Supporting Information

A stable and highly selective metalloporphyrin based framework for catalytic oxidation of cyclohexene

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Characterization techniques

IR spectra were collected from KBr pellets on an Agilent Technologies Cary 630 FTIR spectrophotometer. Thermogravimetric analyses (TGA) were performed on a PerkinElmer TGA instrument heating from room temperature to 800°C in N_2 atmosphere at the rate of 10°C min^{-1}. GC spectra were recorded on a Agilent Technologies 7820A. Powder X-ray diffraction (XRD) pattern for sample was recorded ranging from 5° to 40° at room temperature on a Siemens D5005 diffractometer with Cu-Ka (λ= 1.5418 Å) radiation. X-ray photoelectron spectroscopy (XPS) was carried out on a USWHA150 photoelectron spectrometer using monochromatic Al Kα radiation as the excitation source. Morphology analyses was characterized by adopting a scanning electron microscope (Hitachi SU-8000 FE-SEM) equipped with an energy-dispersive X-ray (EDX) analyzer.

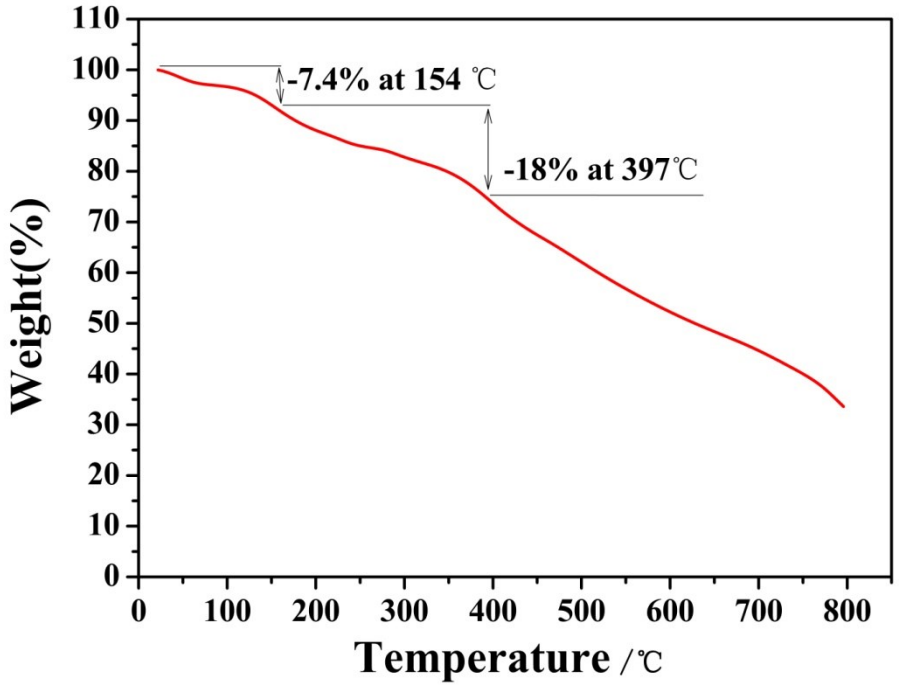

Fig. S1 TGA plots of the Mo_2TCPP.

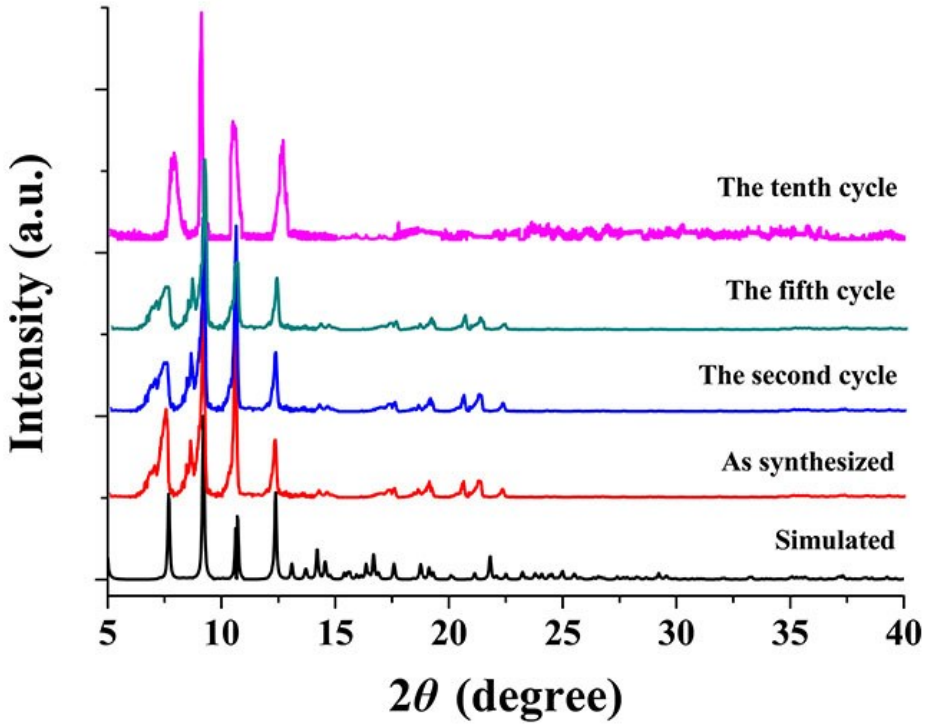

Fig. S2 The X-ray diffraction pattern of the catalyst Mo_2TCPP after several cycles

