Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

Dual-functional ionic porous organic framework for palladium scavenging and heterogeneous catalysis

Shun-Shun Qin,[a] Ze-Kun Wang,[a] Lei Hu,[a] Xing-Hao Du,[a] Zheng Wu,[a] Maria Strømme,[b] Qian-Feng Zhang,[a] Chao Xu*[ab]

a. Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, 243002, P. R. China

b. Department of Materials Science and Engineering, Uppsala University, The Ångström Laboratory, Box 35, 751 03 Uppsala, Sweden

Experimental section

Materials

1,3,5-triformylphloroglucinol (TFP) was purchased from Shanghai Tensus Bio-tech. triaminoguanidinium chloride (TGCl) was synthesized according to reported method.[1] Other chemicals and solvents were purchased from Sigma Aldrich and used without further purification.

Characterizations

Infrared spectra were collected on a Bruker Tensor 27 spectrometer. Solid-state ^{13}C nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker AVWBIII600 spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker Focus D8 diffractometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Physical Electronics ESCA. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100 TEM instrument. N_2 adsorption and desorption isotherms were recorded on a Micromeritics ASAP 2020 surface area and porosity analyzer at 77 K. The samples were degassed at 100 °C for 10 h under a kinetic vacuum ($<10^{-5}$ mmHg) prior to analysis. Thermal gravimetric analysis (TGA) data was collected on a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer. The experiment was carried out under N_2 or air atmosphere with a flow rate of 60 mL/min. UV-vis spectra were recorded on a Shimadzu UV-2600 UV-VIS spectrophotometer. The concentration of Pd content in the aqueous solutions was analyzed by ICPS-7510 ICP emission spectrometer.

Synthesis of IPOF-Cl[1]

TFP (0.2 mmol, 42 mg) and TGCl (0.2 mmol, 28 mg) was added to a mixture solvent of dioxane (2.0 mL)/water (0.6 mL). The mixture was charged into a Pyrex tube and sonicated for 20 min at room temperature. After the mixture was degassed by three freeze-pump-thaw cycles, the Pyrex tube was sealed and then heated in an oven at 120 °C for 3 days. The obtained yellow precipitate was washed by water and acetone several times, and then further purified by Soxhlet extraction in methanol for 24 h. The purified powder was dried in an oven at 100 °C for 24 h.

Synthesis of IPOF-$PdCl_4$(II)

60 mg IPOF-Cl was added in an aqueous solution of $Na_2[PdCl_4]$ (0.8 mg/mL, 75 mL). The mixture was stirred at room temperature for 6 h and then centrifuged. The obtained brown precipitate was washed by water several times and then dried in an oven at 100 °C for 24 h.

Synthesis of IPOF-Pd(0)

$NaBH_4$ (0.4 mmol, 15 mg) was added to a suspension of 100 mg IPOF-$PdCl_4$ dispersed in 20 mL water. The mixture was stirred for 10 h at room temperature. The obtained dark brown precipitate was washed by water several times and then dried in an oven at 100 °C for 24 h.

Stability study of IPOF-Cl

A comparison experiment was carried out to investigate the chemical stability of IPOF-Cl in aqueous solution in the presence of $NaBH_4$. Specifically, $NaBH_4$ (0.4 mmol, 15 mg) was added to a suspension of 100 mg IPOF-Cl dispersed in 20 mL water and the mixture was stirred for 3 h at room temperature. The solid was collected and washed by water several times and then dried in an oven at 100 °C for 24 h. The obtained sample was characterized by both infrared spectroscopy and XRD.

Kinetic study of $Na_2[PdCl_4]$ capture on IPOF-Cl

An aqueous solution of $Na_2[PdCl_4]$ (33 mL, 0.6 mg/mL) was prepared. 20 mg grinded IPOF-Cl was added to the above solution and the mixture was stirred at room temperature. Aliquots of 2 mL were withdrawn from the suspension at intervals of 5, 30, 90, 150, and 240 min. The dispersed IPOF-Cl powder in the withdrawn mixture was removed by centrifugation to give clear solutions. The Pd concentration of the clear solution was analyzed by ICP-AES. The adsorption capacity was calculated and the capture kinetic curve was fitted by pseudo-second order kinetic equation:

$$q = \frac{{q_e}^2 kt}{1 + (q_e kt)}$$

where q is the adsorption capacity (mg/g) at different intervals, q_e is the equilibrium adsorption capacity (mg/g), k is the rate constant (g/(mg × min)), and t is time (min).

