Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Coordinate-polymerized organic ligand towards efficient catalyst for selective hydrocarbons oxidation

Table S1. Selected bond lengths (Å) and angles (°) for **1-3.**

1			
Co1-O1	2.145(2)	Co1-N1	2.091(2)
Co1-O2	2.1914(19)	Co1-N2	2.115(2)
Co1-O4	2.115(2)	Co1-C14	2.511(3)
Co1-O5	2.212(2)	Co1-C25	2.490(3)
O1-Co1-O2	60.37(7)	O5-Co1-C25	30.05(8)
O1-Co1-O5	101.04(8)	N1-Co1-O1	94.09(8)
O1-Co1-C14	30.25(8)	N1-Co1-O2	96.64(8)
O1-Co1-C25	95.94(9)	N1-Co1-O4	155.30(8)
O2-Co1-O5	158.76(8)	N1-Co1-O5	94.80(8)
O2-Co1-C14	30.12(8)	N1-Co1-N2	94.72(9)
O2-Co1-C25	134.73(9)	N1-Co1-C14	96.19(8)
O4-Co1-O1	89.62(9)	N1-Co1-C25	124.83(9)
O4-Co1-O2	106.35(8)	N2-Co1-O1	158.70(9)
O4-Co1-O5	60.55(7)	N2-Co1-O2	99.32(8)
O4-Co1-N2	90.44(9)	N2-Co1-O5	97.51(8)
O4-Co1-C14	99.19(9)	N2-Co1-C14	129.18(9)
O4-Co1-C25	30.50(8)	N2-Co1-C25	94.87(9)
O5-Co1-C14	130.60(9)	C25-Co1-C14	117.90(9)
2			
Zn1-O1	1.990(4)	Zn1-N1	2.048(3)
Zn1-O5	1.959(3)	Zn1-N2	2.088(3)
O1-Zn1-N1	100.01(14)	O5-Zn1-N1	133.90(14)
O1-Zn1-N2	142.49(16)	O5-Zn1-N2	95.99(13)
O5-Zn1-O1	96.57(14)	N1-Zn1-N2	96.28(12)
3			
Cd1-O1	2.3752(17)	Cd1-O5	2.2812(17)
Cd1-O1W	2.2904(15)	Cd1-N1	2.3713(17)
Cd1-O2	2.5227(16)	Cd1-N2	2.3223(18)
Cd1-O4	2.6220(18)	O5-Cd1-O2	83.80(6)
O1-Cd1-O2	53.08(6)	O5-Cd1-O4	52.44(5)
O1-Cd1-O4	170.08(6)	O5-Cd1-N1	85.97(6)
O1W-Cd1-O1	91.39(6)	O5-Cd1-N2	136.03(6)
O1W-Cd1-O2	97.73(6)	N1-Cd1-O1	92.45(6)
O1W-Cd1-O4	84.12(6)	N1-Cd1-O2	83.36(6)
O1W-Cd1-N1	175.85(6)	N1-Cd1-O4	92.32(6)
O1W-Cd1-N2	87.02(6)	N2-Cd1-O1	87.30(6)
O2-Cd1-O4	136.24(6)	N2-Cd1-O2	140.04(6)
O5-Cd1-O1	136.66(6)	N2-Cd1-O4	83.65(6)
O5-Cd1-O1W	90.17(6)	N2-Cd1-N1	94.71(6)

Table S2. Hydrogen-bonding parameters (Å, °) for **1-3**.