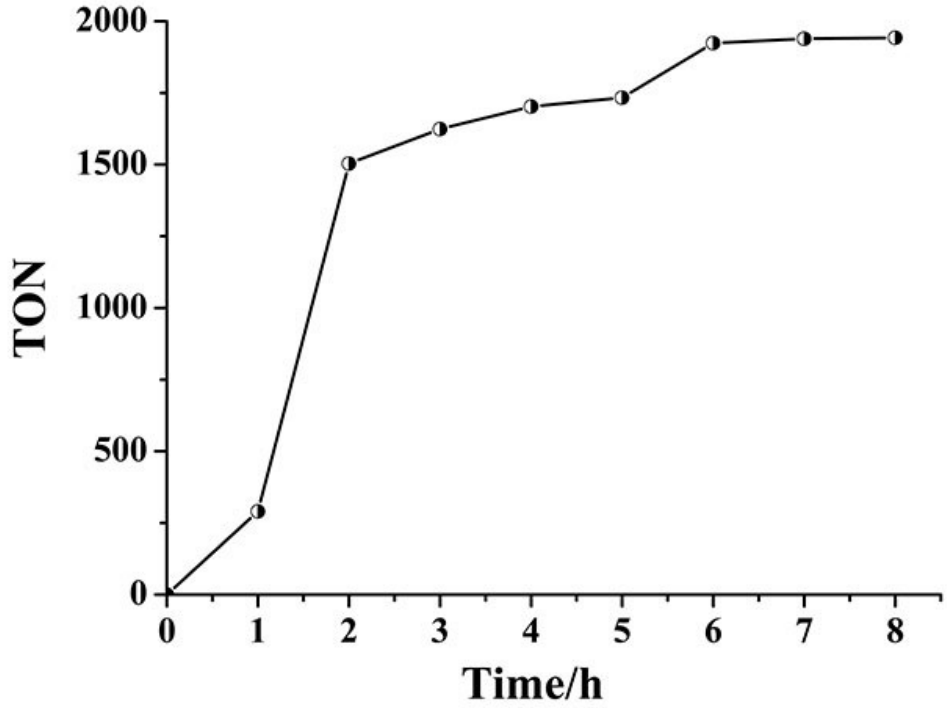

Fig. S3 The catalyst turnovers in 8 hours.

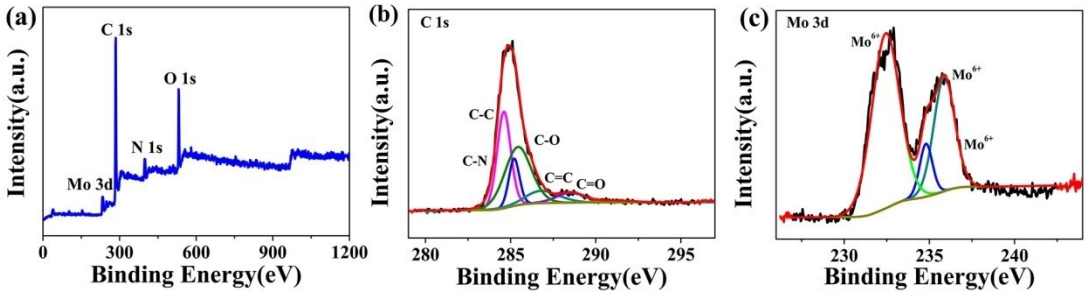

Fig. S4 XPS analysis of Mo_2TCPP. (a) survey scan; (b) C 1s; (c) Mo 3d. the binding energies of C, N and O are 285eV, 398eV and 531eV, respectively, and the valence of the three elements are in common state. In Fig. 8c, the two strong peaks at 232.45eV and 235.8eV belong to Mo3d binding energies, so the valence state of Mo element is Mo^{6+}.

