Supporting Information

Amine-functionalized Metal-Organic Frameworks for transesterification of triglycerides

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Experimental

1. Chemicals

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. Terephthalic acid (BDC), 2-aminoterephthalic acid ($BDC-NH_2$), 4,4′-biphenyldicarboxylic acid (BPDC), zinc nitrate hexahydrate ($Zn(NO_3)_2·6H_2O$), ethanediamine (ED), 4-dimethylamiopryidine (DMAP), 2-chloro-*N*,*N*-dimethylethylamine hydrochloride, glyceryl triacetate, glyceryl tributyrate, methyl acetate, and methyl butyrate were purchased from Aladdin Industrial Inc. (Shanghai, P. R. China). Methanol, toluene (internal standard), potassium carbonate, *N*,*N*-dimethylformamide (DMF), triethylamine, acetone, trichloromethane, and aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). Nitrogen gas (>99.999%) was obtained from Huate Co. Ltd. (foshan, P. R. China). De-ionized pure water from Millipore Milli-Q Plus System was used as solvent.

2. Characterization

Surface area**:** The BET surface area measurements were performed with N_2 adsorption-desorption isotherms at 77 K (SI-MP-10/PoreMaster 33, Quantachrome). After degassing the samples under vacuum at 393 K for 24 h and then the isotherms were measured over the range of $10^{-6} < P/P0 < 0.1$. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method in the p/p_0 range 0.05 to 0.3. Pore size distribution curves were calculated using the adsorption branch of the isotherms and the Barrett-Joyner-Halenda (BJH) method, and pore sizes were obtained from the peak positions of the distribution curves.

Fourier transform infrared (FT-IR)**:** Approximately 2 mg sample and 100 mg KBr were mixed in a quartz cell. The mixture was crush into power and were pressed (107 Pa) into self-supported discs (2 cm^2 area). FT-IR analysis of the discs including sample were carried out using Bruker Tensor 27 spectrotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-3} and accumulations of 128 scans. Spectra were recorded at room temperature under dinitrogen atmosphere.

Powder X-ray diffraction (XRD)**:** XRD patterns of the as-prepared and functionalized MOF samples were obtained by a Bruker Advance D8 diffractometer at 40 KV and 40 mA, using Ni-filtered Cu-Kα radiation with a scan speed of 0.3 sec/step, a step size of 0.02° in 2θ, and a 2θ range of 5–50. Approximately 15 mg sample was dehydrated under high vacuum at 100°C before XRD analysis.

Thermal gravimetric analysis (TGA)**:** Approximately 10–14 mg sample was used for thermogravimetric analysis. The sample was analyzed under a stream of dinitrogen using a TA Instrument Q600 SDT from room temperature to 600°C with a scan rate of 10 K/min.

***^{1}H NMR*:** ^{1}H NMR spectra were recorded on Varian FT-NMR spectrometers (400 MHz). Approximately 10 mg of sample were digested by sonication in the mixture of 500 μL DMSO-d_6 and 100 μL DCl (20%). Upon complete dissolution of the sample, this solution was used for ^{1}H NMR analysis.

***GC and GC-MS analysis*:** GC and GC-MS analysis were recorded on Agilent 6890 and ThermoQuest Trace 2000, respectively, equipped with a FID detector and a packed column (0.32 mm × 30 m KB-5 capillary column) with He as carrier gas. The GC and GC-MS conditions for the product analysis: the Injector and Detector Temperature were fixed at 260°C. Product separation was achieved using temperature ramps 60°C for 1 min, 5°C/min to 75°C, held at 75°C for 0.5 min, 30°C/min to 260°C, and held at 260°C for 2 min.

X-ray photoelectron spectroscopy (XPS) spectra analysis: the XPS spectra was performed with a Kratos Axis Ultra (DLD) photoelectron spectrometer operated at 15 kV and 10 mA at a pressure of about 5×10^{-9} torr using AlKa as the exciting source (1486.6 eV). C 1s photoelectron peak (BE = 284.2 eV) was used for the binding energy calibration.

