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Pd@COF-QA: A phase transfer composite catalyst for aqueous Suzuki-Miyaura coupling reaction

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A Pd NP loaded and paraffin-chain quaternary ammonium salt decorated covalent framework Pd@COF-QA and its chitosan aerogel-based continuous flow-through reactor, which can be an excellent phase transfer catalyst to promote aqueous Suzuki-Miyaura coupling reaction, is reported.

Although covalent organic frameworks (COFs) being in their early teens,¹ as a typical class of organic crystalline porous species, they have already been found to be the promising functional materials in gas adsorption,² separation,³ proton conduction,⁴ optical devices,⁵ drug delivery,⁶ chemical sensing,⁷ energy storage,⁸ and catalysis.⁹

Taking their advantages of the tuneable and permanent porosity and excellent chemical stability, a predestined ambit for COFs could be the ideal carriers for loading active catalytic species such as metal nanoparticles (M NPs) to fabricate heterogeneous composite catalytic systems (M@COFs).¹⁰⁻¹² For example, palladium loaded COFs (Pd@COFs) have been found to be highly efficient heterogeneous catalysts to promote Suzuki-Miyaura coupling reaction, 13-17 which is one of the most important class of C-C coupling reactions. 18 However, the most reported COF-catalysed coupling reactions were performed at relatively high temperature and in organic media such as toluene, p-xylene, methanol, ethanol, and DMF, which did not meet the resource conservation and environment-friendly requirements. Therefore. the development of COF-based green catalysts for Suzuki-Miyaura coupling reaction is of great significance.

Phase-transfer catalysis (PTC) is a promising green technique for organic transformation due to its simple operation, aqueous medium and mild reaction conditions.¹⁹ Very recently, our group developed a series of MOF-based PTC catalytic systems which can well promote the organic transformations in aqueous phase.^{20,21} As a promising alternative to MOFs, the covalent bond driven COFs should be more stable in aqueous phase, and their PTC behaviour is really worth pursuing.

Herein, we report a Pd NP loaded and *N*, *N*-dimethyldodecyl ammonium bromide decorated COF. The obtained **Pd@COF**-**QA** and its chitosan aerogel-based continuous flow-through reactor can be an excellent phase transfer catalyst to promote Suzuki-Miyaura coupling reaction in water under mild conditions even at gram scale level.

As shown in Scheme 1, the quaternary ammonium salt decorated dihydrazide (L-QA) was prepared from 2, 5-di-(4-methoxycarbonylphenyl) toluene (A) via three steps. **COF-QA** was synthesized as light-yellow crystalline solids through the Schiff-base condensation between L-QA and 1,3,5-triformylbenzene under solvothermal conditions (ESI⁺). The as-synthesized **COF-QA** was characterized by FT-IR and solid-state CP-MAS spectroscopies, and the formation of **COF-QA** from L-QA and tribenzaldehyde was directly evidenced (ESI⁺).

As shown in Fig. 1, the collected PXRD data revealed that the obtained COF-QA was crystalline and its structural modeling was thus conducted with the software of Materials Studio (ver. 5.0) (ESI⁺).²² The most probable structure of COF-QA was a typical 2D layered hexagonal network with the space group of P₃. As shown in Fig. 1, COF-QA showed a main Bragg diffraction peak at 2.3° corresponding to the (100) plane, and three weak peaks at 4.6°, 6.1° and 7.9°, and a broad peak within the range of 17.5-26.2°. These observed peaks are respectively associated with (200), (210), (220) and (002) planes. The broad PXRD peaks, especially the (002) peak, which should be caused by the long alkyl chains, which can disturb both the packing of layers and the size of unit cells. ²³⁻²⁵ A Pawley refinement of COF-QA based on the experimental PXRD and model PXRD patterns gave the fitting parameters of Rwp = 1.88 and Rp = 1.46%, respectively. After Pawley refinement, the unit cell parameters were determined as a = b= 44.4, and c = 5.6 Å; α = β = 90°, and γ = 120° (ESI⁺).

