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Bottom-up Approach to Direct a Molybdenum-doped Covalent-Organic Framework Catalyst for Selective Oxidation Reaction

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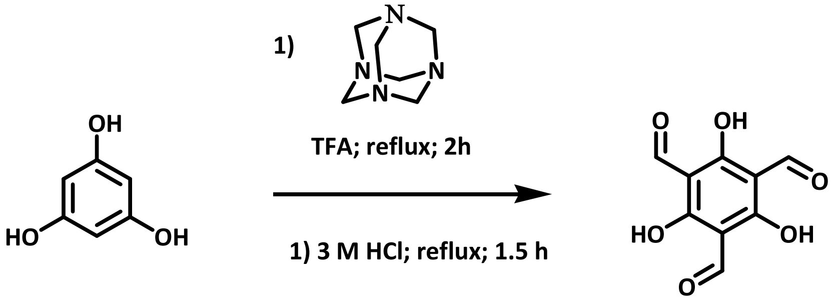
S1. General information and synthetic procedures.

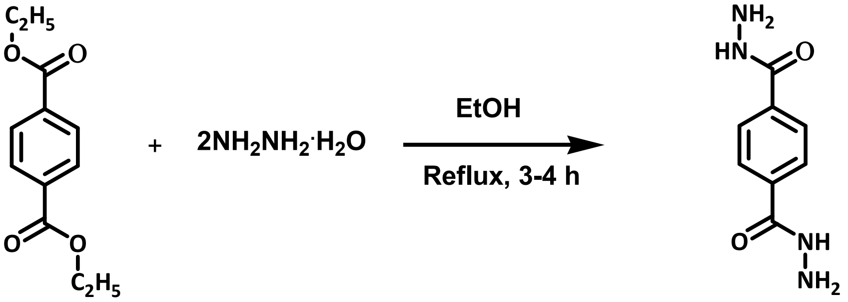
Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ= 1.54178) at 40 kV and 40 mA. Thermogravimetry analysis (TGA) was conducted on a TGA-50 (SHIMADZU) thermogravimetric analyzer. Fourier transform infrared (IR) measurements were recorded on a Bruker Optics ALPHA-E spectrometer. TG of the samples was recorded using a Mettler TGA/SDTA 851 E analyzer in the temperature range 50-800 °C at a heating rate of 20 °C/min. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$, and the chemical shifts were reported relative to the internal standard TMS (d=0 ppm). X-ray photoelectron spectroscopy (XPS) was recorded by a Kratos Ultra DLD imaging spectrometer (UK) using an Al Kα Rradiation (1486.6 eV) in East China University of Science and Technology. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6360 microscope using JEOL JFC-1600 Auto fine coater. The Steady-state UV-vis spectroscopic measurements were recorded on a Shimadzu UV3600 spectrometer with $BaSO_4$ as the diffuse reflectance.

1) $MoO_2(acac)_2$ was synthesized according to the published procedure.[1]
2) 1,3,5-triformylphloroglucinol was synthesized following previously reported procedure and characterization matched that in the literature.[2]



In a typical synthesis, 3 g phloroglucinol was activated by drying in a 90 °C oven overnight. This activated phloroglucinol was mixed with 7.4 g hexamine and 40 mL of trifluoroacetic acid and heated to reflux for 3 h under nitrogen atmosphere. To this 3 M HCl was added slowly with continuous stirring and again reflux for 1 h. After cooling to room temperature, the reaction mixture was extracted three times with ethyl acetate. The organic part was repeatedly washed with saturated brine solution and then dried over anhydride Na_2SO_4. The combined organic part was concentrated by a rotary evaporator to get an orange colored solid. The solid was washed repeatedly by hot ethanol to obtain pale yellowish powder. ^{1}H NMR (300 MHz, DMSO) δ 9.97 (s, 8H).

3) 1,4-dicarbonyl-phenyl-dihydrazide was prepared according to a previous procedure.[3]



A mixture of diethyl ester of terephthalic acid (2.22 g) and hydrazine hydrate (98% 2 mL) in ethanol was refluxed for 4-5h. The reaction mixture was allowed to cool to the room temperature Then, the cooled solution was poured onto ice cold water. The dihydrazide of terephthalic acid was thus obtained, filtered and recrystallized from ethanol.