3. Preparation of MOFs

***MOF-5*:** zinc nitrate hexahydrate $Zn(NO_3)_2\cdot6H_2O$ (2.4 g, 8.1 mmol) and terephthalic acid (0.66 g, 3.97 mmol) were dissolved in 80 mL of *N*,*N*-dimethylformamide (DMF). The precipitation took place instantaneously at room temperature upon drop wise addition of 1.5 ml (16 mmol) of pure Et_3N, After 90 min of stirring, the white powder was filtered and washed three times with DMF. The solid was then immersed in chloroform for 3 days with fresh chloroform added every 24 h. The solvent was filtered and the solid was dried under vacuum at 343 K. (L. M. Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun, D. Y. Zhao and Y. S. Yan, *Microporous Mesoporous Mater.*, 2003, **58**, 105-114.)

***IRMOF-10*:** zinc nitrate hexahydrate $Zn(NO_3)_2\cdot6(H_2O)$ (1.8 g, 6.9 mmol,) and 4,4′-biphenyldicarboxylic acid (0.3 g, 1.2 mmol) were stirred for 15 min in 100 mL of *N*,*N*-dimethylformamide (DMF) in a 1-L wide mouth glass jar. The mixture was introduced into a stainless steel autoclave and placed in oven at 373 K for 18 h to yield rectangular prismatic crystals. After decanting the hot mother liquor and rinsing with DMF, the product was immersed in chloroform for 3 days, during which the activation solvent was decanted, freshly replenished three times every 24 h. The solvent was removed and the solid was dried under vacuum at 343 K. (Lit. M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O′Keeffe, O. M. Yaghi, *Science*, **2002**, *295*, 469–472.)

***MIL-53(Al)-NH$_2$*:** Aluminum nitrate nonahydrate $Al(NO_3)_3 \cdot 9H_2O$ (0.878 g, 2.10 mmol) and 2-amino-1,4-benzenedicarboxylic acid (0.564 g, 3.12 mmol) dissolved in 30 mL DMF were mixed in a Teflon insert and placed in an autoclave. The autoclave was heated in an oven at 403 K for 3 days. The yellow gel product was filtered off and washed with acetone. After removal of the acetone under reduced pressure, the product was washed overnight with methanol under reflux and dried at 383 K under vacuum for 10 h. (Lit. J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. van Klink, F. Kapteijn, *J. Catal.* 2009, **261**, 75–87.)

4. Characterization of basic site density and apparent pH value for MOFs

***Basic site density*:** the basicity properties and the number of accessible basic sites were characterized by acid-base titration with HCl as the titrant. The total number of basic groups (basic site density) was calculated by the amount of HCl (10 mM) added to the corresponding amine-functionalized MOFs (60 mg) in an aqueous KCl solution (60 mL, 1 mM).

***Apparent pH value*:** the apparent pH value was generated by suspending the corresponding amine-functionalized MOFs (30 mg) in an aqueous KCl solution (20 mL, 1 mM) (Lit. A. Villa, J.-P. Tessonnier, O. Majoulet, D. S. Su, R. Schlögl, *ChemSusChem* 2010, **3**, 241–245).

Table S1. The textural properties of various amine-functionalized MOFs

Sample	surface area (m^2g^{-1})[a]	microporous volume (cm^3g^{-1})[b]
MOF-5[c]	872	1.01
MOF-5-ED	391	1.28
MOF-5-DMAP	348	0.20
IRMOF-10[d]	1904	/
IRMOF-10-ED	523	0.62
IRMOF-10-DMAP	420	0.39

[a] Obtained by BET method. [b] Obtained by BJH method. [c] Referred to S. X. Gao, N. Zhao, M. H. Shu, S. N. Che, *Appl. Catal. A* 2010, **388**, 196–201. [d] Referred to Jesse. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* 2006, **128**, 1304–1315.

