Supporting Information

Dual Functionalized Cages in Metal-Organic Frameworks via Stepwise Post-Synthetic Modification

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Experimental

Materials Synthesis

Synthesis of MIL-101-Cr[1]

A solution containing $Cr(NO_3)_3 \cdot 9\ H_2O$ (800 mg), 1,4-benzene dicarboxylic acid (332 mg), hydrofluoric acid (0.077 mL, 40 % in water) and H_2O (10 mL) was introduced in a 20 mL Teflon-liner. The mixture was heated to 220 ºC in an autoclave for 8 h. Upon cooling, the reaction mixture was doubly filtered to remove the free terephthalic acid. Then a solvothermal treatment was sequentially performed using ethanol (95 %) at 80 ºC for 24 h. The resulting solid was soaked in 1 M of NH_4F solution at 70 ºC for 24 h and immediately filtered, washed three times by hot water. The solid was finally dried overnight at 150 ºC.

Synthesis of MIL-101-ED

MIL-101-ED was prepared according to the literature.[1] MIL-101-Cr (0.5 g), dehydrated at 433 K for 12 h, was suspended in anhydrous benzene (30 mL). To this suspension, 1.5 mmol of ethylenediamine was added, and the mixture was stirred with heating to reflux for 24 h. The product was recovered by filtration and washed with de-ionized water/ethanol, and then dried at room temperature. Element analysis: C:17.80%, H:2.42%, N:6.73%. ICP: Cr: 19.54%.

Synthesis of MIL-101-NH_2

MIL-101-Cr-NH_2 was prepared according to the literature.[2] $CrCl_3$(266 mg), nitroterephthalic acid (211 mg)and water (5 mL)were put into a 23 mL autoclave with teflon vessel. The autoclave was kept at 180 ºC for 96 h. The green solid was centrifuged and activated by using water and ethanol. The resulting green solid MIL-101-NO_2 was dried at 70 ºC for 12 h. The 500 mg dry MIL-101-NO_2 and 18 g $SnCl_2 \cdot 2H_2O$ were suspended in 120 mL ethanol for 10 h at 70 ºC. The greenish solid was centrifuged and washed by concentrated hydrochloric acid, water, and ethanol for several times. MIL-101-NH_2 was obtained and dried at 70 ºC for 12 h.

Synthesis of MIL-101-NH_2-PW

The same synthetic procedure as for MIL-101-ED-PW was used except that MIL-101-ED was replaced by MIL-101-NH_2.

Synthesis of MIL-101-NHCH$_2$CH$_2$NH$_2$-PW

500 mg MIL-101-NH$_2$-PW was suspended in 25 mL dry CH$_3$CN. Then 210 mg BrCH$_2$CH$_2$NH$_2$·HCl and 180 mg ethylamine in methanol were added, and the mixture was stirred under reflux for 10 h. The product was achieved by filtration and washed with methanol and water, and then dried at room temperature. Elemental Analysis: C: 24.21%, H: 1.67%, N: 4.23%, ICP: Cr:12.58%, W:28.85%.

Synthesis of (R,R)-N,N'-Dibenzylidene-l,2-diaminocyclohexane

(R,R)-N,N'-Dibenzylidene-l,2-diaminocyclohexane was prepared according to the literature[3] with minor revision. A mixture of benzaldehyde (10.6 g, 100 mmol) and (R, R)-l,2-diaminocyclohexane (5.2 g, 50 mmol) in benzene (100 mL) was stirred at room temperature for 1 h. Then the mixture was refluxed under nitrogen with a Dean–Stark adapter until all the water had been removed. The solution was evaporated to dryness and the yellow resultant was recrystallized from petroleum ether to give 10.6 g product.

Synthesis of (R, R)-N,N'-Dibenzyl-l,2-diaminocyelohexane

(R, R)-N,N'-Dibenzyl-l,2-diaminocyelohexane was prepared according to the literature[4] with minor revision. To a 250 mL flask was added (R,R)-N,N'-dibenzylidene-l,2-diaminocyclohexane (5.0 g, 17.2 mmol), methanol (100 mL) and the mixture was cooled to 0°C. NaBH$_4$ (1.5 g) was added portionwise and the mixture was stirred at 25°C for 4 h. The solvent was evaporated and 100 mL H$_2$O was added and then extracted with CH$_2$C1$_2$ (3 × 150 mL). The organic layer was dried over MgSO$_4$ and the solvent evaporated to give the product (~ 4 g) as a yellow oil, which was used without further purification.

Synthesis of Ni(II)-bis[(R,R)-N,N'-dibenzylcyclohexane-1,2-diamine]Br$_2$

The catalyst Ni(II)-bis[(R,R)-N,N'-dibenzylcyclohexane-1,2-diamine]Br$_2$ was prepared following the method described by the literature.[4]

Synthesis of SBA-15

SBA-15 was prepared following the method described by Zhao et al.[5] The surfactant was removed by extraction with the HCl (37 wt %)/EtOH (V_{HCl}/V_{EtOH} = 1.5/98.5) solution in a Soxhlet apparatus for 24 h. The SBA-15 solid product was dried at 50 °C under vacuum for 12 h.