Study of $Na_2[PdCl_4]$ adsorption isotherm of IPOF

10 mg grinded IPOF-Cl was added to aqueous $Na_2[PdCl_4]$ solutions with different concentrations (0.276 mg/mL, 36 mL; 0.4 mg/mL, 25 mL, 0.5 mg/mL, 20 mL; 0.7 mg/mL, 14.3 mL; 0.8 mg/mL, 12.5 mL). The total amount of $Na_2[PdCl_4]$ in the solution was fixed at ~10 mg. The mixture was stirred at room temperature for 6 h to reach the adsorption equilibration. Subsequently, the mixture was treated by

centrifugation and the obtained clear solution was analyzed by ICP-AES to determine the Pd concentration. The adsorption capacity was calculated and the adsorption isotherm was plotted and fitted by Langmuir equation:

$$q = \frac{q_m k C}{1 + kC}$$

where q is the adsorption capacity (mg/g), q_m is the maximum adsorption capacity (mg/g), k is the Langmuir isotherm constant (mL/mg), and C is the concentration (mg/mL).

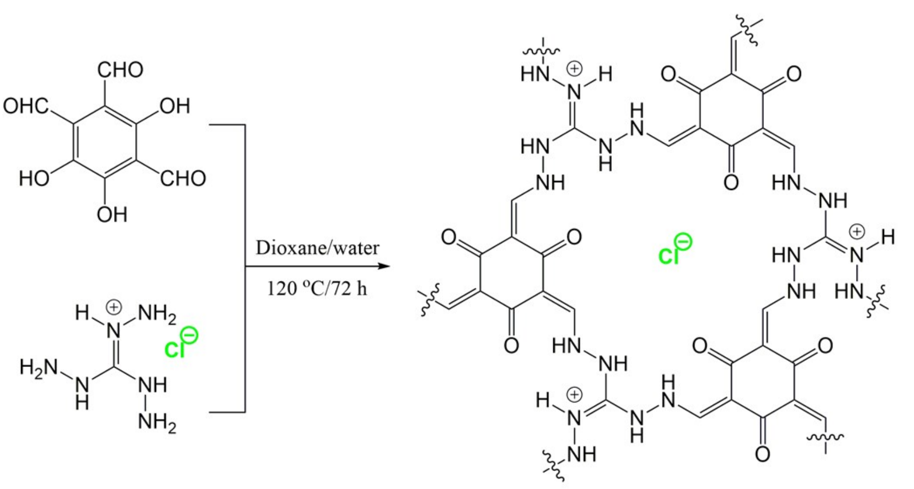
Scavenging study of IPOF towards $Na_2[PdCl_4]$

10 mg grinded IPOF-Cl was added to an aqueous solution of $Na_2[PdCl_4]$ (9 mL, 0.276 mg/mL, equal to 100 ppm Pd). The mixture was stirred at room temperature for 60 min. Subsequently, the solid was removed by centrifugation and the obtained clear solution was analyzed by ICP-AES to determine the Pd content. The result indicated that the residual Pd content in the solution was less than 0.1 ppm.

General procedure for heterogeneous catalysis

All catalytic reactions were carried out under N_2 atmosphere using Schlenk technique. Aryl halide (1.0 mmol, 1.0 equiv.), aryl boronic acid (1.2 mmol, 1.2 equiv.), IPOF-Pd(0) (25.4 wt% Pd) (4.2 mg, 1 mol%), K_3PO_4 (637 mg, 3.0 mmol, 3.0 equiv.) was loaded in a 50 mL three-neck round bottom flask. After this, H_2O (2 mL) and ethanol (3 mL) were added. The reaction mixture was stirred at 85 °C for 3 h. The solid catalyst was separated from the mixture by centrifugation and washed by 5 mL acetone 3 times. The acetone solution was combined with crude product and the mixture was concentrated by rotary evaporator. The product was then subjected to flash chromatography on silica (CH_2Cl_2: petroleum ether = 1:10) giving the pure biphenyl products. The purified products were analyzed by ^1H NMR spectroscopy on a Bruker-400 MHz spectrometer.

For recycling catalysis reactions, the scale was doubled. The solid catalyst was collected by centrifugation and washed by acetone 3 times. The catalyst was dried and then used in the next cycle. In order to investigate the chemical and structural stability of the catalyst during the catalytic conversions, a ten times scaled-up Suzuki coupling reaction was carried out and the recycled catalyst was characterized by both infrared spectroscopy and XRD.



Scheme S1 Synthesis of IPOF-Cl by polycondensation of 1,3,5-triformylphloroglucinol and triaminoguanidinium chloride.[1]

