Electronic Supplementary Information

Hydrogen Bond-Directed Encapsulation of Metalloporphyrin into the Microcages of Zeolite Imidazolate Framework for Synergistically Biomimetic Catalysis

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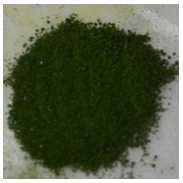
Table S1. Photographs and optical images of por@ZIF-8 and ZIF-8

			
Mn-TAPP@ZIF-8	TAPP@ZIF-8	Mn-TPP@ZIF-8	ZIF-8

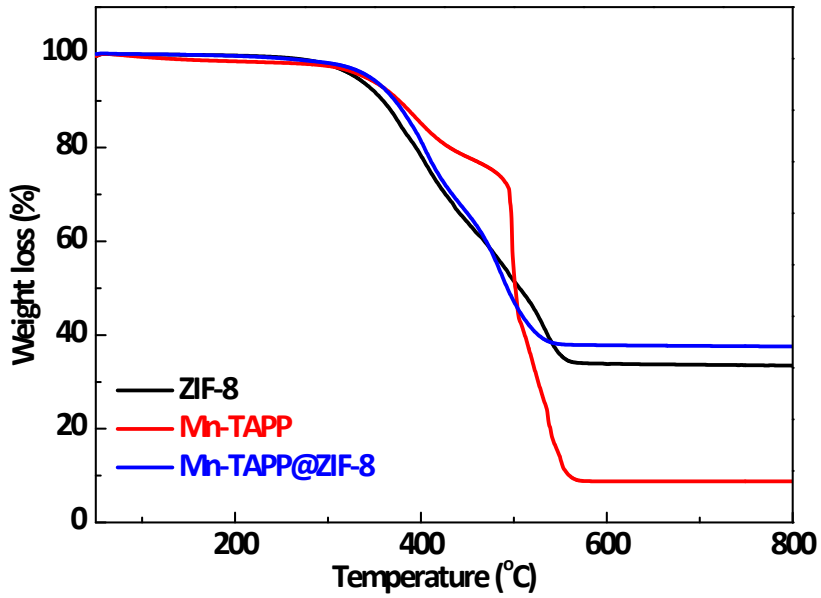


Figure S1. The TG curves of ZIF-8 (black line), Mn-TAPP (red line) and Mn-TAPP@ZIF-8 (blue line).

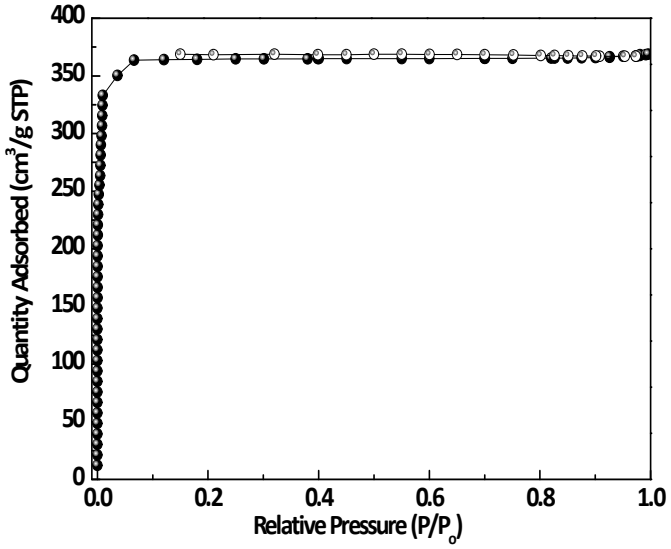


Figure S2. Representative N_2 adsorption and desorption isotherms of Mn-TPP@ZIF-8.