Synthesis of SBA-15-NH_2[1]

SBA-15-NH_2 was achieved by reacting aminopropyltrimethoxysilane with dry SBA-15 for 24 h under reflux in toluene.

Catalytic Reactions

Amine Poison Experiments

The amine poison experiments were performed using procedures similar to those for the synthesis of MIL-101-ED-PW. Typically, a methanolic solution containing phosphotungstic acid or tetrasulfophthalocyanine (Zn) or 1,5-naphthalenedisulfonic acid (0.11 mmol) was added to the water solution of MIL-101-ED (containing 0.1 mmol amine), and the mixture was stirred at room temperature for 1 h. The product was recovered by filtration and washed with methanol and hot water, and then dried at room temperature. The amine poison experiments performed on SBA-15-NH_2 followed procedures similar to the above except that MIL-101-ED was replaced by SBA-15-NH_2.

Deacetalization Control Experiment for MIL-101-Cr, HKUST-1, and MIL-101-ED-PW

To further demonstrate the advantages of our DPF-MOFcatalysts, we conducted additional control experiments on some benchmark catalysts such as the Cu(II)-based HKUST-1[6] and Cr(III)-based MIL-101-Cr, which can also catalyze the first step of deacetalization reaction. Our results indicated that the conversion was only 87% for MIL-101-Cr over 24 h and 97.5% for HKUST-1 over 11 h, whereas 98% conversion was achieved within just 1 h when MIL-101-ED-PW was used under the same conditions. This clearly shows that our strategy has its unique advantages which can introduce desired catalytic sites into MOFs for different reactions. Experiment procedure: A mixture of benzaldehyde dimethyl acetal (1 mmol), toluene (5 mL), water (0.2 mL) and catalyst (50 mg) was kept at 90 ºC under magnetic stirring.

Control Experiment for Mixture of MIL-101-Cr and Solid PW

We performed the deacetalization-Henry reaction using the mixture of MIL-101-Cr and PW powder as catalysts. We can only obtain the product of the first step reaction with 98% yield with no final product obtained, and we reasoned that the inability to catalyze the second step reaction for the mixture of MIL-101-Cr and PW powder should be due to the lack of Lewis base sites in the reaction system, which on the other hand highlights the advantage of our DPF-MOF.

Control Experiment for Mixture of MIL-101-ED and MIL-101-PW

We performed the deacetalization-Henry reaction using the mixture of MIL-101-ED (29 mg, contained 4.2 mg ED) and MIL-101-PW (45 mg, contained 18 mg PW) as catalysts.The same procedure as for MIL-101-ED-PW was used for mixture.

Control Experiment for Mixture of Two Homogeneous ED and PW

We performed the deacetalization-Henry reaction using the mixture of ED and PW powder (1.6:1 mmol) as catalysts. Only a negligible amount of **3** was observed. While we used ED and PW powder (1:1 mmol) as catalysts, we could only obtain **2** with 97% yield but without **3** formed. This fact obviously illustrates that two free catalysts will poison the activity of each other under the free situation probably due to the formation of ion pairs.

Preparation Process for Sections of MIL-101-ED-PW

A mixture of SPI-Pon812 (16.2 g), DDSA (10.0 g), NMA (8.9 g), DMP-30 (0.6 g) was added MIL-101-ED-PW (20 mg) and stirred 4 h at room temperature. Then obtained mixture was put into a mould and heated at 37 ^{o}C for 12 h, 45 ^{o}C for 12 h, and 60 ^{o}C for 48 h respectively. The resin after solidification was finally cut into extra-thin sections by LEICA EM UC7 microtome.

Methods

Commercially available reagents were purchased in high purity and used without further purification. PXRD data were collected on a Rigaku D/max 2550 Powder X-ray Diffractometer. N_2 gas sorption experiments were carried out on a Micrometrics ASAP 2020 M volumetric gas sorption instrument, and pore size distribution were caculated by Horvath-Kawazoe model. Elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. Inductively coupledplasma (ICP) analysis was performed on a Perkin–ElmerOptima 3300DV spectrometer.IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. XPS measurements were performed on an ESCALAB 250 X-ray photoelectron spectroscopy, using Mg Kα X-ray as the excitation source. High-performance liquid chromatograms (HPLC) were performed using the UltiMateTM 3000 system, including autosampler ASI-100, degasser DG-1210, pump P680 and Detector VWD-3400, the detect wavelength is 254 nm. HPLC-MS was performed on a High Capacity Ion Trap Mass Spectrometer of Bruker Daltonics Inc. HRTEM-EDS analysis was performed in a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gantan multiple CCD camera. The FEI tecnai G2S-Twin is equipped with an EDS detector, which was used for elemental analysis of the nanocrystal composition.