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	<(D–H···A)
1				
C1–H1A···O5	0.9300	2.5800	3.175(4)	122.00
C5–H5A···O2	0.9300	2.6000	3.215(4)	124.00
2				
C1–H1A···O2	0.9300	2.5700	3.2699	132.00
C6–H6A···O4	0.9300	2.4000	3.1035	132.00
C10-H10A···O2	0.9300	2.5500	3.2946	138.00
C24-H24A···O1	0.9600	2.4200	3.0611	123.00
C34-H34A···O4	0.9300	2.5800	3.0215	109.00
3				
O1W-H1WA···O2	0.8500	1.9900	2.811(2)	163.00
O1W-H1WB···O5	0.8500	2.0000	2.738(2)	144.00
C1-H1A···O2	0.9300	2.5200	3.155(3)	125.00
C6-H6A···O1	0.9300	2.4600	3.108(3)	127.00
C10-H10A···O4	0.9300	2.4600	3.168(3)	133.00
C13-H13B···N3	0.9700	2.5400	3.367(3)	144.00

Table S3. The final detailed data of mpca, bpp and metal ion.

Time (h)	Mpca		Bpp		Co^{2+} ion	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
12	6.00	66.67	2.28	94.48	7.67	96.03
24	10.33	85.59	2.07	93.94	10.6	96.66
36	16.20	86.13	2.30	95.83	14.83	96.22
48	19.98	86.26	2.20	94.96	17.27	94.18

Table S4. The final detailed data of compound **1** and physical mixture materials of **1.**

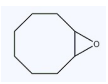
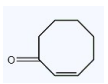
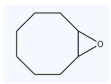
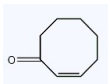
Time (h)	Compound **1**				Materials of **1**			
	Conversion (%)	Product selectivity (%)			Conversion (%)	Product selectivity (%)		
				Σ_{sel}C8[b] (%)				Σ_{sel}C8[b] (%)
12	14.63	75.28	22.76	98.04	8.12	89.12	10.56	99.68
24	24.32	82.64	15.46	98.10	15.95	94.57	5.31	99.88
36	33.72	90.07	8.79	98.86	26.52	96.65	3.22	99.87
48	45.77	90.85	9.08	99.93	30.15	96.72	3.05	99.77

Table S5. The final detailed data of compound **2** and physical mixture materials of **2.**

Time (h)	Compound **2**		Materials of **2**	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
12	14.40	79.93	14.47	84.93
24	21.20	88.39	22.05	80.52
36	27.27	80.35	26.13	83.34
48	37.78	81.02	30.33	87.92

Table S6. The final detailed data of compound **3** and physical mixture materials of **3.**

Time (h)	Compound **3**		Materials of **3**	
	Conversion (%)	Product selectivity (%)	Conversion (%)	Product selectivity (%)
12	12.93	86.90	7.67	77.18
24	20.25	90.07	17.00	90.74
36	32.70	90.08	20.30	92.41
48	39.08	85.65	30.67	90.24

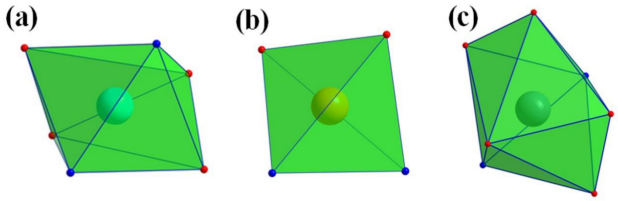


Fig. S1 The coordination polyhedrons of metal centres in compounds **1** (a), **2** (b) and **3** (c), respectively.

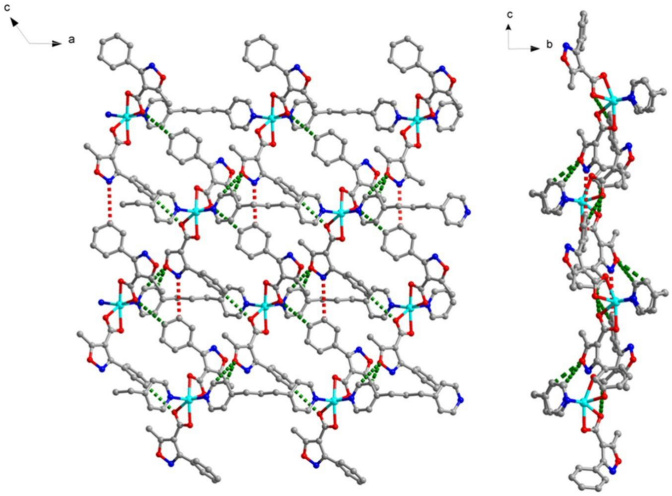


Fig. S2 The double layer structure of **1**. Red dotted lines between two chains are hydrogen bonds in the same layer. Green dotted lines between two chains are hydrogen bonds in the different layer.