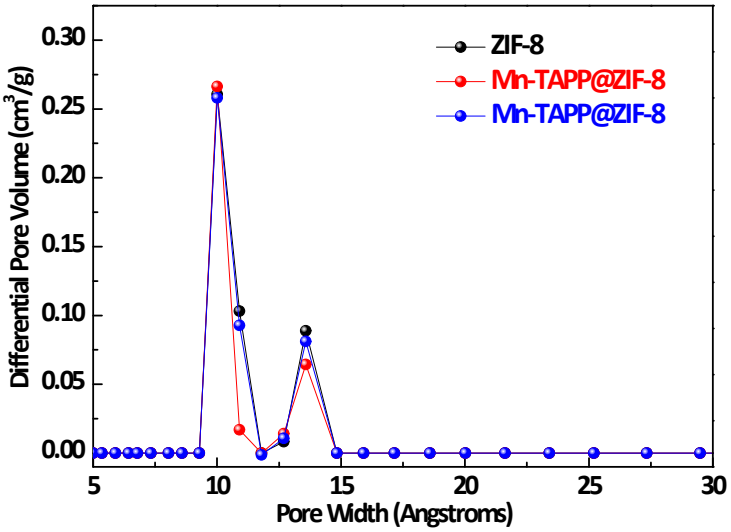


Figure S3. Pore size distribution data of ZIF-8 and Mn-TAPP@ZIF-8.

Figure S4. Contact angle for a droplet of (a) water on Mn-TAPP, (b) water on Mn-TPP

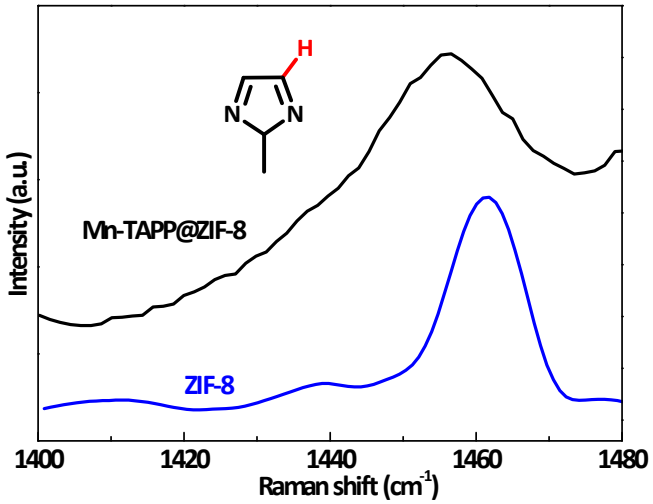


Figure S5. Raman spectrum of Mn-TAPP@ZIF-8 (black line) and ZIF-8 (blue line).

