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Electronic Supplementary Information

Light-Enhanced Acid Catalysis over a Metal-Organic Framework

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S1. Materials and Instrumentation

All chemicals were obtained from commercial sources and were used without further purification. Monosodium 2-sulfoterephthalic acid (TCI, >99.0%), chromium trioxide (CrO_3, Sigma-Aldrich, 99%), hydrochloric acid (HCl, Sinopharm Chemical Reagent Co., Ltd., AR), sulfuric acid (H_2SO_4, Sinopharm Chemical Reagent Co., Ltd., AR), N,N-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR), acetic acid (CH_3COOH, Sinopharm Chemical Reagent Co., Ltd., AR), propionic acid (CH_3CH_2COOH, Energy Chemical, AR), methanol (CH_3OH, Sinopharm Chemical Reagent Co., Ltd., AR), benzyl alcohol (Energy Chemical, AR), Hantzsch ester (HEH, Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate, Energy Chemical, AR), N-benzylideneaniline (Energy Chemical, AR), N-phenylbenzylamine (Energy Chemical, AR), cyclohexanol (Sinopharm Chemical Reagent Co., Ltd., AR), cyclohexanone oxime (Energy Chemical, 98%), benzonitrile (Aladdin Industrial Inc., 98.5%), benzaldehyde (Aladdin Industrial Inc., 98.5%), ethylene glycol (Sinopharm Chemical Reagent Co., Ltd., AR), aniline (Sinopharm Chemical Reagent Co., Ltd., AR), tetrahydro pyrrole (Energy Chemical, 99%) and toluene (Sinopharm Chemical Reagent Co., Ltd., AR) were used as received.

Deionized water with the specific resistance of 18.25 MΩ·cm was acquired by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction (XRD) studies were carried out on a Japan Rigaku SmartLabTM rotation anode X-ray diffractometer or Holland X'Pert PRO fixed anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.54$ Å). UV-Vis absorption spectrum was recorded on a Shimadzu UV-2700 spectrophotometer and a white standard of $BaSO_4$ was used as a reference. Steady-state photoluminescence (PL) emission spectra were obtained over a LS-55 fluorescence spectrometer made by PerkinElmer. The conversion and selectivity were determined by using a Shimadzu gas chromatograph (GC-2010 Plus with a 0.25 mm × 30 m Rtx®-5 capillary column) with an FID detector and high purity nitrogen as the carrier gas. Nitrogen sorption isotherms were measured by using automatic volumetric adsorption equipment (Micrometritics ASAP 2020). The products were determined by using the Agilent technologies 7890A GC and a mass spectrometer Agilent technologies 5975C as detector. The light irradiation was obtained by 300 W Xenon lamp (LX300F, Japan) otherwise stated. ^1H NMR spectra were recorded on Bruker-400 MHz NMR spectrometer. The ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$(TMS) at δ 0.0 or at the signal of a residual protonated solvent: $CDCl_3$ δ 7.26 or DMSO-d_6 δ 2.50. Prior to N_2 adsorption/desorption measurements, the samples were dried overnight at 150 °C under vacuum first and then degassed at 120 °C for 6 h using the “degassing” function of the ASAP equipment.

S2. Experimental Section

2.1 Preparation of MIL-101-SO_3H.

The one-pot synthesis of the sulfonic acid-functionalized MIL-101 was based on the reported method.[S1] Typically, monosodium 2-sulfoterephthalic acid (0.67 g, 2.5 mmol), CrO_3 (0.25 g, 2.5 mmol), and concentrated HCl (0.16 mL, 12 M, 5 mmol) were dissolved in deionized water (10 mL), and then transferred to a Teflon-lined stainless steel autoclave (20 mL). The prepared solution was heated at 180 °C for 6 d under the hydrothermal conditions. The products were filtered and washed with 200 mL deionized water and 100 mL methanol, then dried in air. The obtained green powder was purified in 150 mL DMF at 120 °C for 24 h to wash out the unreacted organic ligand stayed within the MOF pores. Then the sample was added into a mixed solution of 50 mL methanol and 100 mL H_2O at 90 °C for 12 h to remove the remaining DMF. To acidize the resultant solid and exchange out the Na^+, giving a sufficiently protonated MIL-101-SO_3H, the product was treated in a mixed solution of diluted HCl (0.08 M) in 50 mL methanol and 100 mL water according to the reported procedure.[S2] The product after acidification was further treated in 50 mL methanol and 100 mL water at 90 °C for 6 h to eliminate additional HCl and finally dried at 120 °C for 24 h under vacuum prior to the further use.

