

Electronic Supplementary Information

Dual Functionalization of Porous Aromatic Framework as a New Platform for Heterogeneous Cascade Catalysis

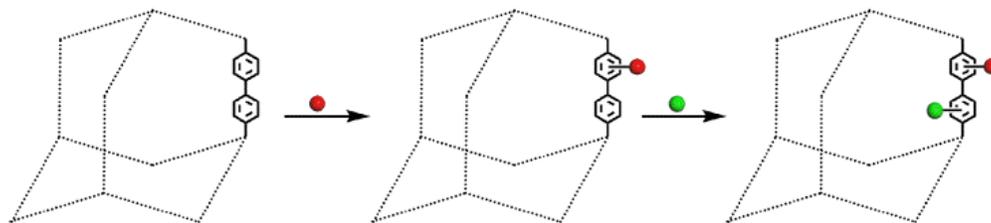
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Scheme S1 Illustration of stepwise post-synthetic modification of PAF-1 with two types of functional groups (red sphere: type A functional group; green sphere: type B functional group).

1. Experimental Details

All reagents were purchased from Sigma-Aldrich or Alfa and used as received unless otherwise indicated. PAF-1¹ was synthesized according to the procedures reported previously

1.1 Synthesis of PAF-1-NO₂

PAF-1 (100 mg) was suspended in Ac₂O (50 mL). To this suspension at an ice bath, 3.0 g of HNO₃ was gradually added, and the reaction mixture was then stirred at room temperature for two days. Subsequently, the mixture was poured into a large amount of water, and the solid was filtrated, washed with water substantially, and then dried to give PAF-1-NO₂.

1.2 Synthesis of PAF-1-NH₂

100 mg PAF-1-NO₂ and 3.26 g SnCl₂·2H₂O were suspended in 20mL ethanol. The mixture was heated at 70 °C for 8 h. The solid was centrifuged and suspended in 20 mL concentrated hydrochloric acid. Afterwards, the solid was centrifuged, washed three times with 15 mL H₂O each and one time with ethanol. The product was dried to produce PAF-1-NH₂.

1.3 Synthesis of PAF-1-NHCH₂CH₂NHBOC

PAF-1-NH₂ sample (240 mg) dehydrated at 120 °C for 12 h was suspended a solution of 30 mL of anhydrous benzene, 330 mg of triethylamine and 5 mL of ethanol. To this suspension, 2-(Boc-amino)ethyl bromide (500 mg) was added and the mixture was stirred under N₂ for 12 h

at 70 °C. The product was recovered by filtration and washed with ethanol, and then dried at 120 °C.

1.4 Synthesis of PAF-1-NHCH₂CH₂NHBOC-SO₃H

PAF-1-NHCH₂CH₂NHBOC was degassed at 120 °C under vacuum for 5 h. The activated PAF-NHCH₂CH₂NHBOC (180 mg) was stirred in 30 mL CH₂Cl₂ at an ice bath, and ClSO₃H (250 mg) was dropwisely added to the mixture, which was stirred at room temperature for 8 h. The solid was collected by filtration, washed several times with CH₂Cl₂, and then washed with 200 mL H₂O, and dried to give PAF-1-NHCH₂CH₂NHBOC-SO₃H.

1.5 Synthesis of PAF-1-NHCH₂CH₂NH₂-SO₃H

A sample of PAF-1-NHCH₂CH₂NHBOC-SO₃H (100 mg) was suspended in a mixture of 10 mL of ethanol and 10 mL of concentrated HCl. The reaction mixture was stirred at room temperature for 7 h. The solid was collected by filtration, washed several times with H₂O and ethanol followed by drying under vacuum. Elemental Analysis: C: 63.44%; H: 5.93%; N: 4.67%; S: 2.54%.

1.6 Synthesis of PAF-1-SO₃H

PAF-1-SO₃H was synthesized according to the procedures reported in the reference.² Elemental Analysis: C: 62.34%; H: 4.53%; N: 0.27%; S: 8.80%.

1.7 Synthesis of PAF-1-CH₂NH₂

PAF-1-CH₂NH₂ was synthesized according to the procedures reported in the reference with NH₃·H₂O instead of ethylenediamine.³ Elemental Analysis: C: 84.55%; H: 6.26%; N: 7.37%.