Synthesis of COF. An DMA (1mL) mixture of 1,3,5-triformylphloroglucinol (0.096 mmol, 20mg) and 1,4-dicarbonyl-phenyl-dihydrazide (0.142 mmol, 27 mg) in the presence of acetic acid catalyst (6M, 50 uL) in a Pyrex tube (10 mL) was degassed by three freeze-pump-thaw cycles. The tube was sealed off by flame and heated at 120 ^oC for 3 days. The precipitate was collected via centrifuge, washed with THF for 6 times, and washed with acetone 3 times. The slight yellow powder was dried at 120 ^oC under vacuum overnight to give the corresponding CPF-1 in isolated yields of 60 %. Anal. Calcld (%). For $(C_7O_2N_2H_4)_n$: C, 57.8; H, 3.7; N, 18.9; found: C, 51.3; H, 3.9; N, 19.3.

Synthesis of Mo-COF catalyst. A mixture of COF (0.16 g) and $MoO_2(acac)_2$ (0.03 g) was refluxed for 24 h in methanol. The complex separated was filtered, washed with methanol, then further purification was carried out by Soxhlet extraction in methanol for 48 h and dried at 120 ^oC under vacuum for 24 h to yield Mo-COF as a orange-red powder (93 % yield).

Mo-benzoyl salicylal hydrazine Schiff base, namely $Mo(HSY)_2$ was prepared in a manner similar to a reported procedures.[4]

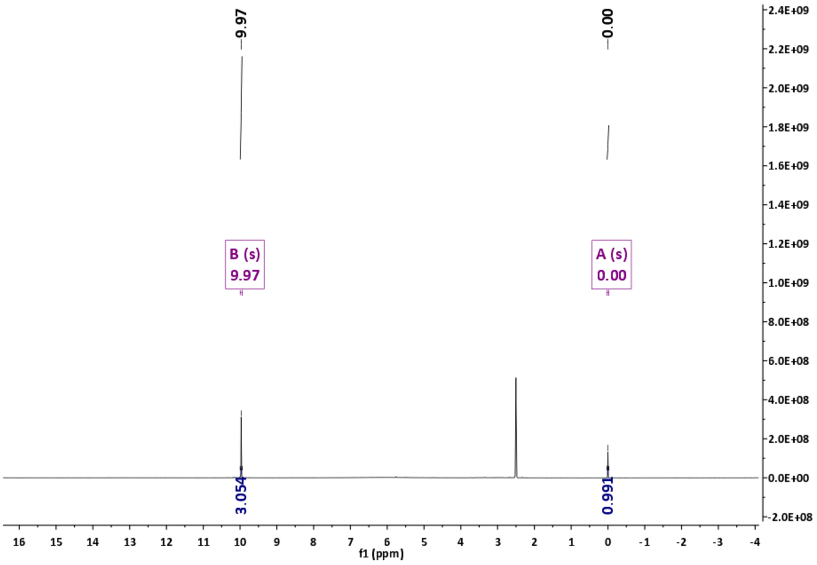


Figure S1. ^{1}H NMR spectrum of 1,3,5-triformylphloroglucinol.

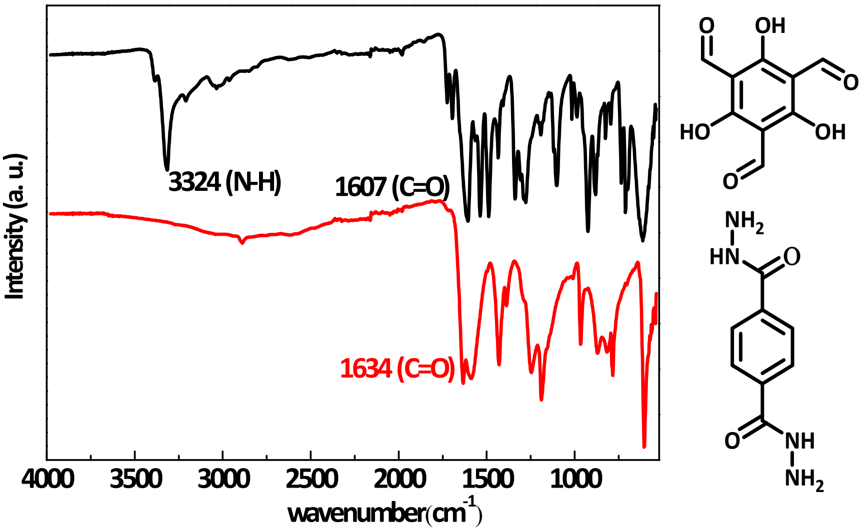


Figure S2. FT-IR spectra of 1,3,5-triformylphloroglucinol (black line) and 1,4-dicarbonyl-phenyl-dihydrazide (red line)

S2. XPS and steady-state UV-vis analysis.