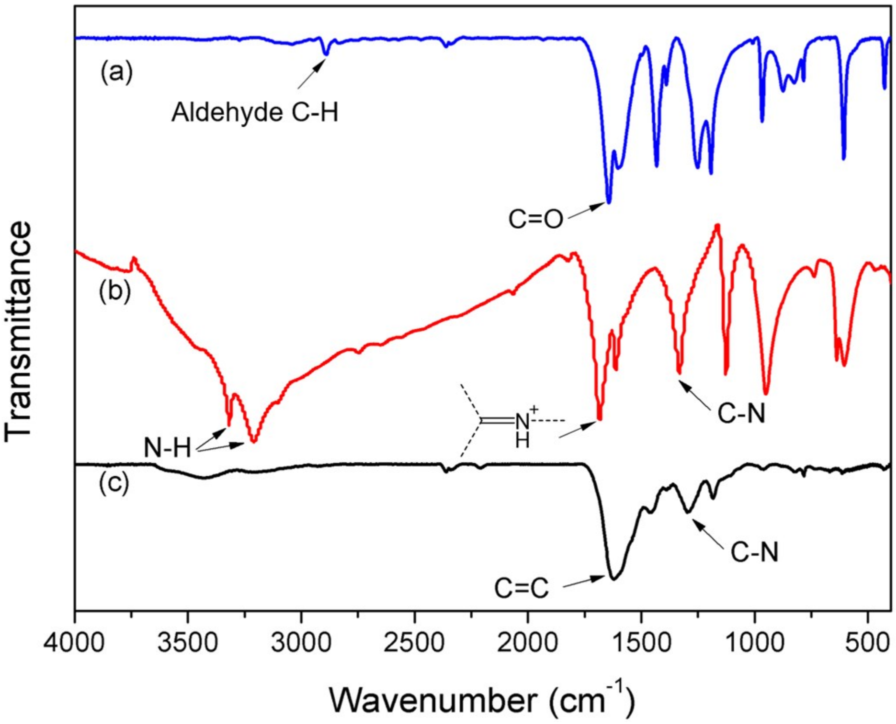


Fig. S1 Infrared spectra of (a) 1,3,5-triformylphloroglucinol, (b) triaminoguanidinium chloride, and (c) IPOF-Cl.

