapsulation in a single pot (Scheme 1b), thereby drastically reducing the preparation time of the Pd/COF catalyst from the conventional 4 days to merely 1 h. Moreover, this strategy can be implemented on a gram scale and is applicable

to a range of Pd/COFs. As a proof of concept, the resultant Pd/DMTP-TPB was employed to catalyze the Suzuki-Miyaura coupling reaction of aryl bromides and arylboronic acids, exhibiting outstanding catalytic activity at room temperature, broad functional group tolerance, and good reusability. Notably, its catalytic performance surpasses that of commercial Pd/carbon, Pd/DMTP-TPB made by solution chemistry, and most existing Pd/COF catalysts. To the best of our knowledge, this work represents the first endeavor in the synthesis of metalated COF catalysts via mechanochemistry.

We initiated our study by using a prototypical 2D imine COF, DMTP-TPB, which consists of 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (DMTP) and 1,3,5-tris(4-aminophenyl)benzene (TPB) (Figure 1a).⁵² To implement the mechanochemical *in situ* encapsulation strategy, COF monomers (DMTP and TPB) and palladium acetate ($\text{Pd}(\text{OAc})_2$) were ball milled under air at room temperature for 1 h in the presence of liquid additives. To achieve the highly crystalline Pd/DMTP-TPB, various synthetic parameters including liquid additive, Pd amount, and milling frequency have been systematically screened. It was found that the mesitylene/1,4-dioxane mixture was the optimal liquid additive, outperforming other liquids such as methanol, acetonitrile, *n*-butanol, 1,4-dioxane, mesitylene, and *o*-dichlorobenzene/*n*-butanol (Figure S1). Furthermore, the influence of the amount of $\text{Pd}(\text{OAc})_2$ on the crystallinity of Pd/COF was investigated, revealing that 2 mg of $\text{Pd}(\text{OAc})_2$ resulted in the highest crystallinity (Figure S2). Lastly, the impact of frequency was examined, and 20 Hz was identified as the optimal frequency compared to 10 Hz and 30 Hz (Figure S3). Highly crystalline Pd/DMTP-TPB was synthesized by milling DMTP (0.105 mmol) and TPB (0.07 mmol) in a 5 mL-stainless steel jar at 20 Hz for 1 h, using AcOH (15 μL) as a catalyst and mesitylene/1,4-dioxane (15 μL /15 μL) as

a liquid additive. Notably, Pd/DMTP-TPB was obtained as a light brown powder (see supporting information), which contrasts with the bright yellowish color of Pd-free COF (DMTP-TPB), signifying the successful encapsulation of Pd species into the COF. This was further corroborated by the X-ray photoelectron spectroscopy (XPS) survey spectrum of Pd/DMTP-TPB, which revealed the presence of Pd (Figure S4). In addition, the Pd content in the COF was determined to be 4.1 wt.% based on inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements. It is worth noting that the large-scale synthesis of Pd/DMTP-TPB was conducted by amplifying the substrate 40-fold using a 25 mL-stainless steel jar, giving rise to ~1.3 g of highly crystalline Pd/DMTP-TPB within an hour (inset Figure 1a and Figure S5). The scalability further underscores the advantage of the mechanochemical *in situ* encapsulation strategy compared to the traditional *ex situ* encapsulation approach.