2.2 General procedure for esterification reactions.

The typical procedure for esterification reactions was as follows: 10 mmol of benzyl alcohol with 40 mmol of acetic acid (or 10 mmol of cyclohexanol with 40 mmol of acetic acid, or 10 mmol of benzyl alcohol with 40 mmol of propanoic acid) and the catalyst (30 mg MIL-101-SO_3H, or 1.6 μL concentrated H_2SO_4, or 21.6 mg MIL-101) were charged successively into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 80 °C in an oil bath for a desired time length under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction mixture was sampled periodically and analyzed using a GC, and further confirmed by GC-MS.

2.3 Recycling experiment of the MIL-101-SO_3H catalyst.

The recyclability of the catalyst toward the esterification reaction between benzyl alcohol (10 mmol) and acetic acid (40 mmol) was examined. Typically, the catalyst was filtered out after the reaction, washed with acetic acid for 2 times. Then the catalyst was reused for a subsequent run with fresh benzyl alcohol (10 mmol) and acetic acid (40 mmol).

2.4 The pH change under different light intensities and different concentrations of MIL-101-SO_3H.

The pH change (ΔpH) under different light intensities and different concentrations of MIL-101-SO_3H was measured by a pH-meter (Mettler-Toledo FE 20). The concentrations of the MIL-101-SO_3H in the aqueous solution were 1, 3, and 5 mg/mL, respectively. The volume of the solution for test was 30 mL and the light was emitted by a 300 W Xenon lamp. The temperature of the reaction solution was controlled by a water cooling system and the temperature change was negligible. The probe of pH meter was shielded from direct exposure to the light. The catalyst suspension solution was stirred in water until dissociation equilibrium to obtain pH_{eq1} in advance. Obviously, the pH_{eq1} decreased gradually with the increased concentration of MIL-101-SO_3H suspension solution. After a new dissociation equilibrium was reached (in ~0.5 h), the pH_{eq2} was measured at fixed concentration and light intensity under stirring ($\Delta pH = pH_{eq2} - pH_{eq1} = -\log([H^+]_{eq2}/[H^+]_{eq1})$).

2.5 Acid-base titration.

Prior to the test, ~0.5 g of MIL-101-SO_3H was dried at 393 K under vacuum for 12 h, then cooled to room temperature under N_2 atmosphere. The solid was weighed and dispersed in 200 mL of saturated NaCl solution and stirred at room temperature for 24 h. The supernatant was collected via centrifugation, and analysed by 0.1 M NaOH solution. The H^+ amount was determined to be 1.75 mmol/g based on acid-base titration.

2.6 Ring-opening of styrene oxide over MIL-101-SO_3H by two different

nucleophiles, aniline and tetrahydro pyrrole.

The typical procedure for ring-opening reaction with aniline was as follows: 1 mmol styrene oxide, 1.1 mmol aniline, 30 mg MIL-101-SO_3H and 2 mL toluene, were charged successively into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 80 °C in an oil bath for a desired time length under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction of styrene oxide with aniline yielded two types of isomers. The reaction mixture was sampled periodically and analyzed using a GC-MS and further confirmed by ^1H NMR.

The typical procedure for ring-opening reaction with tetrahydro pyrrole was as follows: 2 mmol styrene oxide, 1.64 mL tetrahydro pyrrole, 20 mg MIL-101-SO_3H and 3 mL toluene, were charged successively into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 80 °C in an oil bath for a desired time length under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction of styrene oxide with tetrahydro pyrrole (their molar ratio was set to 1/20) yielded two types of isomers. The reaction mixtures were sampled periodically and analyzed using a GC-MS and further confirmed by ^1H NMR.

2.7 Different catalytic reactions over MIL-101-SO_3H and homogeneous H_2SO_4.

Diverse Brønsted acid-catalyzed organic reactions, such as Beckmann rearrangement reaction and acetalization of aldehyde with diol, were examined to demonstrate the generality of light-enhanced activity based on MIL-101-SO_3H and homogeneous H_2SO_4 catalyst.

Typical procedure for Peckmann rearrangement reaction: cyclohexanone oxime (56 mg, 0.5 mmol), catalyst (MIL-101-SO_3H, 20 mg or concentrated H_2SO_4, 1.08 μL) and 6 mL benzonitrile, were added into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 130 °C in an oil bath for 10 h under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction mixture was sampled periodically and analyzed using a GC, and further confirmed by 1H NMR.