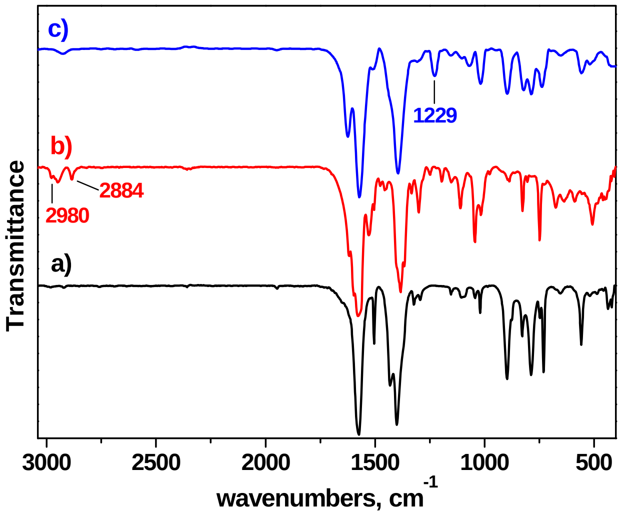


Figure S1. FT-IR spectra of a) MOF-5, b) MOF-5-ED and c) MOF-5-DMAP.

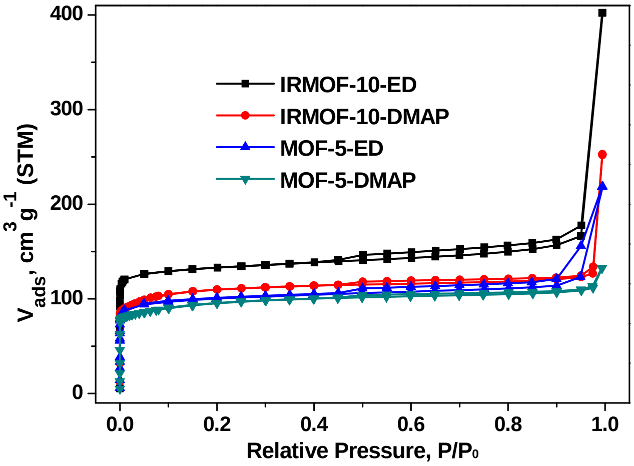


Figure S2. N_2 adsorption/desorption isotherms of MOF-5-ED, MOF-5-DMAP, IRMOF-10-ED and IRMOF-10-DMAP

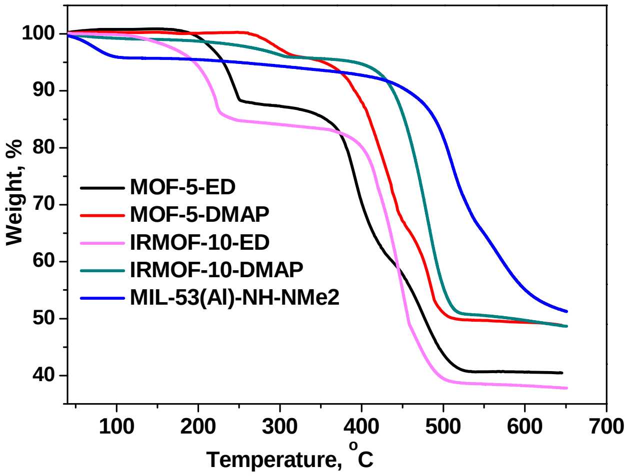
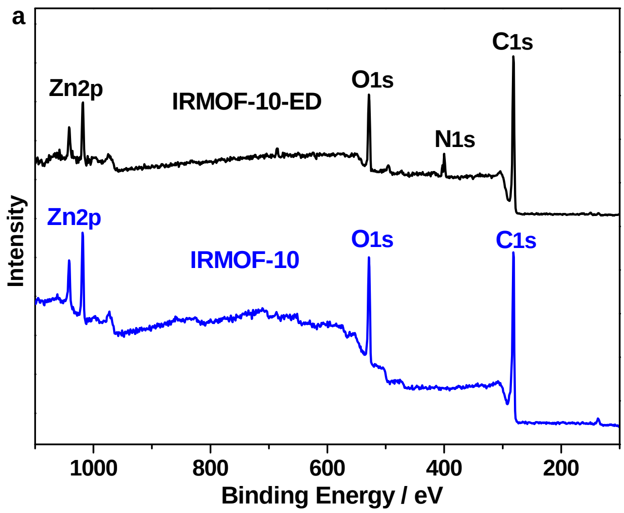