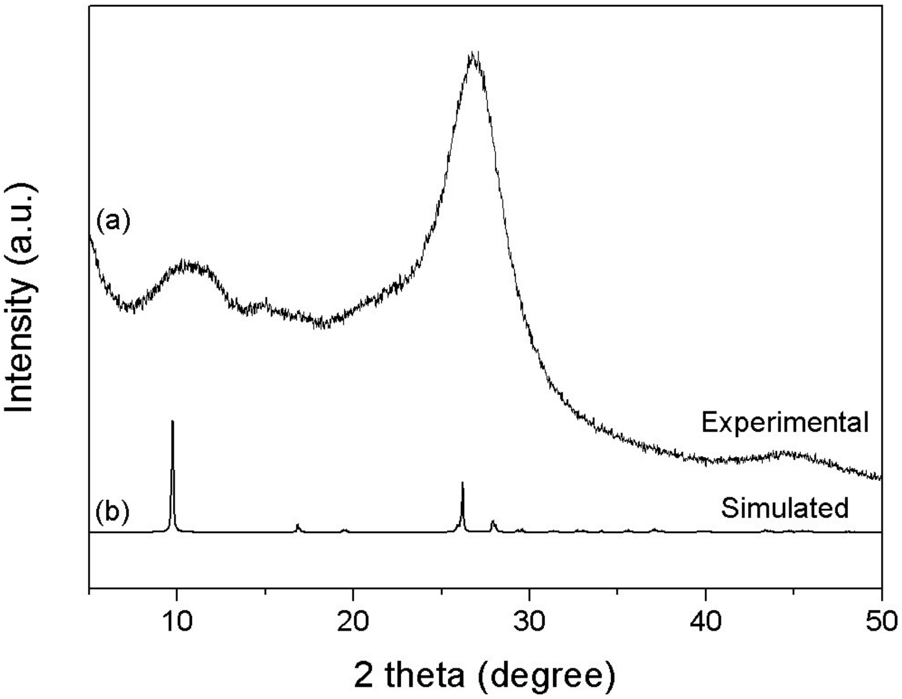
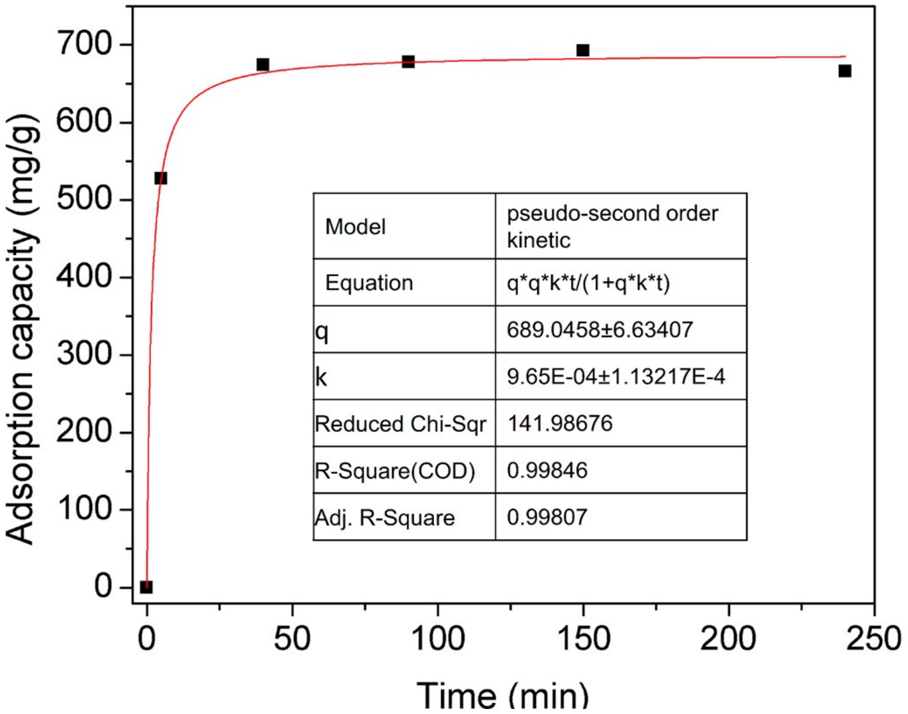
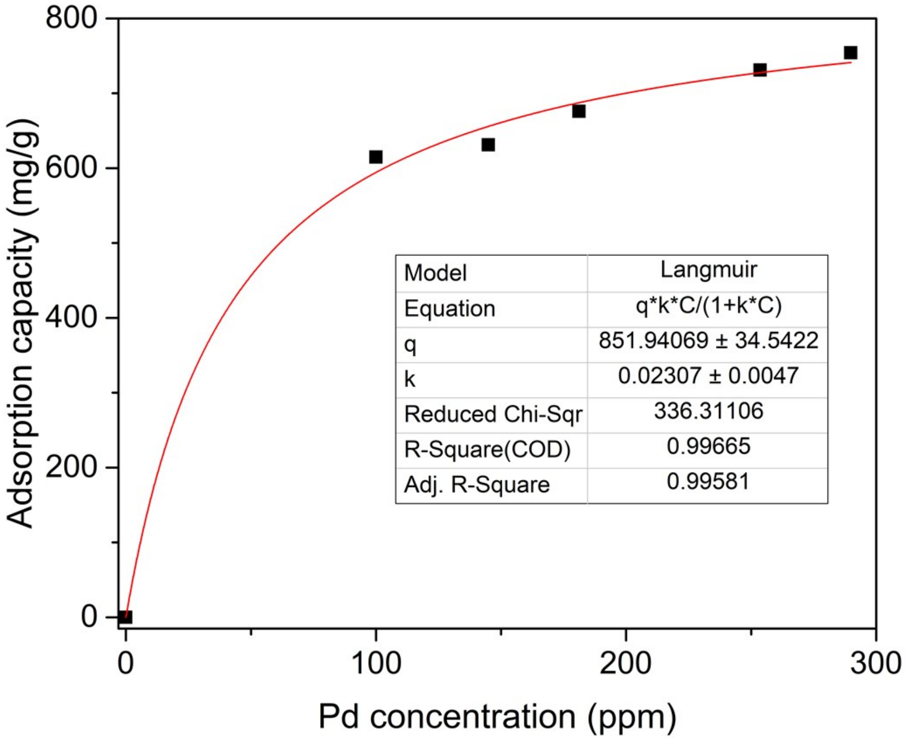