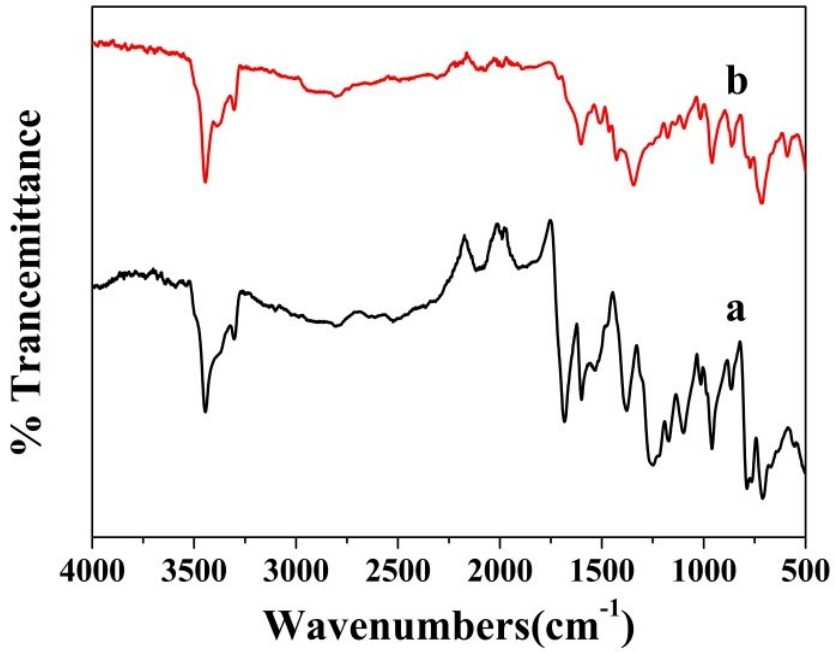

Fig. S5 FTIR spectra of H_4TCPP (a) and Mo_2TCPP (b). The peaks at 865 and 590 cm^{-1} are attributed to Mo-O vibration peaks in Mo_2TCPP. Because the coordination of metals to the ligands, the peak value in the spectrum shifts slightly compared to the TCPP ligands.

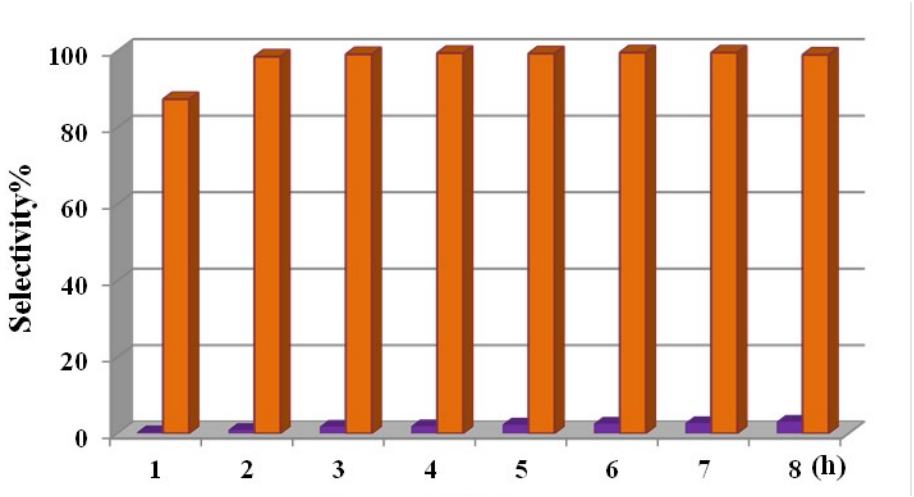

Fig. S6 H_2O_2 as oxidant, the selectivity of epoxycyclohexane after catalytic oxidation by TCPP (purple) and Mo_2TCPP (orange) at different time.