Figure S3. TGA of MOF-5-ED, MOF-5-DMAP, IRMOF-10-ED, IRMOF-10-DMAP, MIL-53(Al)-NH-NMe_2



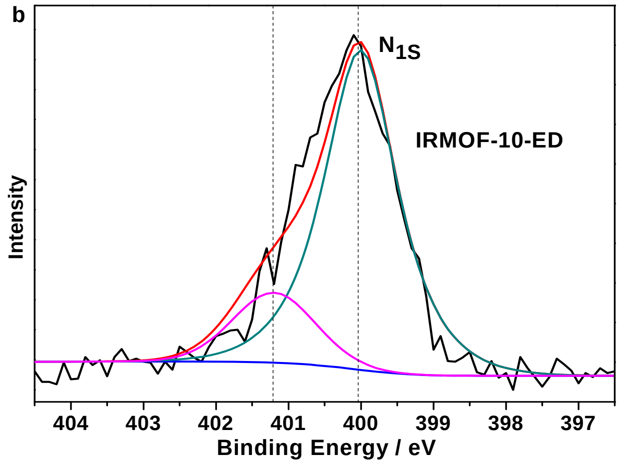


Figure S4. a) XPS scan survey for IRMOF-10 and IRMOF-10-ED; b) N 1s XPS spectra of IRMOF-10-ED

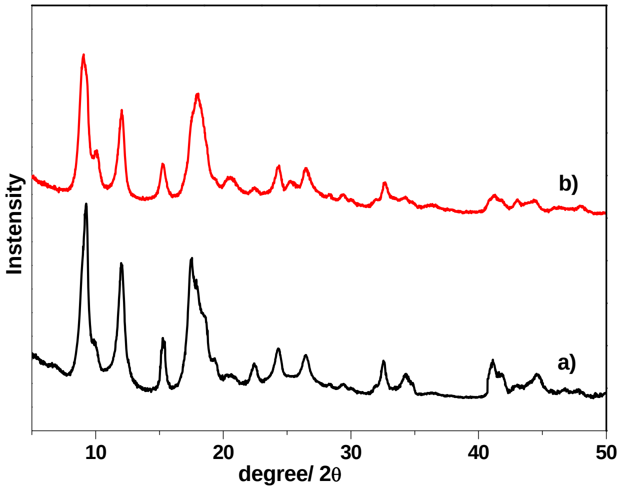


Figure S5. The XRD patterns of a) MIL-53(Al)-NH_2, b) MIL-53(Al)-NH-NMe_2

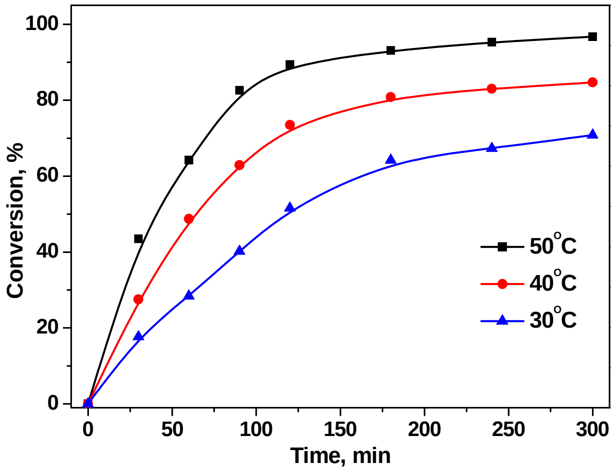


Figure S6. IRMOF-10-ED catalyzed transesterification of glyceryl triacetate with methanol (reaction conditions: IRMOF-10-ED, 120 mg; methanol, 35 mL; glyceryl triacetate, 1831 mg; molar ratio of methanol to triacetate, 90:1; temperature, 50, 40, and 30°C, respectively).