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Scheme 1. Synthesis of ligand LA-QA, COF-Me and COF-QA. i) NBS, AIBN, CCl₄, 90°C. ii) C₁₄H₃₁N, MeCN, 78°C. iii) and iv) N₂H₄·H₂O, MeOH, reflux. v) and vi) 1,4dioxane/mesitylene/HOAc, 120°C, 3 days. vii) and viii) Pd(OAc)₂/CH₂Cl₂/24 h, TEA/50°C/24h. Crystal packing patterns of COF-Me and COF-QA viewed down the crystallographic c axis are shown. The sample photographs of COF-Me, COF-QA, Pd@COF-Me and Pd@COF-QA are inserted.



As indicated in Scheme 1, Pd@COF-QA was prepared as deep brown crystalline solids by solution impregnating and in situ reduction process, in which the unreacted free end formamide groups on COF-QA acted as the reducing reagent (ESI⁺).

Scanning Electronic Microscopy (SEM) measurement showed that most of the larger particles of **COF-QA** were broken into smaller pieces in **Pd@COF-QA** after the palladium loading and

the in situ reduction processes but with the same crystal structure based on their PXRD patterns (Fig. 2a-b, and ESI+). In addition, the high-resolution transmission electron microscopy (HR-TEM) revealed that the loaded Pd NPs were well dispersed in the COF-QA matrix with an average particle centred at ca. 2.4 nm based on the statistic histogram for more than 100 randomly chosen particles and the atomic lattice fringes had an interplanar spacing of 0.22 nm associated with the (111) plane of the loaded Pd NPs (Figs. 2c-d). As indicated in Fig. 2e, the oxidation state of the loaded Pd NPs in Pd@COF-QA were found to be zero based on the Pd 3d binding energy at 335.05 (Pd-3d_{5/2}) and 339.92 eV (Pd-3d_{3/2}) in its measured X-ray photoelectron spectroscopy (XPS),^{10, 11} implying that the in situ reduction of palladium from Pd(II) to Pd(0) herein is successful. The uniform texture of Pd@COF-QA was further confirmed by SEM-EDX mapping, which showed a homogeneous distribution of Pd, N, and C elements in the COF matrix (Fig. 2f). Inductively coupled plasma (ICP) analysis indicated that the Pd loading amount in Pd@COF-QA was 9.2 wt% (ESI+).

Thermogravimetric analysis (TGA) trace indicated that Pd@COF-QA remained intact till temperature over 200°C,

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suggesting its good thermal stability (ESI⁺). As we know, the common molecular quaternary ammonium salts are generally stable up to ca. 100°C.²⁰ Notably, after covalently grafting on COF framework, their thermal stability was largely enhanced, which would effectively expand their application temperature range, and make them more suitable to catalyse organic reactions at relative higher temperature.

The porosity difference before and after Pd NP loading was demonstrated gas bv the adsorption-desorption measurement. N₂ absorption amount of COF-QA and Pd@COF-QA at 77 K is 61.9 and 47.0 cm³ g⁻¹, respectively. Their corresponding surface areas calculated on basis of the BET model are 59.0 (COF-QA), 26.0 (Pd@COF-QA) m² g⁻¹, respectively. The decreased N₂ adsorption and the reduced surface area in Pd@COF-QA were obviously caused by the Pd NP loading. The pore sizes distribution curves, generated from Barrett-Joyner-Halenda analysis, showed that COF-QA and Pd@COF-QA having the major contribution of the pore widths at ca. 3.8 and 3.4 nm, respectively, which is well consistent with their simulated structure.



Fig. 2 a) and b) SEM images of COF-QA and Pd@COF-QA. c) HRTEM image of Pd@COF-QA. d) Pd NP size distribution in Pd@COF-QA. e) XPS spectrum of the Pd 3d in COF-QA. f) SEM-EDX spectrum of Pd@COF-QA.

We expected that the **Pd@COF-QA** with PTC functionality herein could bypass those adverse issues such as organic solvents or relatively high temperature in the reported Suzuki-Miyaura coupling reaction. For this, its catalytic activity was preliminarily examined by the PhI and PhB(OH)₂ coupling in water.