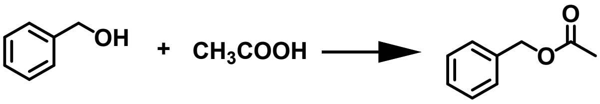
Typical procedure for acetalization reaction: benzaldehyde (3 mL, 30 mmol), glycol (3 mL, 60 mmol), catalyst (MIL-101-SO_3H, 20 mg or concentrated H_2SO_4, 1.08 μL), were charged successively into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 80 °C in an oil bath for 10 h under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction mixture was sampled periodically and analyzed using a GC, and further confirmed by MS.

Typical procedure for transfer hydrogenation of imines: N-benzylideneaniline (0.2 mmol), Hantzsch ester (HEH, 1.3 equiv, 0.26 mmol), and toluene (6.0 mL), catalyst (30 mg MIL-101-SO_3H or 1.6 μL concentrated H_2SO_4), were charged successively into the photo-reactor, irradiated by a 300 W Xe lamp (full-spectrum) and heated at 30 °C in an oil bath under stirring. For control experiment, no light irradiation exists during the catalytic reaction. The reaction mixture was sampled periodically and analyzed using a GC, and further confirmed by MS.[S3]

S3. Computational Details.

DFT calculations are performed by using Vienna Ab Initio Simulation Package (VASP).[S4] The exchange-correlation energy and potential are described by the generalized gradient approximation in the form of PW91 functional.[S5] Plane waves with a cutoff of 400 eV and a Brillouin-zone sampling restricted to the Γ-point have been used for projector augmented wave (PAW) potentials.[S6] All structures are fully optimized under the scheme of spin-polarized density functional theory. The criteria for the convergence in the structural relaxation are the residual force less than 0.05 eV $Å^{-1}$. A three-membered ring-like building unit, composed by three Cr-oxo clusters and three BDC-SO_3^-/SO_3H ligands from the structure of MIL-101-SO_3H, was selected as a calculation model. To balance one positive charge of Cr-oxo cluster, it is assumed that one of the three SO_3H groups (from three BDC-SO_3H ligands) presents its anionic form (that is, SO_3^-) in MIL-101-SO_3H. Or else, chloride ions would be included in the skeleton to achieve electroneutrality. Sulfonic acid is a kind of strong acid, which tends to dissociate completely (deprotonation) in polar solvent. MIL-101-SO_3H always lies in dynamic disassociation equilibrium in solvents. Therefore, two circumstances, initial disassociation (two -SO_3H and one -SO_3^-) and complete disassociation (three -SO_3^-), were selected as calculation models, respectively (Fig. S7).

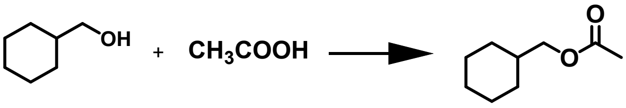
Table S1 The activity of the esterification reaction between benzyl alcohol and acetic acid over various catalysts.[a]



Catalyst	Time/[min]	Conversion/[%][b]	Selectivity/[%]
MIL-101-SO_3H (hν)	160	97	100
MIL-101-SO_3H	322	83.8	100
H_2SO_4	300	87	100
MIL-101	322	26.3	100

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The esterification reaction was carried out with 30 mg MIL-101-SO_3H, 21.6 mg MIL-101 or 1.6 µL concentrated H_2SO_4, 10 mmol of benzyl alcohol, 40 mmol acetic acid, and a reaction temperature of 80 °C, hν = light irradiation with a 300 W Xenon lamp. [b] Determined by GC/GC-MS.

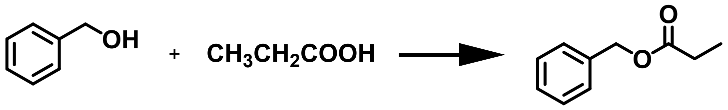
Table S2 The activity of the esterification reaction between cyclohexanol and acetic acid over various catalysts.[a]



Catalyst	Time/[min]	Conversion/[%][b]	Selectivity/[%]
MIL-101-SO_3H (hν)	390	90.1	100
MIL-101-SO_3H	690	63.1	100
H_2SO_4	690	79.3	100
MIL-101	690	25.3	100

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The esterification reaction was carried out with 30 mg MIL-101-SO_3H, 21.6 mg MIL-101 or 1.6 µL concentrated H_2SO_4, 10 mmol of cyclohexanol, 40 mmol acetic acid, and a reaction temperature of 80 °C, hν = light irradiation with a 300 W Xenon lamp. [b] Determined by GC/GC-MS.