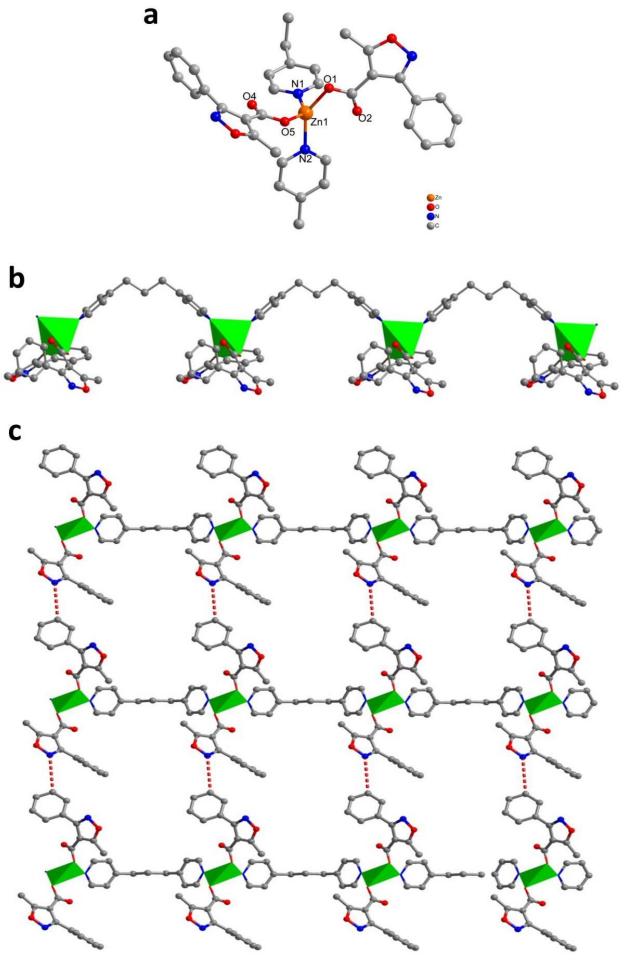


Fig. S3 (a) The coordination environment view of compound **2**. All hydrogen atoms had been omitted for clarity. (b) The 1D waved-liked chain of compound **2**. (c) The 2D stick/polyhedral layer of compound **2**. The hydrogen bonds were replaced by the red dotted line.