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 Table 1. Optimization of reaction conditions for the model Suzuki-Mixaura: (coupling reaction in water^a
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$ + \bigcup_{H_2O}^{B(OH)_2} - \bigcup_{H_2O}^{Catalyst} $						
entry	catalyst	base	T (°C)/t (h)	Yield ^b (%)		
1	Pd@COF-QA	TEA	25/1	32		
2	Pd@COF-QA	TEA	35/1	61		
3	Pd@COF-QA	TEA	50/1	81		
4	Pd@COF-QA	TEA	50/3	88		
5	Pd@COF-QA	TEA	50/6	>99		
6	Pd@COF-QA	K ₂ CO ₃	50/6	58		
7	Pd@COF-QA	Na ₂ CO ₃	50/6	66		
8	Pd/C	TEA	50/6	13		
9	Pd@COF-Me	TEA	50/6	79		
10 ^c	Pd@COF-Et	TEA	50/6	82		

 o Reaction condition: I-Ph (0.2 mmol), phenylboronic acid (0.24 mmol), base (0.4 mmol), catalyst (1.7 mol % Pd equiv), H₂O (2.0 mL), in air. b Determined by GC (ESI†). c Reaction condition: I-Ph (0.2 mmol), phenylboronic acid (0.24 mmol), base (0.4 mmol), catalyst (3.4 mol % Pd equiv), H₂O (2.0 mL), in air.

As shown in Table 1, the influence of different temperature, time and base were examined for the model coupling reaction in water. When triethylamine (TEA) was employed, the coupling yield increased along with the reaction temperature (Table 1, entries 1–3) and time (Table 1, entries 3–5) increase. The best results were observed when the reaction was conducted at 50 °C for 6h in water, giving the desired diphenyl in 99% yield (Table 1, entry 5). In addition, when the reaction was carried out with inorganic base such as K_2CO_3 or Na_2CO_3 , the coupled product was obtained in much lower yields under the given conditions (Table 1, entries 6 and 7). Worth mentioning, when the reaction was carried out with commercialized Pd/C under the optimal conditions, the desired product was obtained in only 13% yield (Table 1, entry 8).

The heterogeneous nature of Pd@COF-QA was well demonstrated by the leaching test (ESI⁺), and no further reaction took place without Pd@COF-QA after triggering of the coupling reaction at 1.5 h. In addition, Pd@COF-QA could be easily recovered by centrifugation and directly reused in the next catalytic run under the same PTC conditions. As shown in Fig. 3a, still 90% yield was observed after ten runs. The structural integrity and morphology of Pd@COF-QA were well preserved after multiple catalytic runs, which was well supported by its PXRD pattern and SEM image (ESI⁺). HR-TEM image indicated that the loaded Pd species was still equally distributed (ESI+), and the XPS spectrum showed that less than 20% of Pd(0) changed to Pd(II) after ten catalytic cycles (Fig. 3b). Notably, the average size of Pd NPs was ca. 2.50 nm in diameter based on more than 100 randomly chosen particles, indicating that basically no Pd NPs aggregation occurred over multiple recycles (Fig. 3c). In addition, ICP analysis showed the encapsulated Pd species amount was ca. 8.7 wt%, indicating

only ca. 5% Pd loss after ten catalytic runs. Therefore, COF-QA herein is an ideal support to load Pd NP for heterogeneous catalysis.



With the optimized conditions in hand, we then investigated the scope of the Pd@-COF-QA-catalyzed Suzuki-Miyaura coupling utilizing various substituted halobenzene and phenylboronic acids (Table 2, entries 1-27). Under the optimized PTC conditions, the excellent catalytic activity of Pd@COF-QA was observed for the various substituted iodobenzene and bromobenzene with substituted phenylbonic acids regardless of electron-withdrawing or electron-donating groups at different substituted positions (Table 2, entries 1, 3-7, 9-11, 13-22, 90-99%) except -OMe substituted iodobenzene (Table 2, entry 2, 85%), bromobenzene (Table 2, entry 12, 86%) and -OH substituted phenylboronic acid (Table, entry 8, 83%). It is noteworthy to point out that the Pd@COF-QA herein exhibited excellent catalytic behavior for the chlorobenzene-(Table 2, entry 23, 99%) and 3-nitrochlorobenzenephenylboronic acid coupling in water. For -NO₂, -OMe, -CHO and -CN substituted chlorobenzenes, it showed less catalytic activity and provided the coupling yields in the range of 42-63% heterogeneous catalysts for the aqueous chlorobenzene-based (Table 2, entries 25-27).