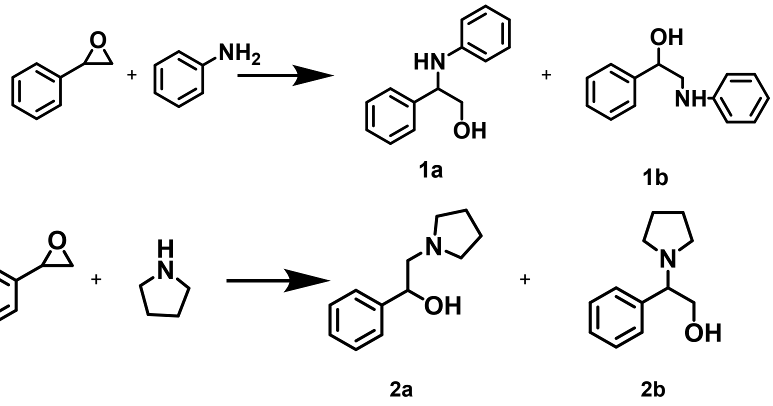
Table S3 The activity of the esterification reaction between benzyl alcohol and propionic acid over various catalysts.[a]



Catalyst	Time (min)	Conversion/[%][b]	Selectivity/[%]
MIL-101-SO_3H (hν)	187	96	100
MIL-101-SO_3H	570	89	100
H_2SO_4	240	93.2	100
MIL-101	576	28.6	100

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The esterification reaction was carried out with 30 mg MIL-101-SO_3H, 21.6 mg MIL-101 or 1.6 μL concentrated H_2SO_4, 10 mmol of benzyl alcohol, 40 mmol propionic acid, and a reaction temperature of 80 °C, hν = light irradiation with a 300 W Xenon lamp. [b] Determined by GC/GC-MS.

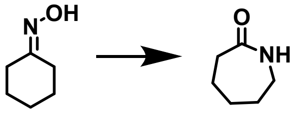
Table S4 Catalytic activity and regioselectivity toward ring-opening of styrene oxide over MIL-101-SO_3H by two different nucleophiles, aniline and tetrahydro pyrrole, in the presence or absence of light irradiation.[a]



Nucleophile	Light	Time [min]	Conversion [%][b]	Regioselectivity to **1a,2a** [%][c]
aniline	with light	90	96.1	100
aniline	without light	90	60	100
aniline	without light	240	83.4	100
tetrahydro pyrrole	with light	135	98.7	100
tetrahydro pyrrole	without light	135	80.3	100
tetrahydro pyrrole	without light	225	93.5	100

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The ring-opening of styrene oxide by aniline was carried out with 30 mg MIL-101-SO_3H, 1 mmol styrene oxide, 1.1 mmol aniline, 2 mL of toluene as solvent and a reaction temperature of 80 °C. The ring-opening of styrene oxide by tetrahydro pyrrole was carried out with 20 mg MIL-101-SO_3H, 2 mmol styrene oxide, 1.64 mL of tetrahydro pyrrole, 3 mL of toluene as solvent and a reaction temperature of 80 °C. [b,c] Determined by GC-MS/^{1}H NMR.

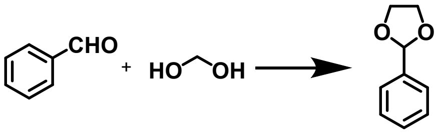
Table S5 Catalytic activity in the Peckmann rearrangement reaction over MIL-101-SO_3H and homogeneous H_2SO_4.[a]



Catalyst	Light	Conversion/[%]	Yield/[%]
MIL-101-SO_3H	with light	100	83.3
MIL-101-SO_3H	without light	76.2	62.2
H_2SO_4[b]	day light	48.5	25.8

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The Peckmann rearrangement was carried out with 20 mg MIL-101-SO_3H or 1.08 μL concentrated H_2SO_4, 0.5 mmol cyclohexanone oxime, 6 mL of benzonitrile as solvent and a reaction temperature of 130 °C and the reaction time length of 10 h. [b] The same amount of catalytic sites as that in MIL-101-SO_3H.

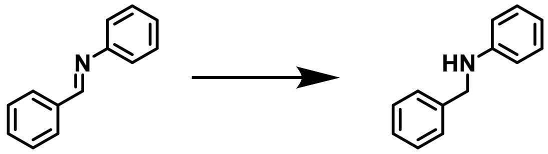
Table S6 Catalytic activity in the acetalization of aldehyde with diol over MIL-101-SO_3H and homogeneous H_2SO_4.[a]



Catalyst	Light	Conversion/[%]	Yield/[%]
MIL-101-SO_3H	with light	80	68.6
MIL-101-SO_3H	without light	51.2	49.5
H_2SO_4[b]	day light	51.3	49.6

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The acetalization reaction was carried out with 20 mg MIL-101-SO_3H or 1.08 μL concentrated H_2SO_4, 30 mmol benzaldehyde, 60 mmol glycol, and a reaction temperature of 80 °C and the reaction time length of 10 h. [b] The same amount of catalytic sites as that in MIL-101-SO_3H.