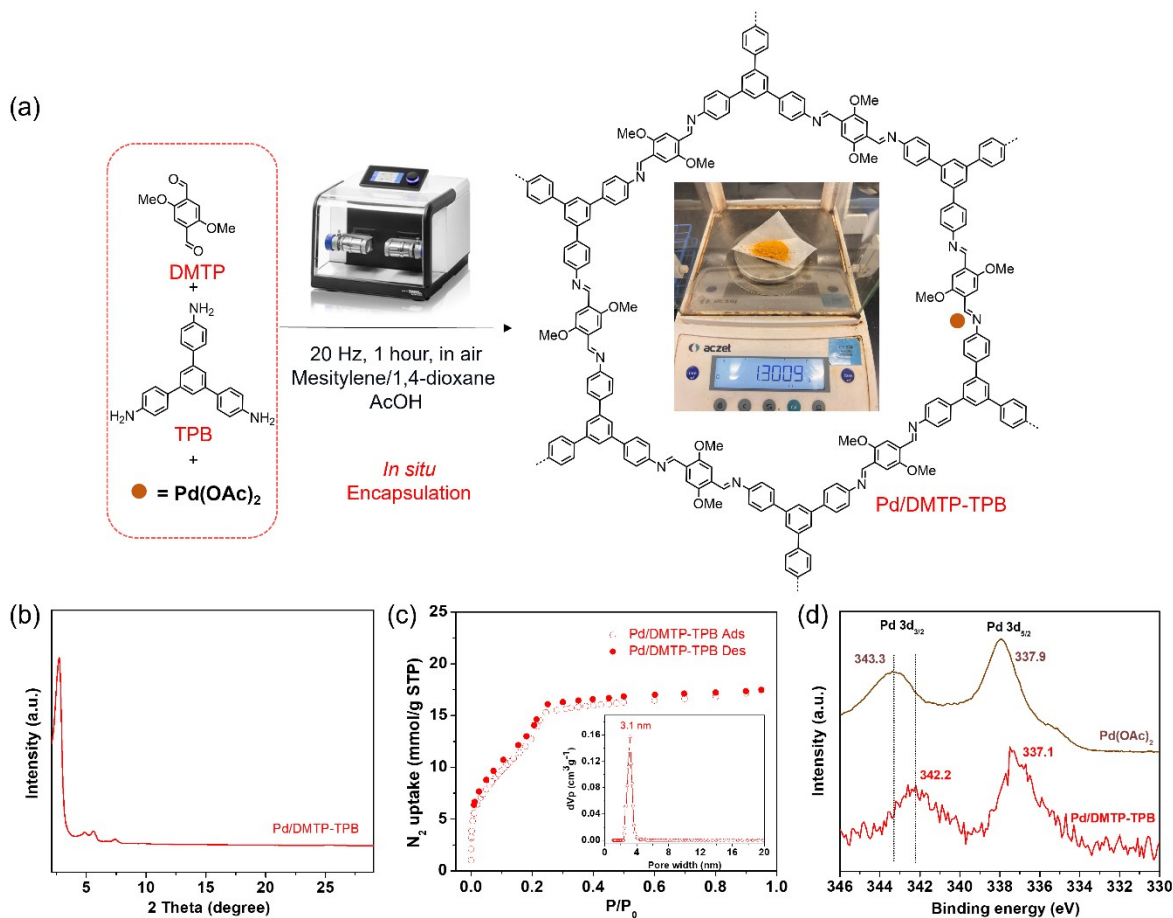


Figure 1. (a) One-step synthesis of Pd/DMTP-TPB via the mechanochemical *in situ* encapsulation strategy. Inset is the Restch Mixer Mill MM 400 and the gram-scale synthesis of Pd/DMTP-TPB powder. (b) PXRD pattern. (c) N₂ adsorption-desorption isotherm. Inset is the pore size distribution profile calculated by NLDFT. (d) XPS Pd 3d spectra of bare Pd(OAc)₂ and Pd/DMTP-TPB.

The resulting Pd/DMTP-TPB was characterized by various analytical techniques. Fourier transform infrared (FTIR) spectroscopy revealed the characteristic imine stretch at 1612 cm⁻¹ and the disappearance of N–H stretch (3100–3300 cm⁻¹) in the starting monomer TPB, confirming the successful Schiff-base condensation (Figure S6). In addition, the vibration peaks at ~1700 cm⁻¹ correspond to the unreacted -CHO groups located at the defective edges of the COF. The

