

Supporting information:

From Single Helix to Helix Porous Metalloenzyme Catalyst Based on Temperature Sensitive Polyionic Liquid

Xinjuan Li,* Zhangquan Zhou, Jiaxin Dong, Yanping Sun, Guanglei Ma, Qingcong Wei, Nana Ma*, Xianbin Jia*

Henan Key Laboratory of Green Chemistry, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, 453007, P. R. China

1. Experimental part

1.1 Main raw materials

Palladium acetate (II) (99%) was obtained from Aldrich and used as accepted. Iodotoluene and 4-hydroxymethylphenylboronic acid from Alfa Aesar and use them directly. Other phenylboronic acids and aryl halides obtained from Aldrich are used directly. Ethyl acetate, dimethyl sulfoxide, dimethylformamide and acetonitrile (99.7%, Aldrich) do not need further purification.

1.2 Synthesis and characterization of catalyst

1.2.1 Synthesis of PILs

PIL is synthesized by the reaction of polyepoxychloropropane ($M_n=1000$, $PDI=1.12$) and methylimidazole. The experiment is as follows: PECH (1 g, 0.50 mmol) was added to a single neck round bottom flask (100 mL). After degassing for 30 minutes, methylimidazole (0.023 g, 0.28 mol) was added with a syringe. The molar ratio of PECH to methylimidazole was 1.8:1.0. Stir until completely dissolved, sealed

the flask and immersed it in an oil bath at 80 °C for 10 hours. The crude product (PIL-1) was then collected by ether precipitation, washed several times with ether until there was no small molecular impurity, and dried in vacuum at 60 °C for 48 hours.

PIL-1 with part of Cl⁻ and part of [NTf₂]⁻ was prepared by partial ion exchange with the above PIL. PIL (29.30 g, 0.067 mmol) and LiNTf₂ (4.86 g, 0.034 mmol) were dissolved in 100 mL of distilled water to form a clear mixture solution. The crude product was washed with water and ether respectively, and dried in vacuum at 60 °C for use. The yield was 91%.

PIL-2 with part of Cl⁻ and part of [NTf₂]⁻ was prepared by partial ion exchange and the synthesis was the same as that of PIL-2. PIL (29.30 g, 0.067 mmol) and LiNTf₂ (9.62 g, 0.034 mmol) were dissolved in 100 mL of distilled water to form a clear mixture solution. The crude product was washed with water and ether respectively, and dried in vacuum at 60 °C for use. The yield was 91%.

PIL-3 was prepared by partial ion exchange with PIL. PIL (29.30 g, 0.067 mmol) and LiNTf₂ (14.43 g, 0.051 mmol) were dissolved in 100 mL distilled water to form a clear mixture solution. The mixture was stirred at 25 °C for 5 hours to form an insoluble oil like substance. The crude product was collected by centrifugation, washed with water and ether respectively, and dried in vacuum at 60 °C with a yield of 93%.

PIL-4 was prepared by partial ion exchange with PIL. PIL (29.30 g, 0.067 mmol) and LiNTf₂ (17.32 g, 0.06 mmol) were dissolved in 100 ml distilled water to form a clear mixture solution. The mixture was stirred at 25 °C for 5 hours to form an

insoluble oil like substance. The crude product was collected by centrifugation, washed with water and ether respectively, and dried in vacuum at 60 °C with a yield of 90%.

1.2.2 Palladium catalysts

Polyionic liquid (500 mg, 6.88 mmol) and palladium acetate (57 mg, 0.25 mmol) were dissolved in dimethyl sulfoxide (5 ml). Stir the solution at 60 °C for 12 hours under N₂, purify the resulting polymer by precipitation in dichloromethane, and dry under vacuum to obtain the catalyst.