Table S7 Catalytic activity in the transfer hydrogenation of imines over MIL-101-SO_3H or homogeneous H_2SO_4.[a]



Catalyst	Light	Time/[min]	Conversion/[%]	Yield/[%]
MIL-101-SO_3H	with light	50	100	100
MIL-101-SO_3H	without light	50	87	100
MIL-101-SO_3H	without light	60	100	100
H_2SO_4[b]	day light	60	51	51

[a] Reaction conditions: all reactions were performed in a photo-reactor equipped with a quartz window. The transfer hydrogenation of imines was carried out with 30 mg MIL-101-SO_3H or 1.6 μL concentrated H_2SO_4. [b] The same amount of catalytic sites as that in MIL-101-SO_3H.

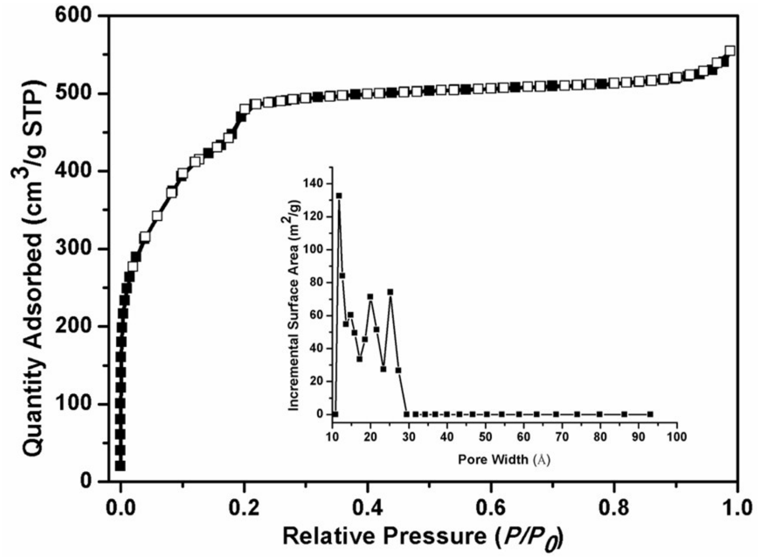


Fig. S1 Nitrogen adsorption and desorption isotherms for MIL-101-SO_3H at 77 K. Inset: pore-size distribution analysis for MIL-101-SO_3H (DFT method).

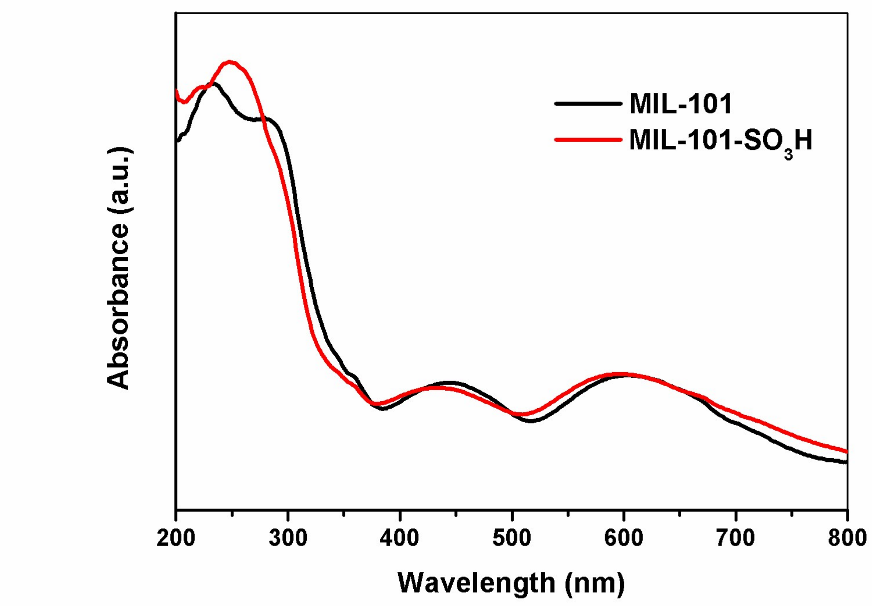


Fig. S2 UV-Vis spectra of MIL-101 and MIL-101-SO_3H.