high crystallinity of the as-synthesized Pd/COF was ascertained by powder X-ray diffraction (PXRD) analysis. Pd/DMTP-TPB displayed a sharp first peak at 2.72° and minor peaks at 5.03° , 5.65° , 7.55° , 9.82° , and 25.7° (Figure 1b), corresponding to the (100), (110), (200), (210), (220), and (001) facets, respectively. This experimental PXRD pattern was similar to the previously reported one,⁵³ suggesting the retained crystallinity of COF support upon the Pd encapsulation (Figure 1b).⁵⁴ N_2 sorption analysis showed a type-IV adsorption isotherm for Pd/DMTP-TPB (Figure 1c), revealing its mesoporous nature. The Brunauer-Emmett-Teller (BET) surface area of Pd/DMTP-TPB was evaluated to be $625 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution estimated by using the non-local density functional theory (NLDFT) model revealed a pore with of 3.1 nm (Inset of Figure 1c), consistent with the reported pore size of DMTP-TPB.²⁸ XPS analysis was employed to probe the oxidation state of the encapsulated Pd in the COF. Pd/DMTP-TPB displayed two broad peaks at 337.1 eV and 342.2 eV, (Figure 1d), which were assignable to core energy levels of Pd(II)3d_{5/2} and Pd(II)3d_{3/2}, respectively.²³ Notably, the binding energy of Pd(II)3d_{3/2} for Pd/DMTP-TPB shifted upfield by ~ 1.0 eV compared to that of bare Pd(OAc)₂, indicating the strong interaction between Pd(II) and the COF support. This observation aligns with prior findings in Pd/COF systems, where a similar upfield shift of Pd energy level was noted.¹² High-resolution transmission electron microscopy (HRTEM) analysis indicates that Pd/DMTP-TPB adopts irregular sheet morphology and heterogeneous particle size (Figure S7). Importantly, HRTEM images (Figure S8) reveal no discernible Pd nanoparticles (NPs). Furthermore, PXRD pattern of the Pd/COF (Figure S9) lacks any diffraction peaks attributable to Pd NPs. These observations are consistent with the XPS analysis, suggesting the presence of Pd(II) species within the COF framework. The Pd distribution was evaluated by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive

spectroscopy (EDS) measurements. The EDS mapping of Pd/DMTP-TPB revealed the uniform distribution of C, N, O, and Pd elements throughout the framework (Figure 2).

Thermogravimetric analysis (TGA) indicated that Pd/DMTP-TPB is thermally stable up to 400 °C under nitrogen (Figure S10). Furthermore, the chemical stability of Pd/DMTP-TPB was assessed by immersing COF samples into aqueous solutions of HCl (12 M), and NaOH (14 M) for 3 days at room temperature (Figure S11). PXRD profiles showed the crystallinity of Pd/DMTP-TPB was well preserved after chemical treatment, indicating the robust chemical stability of the COF host. The high stability of Pd/DMTP-TPB is crucially important for its durable catalytic performance in heterogeneous catalysis, which may require stringent conditions like high temperatures and acidic or alkaline environments.