Fig. S2 Comparison of (a) experimental and (b) simulated powder X-ray diffraction pattern (XRD) of IPOF-Cl. The simulated XRD pattern is created based on reported Crystallographic Information File (CIF). [1]



Model	pseudo-second order kinetic
Equation	q*q*k*t/(1+q*k*t)
q	689.0458±6.63407
k	9.65E-04±1.13217E-4
Reduced Chi-Sqr	141.98676
R-Square(COD)	0.99846
Adj. R-Square	0.99807

Fig. S3 Kinetic curve of Na_2PdCl_4 capture on IPOF-Cl and its fitted results according to the pseudo-second order kinetic model.



Model	Langmuir
Equation	q*k*C/(1+k*C)
q	851.94069 ± 34.5422
k	0.02307 ± 0.0047
Reduced Chi-Sqr	336.31106
R-Square(COD)	0.99665
Adj. R-Square	0.99581

Fig. S4 Na_2PdCl_4 adsorption isotherm of IPOF-Cl and its fitted results according to the Langmuir model.

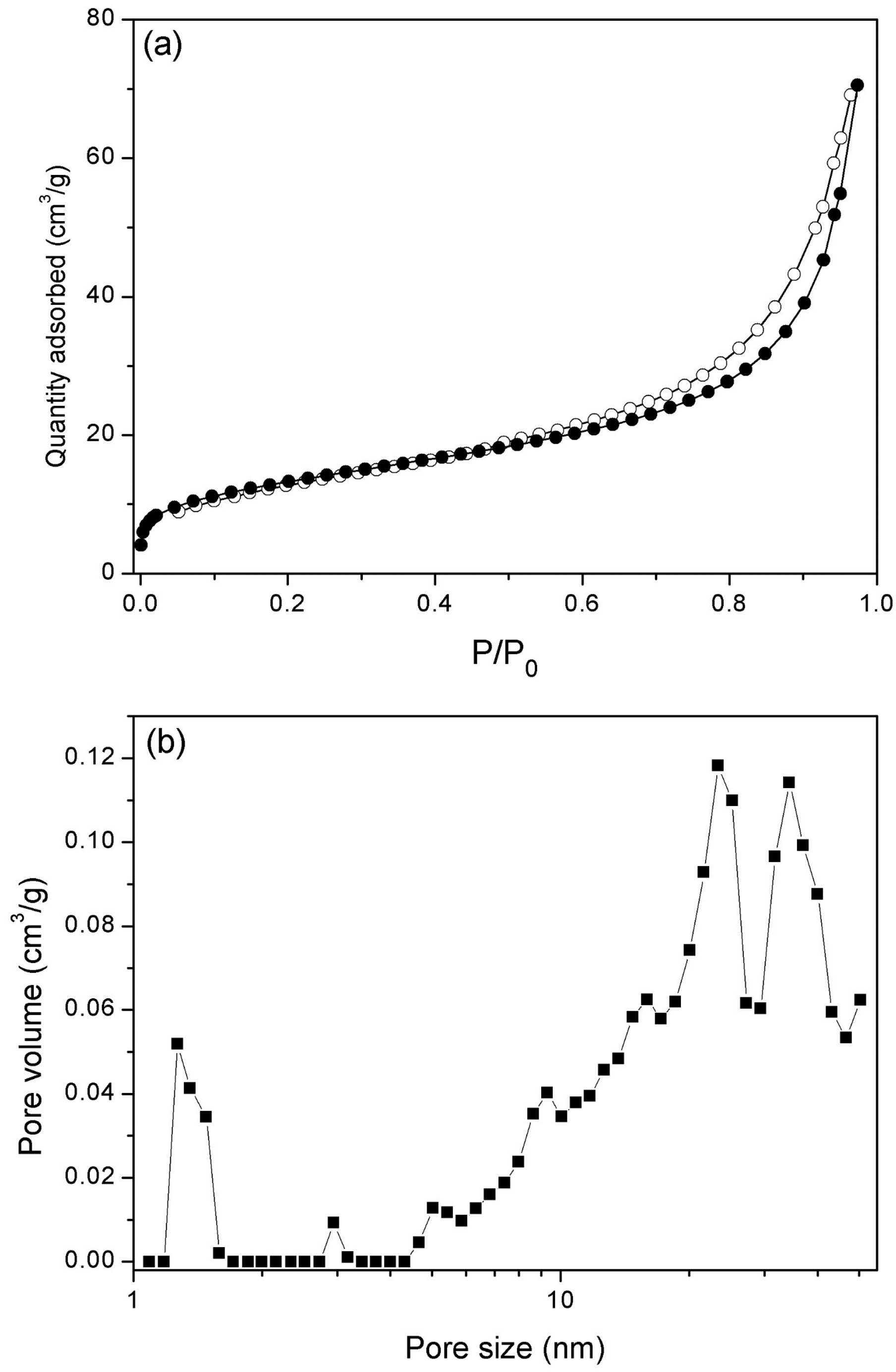


Fig. S5 (a) N_2 adsorption and desorption isotherms of IPOF-$PdCl_4$ recorded at 77 K. (b) Pore size distribution of IPOF-$PdCl_4$ calculated from the adsorption branch using the density functional theory model.