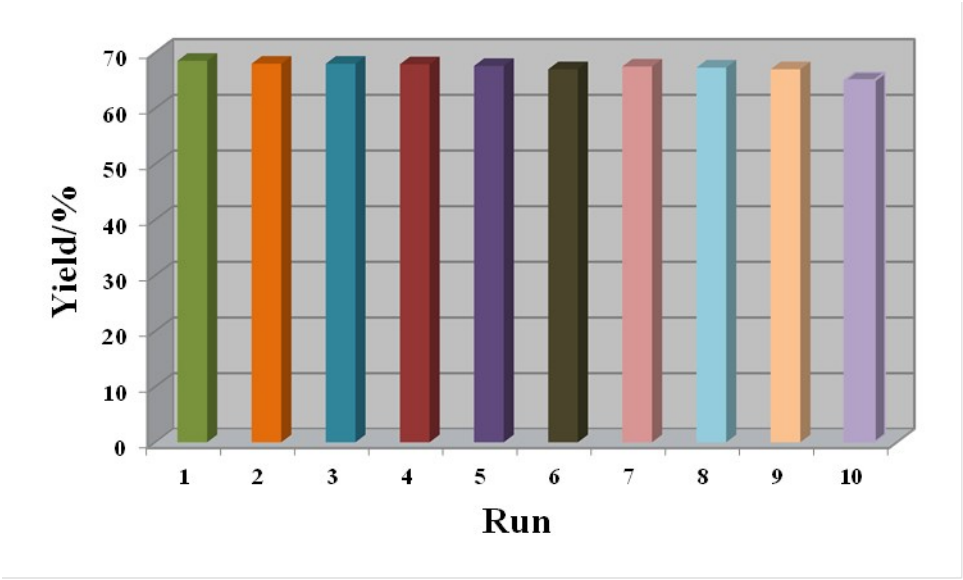

Fig. S7 H_2O_2 as oxidant, the productivity of epoxycyclohexane by Mo_2TCPP with cyclohexene at different runs.

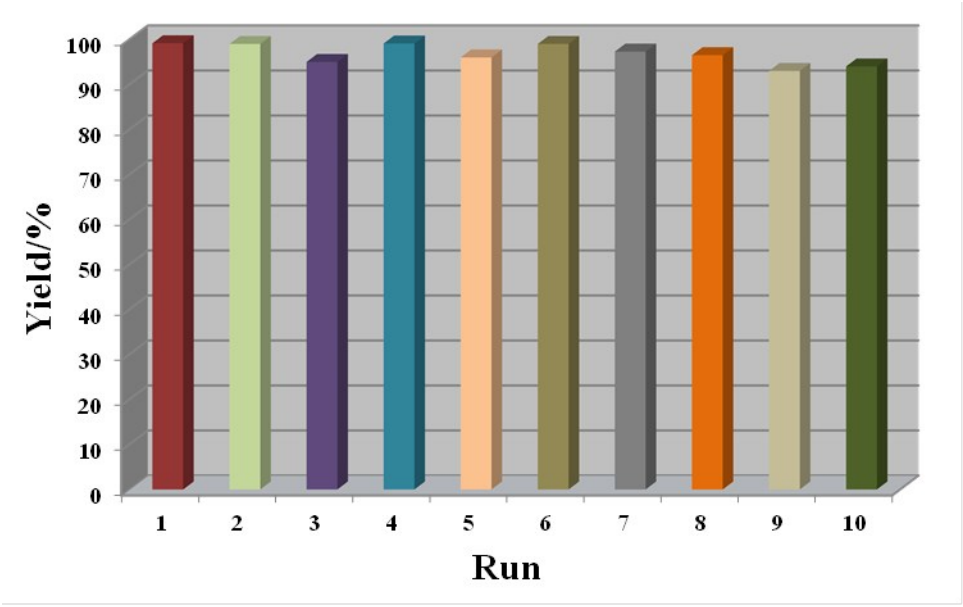

Fig. S8 CHP as oxidant, the productivity of epoxycyclohexane by Mo_2TCPP with cyclohexene at different runs.

Table S1 Crystal data and structure refinements.

Compounds	Mo_2TCPP
Empirical formula	$C_{54}H_{59}Mo_2N_7O_{19}$
Formula weight	1325.77
Crystal system	Orthorhombic
Space group	*P*nma
***a* (Å)**	24.2727(9)
***b* (Å)**	35.9510(13)
***c* (Å)**	7.6427(3)
Volume (Å ^{3})	6669.2(4)
Z	4
ρ (g·cm $^{-3}$)	1.320
F(000)	2360
μ (mm $^{-1}$)	0.433
R_{all}	0.0867
Data / parameters	2664/321
Goodness-of-fit on F ^{2}	1.014
R_1 (wR_2) [I > 2σ(I)]	0.0778
R_1 (wR_2) (all data)	0.1952

Table S2 Catalytic performence of different catalysts in the oxidation of cyclooctane with H_2O_2[a].

Catalyst	Cyclooctane conversion (%)	Cyclooctanone yield (%)	Cyclooctane-1,4-dione yield (%)	Cyclooctanol yield(%)	Cyclooctane selectivity (%)
None	0	-	-	-	-
Na_2MoO_4	0	-	-	-	-
H_4TCPP	0	-	-	-	-
Mo_2TCPP	68.6	46	14.4	8.2	67

[a] Reaction conditions: 3 ml cyclooctane, 4ml H_2O_2, 80°C, 8 h and Mo_2TCPP 0.02 g.

Table S3 Catalytic performance of different catalysts in the oxidation of benzene with H_2O_2[b].

Catalyst	Benzene conversion(%)	Phenol yield(%)	Quinones yield(%))	Phenol selectivity(%)
None	0	-	-	-
Na_2MoO_4	0	-	-	-
H_4TCPP	0	-	-	-
Mo_2TCPP	71	47.9	23.1	67.5

[b] Reaction conditions: 8mmol benzene, 3ml H_2O_2, 80°C, 8 h and Mo_2TCPP 0.02 g.