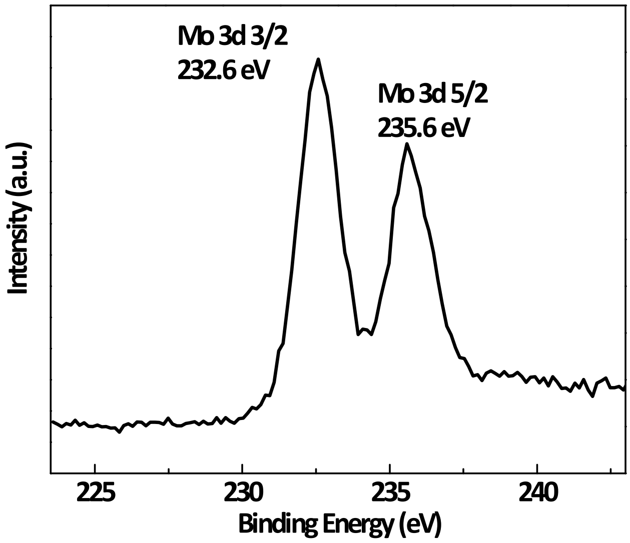


Figure S3. XPS spectra of Mo-COF, Mo 3d region.

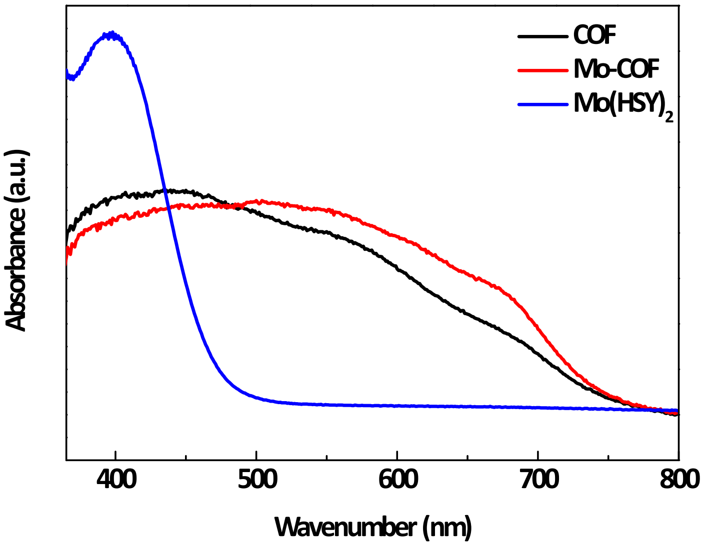


Figure S4. UV/Vis spectra of solid COF (black line) and Mo-COF (red line) and Mo(HSY)$_2$ (blue line) in in CH_3OH solution

S3. Powder X-ray diffraction and crystal data.

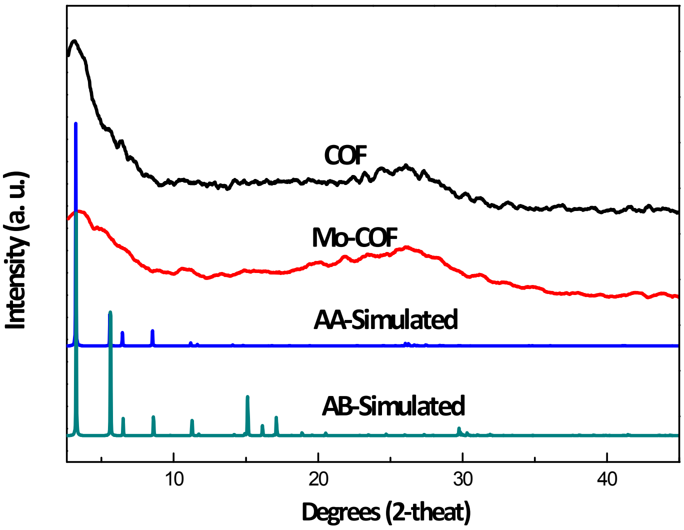


Figure S5. PXRD pattern of COF and Mo-COF compared with AA (blue) eclipsed and AB staggered (green) stacking models.