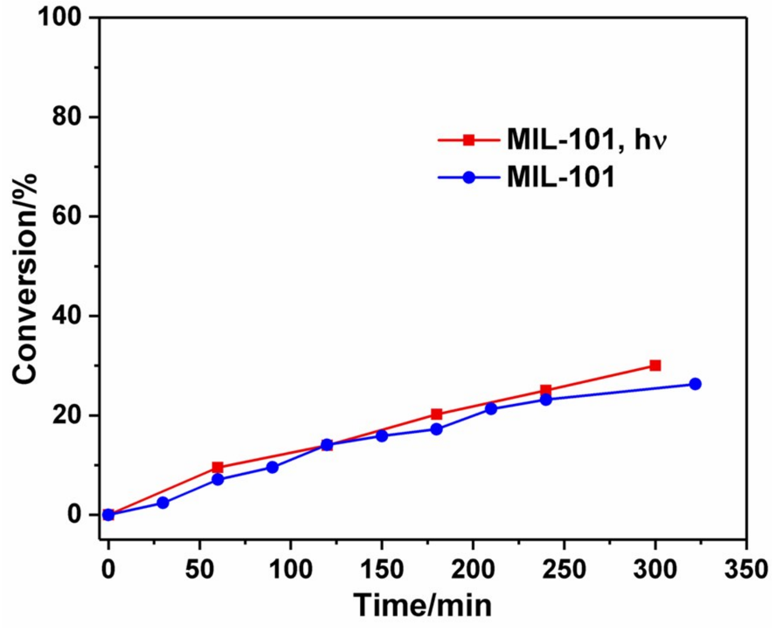


Fig. S3 The time-conversion plot of the esterification reaction between benzyl alcohol and acetic acid over MIL-101 in the presence or absence of light irradiation.

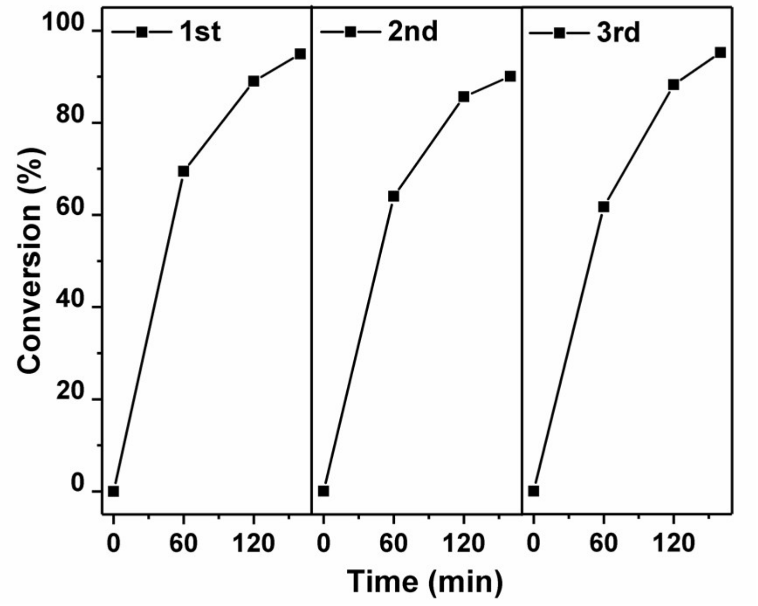


Fig. S4 The three runs of time-conversion plots for the esterification reaction between benzyl alcohol and acetic acid.

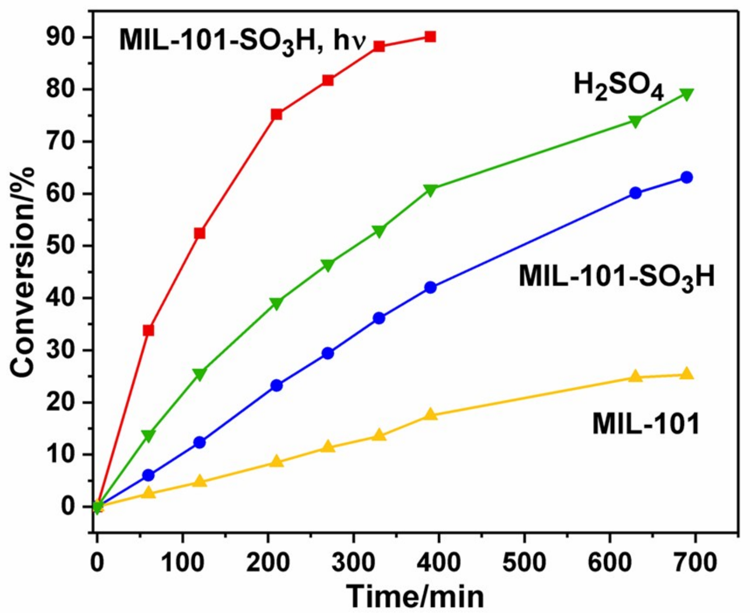


Fig. S5 Time courses of the esterification reaction between cyclohexanol and acetic acid over various catalysts.