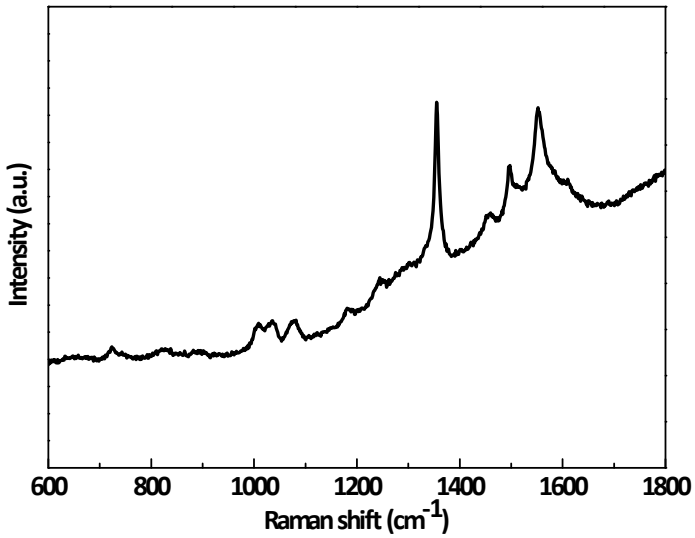


Figure S6. Raman spectrum of Mn-TAPP@ZIF-8

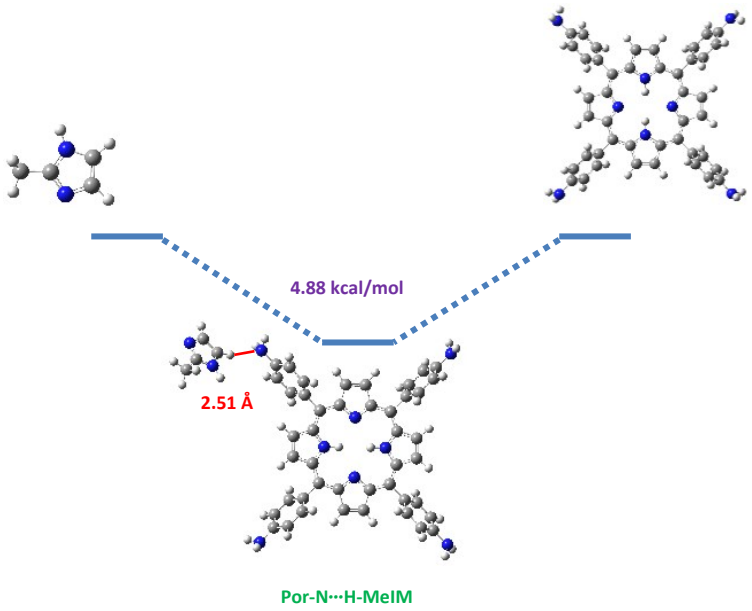
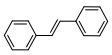
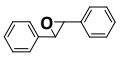


Figure S7. Energy profiles for Por-N···H-MeIM.

Table S2. Scope of Mn-TAPP@ZIF-8 catalyzed epoxidation of alkenes.[a]

Entry	Substrate	product	Conversion (%)[b]	Yield (%)
1			96	96
2			91	91
3			62	62
4			84	84
5			78	78
6			74	74
7			54	54
8			39	39
9			25	25
10			-	-

[a] Substrate (250 mM), TBHP (500 mM), catalyst (5 mg, 2.5 μmol), acetonitrile (0.5 mL) and bromobenzene 10 mg as internal standard sealed in a Teflon-lined screwcap vial were stirred at 80 °C. [b] Conversion (%) was measured relative to the starting substrate.

Table S3. Selective epoxidation of cyclohexene catalyzed by different catalysts. [a]

Entry	Catalyst	Conversion (%)[b]	Yield (%)
1	Mn-TAPP@ZIF-8	96	96
2	Mn-TPP@ZIF-8	72	29
3	Filtrate[c]	53	53
4	Mn-TAPP	93	48
5	Mn-TPP	86	65
6	$MnCl_2$	45	35
7	Recycle	96	96
8	Blank	19	-