1.8 Synthesis of PAF-1-NH₂-SO₃H

PAF-1-NH₂-SO₃H was synthesized by sulfonation of PAF-1-NO₂ following the reduction reaction similar as PAF-1-NH₂.

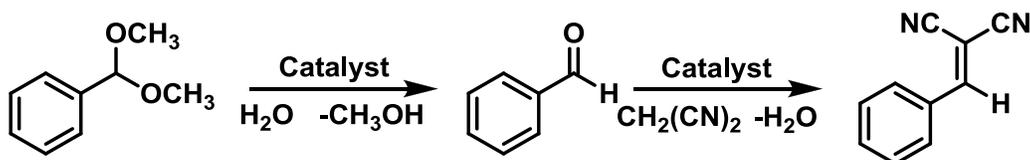
1.9 One pot deacetalization-Henry reaction

A mixture of benzaldehyde dimethyl acetal (1.0 mmol), nitromethane (5.0 mL), and catalyst (50 mg) was kept at 90 °C under magnetic stirring. The reaction mixture was then stirred under a nitrogen atmosphere for 24 h and the sample mixture was removed with a filter syringe and

evaluated by GC-MS to determine the yield.

1.10 One pot deacetalization–Knoevenagel reaction

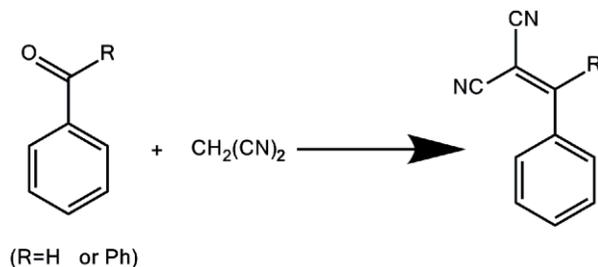
A mixture of benzaldehyde dimethyl acetal (1.0 mmol), 2.0 mmol malonitrile, and 50 mg of PAF-1-NHCH₂CH₂NH₂-SO₃H in 25 ml toluene was kept at 90 °C under magnetic stirring. The reaction mixture was then stirred under a nitrogen atmosphere for 3 h and the sample mixture was removed with a filter syringe and evaluated by GC-MS to determine the yield. For the control experiment, the quantity of catalysts was used with the same amount of free -NH₂ and -SO₃H groups.



Scheme S2. The tandem deacetalization-Knoevenagel reaction catalyzed by bifunctional PAF-1-NHCH₂CH₂NH₂-SO₃H.

1.11 Size selectivity experiment

The size selectivity experiment was performed based on the Knoevenagel reaction with the same process as deacetalization–Knoevenagel reaction.



R	Yield
H	99%
Ph	8%

Scheme S3. Size selectivity experiment based on Knoevenagel reaction catalyzed by PAF-1-NHCH₂CH₂NH₂-SO₃H.

2. Characterization

Gas sorption experiments were carried out on the surface area analyzer ASAP-2020. N₂ gas adsorption isotherm was measured at 77 K using a liquid N₂ bath. Prior to the measurements, PAF-1 was treated by the literature and the other samples were degassed for 10 h at 120 °C. FT-IR data were recorded on an IRAffinity-1 instrument. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res.

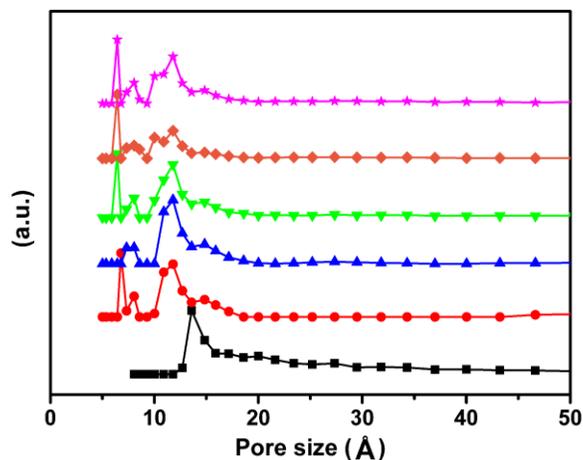


Fig. S1 The pore size distributions for: PAF-1 (black); PAF-1-NO₂ (red), PAF-1-NH₂ (blue), PAF-1-NHCH₂CH₂NHBOC (green), PAF-1-NHCH₂CH₂NHBOC-SO₃H (orange), and PAF-1-NHCH₂CH₂NH₂-SO₃H (magenta).