Table 2. Substrate scope for Pd@-COF-QA-catalyzed Suzuki-Miyaura coupling reaction	а
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B(OH)

î	L L	2	
		Pd@COF-QA	
لي ال		H ₂ O, TEA, 50°C R1	
N1	1.2		

Entry	PhX	PhB(OH) ₂	Yield ^b (%)	TOF[h ⁻¹]℃
1	R ₁ =H, X=I	R ₂ = H	a : 99	9.7
2	R ₁ = 2-OCH ₃ , X = I	R ₂ = H	b : 85	8.3
3	R ₁ = 2-CF ₃ , X = I	R ₂ = H	c : 93	9.1
4	R ₁ = 3-NO ₂ , X = I	R ₂ = H	d : 99	9.7
5	R ₁ = 4-NO ₂ , X = I	R ₂ = H	e : 98	9.6

6	R ₁ = 4-CO ₂ CH ₃ , X = I	R ₂ = H	f : 90 _{Vi}	ew Article Online
7	R ₁ = 4-CN, X= I	R ₂ = H	DOI: 10,1039, g: 98	C9GC03/18G
8	R ₁ = H, X = I	R ₂ = 3-OH	h : 83	8.1
9	R ₁ = H, X = I	R ₂ = 4-CN	g : 92	9.0
10	$R_1 = H, X = Br$	R ₂ = H	a : 99	9.7
11	R ₁ = 2-CN, X = Br	R ₂ = H	i: 97	9.5
12	R ₁ = 2-OCH ₃ , X = Br	R ₂ = H	b : 86	8.4
13	R ₁ = 2-NO ₂ , X= Br	R ₂ = H	j : 96	9.4
14	R ₁ = 3-OCH ₃ , X = Br	R ₂ = H	k : 93	9.1
15	$R_1 = 3-NH_2$, X = Br	R ₂ = H	l: 92	9.0
16	R ₁ = 3-OH, X = Br	R ₂ = H	h : 92	9.0
17	R ₁ = 3-COOH, X = Br	R ₂ = H	m : 96	9.4
18	R ₁ = 4-NO ₂ , X = Br	R ₂ = H	e : 95	9.3
19	$R_1 = H, X = Br$	R ₂ = 4-CHO	n : 96	9.4
20	R ₁ = H, X= Br	R ₂ = 4-CO ₂ CH ₃	f : 99	9.7
21	R ₁ = H, X = Br	R ₂ = 4-OH	o : 92	9.0
22	R ₁ = H, X = Br	R ₂ = 4-CN	g : 98	9.6
23	R ₁ = H, X = Cl	R ₂ = H	a : 99	9.7
24	R ₁ = 3-NO ₂ , X = Cl	R ₂ = H	d : 95	9.3
25	R ₁ = 4-OCH ₃ , X = Cl	R ₂ = H	p : 62	6.1
26	R ₁ = 4-CHO, X = Cl	R ₂ = H	n : 63	6.2
27	R ₁ = 4-CN, X = Cl	R ₂ = H	g : 42	4.1

^a Reaction condition: PhX (0.2 mmol), PhB(OH)₂ (0.24 mmol), TEA (0.4 mmol), Pd@COF-QA (1.7 mol % Pd equiv), H₂O (2.0 mL), 50 °C, 6h, in air. ^b Determined by GC (ESI⁺). ^CTOF = conversion (mmol of substrate/mmol of cat., h).