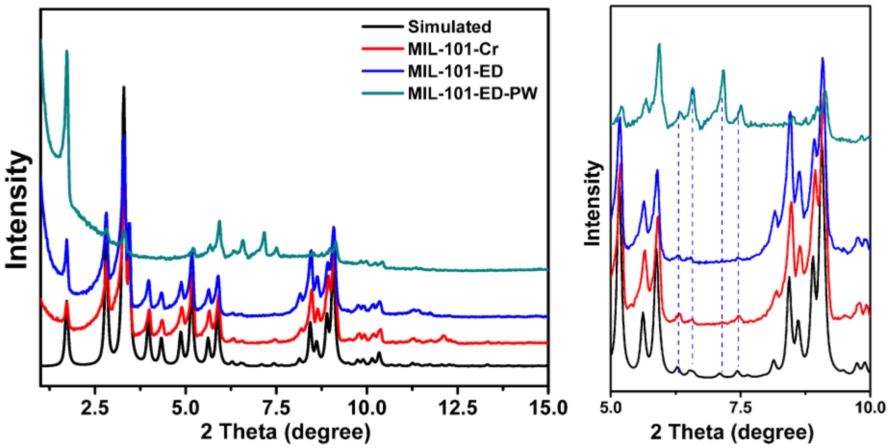


Figure S1. PXRD of MIL-101-Cr (simulated), MIL-101-Cr (as-synthesized), MIL-101-ED, and MIL-101-ED-PW.

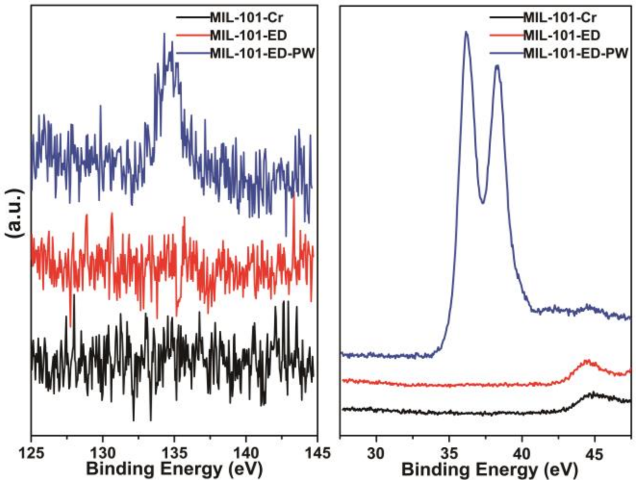


Figure S2. XPS spectra of MIL-101-Cr, MIL-101-ED, and MIL-101-ED-PW (left:P XPS spectra, right: W XPS spectra).

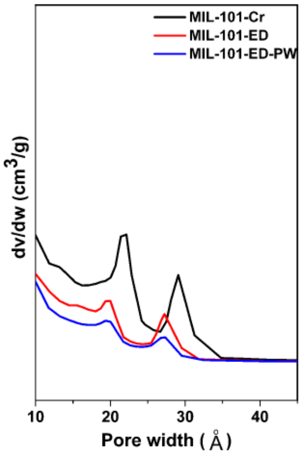


Figure S3. The pore size of MIL-101-Cr, MIL-101-ED and MIL-101-ED-PW.

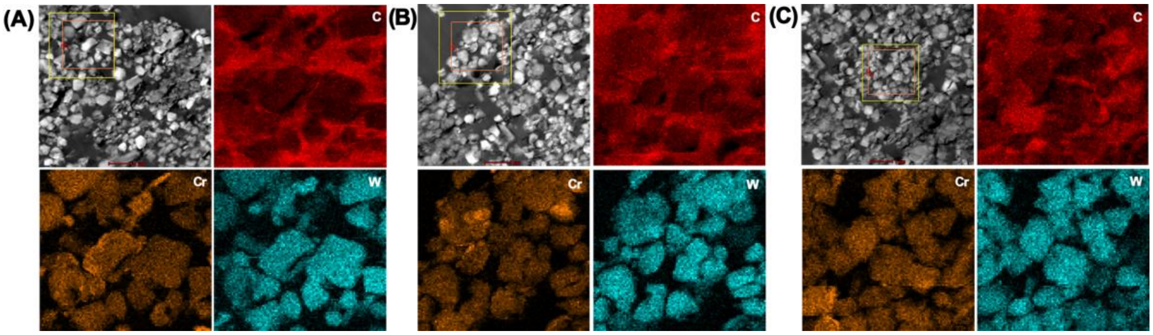


Figure S4.HRTEM-EDS analysis for three different areas in sections of a MIL-101-ED-PW sample (the length of red bar in every picture is 1μm, the other three pictures in each section are enlargements).

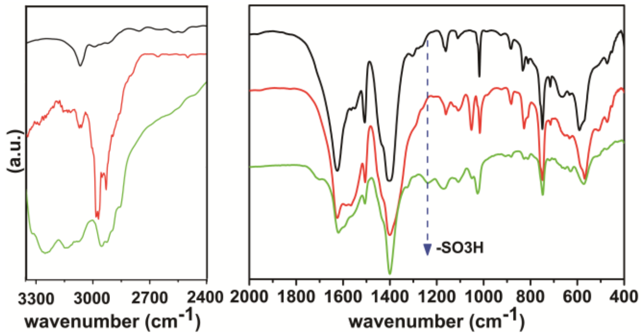


Figure S5. (a) FT-IR spectra of the dehydrated samples under vacuum, (b) FT-IR spectra of as-synthesized sample as a KBr tablet. MIL-101-Cr (black), MIL-101-ED (red), MIL-101-ED-TSP (green).