1.2.3 Characterization of catalysts

¹H NMR spectra were measured on a Bruker 400 MHz NMR spectrometer. A Thermo FLASH 1112 elemental analyzer was used to determine the elemental analysis. The IR measurements were carried out on a Fourier transform infrared spectrometer (Nicolet 94 NEXUS). HPLC method was performed on an Agilent TM 1100. Transmission electron microscopy (JEOL-2010, 200 kV) and field emission scanning electron microscopy (NovaNano SEM450) were used to characterize the morphology of the catalyst. TEM image at 60 °C refers to the preparation of the sample after it is dispersed in the solution and heated to 60 °C, and then tested at room temperature. DSC was performed on a custom-made PCT-1A thermal analysis system. XPS spectra were obtained on a VG ESCALAB MK II spectrograph. The X-ray powder diffraction measurements of samples were detected by Bruker AXS D8 advanced automated diffractometer with Cu-K α radiation. The average diameter (D_n) was determined using TEM and were calculated using the following

formula:

$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i} \quad (1)$$

Where k was the total number of measured particles, D_i was the measured particle diameter, and n_i was the particle number with diameter D_i .

1.2.4 Suzuki coupling and one pot Suzuki-Knoevenagel reaction

Iodotoluene (480 mg, 2.2 mmol), 4-hydroxymethylphenylboric acid (1.2 Eq., 401 mg, 2.6 mmol) and potassium carbonate (3 eq., 912 mg, 6.6 mmol) were put into Shrek tube. The catalyst (0.1 mol% of toluene iodide) was added and the solution was stirred in argon for 20 minutes and then reacted at 60 °C. After cooling to room temperature, the mixture was extracted with ether (3 × 20 ml). Combine organic phase, dry with magnesium sulfate, and remove solvent by rotary evaporation.

One pot Suzuki-Knoevenagel reaction: Suzuki coupling was carried out first, and then nitromethane was added. After the reaction, it was separated by column chromatography.

2. Results and discussion

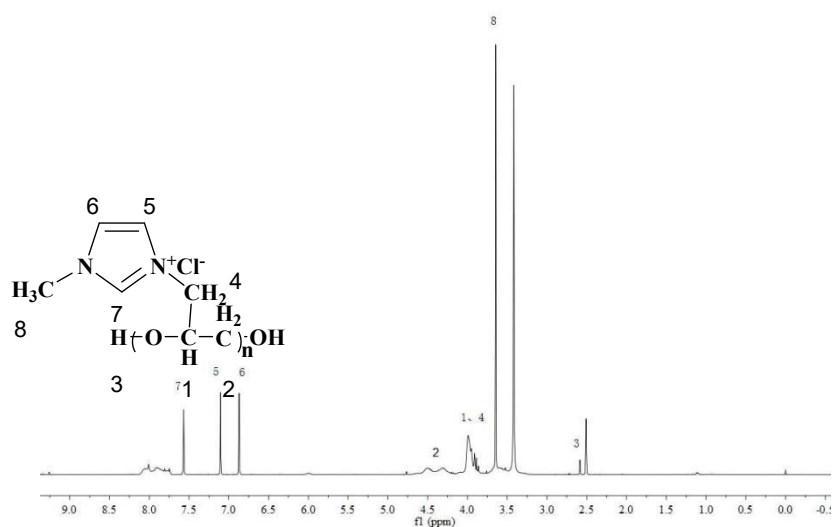


Fig. S1 ^1H NMR of PIL-1 in DMSO-d_6

Table. S1 Tg of PILs from DSC results and Cl^- content of PILs from ion chromatography.

PIL	PIL-1	PIL-2	PIL-3	PIL-4
Tg ($^{\circ}\text{C}$)	-14.3	-10.0	-57.1	-61.7
Cl^- content (mg/kg)	31.6	24.7	21.5	0
m:n	0	1:2.21	1:1.5	-