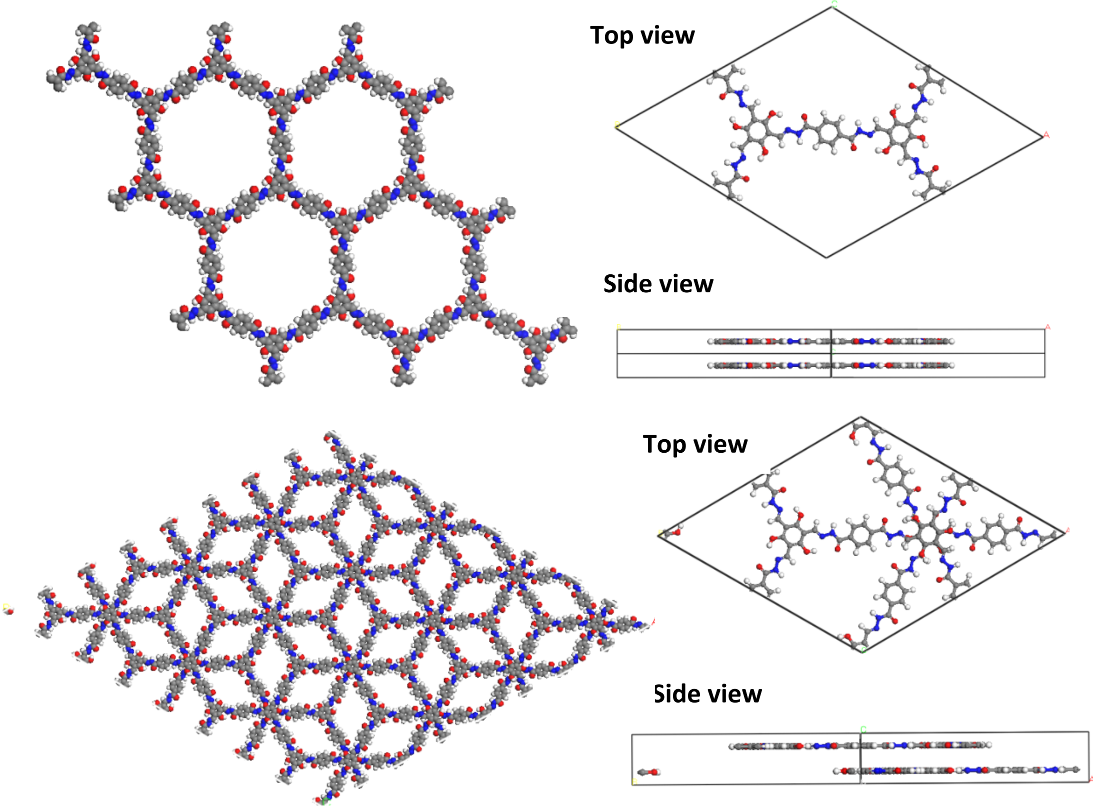


Figure S6. The simulated pattern for an AA and AB stacking mode. Top and side views of the hexagonal pore of the COF.

S4. Infrared analysis of catalyst.

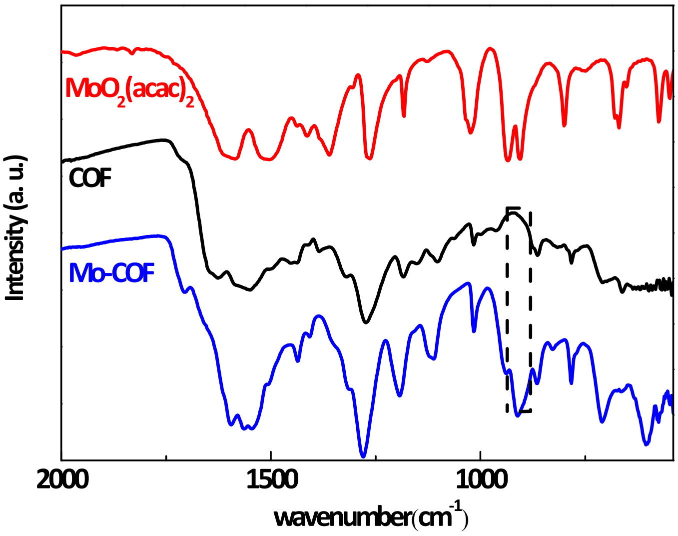


Figure S7. FT-IR spectra of $MoO_2(acac)_2$ (red line), COF (black line) and Mo-COF (blue line).