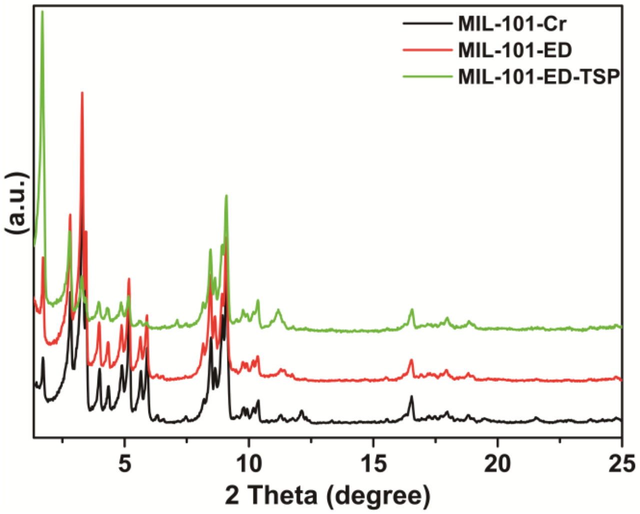


Figure S6.PXRD of MIL-101-Cr, MIL-101-ED, and MIL-101-ED-TSP.

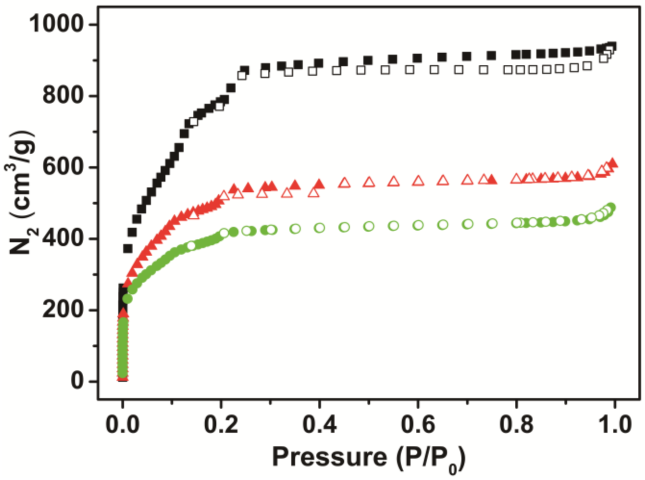


Figure S7. N_2 adsorption-desorption isotherms of MIL-101-ED-TSP and other intermediates. MIL-101-Cr (black), MIL-101-ED (red), and MIL-101-ED-TSP (green).

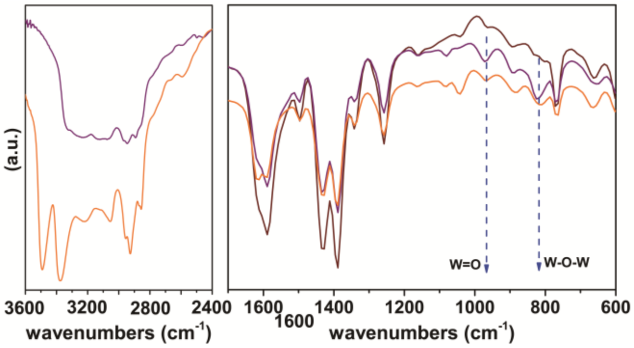


Figure S8.(a) FT-IR spectra of dehydrated samples under vacuum (left), (b) FT-IR spectra of as-synthesized sample as KBr tablets (right). MIL-101-NH_2 (brown), MIL-101-NH_2-PW (purple), MIL-101-$NHCH_2CH_2NH_2$-PW (orange).

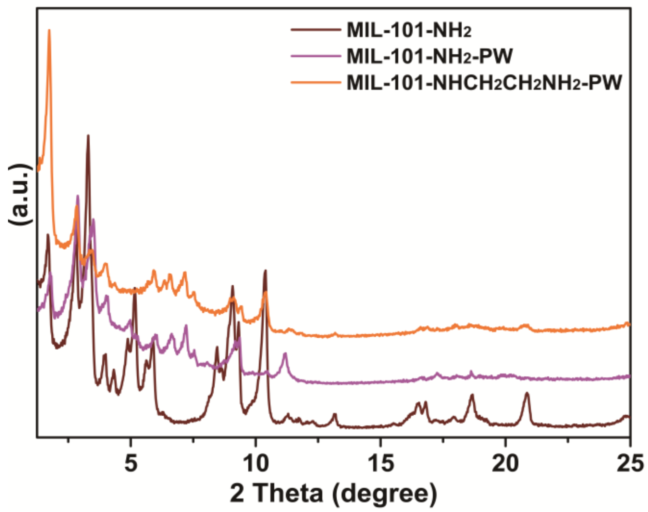


Figure S9.PXRD of MIL-101-NH_2, MIL-101-NH_2-PW, and MIL-101-$NHCH_2CH_2NH_2$-PW.