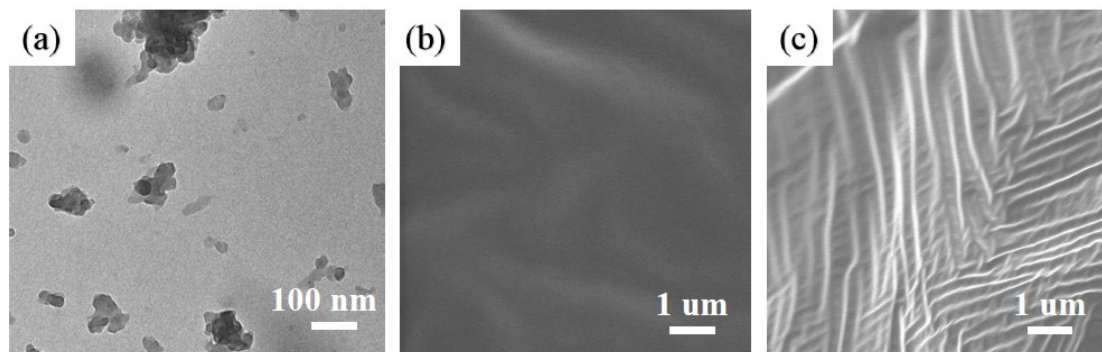


Fig. S2 TEM images of PIL-1 (a), SEM images of PIL-3 (b), and PIL-4 (c).

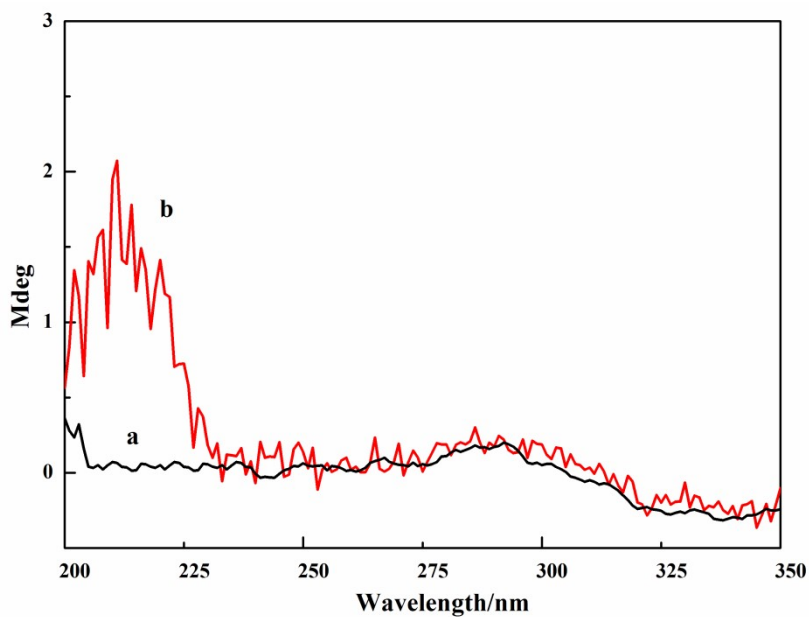
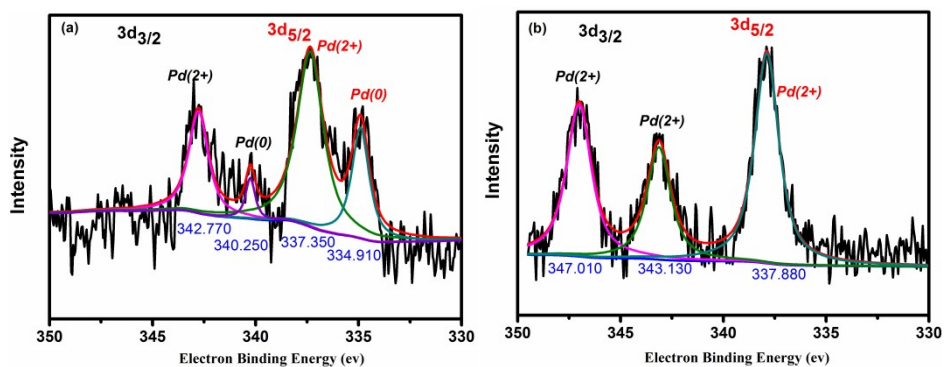


Fig. S3 CD spectrum of PIL-2 in DMSO at 25 $^{\circ}\text{C}$ (a) and 60 $^{\circ}\text{C}$ (b).