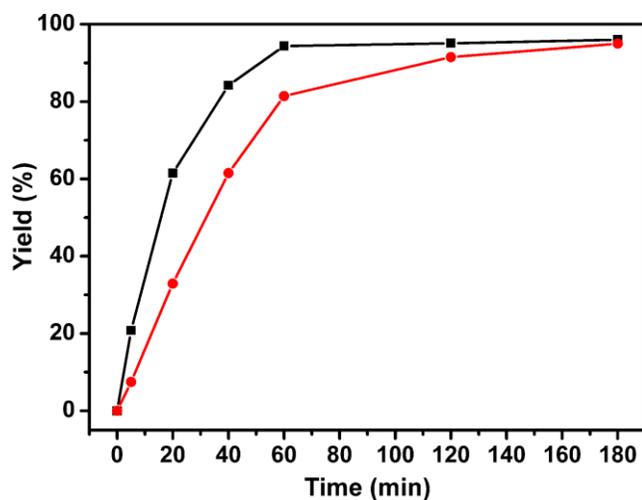


Fig. S2 Tandem deacetalization-Knoevenagel reaction catalyzed by PAF-NHCH₂CH₂NH₂-SO₃H (black) and mixture (red) of PAF-1-SO₃H and PAF-1-CH₂NH₂.

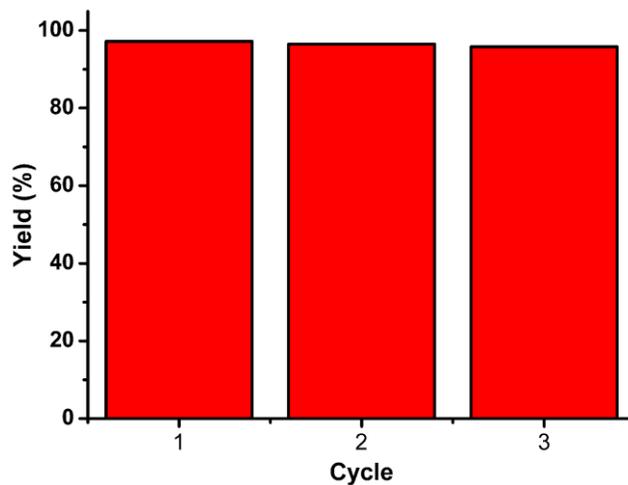


Fig. S3 The cycle of PAF-1-NHCH₂CH₂NH₂-SO₃H for deacetalization-Henry reaction.

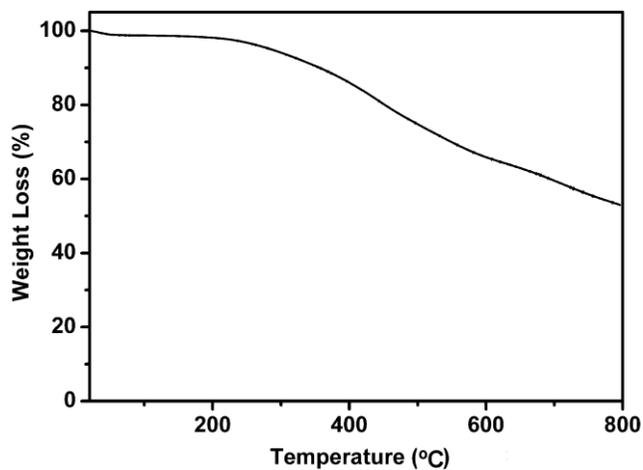


Fig. S4 Thermogravimetric analysis (TGA) of PAF-1-NHCH₂CH₂NH₂-SO₃H.

Reference

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- 3 W. Lu, J. P. Sculley, D. Yuan, R. Krishna, Z. Wei, and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 7480.