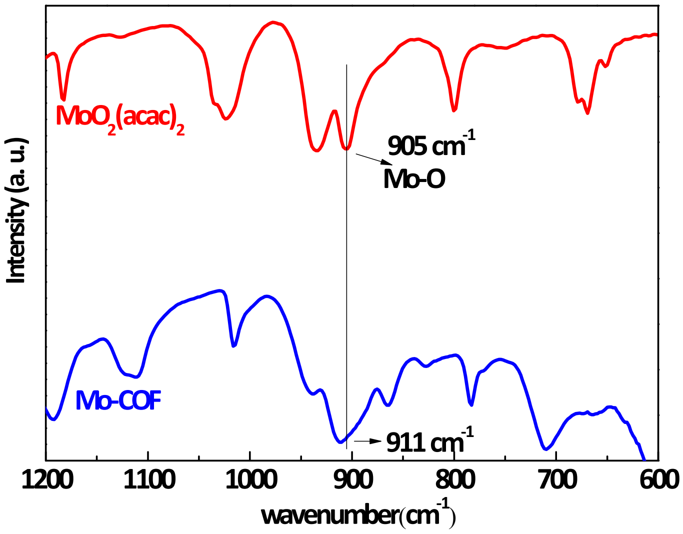


Figure S8. FT-IR spectra of $MoO_2(acac)_2$ (red line) and Mo-COF (blue line).

S5. BET, Thermal Stability and SEM.

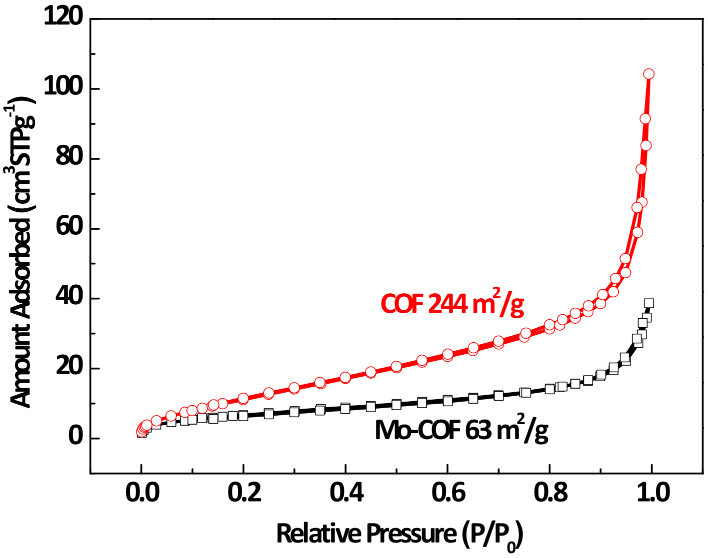


Figure S9. Representative N_2 adsorption (closed circles) and desorption (open circles) isotherms of COF (red) and Mo-COF (black)