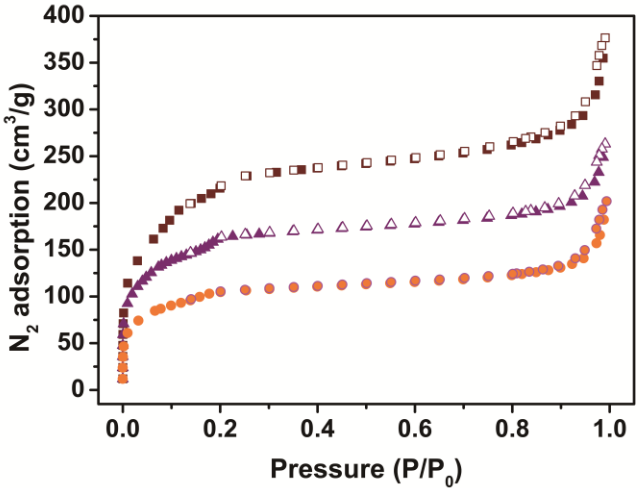


Figure S10. N_2 adsorption-desorption isotherms of MIL-101-NH_2 (brown), MIL-101-NH_2-PW (purple) and MIL-101-$NHCH_2CH_2NH_2$-PW (orange).

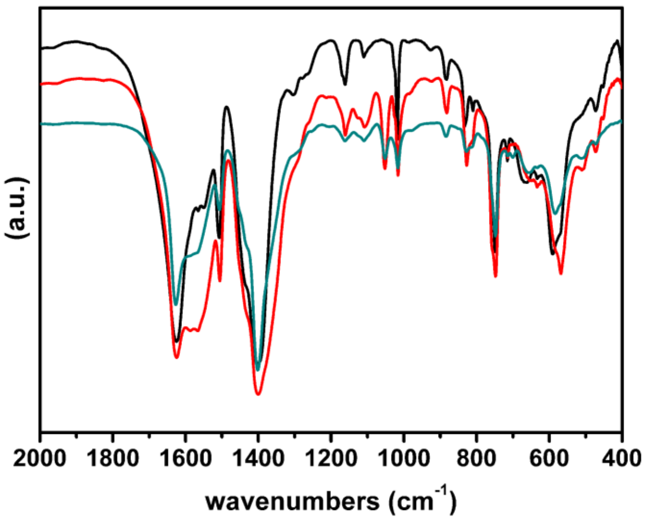


Figure S11. FT-IR spectra of as-synthesized samples as KBr tablets. MIL-101 (black), MIL-101-ED (red), MIL-101-ED-Ni-BDCDBr (deep blue).

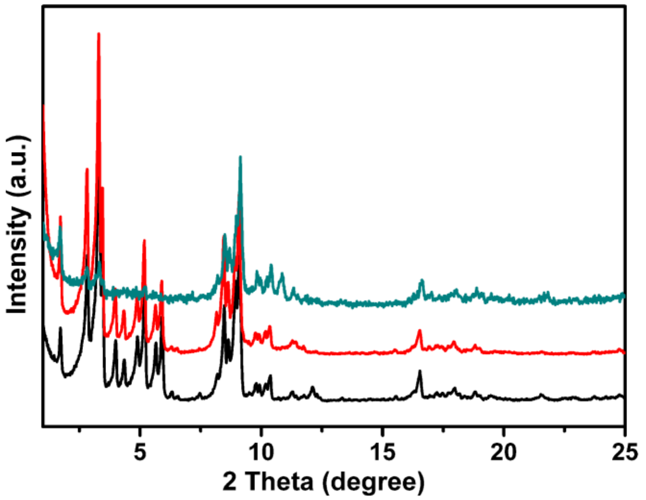


Figure S12. PXRD of MIL-101 (black), MIL-101-ED (red), MIL-101-ED-Ni-BDCDBr (deep blue).

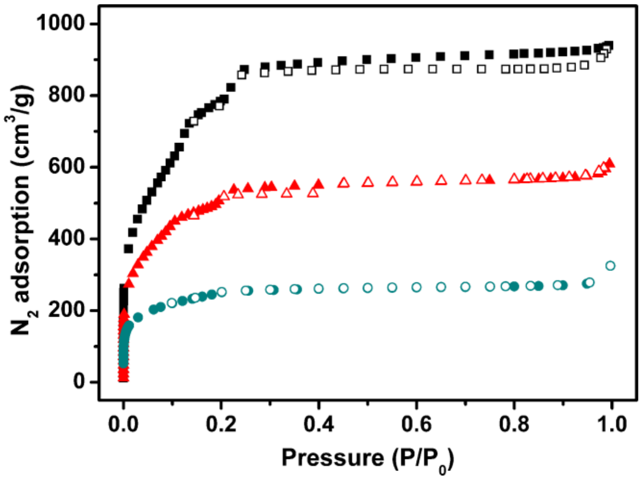


Figure S13. N_2 adsorption-desorption isotherms of MIL-101 (black), MIL-101-ED (red), MIL-101-ED-Ni-BDCDBr (deep blue).