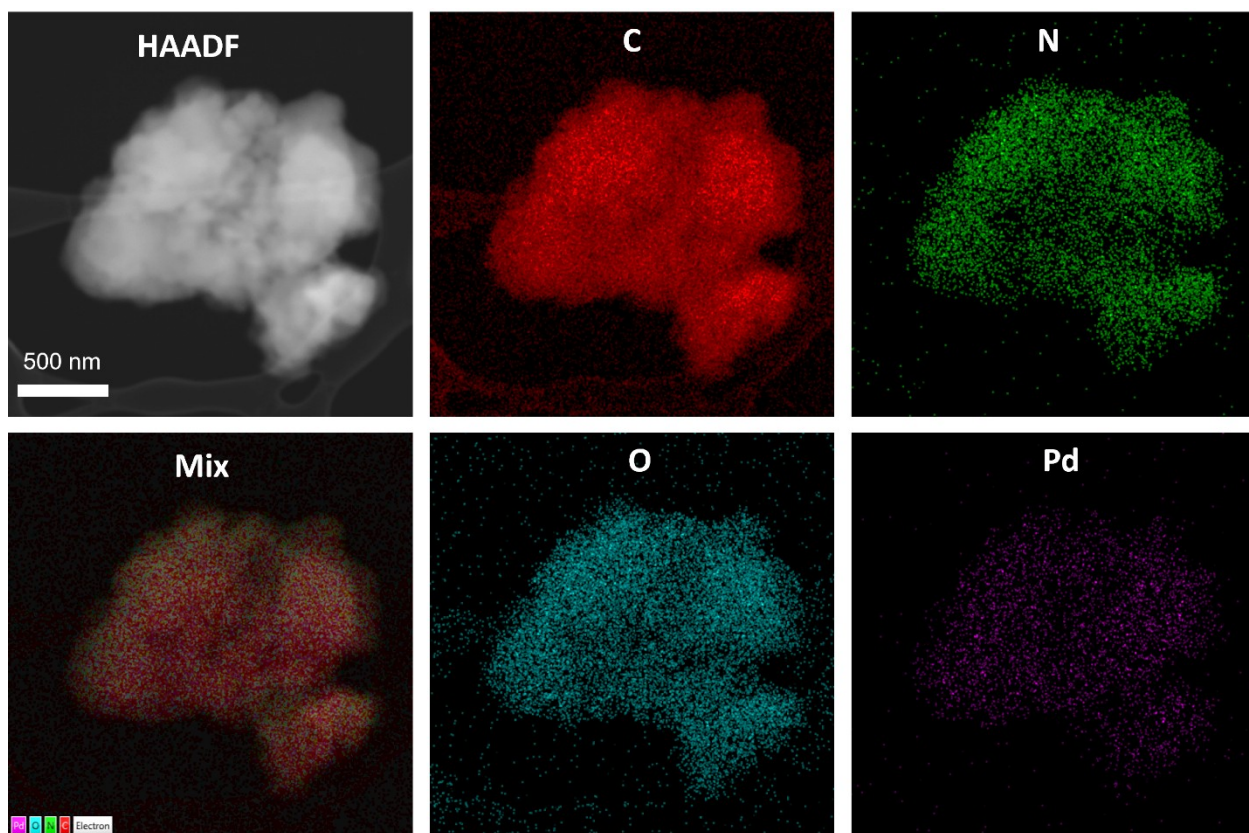


Figure 2. HAADF-STEM image and the corresponding EDS map of Pd/DMTP-TPB.

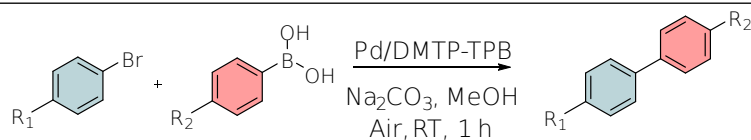
Enlightened by the high crystallinity, permanent porosity, uniform Pd dispersion, strong metal-support interaction, and robust structure of Pd/DMTP-TPB, we proceeded to investigate its catalytic performance for the Suzuki-Miyaura coupling reaction, which stands as a cornerstone in organic synthesis, enabling the formation of carbon-carbon (C-C) bonds with exceptional efficiency and selectivity.⁵⁵⁻⁵⁸ To optimize the reaction condition, we selected the coupling reaction of 4-bromotoluene and phenylboronic acid at 1 mol% catalyst loading as the model reaction. The results of the optimization and control experiments are summarized in Table S1. A comparison of various bases showed that Na₂CO₃ is superior to K₂CO₃ and triethylamine (Table S1, entries 1-3). Solvent screening indicated that methanol is a better solvent than ethanol, toluene, methylene chloride, and tetrahydrofuran for the model reaction (Table S1, entries 4-7). The optimized condition used Pd/DMTP-TPB, Na₂CO₃ as the base, and methanol as the solvent in the air at room temperature, exhibiting quantitative yield towards the desired biaryl product. Furthermore, DMTP-TPB COF did not afford any product, confirming that the catalysis occurred at the supported Pd centers (Table S1, entry 8). The superiority of Pd/DMTP-TPB was further validated by a control reaction using commercially available 5%Pd/carbon, which provided an inferior yield of 42% under identical conditions (Table S1, entry 9). This finding further highlights the advantages of Pd/DMTP-TPB over traditional heterogenous catalysts. Under identical conditions, Pd/DMTP-TTA and Pd/TTA-TTB showed 80% and 95% yields in 1 h, respectively (Table S1, entries 10 and 11). This observation underscores the critical role of COF support in catalyst performance. Impressively, compared to the previously reported Pd/COF catalysts for the Suzuki-Miyaura coupling reaction (Table S2), Pd/DMTP-TPB demonstrates