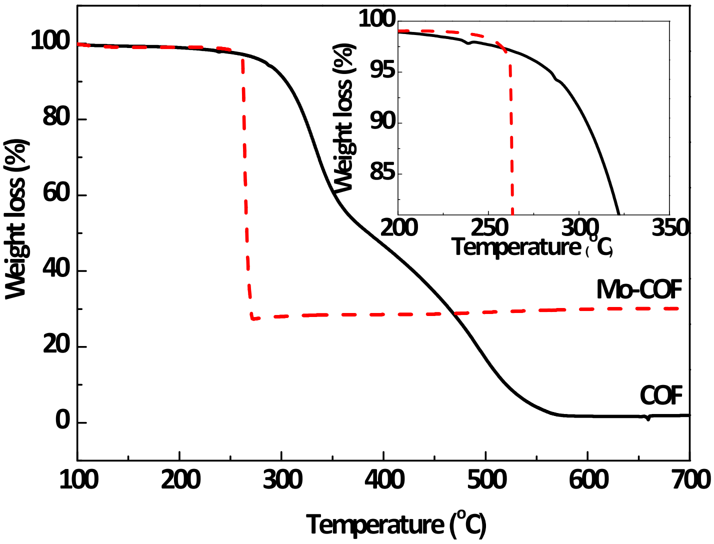


Figure S10. The TG curves of COF (black line) and Mo-COF (red line) under O_2 atmosphere.

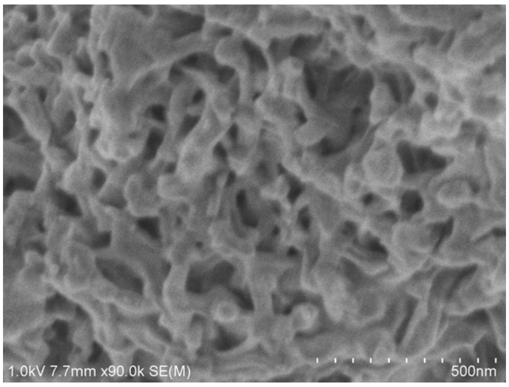


Figure S11. Scanning electron microscope image of Mo-COF

S6. Catalytic Activity Test.

Catalytic activity methods: Olefin (1.0 mmol), TBHP (2.0 mmol), catalyst (0.01 mmol), 1,2-dichloroethane (2.0 mL) and bromobenzene (50 mg) as internal standard sealed in a Teflon-lined screwcap vial were stirred at 80 °C. The progress of reaction was monitored by GC. The catalyst was thoroughly washed with EtOH before reuse.

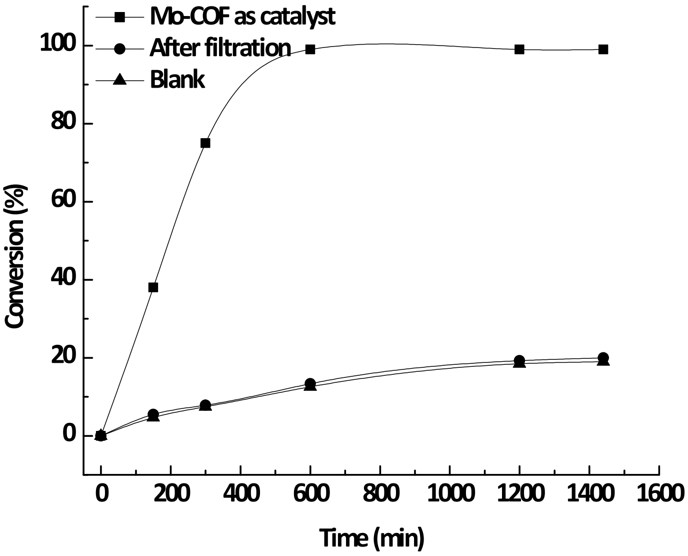
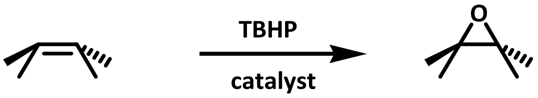


Figure 12. Conversion of cyclohexene into epoxide based on a filtration test.



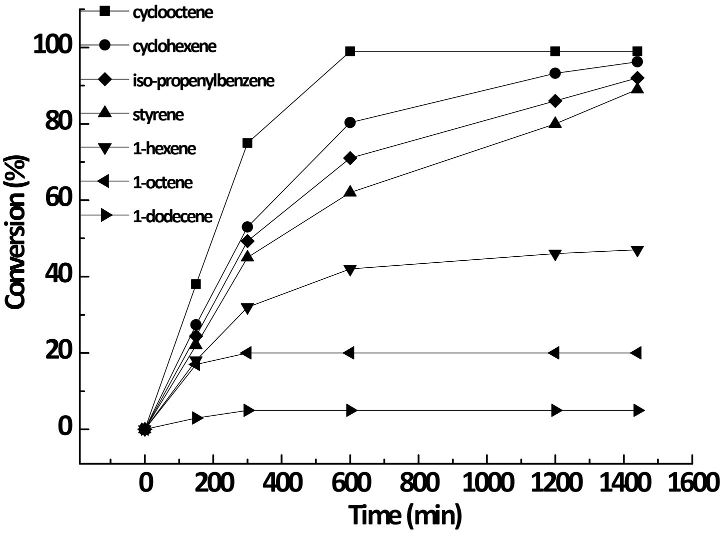


Figure S13. Kinetic traces of various substrates epoxidation catalyzed by Mo-COF (mol ratio olefins/TBHP/catalyst=100:150:1 was used for the catalytic assays).