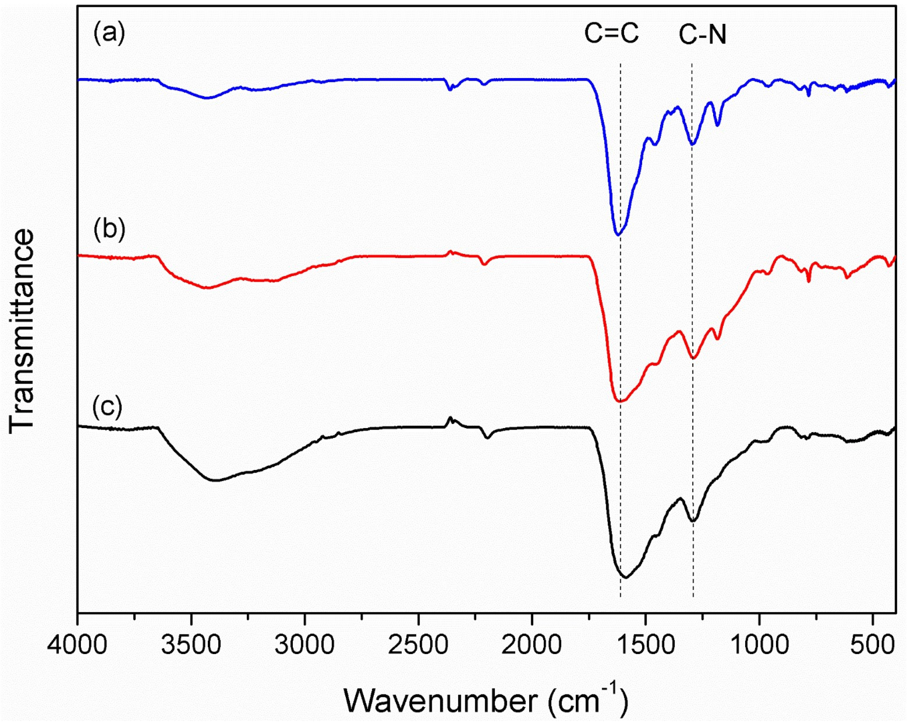


Fig. S6 Infrared spectra of (a) IPOF-Cl, (b) IPOF-PdCl$_4$, and (c) IPOF-Pd(0).

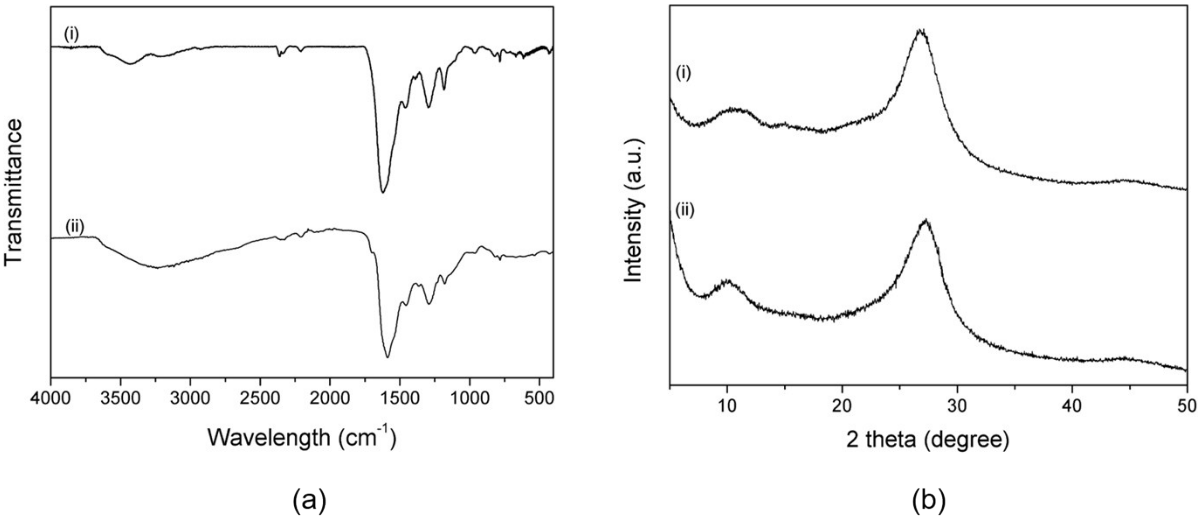


Fig. S7 (a) Infrared (IR) spectra and (b) Powder X-ray diffraction patterns (XRD) for (i) pristine IPOF-Cl and (ii) the treated IPOF-Cl in aqueous solution in the presence of NaBH$_4$. No significant change was observed in the IR spectra and the XRD patterns indicating the high chemical stability of IPOF-Cl.