exceptional catalytic performance in terms of high activity and mild reaction conditions. Pd/DMTP-TPB can achieve a high turnover frequency (TOF) of 97.4 h^{-1} , superior to previously reported Pd/COF catalysts.¹⁴ It is worth noting that the preparation for Pd/DMTP-TPB in this study requires a significantly shorter time (1 h) than most previously reported systems (> 96 hrs) and avoids the usage of toxic solvents. To further underscore the advantage of the mechanochemical *in situ* encapsulation strategy, we prepared the Pd/DMTP-TPB (termed solution-Pd/DMTP-TPB) via a conventional solution impregnation method. This method entails solvothermal synthesis of DMTP-TPB followed by solution impregnation of the Pd precursor (Figure S12A). The obtained solution-Pd/DMTP-TPB exhibits high crystallinity (Figure S12B) and possesses a high BET surface area of $937 \text{ m}^2/\text{g}$ (Figure S12C). When employed as a catalyst in the Suzuki-Miyaura reaction at room temperature, solution-Pd/DMTP-TPB displayed a yield of 98% in 1 h, slightly lower than that of mechanochemically synthesized Pd/DMTP-TPB (Table S1, entry 12). Despite comparable catalytic activity, solution-Pd/DMTP-TPB demands a more tedious protocol and a significantly extended preparation time (>5 d). Altogether, these results not only highlight the advantages of mechanochemical *in situ* encapsulation strategy over traditional protocols in the sustainable synthesis of Pd/COFs but also underscore its considerable potential for heterogeneous catalysis.

With the optimized condition identified, we set out to explore the substrate scope of Pd/DMTP-TPB in the coupling reaction of different aryl bromides and arylboronic acids (Table 1). As shown, Pd/DMTP-TPB demonstrated exceptional functional group tolerance towards a wide range of functional groups, affording the desired biaryl products in high yields (>95%). Aryl bromides bearing electron-donating groups, including methyl and methoxy (Table 1, entries

2 and 3) as well as electron-withdrawing groups such as ketone, nitro, and cyano (entries 4-6) were well tolerated. This catalyst was also effective for heterocyclic arylbromide such as 2-bromothiophene (entry 7). In addition, Pd/DMTP-TPB effectively catalyzed the coupling reactions of bromotoluene with various phenylboronic acids, including those with electron-donating groups such as methyl and methoxy (entries 8 and 9) as well as electron-withdrawing groups like aldehyde, ester, and nitro (entries 10-12). Altogether, these results verified the broad substrate scope of the Pd/DMTP-TPB-catalyzed Suzuki-Miyaura coupling reaction.

Table 1. Substrate Scope of Pd/DMTP-TPB-Catalyzed Suzuki-Miyaura Coupling Reaction ^a



Entry	R ₁ -Ar-Br	R ₂ -Ar'-B(OH) ₂	Product	Yield ^b
1				99%
2				99%
3				98%
4				97%
5				97%
6				96%
7				96%
8				99%
9				98%
10				97%
11				98%
12				96%

^a Reaction conditions: Pd/DMTP-TPB (3 mg, 1 mol% Pd equiv.), aryl bromide (0.113 mmol), arylboronic acid (0.124 mmol), Na₂CO₃ (0.226 mmol), methanol (2 mL), in air, 1 h, stirring at 600 rpm at room temperature.