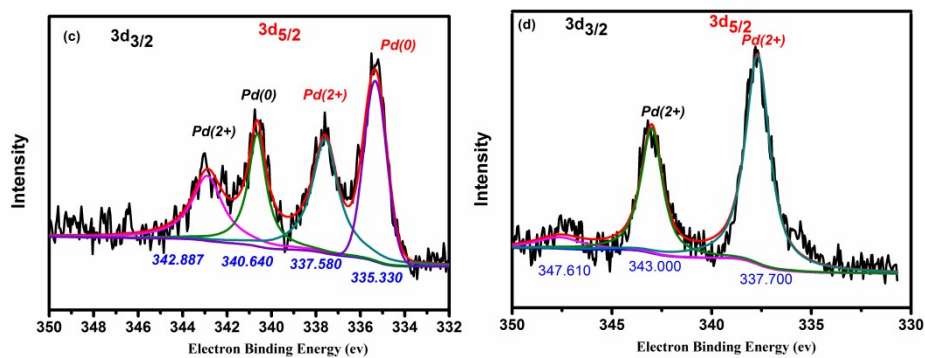


Fig. S4 Pd 3d of Cat-1 (a), Cat-2 (b), Cat-3 (c) and Cat-4 (d).

Fig. S5 EDS mapping of Cat-2.

Table S2. BET results of the prepared catalysts

sample	surf. area (m ² /g)
Cat-1	65.11
Cat-2	98.62
Cat-3	41.36

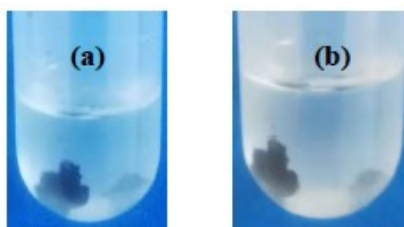


Fig. S6 Cat-2 was immersed in trifluoroacetic acid aqueous solution (10 wt%) for 30 days (a) and then it was immersed in strong sodium oxide aqueous solution (10 wt%) for another 30 days.

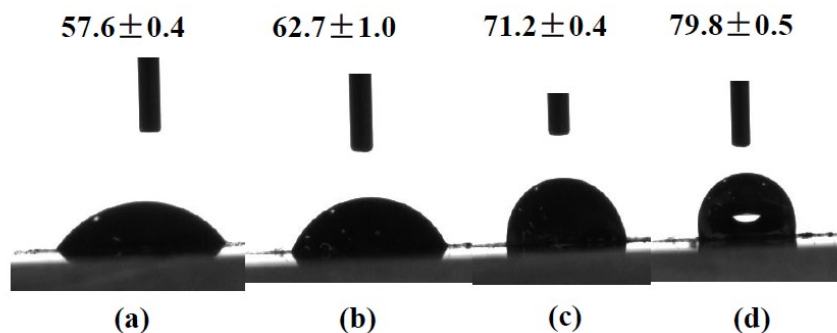


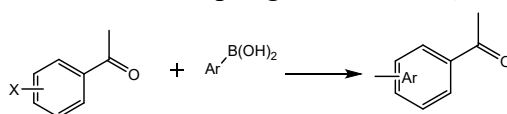
Fig. S7 Hydrophilicity and hydrophobicity was studied by water contact angle method Cat-1 (a), Cat-2 (b), Cat-3 (c) and Cat-4 (d).

Table. S3 Pd loading determined by ICP.