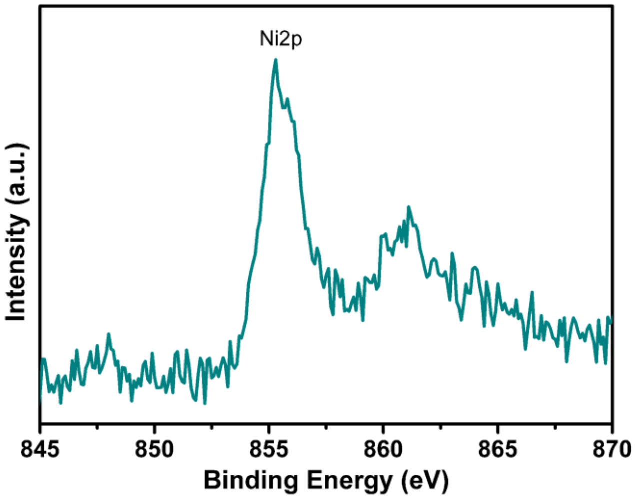


Figure S14. XPS spectra ofMIL-101-ED-Ni-BDCDBr.

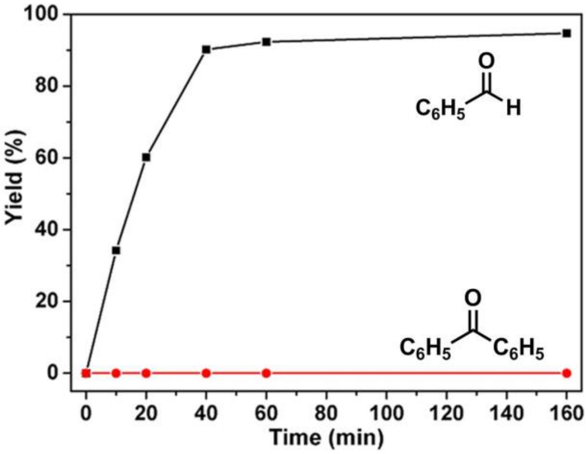


Figure S15. Influence of reaction time on the yield of a Knoevenagel reaction with different starting materials.

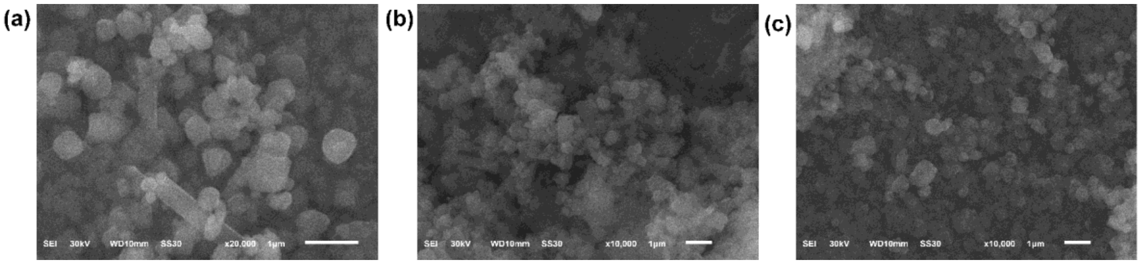
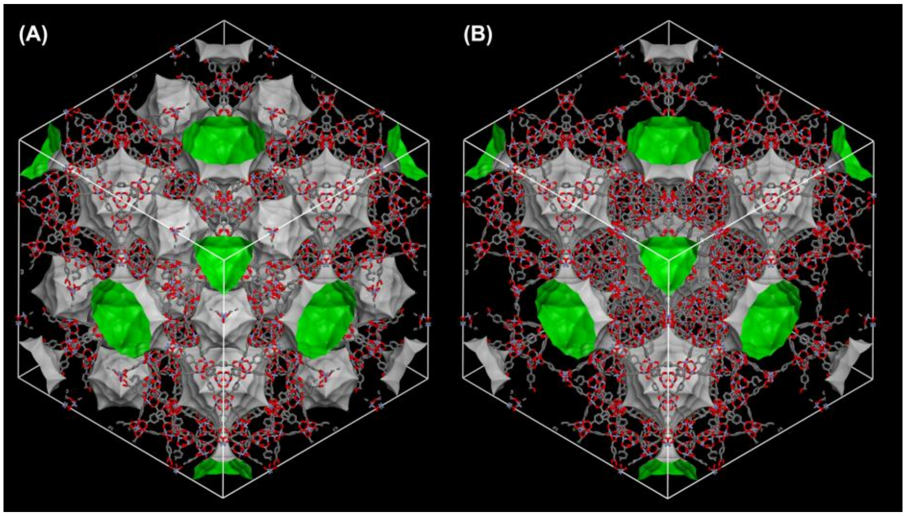


Figure S16. SEM images of MIL-101-ED-PW (a), MIL-101-ED (b), MIL-101-PW (c).