^b Yield was determined by ¹H NMR analysis, based on aryl bromide.

stability and recyclability of Pd catalyst are key parameters in heterogeneous catalysis. To assess the potential leaching of Pd species, Pd/DMTP-TPB was isolated from the reaction solution after

achieving a partial conversion (76%). The isolated reaction filtrate exhibited no further conversion even after several hours, signifying negligible leaching of homogeneous Pd species. The reusability of the Pd/DMTP-TPB catalyst was also evaluated. After each run, the catalyst was isolated by centrifugation, washed with methanol, and reused in the consecutive run. As shown in Figure 3a, Pd/DMTP-TPB consistently displayed excellent yields exceeding 99% over three recycling runs. Extending the recycling process to the 5th cycle demonstrates a slight decrease in yield from >99% to 92% (Figure S13), presumably due to the inevitable loss of COF catalyst during the recycling process. The PXRD pattern of the used Pd/DMTP-TPB remained almost unchanged after catalysis (Figure 3b). The FTIR spectrum of the recovered Pd/DMTP-TPB was nearly identical to that of the pristine one (Figure S14). Moreover, XPS analysis of the recovered catalyst confirmed that the Pd species remained in the Pd(II) state (Figure S15). These characterizations underscore the stability of the Pd/COF catalyst under the catalytic conditions. The exceptional structural stability of the COF support, along with the strong Pd-COF interaction due to the abundant nitrogen sites (>7 wt%) within the framework, collectively contributed to the high reusability of the Pd/DMTP-TPB catalyst. The plausible catalytic mechanism of Pd/DMTP-TPB is depicted in Scheme S1. Initially, the Pd(II) complex embedded in DMTP-TPB generates catalytically active Pd(0) species *in situ*. The Pd(0) species then engage in oxidative addition with aryl bromide (R¹-Br) to afford a R¹-Pd(II)-Br intermediate, which subsequently undergoes transmetalation with aryl boronic acid (R²-B(OH)₂) to form a biaryl palladium complex (R¹-Pd(II)-R²). Finally, reductive elimination yields the desired biaryl product (R¹-R²) and simultaneously regenerates the Pd(0) catalyst, completing the catalytic cycle.⁵⁹

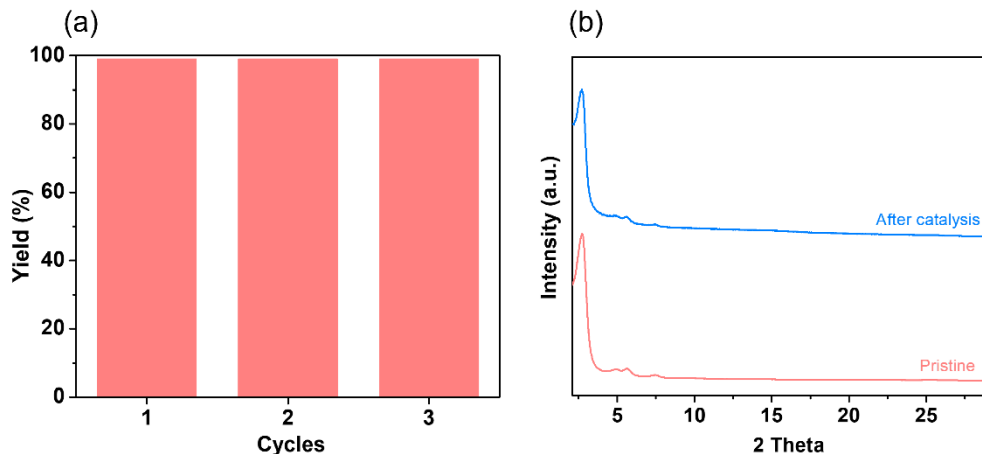


Figure 3. (a) Recycling test of Pd/DMTP-TPB in the Suzuki-Miyaura coupling reaction. (b) PXRD patterns Pd/DMTP-TPB before and after catalysis.