S7. Infrared analysis and catalytic details for recycled catalyst.

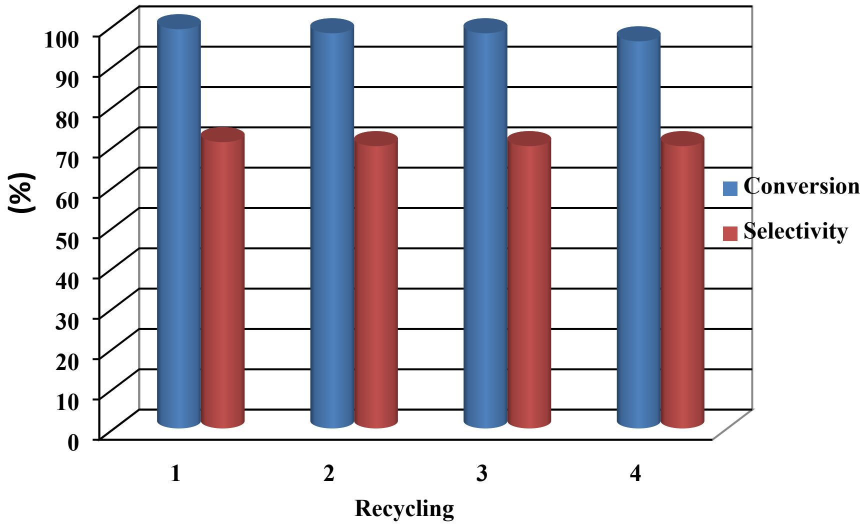


Figure 14. Catalyst recycling in the epoxidation of cyclohexene with Mo-COF as catalyst by TBHP.

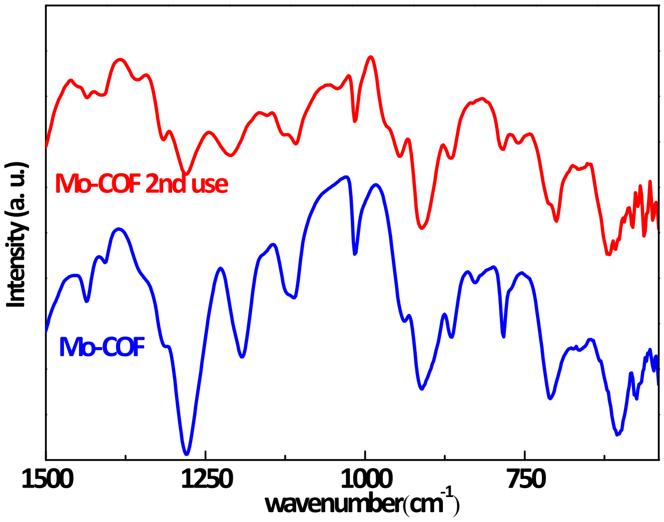


Figure S15. FT-IR spectra of recycled catalyst (red line) and freshly prepared catalyst (black line)

References

1. G. J. J. Chen, J. W. McDonald and W. E. Newton, *Inorg Chem*, 1976, **15**, 2612.
2. J. H. Chong, M. Sauer, B. O. Patrick and M. J. MacLachlan, *Organic Let*, 2003, **5**, 3823.
3. G. Kumar, S. Devi, R. Johari and D. Kumar, *Eur J Med Chem*, 2012, **52**, 269.
4. M. Bagherzadeh and M. Zare, *J Coord Chem*, 2012, **65**, 4054; S. Pasayat, S. P. Dash, Saswati, P. K. Majhi, Y. P. Patil, M. Nethaji, H. R. Dash, S. Das and R. Dinda, *Polyhedron*, 2012, **38**, 198.