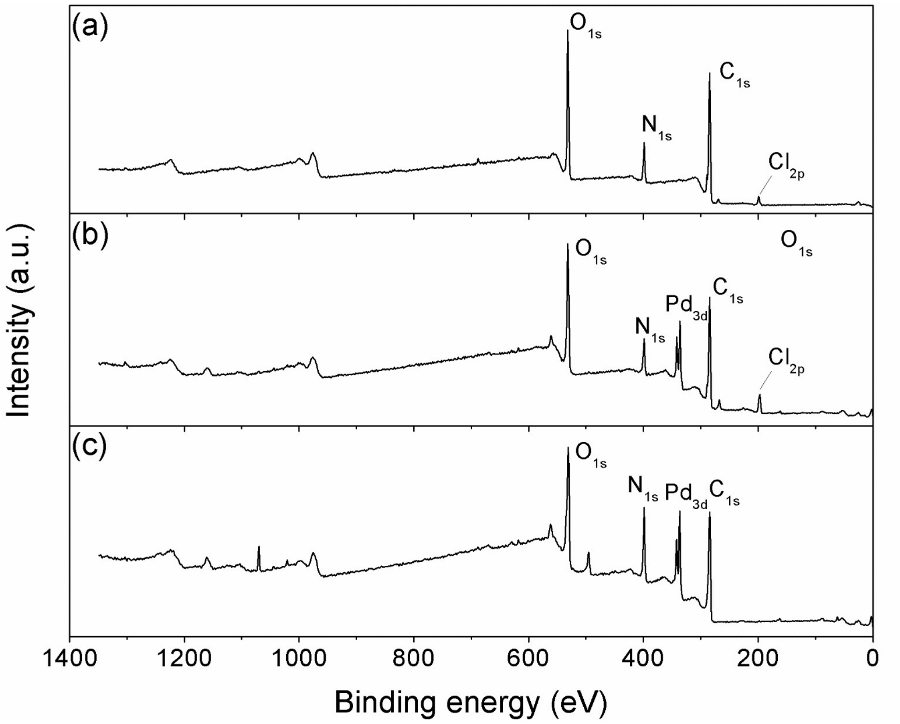


Fig. S8 XPS survey spectra of (a) IPOF-Cl, (b) IPOF-$PdCl_4$, (c) IPOF-Pd(0). The results clearly show that all the IPOF materials contain C, N and O elements. The strong Pd_{3d} peaks observed in the spectra of IPOF-$PdCl_4$ and IPOF-Pd(0) indicate the presence of Pd. In addition, the absence of the Cl_{2p} peak in the spectrum of IPOF-Pd(0) reveals that most Cl was eliminated during the reduction of $[PdCl_4]^{2-}$ into Pd nanoparticles.

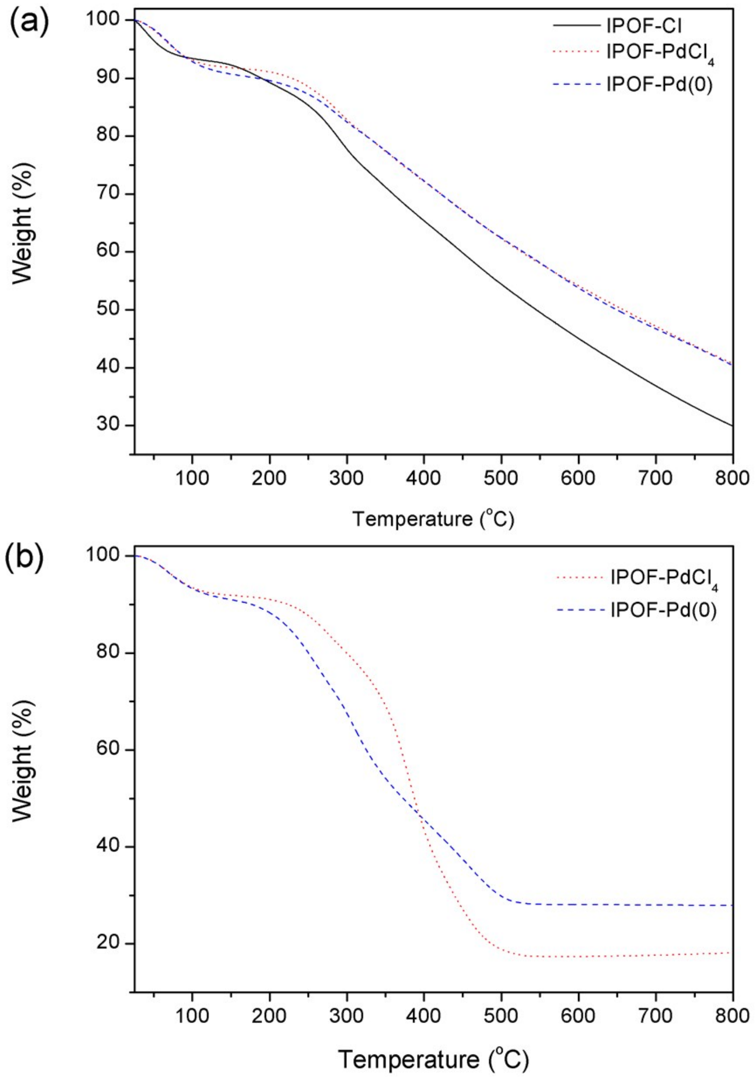


Fig. S9 Thermogravimetric analysis (TGA) curve of (a) IPOF-Cl, IPOF-PdCl$_4$, and IPOF-Pd(0) under N$_2$ atmosphere, (b) IPOF-PdCl$_4$ and IPOF-Pd(0) under air atmosphere. The TGA results indicate that all of the IPOF materials have high thermal stability with decomposition temperature of ~300 °C. In addition, the thermal stability of the IPOF framework was not significantly reduced after the ion exchange and reduction procedures. Since all of the organic components in both IPOF-PdCl$_4$ and IPOF-Pd(0) were removed under the air atmosphere when the temperature reached 800°C, the only residual would be PdO.[2] Therefore, the bulk Pd content in IPOF-PdCl$_4$ and IPOF-Pd(0) was calculated to be 25.4 and 16.6 wt%, respectively. The increased Pd content in IPOF-Pd(0) compared to in IPOF-PdCl$_4$ can be explained by the fact that most of the Cl was eliminated during the reduction procedure.