In comparison with the iodobenzene or bromobenzenebased coupling reactions, the chlorobenzene-based coupling reaction is more significant due to its much lower production cost. Up to now, some attractive Pd loaded and COFs or MOFs or POPs based heterogeneous catalysts for the PhCl-PhB(OH)₂ aqueous Suzuki-Miyaura coupling reaction has been reported. As indicated in Table 3, only a handful catalysts exhibited high catalytic activity for PhCl-PhB(OH)₂ coupling but at higher temperature or with prolonged reaction time.²⁶⁻³⁰ Therefore, Pd@COF-QA herein could be a valuable alternative to the Suzuki-Miyaura coupling reaction. The catalytic performance of Pd@COF-QA herein in water is even comparable to those reported MOF- and COF-based catalysts in organic media (ESI⁺).

Table 3. Summary of the reported Pd loaded COFs, MOFs and POPs-based catalysts for PhCl-PhB(OH)₂ Suzuki-Miyaura coupling reaction in water

catalyst base T (°C) t (h) yield (%) Ref. Pd/MIL-101 NaOMe 80 20 99 26 Pd/Y-MOF K2CO3 80 8 22 27 Pd@MIL-101Cr-NH2 K2CO3 80 6 99 28 Pd/TATAE K2CO3 75 5 65 29 Ru-CP-Pd K3CO3 90 8 23 30	Pd@COF-QA	TEA	50	6	99	This work
catalyst base T (°C) t (h) yield (%) Ref. Pd/MIL-101 NaOMe 80 20 99 26 Pd/Y-MOF K2CO3 80 8 22 27 Pd@MIL-101Cr-NH2 K2CO3 80 6 99 28 Pd/TATAE K2CO3 75 5 65 29	Ru-CP-Pd	K ₂ CO ₃	90	8	23	30
catalyst base T (°C) t (h) yield (%) Ref. Pd/MIL-101 NaOMe 80 20 99 26 Pd/Y-MOF K2CO3 80 8 22 27 Pd@MIL-101Cr-NH2 K2CO3 80 6 99 28	Pd/TATAE	K ₂ CO ₃	75	5	65	29
catalyst base T (°C) t (h) yield (%) Ref. Pd/MIL-101 NaOMe 80 20 99 26 Pd/Y-MOF K ₃ CO ₃ 80 8 22 27	Pd@MIL-101Cr-NH ₂	K ₂ CO ₃	80	6	99	28
catalyst base T (°C) t (h) yield (%) Ref. Pd/MIL-101 NaOMe 80 20 99 26	Pd/Y-MOF	K ₂ CO ₃	80	8	22	27
catalyst base T (°C) t (h) yield (%) Ref.	Pd/MIL-101	NaOMe	80	20	99	26
	catalyst	base	T (°C)	t (h)	yield (%)	Ref.

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For better demonstrating the PTC functionality of Pd@COF-QA in this Pd-catalyzed aqueous coupling reaction, the COF-Me COF without guaternary ammonium salt and its Pd NP loaded Pd@COF-Me were prepared under the same solvothermal conditions (Scheme 1, ESI⁺). The different functional decoration on COF-Me resulted in a different Pd loading amount and particle size. Only 3.3 wt% of Pd NPs with ca. 3 nm in diameter were found in Pd@COF-Me (ESI⁺). As shown in Fig. 1, the obtained COF-Me featured the same 2D structure as that of COF-QA but with the different interlayer distance due to the different substituted groups on the COF framework. Correspondingly, the N2 adsorption absorption amount at 77 K of COF-Me and Pd@COF-Me is 143.4 and 133.4 cm³/g with the surface area of 222.0 and 143.0 m²/g, respectively. Their pore sizes, calculated from Barrett-Joyner-Halenda analysis, respectively centred at 3.8 (COF-Me) and 3.7 nm (Pd@COF-Me) (ESI⁺), which is well agreement with their crystal structures.

The PTC catalytic activity of Pd@COF-Me was examined based on the PhI-PhB(OH)₂ model coupling reaction under the optimized conditions (H₂O, 1.7 mol% Pd equiv, 50°C, 6h, in air). As shown in Table 1 (entry 9), the desired diphenyl product was obtained in only 79% yield (ESI⁺), which is obviously lower than that of Pd@COF-QA case. Therefore, the positive charged Pd@COF-QA might be more suitable for Pd NPs loading and distribution besides PTC function.