Simulations

Scheme S1. PW can Only Enter the Large Cages Based upon Simulations. (a) Gray Areas Represents the Solvent Accessible Cages in MIL-101-Cr, (b) Green Areas Represent Areas into which PW can Diffuse (Large Cages).



The solvent surface is calculated as the locus of the probe center as the probe rolls over the VDW surface of the framework of MIL-101-Cr. The accessible solvent surface is the same as the solvent surface, except that it only encloses those regions externally accessible to the probe. In this study, the radius of the probe is set to 6.5 Å, representing the size of the polyacid molecule. All these calculations are carried out using Materials Studio.[7]

Scheme S2. The Procedure for Synthesizing DPF-MOFs MIL-101-ED-TSP, MIL-101-NHCH$_2$CH$_2$NH$_2$-PW, and MIL-101-ED-Ni-BDCDBr.

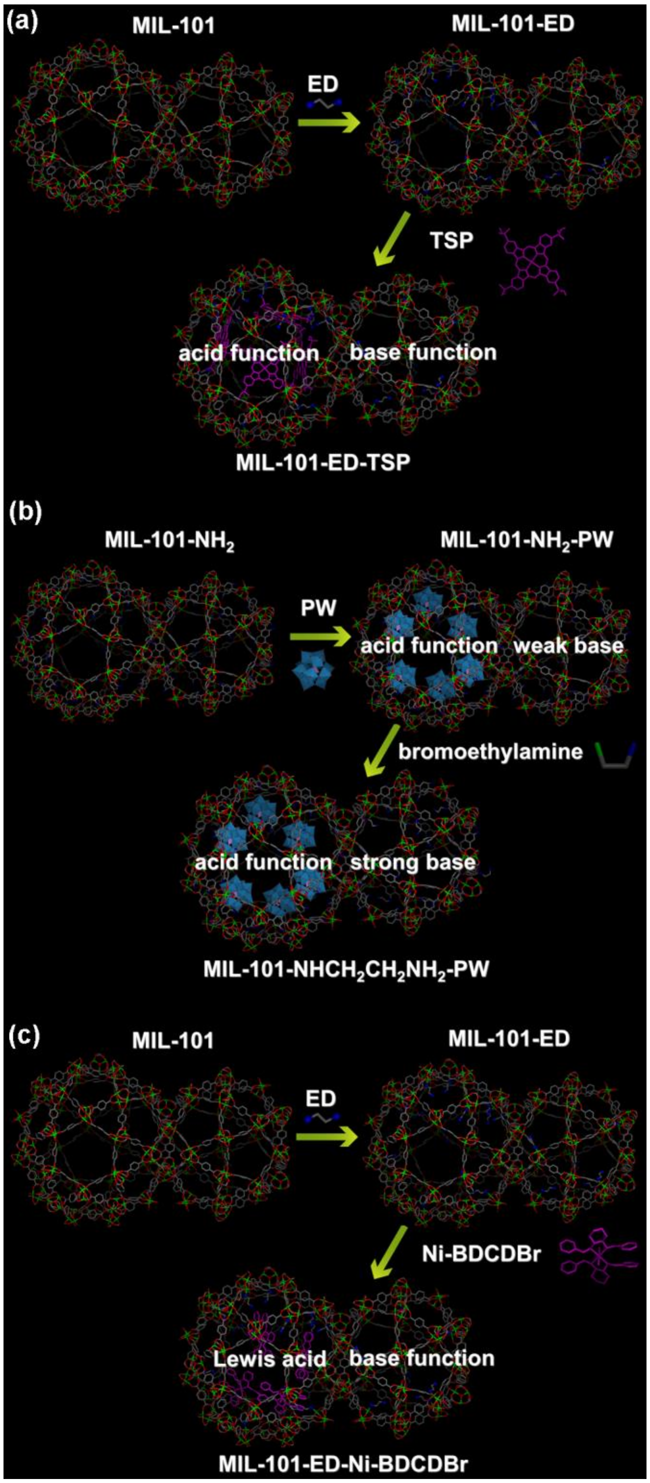
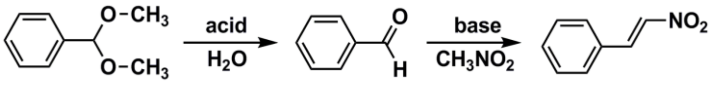


Table S1. In situ XPS Analysis of W/Cr Content for Different Layers of MIL-101-ED-PW.

Layer	1	2	3	4	5	6	7	8	9
W/Cr	0.64	0.65	0.64	0.65	0.63	0.63	0.62	0.62	0.62

The details for in situ XPS analysis : the reduction treatment was performed on a tablet of MIL-101-ED-PW for about 20 nm each time. The content of Cr/W after each reduction was recorded by XPS.