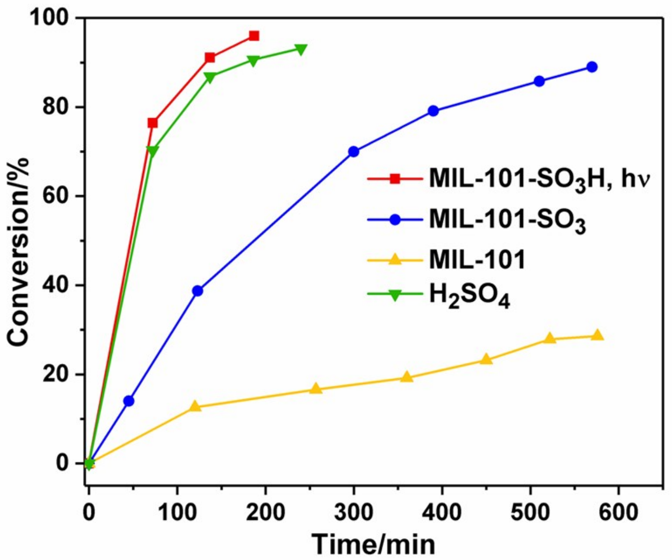


Fig. S6 Time courses of the esterification reaction between benzyl alcohol and propionic acid over various catalysts.

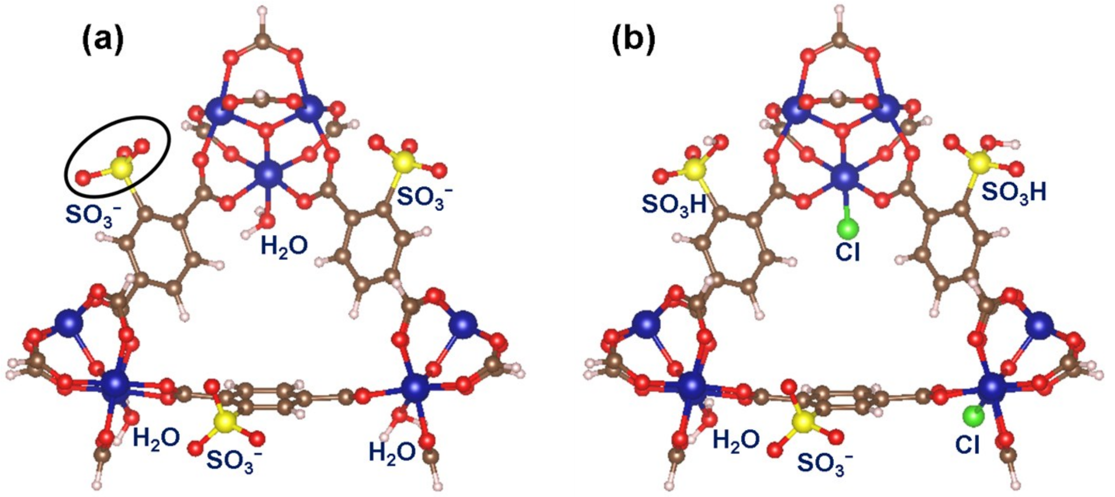
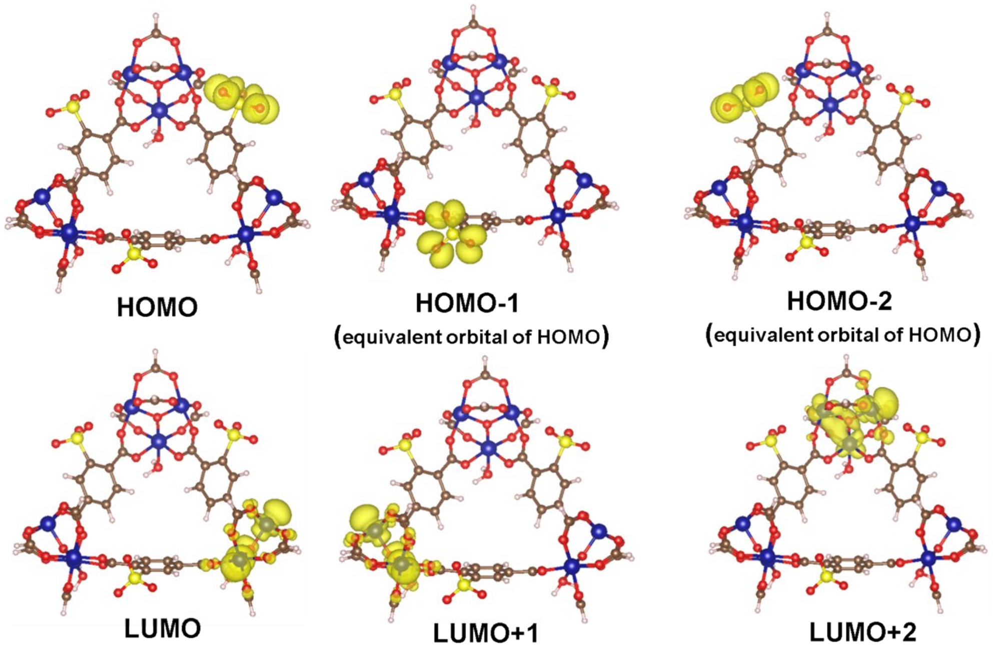