Catalysts	Pd loading (wt.%) (ICP)
Cat-1	1.02
Cat-2	1.06
Cat-3	1.12
Cat-4	1.24
Cat-5	1.08
Cat-2 ^a	1.04

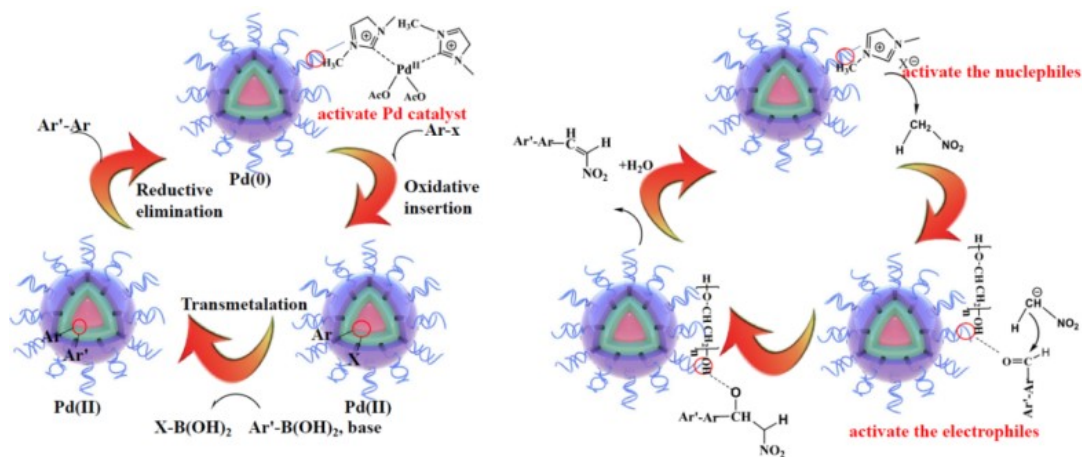
^aAfter 10 cycles for Cat-2.

Table. S4 C-C Suzuki coupling reaction catalyzed by Cat-2.



entry	ArX	Ar-	Time (min)	Yield (%)
1	p-I	Ph	30	99.8
2	p-I	p-FPh	90	97.8
3	p-I	p-ClPh	55	96.7
4	p-I	p-MePh	60	99.2
5	p-I	p-MeOPh	60	99.9
6	p-I	p-CF ₃ Ph	30	98.6
7	p-I	m-ClPh	55	99.9
8	p-I	2,4diMePh	60	96.3
9	m-I	Ph	30	99.2
10	m-I	p-FPh	35	98.5

11	m-I	p-ClPh	30	95.3
12	m-I	p-MePh	120	96.6
13	m-I	p-CF ₃ Ph	30	99.9
14	m-I	p-OMePh	30	97.6
15	m-I	m-ClPh	30	98.2
16	m-I	2,4diMePh	30	94.3



Scheme S1. A plausible mechanism for the Suzuki coupling and Knoevenagel reaction catalyzed by the metal biomimetic enzyme catalyst.

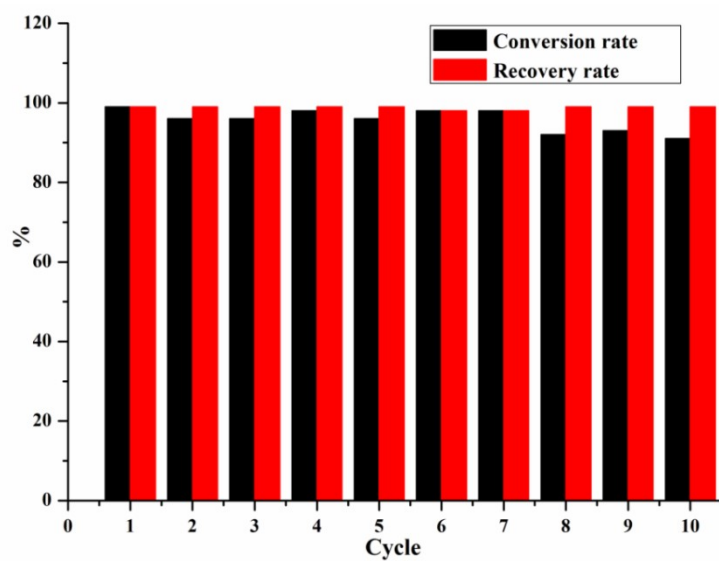


Fig. S8 The one-pot Suzuki-knoevenagel reaction catalyzed by Cat-2 for 10 times.