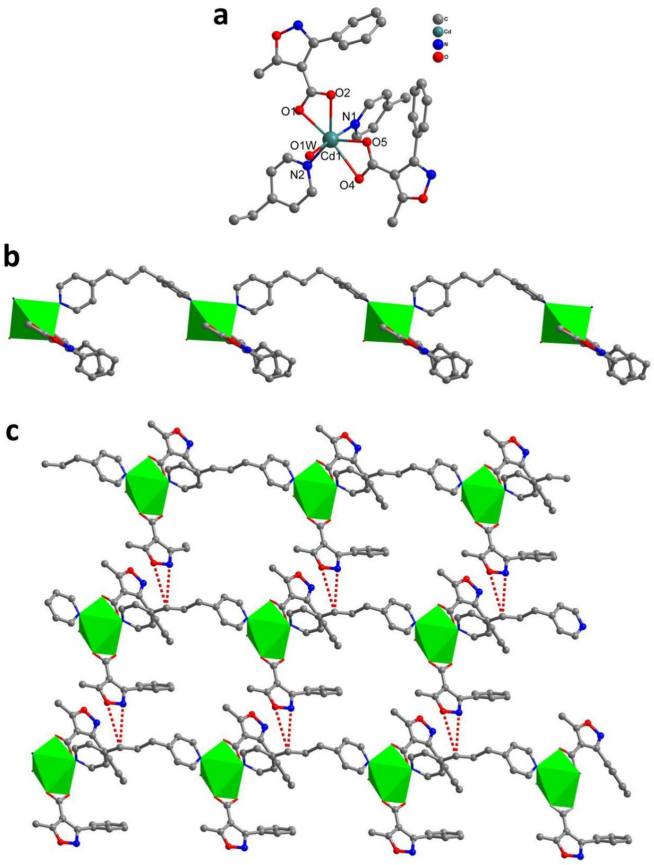


Fig. S4 (a) The coordination environment view of compound **3**. All hydrogen atoms had been omitted for clarity. (b) The 1D wave-liked chain of compound **3**. (c) The 2D stick/polyhedral layer of compound **3**. The hydrogen bonds were replaced by the red dotted line.

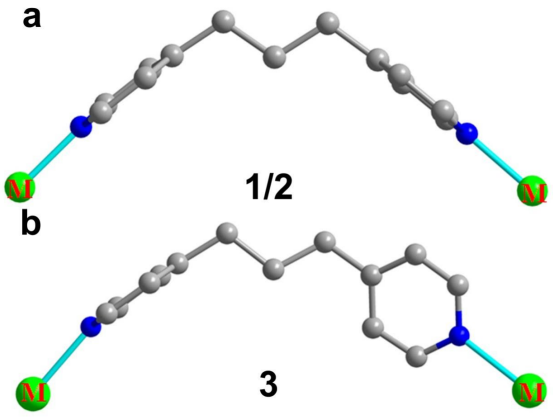


Fig. S5 Different conformation modes of bpp ligand observed in compounds **1**-**3**.

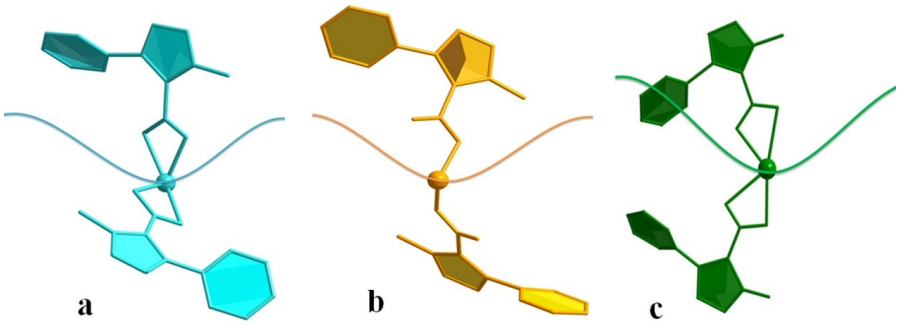


Fig. S6 Arrangements of mpca: head-to-head mode in **1** (a) and **2** (b); shoulder-by-shoulder mode in 3 (c).

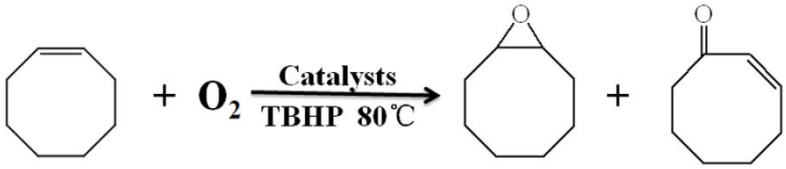


Fig. S7 The equation of cyclooctene epoxidation with catalysts.