Fig. S7 (a) The structure model of a ring-like building unit, composed by three Cr-oxo clusters and three BDC-SO_3^- ligands involving three -SO_3^- groups, serving as the status of "complete disassociation", and (b) the other structure model with two -SO_3H and one -SO_3^-, representing the "initial disassociation", have been built and calculated to investigate the contribution of orbital energy levels. The Cr, O, S, H, C and Cl atoms in the structure with a ball-stick model are drawn in blue, red, yellow, white, brown and green colors, respectively.


HOMO

HOMO-1 (equivalent orbital of HOMO)

HOMO-2 (equivalent orbital of HOMO)

LUMO

LUMO+1

LUMO+2

Fig. S8 Calculated frontier orbitals for a ring-like building unit with three Cr-oxo clusters and three ligands bearing deprotonated SO_3^- groups (shown in Figure S3a). HOMO and LUMO are dominated by SO_3^- groups and Cr-oxo clusters, respectively.

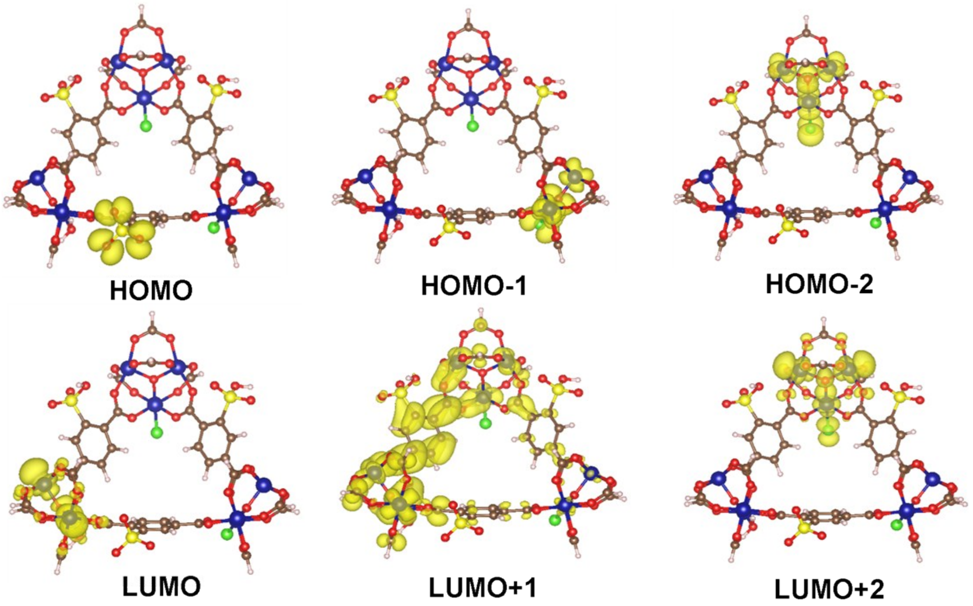


Fig. S9 Calculated frontier orbitals for a ring-like building unit with three Cr-oxo clusters and three ligands bearing two SO_3H groups and one deprotonated $-SO_3^-$ (shown in Figure S3b). HOMO and LUMO are dominated by the SO_3^- groups and Cr-oxo clusters, respectively.

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