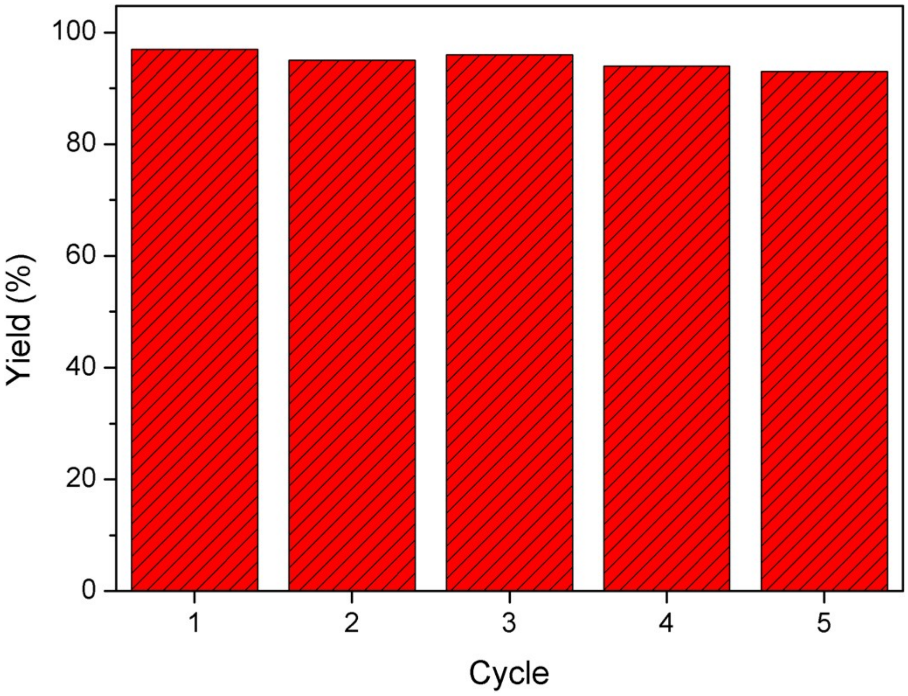
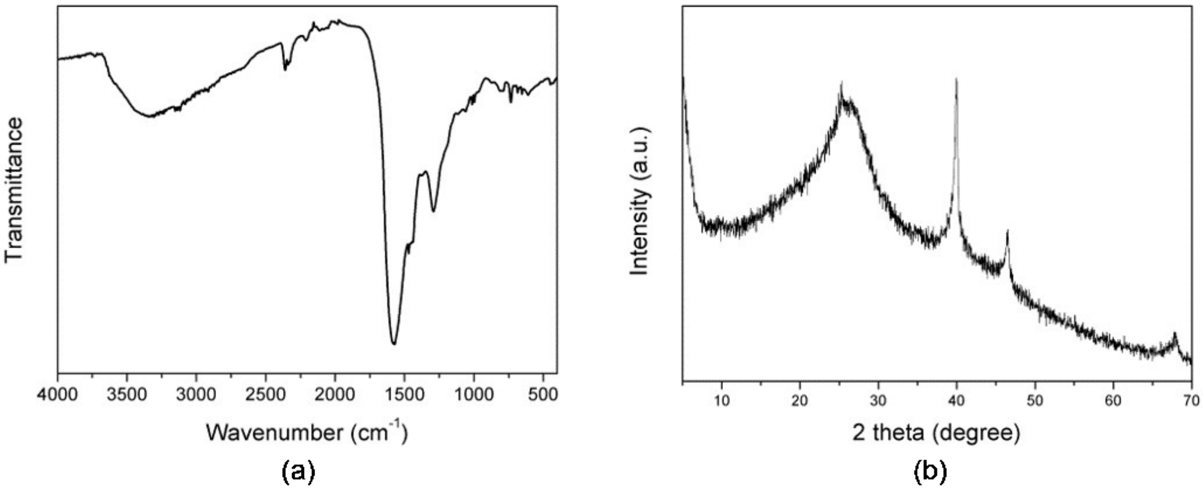


Fig. S10 Recycling performance of the catalyst IPOF-Pd(0) for Suzuki coupling reaction of iodobenzene and phenylboronic acid.



(a)

(b)

Fig. S11 (a) Infrared spectrum and (b) powder X-ray diffraction of the recycled IPOF-Pd(0) catalyst.

References:

[1] S. Mitra, S. Kandambeth, B. P. Biswal, A. Khayum M, C. K. Choudhury, M. Mehta, G. Kaur, S. Banerjee, A. Prabhune, S. Verma, S. Roy, U. K. Kharul and R. Banerjee, *J. Am. Chem. Soc.*, **2016**, *138*, 2823−2828

[2] C. Xu, S. Afewerki, C.-W. Tai, A. Córdova and N. Hedin, *ChemistrySelect*, **2016**, *1*, 5801-5804.