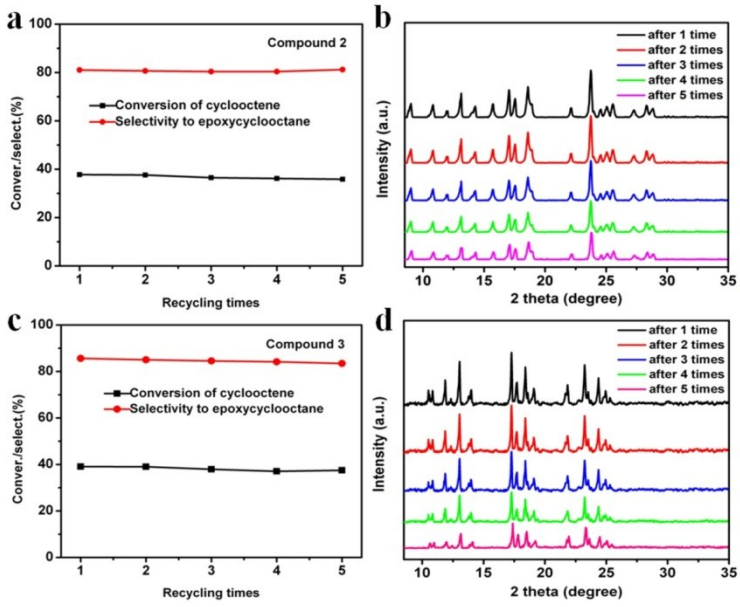


Fig. S8 (a) The relationship between the conversione/selectivity and recycling times with compound **2** as catalyst. (b) The PXRD patterns based on the single-crystal structure of **2**: after 1, 2, 3, 4, and 5 times recycling. (c) The relationship between the conversion/selectivity and recycling times with compound **3** as catalyst. (**d**) The PXRD patterns of **3**: after 1, 2, 3, 4, and 5 times recycling.

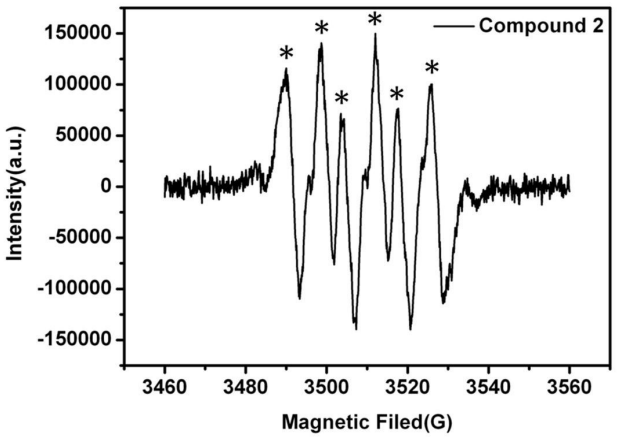


Fig. S9 ESR signals of the DMPO-•O_2^- adducts (compound **2** in methanol solution).

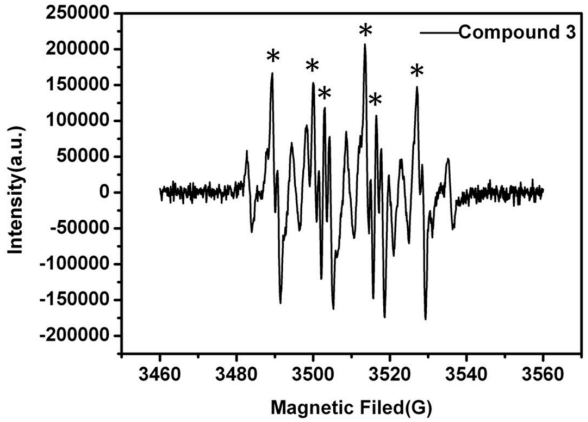


Fig. S10 ESR signals of the DMPO-•O_2^- adducts (compound **3** in methanol solution).