Table S2. OnePot Deacetalization-Henry Reaction[a]



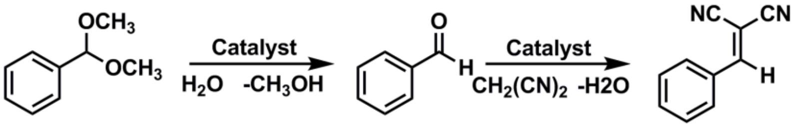
1 2 3

Entry	Catalyst	Conv. of **1** [%]	Yield of **2** [%]	Yield of **3** [%]
1	MIL-101-ED-PW	100	2	97.5
2	MIL-101-PW	100	100	0
3	MIL-101-ED	trace	trace	trace
4	MIL-101-ED-TSP	100	3.6	96
5	MIL-101-ED-PW (excess)	100	5.5	94
6	MIL-101-ED-TSP(excess)	100	6.2	93.8
7	MIL-101-ED-NDSA(excess)	100	100	trace
8	SBA-15-NH_2-PW(excess)[d]	100	100	trace
9	SBA-15-NH_2-TSP(excess)	100	100	trace
10	MIL-101-$NHCH_2CH_2NH_2$-PW[b]	100	4.4	95.6
11	MIL-101-NH_2-PW[b]	100	95.5	4.5
12	MIL-101-ED-PW[c]	100	4.5	95.3

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH_3NO_2 (5 mL), 90 °C, 24 h; [b] reaction time: 48 h; [c] after three cycles; [d] ref. 8.

MIL-101-ED-PW was found to convert benzaldehyde dimethyl acetal (**1**) into 2-nitrovinyl benzene (**3**) in almost quantitative yield after 24 h (entry 1). In comparison, when MIL-101-PW or MIL-101-ED was used alone, only a negligible amount of **3** was observed (entry 2, entry 3). In addition to the tandem deacetalization-Henry reaction, MIL-101-ED-PW also efficiently catalyzes the tandem deacetalization-Knoevenagel reaction (Table S3),[9,10] highlighting the versatility of the DPF-MOF. It is noteworthy that the initial catalytic activity of MIL-101-ED-PW was also higher (~3 times) than physical mixtures of MIL-101-PW and MIL-101-ED (Figure S17). We attribute this enhancement of activity to the lack of proximity of catalytic sites in a physical mixture. The accelerated reaction rate that results from a shortened mass transfer path highlights an advantage of DPF-MOFs.

Table S3.The Tandem Deacetalization-Knoevenagel Reaction Catalyzed by DPF-MOF MIL-101-ED-PW.



Entry	Catalyst	Conv. of 1 [%]	Yield of2 [%]	Yield of 3 [%]
1	MIL-101-ED-PW	100	3.5	94.5
2	MIL-101-PW	100	100	0
3	MIL-101-ED	trace	trace	trace

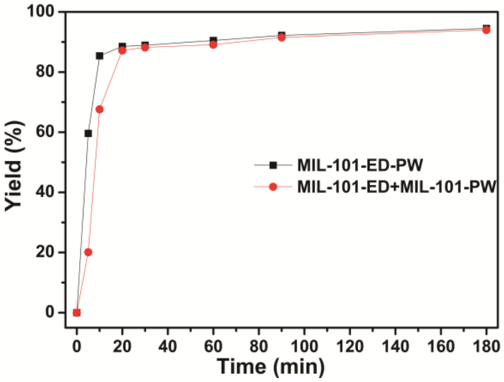


Figure S17. Catalytic activities of MIL-101-ED-PW and physical mixtures of MIL-101-ED and MIL-101-PW in tandem deacetalization-Knoevenagel reaction with benzaldehyde dimethyl acetal and malonitrile.

Table S4. Knoevenagel Reaction of Different Starting Materials Using MIL-101-ED-PW.

Entry	R1	R2	yield of 3 [%]
1	C_6H_5	H	94.7
2	C_6H_5	C_6H_5	0

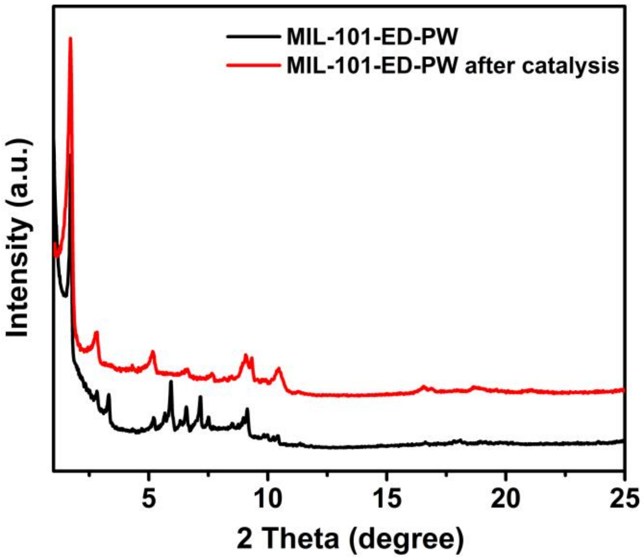


Figure S18. PXRD of MIL-101-ED-PW (black), MIL-101-ED-PW after catalysis (red).

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