It is well known that the phase transfer catalysts with longer paraffin chains are more efficient due to their larger extraction constant.³¹ To verify this, **Pd@COF-Et** with shorter chain quaternary ammonium salt was synthesized and used to catalyse the PhI-PhB(OH)₂ model coupling reaction under the given conditions (Table 1, entry 10). As expected, the coupling product was gotten in relatively low 81% yield (ESI⁺), which illustrated that the longer alkyl chains are necessary for PTC.



Fig. 4 Reaction time examination and schematic representation of Pd@COF-QA@chitosan aerogel reactor based gram scale Suzuki-Miyaura coupling reaction between PhCl and PhB(OH)₂ in water.

For practical application, the gram scale coupling reaction between PhCl and PhB(OH)₂ was carried out based on a continuous flow-through reactor equipped with **Pd@COF-QA**@chitosan aerogel catalyzing column (ESI⁺). As shown in Fig. 4, an aqueous solution (80 mL) of chlorobenzene (1.0 g, 8.9

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mmol), phenylboronic acid (1.3 g, 10.6 mmol) and triethylamine (1.8 g, 17.8 mmol) was pumped through a piece of Pd@COF-QA@chitosan aerogel monolith (150 mg, 60 wt% of Pd@COF-QA, 1.7 mol % Pd equiv) using a peristaltic pump at a flow rate of 1.0 mL/min. The desired biphenyl product was obtained in 88 % yield within ca. 8h. The Pd@COF-QA@chitosan aerogel monolith herein is very stable toward water and common polar organic solvent, and it can be reused three times with almost no yield drop (ESI⁺).

In conclusion, we have developed the paraffin-chain quaternary ammonium salt decorated and Pd NP loaded COFbased composite catalytic system via in situ reduction approach. The obtained **Pd@COF-QA** can be a highly active phase transfer catalyst to promote aqueous Suzuki–Miyaura coupling reaction under mild reaction conditions, especially for PhCI-PhB(OH)₂ coupling. The concept of COF-based multifunctional integration leads the carbon-carbon coupling synthesis to be economical, eco-friendly, and source saving. We believe this approach to be general, effective and viable for the fabrication of many more practical multifunctional composite catalytic materials for a variety of green chemical transformations.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- A. P. Côté, A. I. Benin, N. W. Ockwig, M. Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.
- 2 H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009, **131**, 8875-8883.
- 3 J. W. Colson, A. R. Woll, A. Mukherjee, M. P. Levendorf, E. L. Spitler, V. B. Shields, M. G. Spencer, J. Park and W. R. Dichtel, *Science*, 2011, **332**, 228.
- 4 H. Xu, S. Tao and D. Jiang, *Nat. Mater.*, 2016, **15**, 722.
- 5 H. Ding, J. Li, G. Xie, G. Lin, R. Chen, Z. Peng, C. Yang, B. Wang, J. Sun and C. Wang, *Nat. Commun.*, 2018, **9**, 5234.
- 6 Q. Fang, J. Wang, S. Gu, R. B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu and Y. Yan, J. Am. Chem. Soc., 2015, 137, 8352-8355.
- 7 S. Dalapati, E. Jin, M. Addicoat, T. Heine and D. Jiang, *J. Am. Chem. Soc.*, 2016, **138**, 5797-5800.
- 8 Y. Du, H. Yang, J. M. Whiteley, S. Wan, Y. Jin, S.-H. Lee and W. Zhang, *Angew. Chem. Int. Ed.*, 2016, **55**, 1737-1741.
- 9 S. Dalapati, E. Jin, M. Addicoat, T. Heine and D. Jiang, J. Am. Chem. Soc., 2016, **138**, 5797-5800.