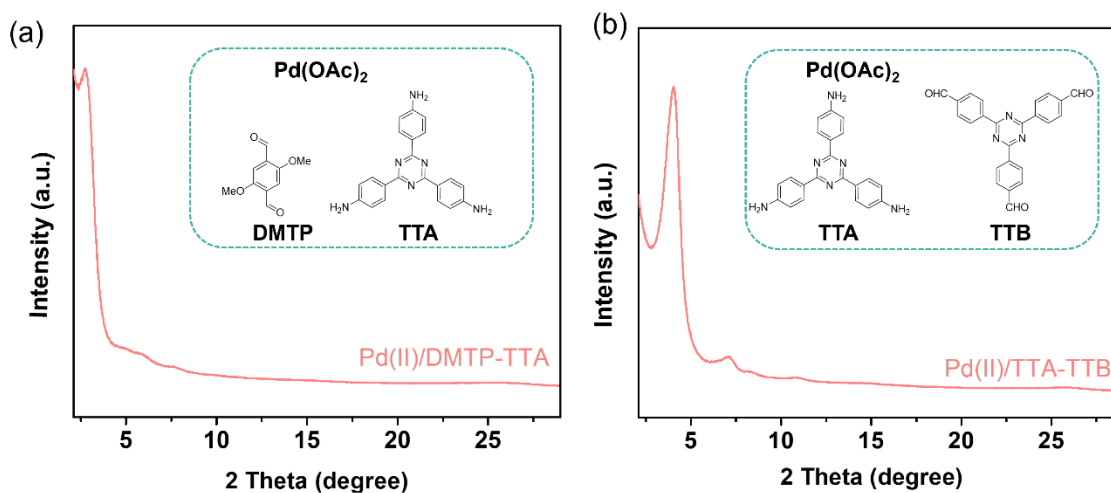


Figure 4. The generality of the mechanochemical *in situ* encapsulation strategy. PXRD patterns of (a) Pd(II)/DMTP-TTA; (b) Pd(II)/TTA-TTB.

To showcase the generality of the mechanochemical *in situ* encapsulation strategy, we encapsulated Pd(II) into another two well-studied COF supports, DMTP-TTA⁶⁰ and TTA-TTB,⁶¹ which are hexagonal imine 2D COFs with distinct pore metrics (Figure 4 A and 4B, see

structures in Supporting Information). After extensive condition optimization, 4.1 wt% Pd/DMTP-TTA was obtained by milling DMTP, 4,4',4''-(1,3,5,-triazine-2,4,6-triyl) trianiline (TTA), and Pd(OAc)₂ using mesitylene as a liquid additive at 20 Hz for 1 h, while 4.2 wt% Pd/TTA-TTB was achieved by milling TTA, 4,4',4''-(1,3,5-triazine-2,4,6-triyl) tribenzaldehyde (TTB), and Pd(OAc)₂ using mesitylene as a liquid additive at 20 Hz for 1 h. Both Pd/COFs were thoroughly characterized by various techniques including PXRD (Figure 4), FTIR (Figure S16), N₂ sorption analysis (Figure S17), and TGA (Figure S18), confirming the formation of Pd/COFs with moderate-to-high crystallinity, large surface areas (>500 m² g⁻¹) and superb thermal stability (>350 °C in N₂). These results unambiguously underscore the versatility of the mechanochemical *in situ* encapsulation strategy in making diverse metal/COF catalysts, allowing for tailored combinations of both metal species and COF supports.

In summary, we have developed a mechanochemical *in situ* encapsulation strategy that enables the one-step synthesis of metal-encapsulated COFs. This strategy is facile, rapid, environmentally benign, scalable, and generalizable, which markedly contrasts with the traditional *ex situ* encapsulation approach for the preparation of Pd/COF catalysts. Thanks to the high crystallinity, permanent porosity, accessible Pd sites, and structural robustness, Pd/DMTP-TPB showed exceptional activity and broad substrate scope for the Suzuki-Miyaura coupling reaction of various substituted aryl bromides and aryl boronic acids within merely one hour. Furthermore, Pd/DMTP-TPB can be reused multiple times without Pd leaching. Given the enormous diversity of COF supports and metal species, we anticipate that the mechanochemical *in situ* encapsulation strategy will open tremendous opportunities for developing multifunctional metal/COF hybrids for sustainable catalysis and beyond.

ASSOCIATED CONTENT

Supporting Information. Additional experimental details, materials, and methods, including detailed experimental setup and protocols, and characterization profiles including PXRD, N₂ sorption analysis, TGA, FTIR, HRTEM, and XPS.

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

There are no financial conflicts to declare.

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