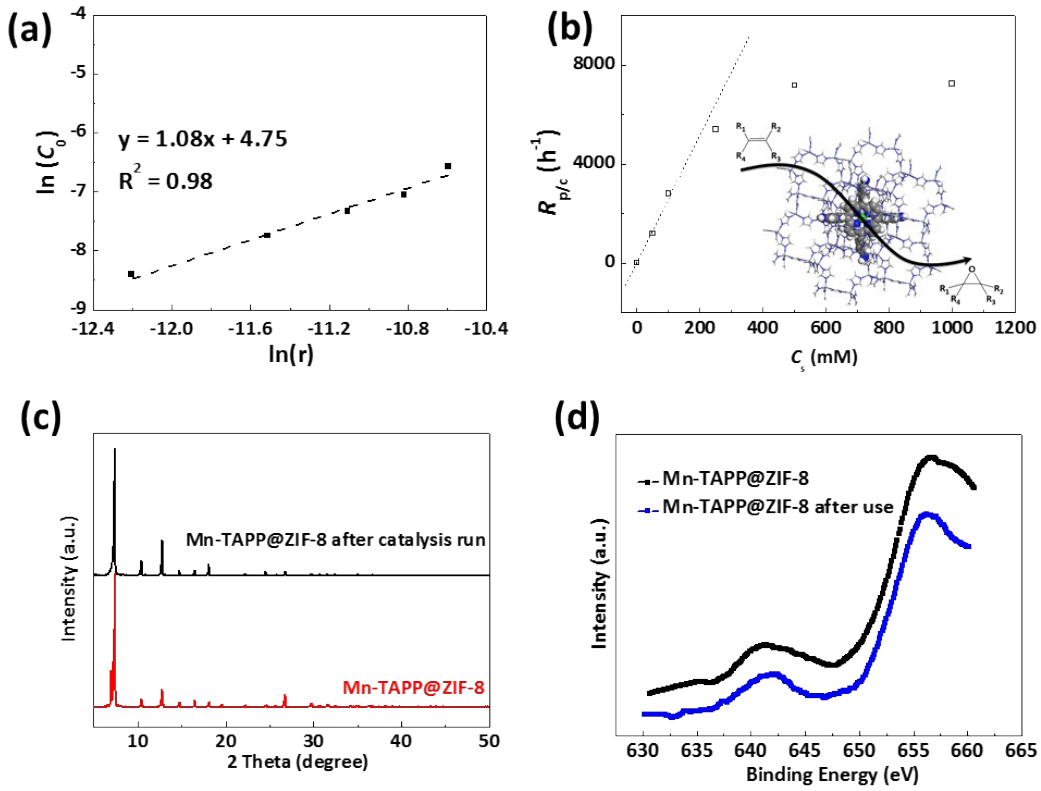


Figure S8. a) Kinetics data for determining Mn-TAPP@ZIF-8 order in the epoxidation of cyclohexene. b) The effect of C_s on reaction rate $R_{p/c}$ which is defined as mol of product per mol of catalyst per hour. c) PXRD patterns of original Mn-TAPP@ZIF-8 (red line) and Mn-TAPP@ZIF-8 after catalytic use (black line). d) XPS spectra for Mn-TAPP@ZIF-8 (blue line) and sample after catalytic use (black line), Mn 2p region.

Table S4. Kinetics data for determining Mn-TAPP@ZIF-8 order in the epoxidation of cyclohexene

Catalyst amount (µmol)	r	ln(r)
0.5	2.4 E-04	-8.3
1.0	4.3 E-04	-7.7
1.5	6.6 E-04	-7.3
2.0	8.3 E-04	-7.1
2.5	1.5 E-03	-6.5

C_t: the concentration of substrate after a certain reaction time

C_o: the initial concentration of catalyst

C_s: the initial concentration of substrate

r: the linear fit of $-ln(C_t/C_s)$ (y axis) and the reaction time (x axis) for different catalyst amount

$R_{p/c}$: mol of product per mol of catalyst per hour

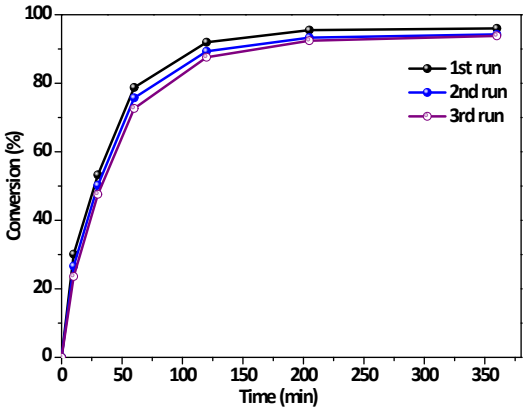


Figure S9. The kinetic profile of different runs for Mn-TAPP@ZIF-8

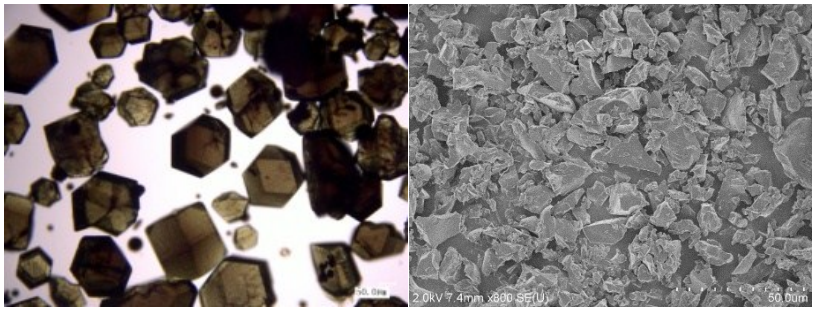


Figure S10. Optical images and SEM spectra of the Mn-TAPP@ZIF-8 before (left) and after catalysis use (right)