- 10 H.-C. Ma, C.-C. Zhao, G.-J. Chen, Y.-B. Dong, *Nat. Commun.*, 2019, **10**, 3368.
- 11 H.-C. Ma, J.-L. Kan, G.-J. Chen, C.-X. Chen, Y.-B. Dong, *Chem. Mater.*, 2017, **29**, 6518–6524.
- 12 G.-J. Chen, X.-B. Li, C.-C. Zhao, H.-C. Ma, J.-L. Kan, Y.-B. Xin, C.-X. Chen, Y.-B. Dong, *Inorg. Chem.*, 2018, **57**, 2678–2685.
- 13 S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su and W. Wang, J. Am. Chem. Soc., 2011, **133**, 19816-19822.
- 14 M. K. Bhunia, S. K. Das, P. Pachfule, R. Banerjee and A. Bhaumik, *Dalton Trans.*, 2012, **41**, 1304-1311.
- 15 R. S. B. Gonçalves, A. B. V. de Oliveira, H. C. Sindra, B. S. Archanjo, M. E. Mendoza, L. S. A. Carneiro, C. D. Buarque and P. M. Esteves, *ChemCatChem*, 2016, **8**, 743-750.
- 16 S. Lu, Y. Hu, S. Wan, R. McCaffrey, Y. Jin, H. Gu and W. Zhang, J. Am. Chem. Soc., 2017, 139, 17082-17088.
- 17 S. Kim, B. Kim, N. A. Dogan and C. T. Yavuz, ACS Sustain. Chem. Eng., 2019, **7**, 10865-10872.
- 18 I. P. Beletskaya, F. Alonso and V. Tyurin, *Coordination Chemistry Reviews*, 2019, **385**, 137-173.
- 19 N. Patel, R. Sood and P. V. Bharatam, Chem. Rev., 2018, 118, 8770-8785.
- 20 J.-C. Wang, J.-P. Ma, Q.-K. Liu, Y.-H. Hu and Y.-B. Dong, *Chem. Commun.*, 2016, **52**, 6989-6992.
- 21 Y.-H. Hu, J.-C. Wang, S. Yang, Y.-A. Li and Y.-B. Dong, *Inorg. Chem.*, 2017, **56**, 8341-8347.
- 22 Materials Studio Release Notes ver. 5.0; Accelrys Software: San Diego, CA, 2008.
- 23 D. B. Shinde, G. Sheng, X. Li, M. Ostwal, A.-H. Emwas, K.-W.
- Huang and Z. Lai, *J. Am. Chem. Soc.*, 2018, **140**, 14342-14349. 24 R. W. Tilford, S. J. Mugavero, 3rd, P. J. Pellechia and J. J.
- Lavigne, *Adv Mater*, 2008, **20**, 2741-2746.
 25 G. Zhang, Y.-L. Hong, Y. Nishiyama, S. Bai, S. Kitagawa, S. Horike. *J. Am. Chem. Soc.*, 2019, **141**, 1227–1234.
- 26 B. Yuan, Y. Pan, Y. Li, B. Yin and H. Jiang, *Angew. Chem. Int. Ed.*, 2010, **49**, 4054-4058.
- 27 J. Huang, W. Wang and H. Li, ACS Catal., 2013, 3, 1526-1536.
- 28 V. Pascanu, Q. Yao, A. Bermejo Gómez, M. Gustafsson, Y. Yun, W. Wan, L. Samain, X. Zou and B. Martín-Matute, *Chem. Eur. J.*, 2013, **19**, 17483-17493.
- 29 V. Sadhasivam, R. Balasaravanan, C. Chithiraikumar and A. Siva, *ChemistrySelect*, 2017, **2**, 1063-1070.
- M. Mondal, J. Joji and J. Choudhury, J. Chem. Sci., 2018, 130, 83.
- 31 G. E. Boyd and Q. V. Larson, *J. Am. Chem. Soc.*, 1967, **89**, 6038.

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A Pd NP loaded and *N*, *N*-dimethyldodecyl ammonium bromide decorated **Pd@COF-QA** and its continuous flow-through reactor was prepared. The obtained COF-based catalyst can highly promote the Suzuki–Miyaura coupling reaction in water under mild conditions even at gram scale level.