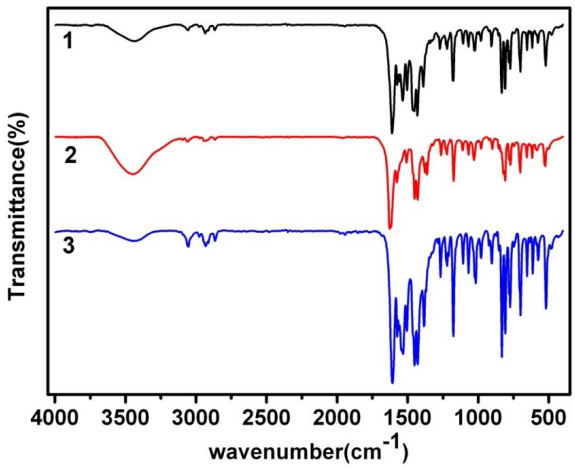


Fig. S11 FT-IR spectra for compounds **1-3**. The broad absorption peaks at around 3425 cm^{-1} represent the –OH groups. The peaks around 3000, 1600 and 1500 cm^{-1} correspond to the C=C stretching vibrations of polycyclic aromatic hydrocarbons. And the characteristic peaks at 2930 and 2860 cm^{-1} are due to the vibrations of sp^2

and sp^3 C—H (J. Hou, L. Wang, P. Zhang, Y. Xu, L. Ding, *Chem. Commun.,* 2015, **51**, 17768.).

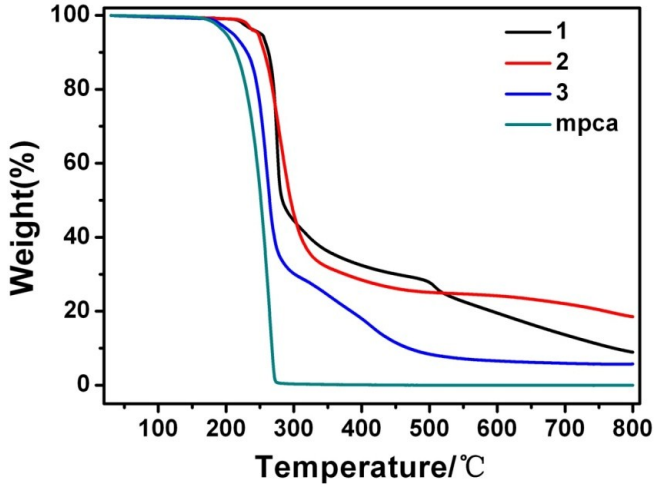


Fig. S12 The TG spectra of compound **1-3** and mpca.

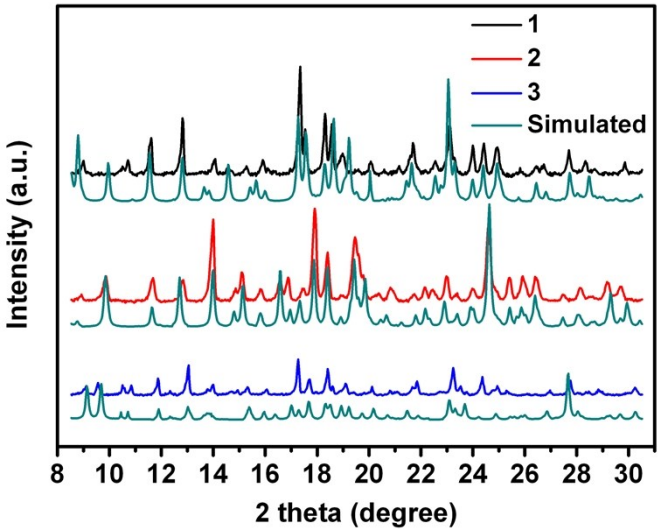
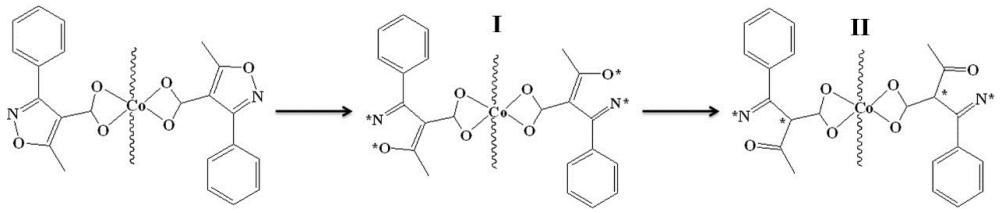


Fig. S13 The PXRD patterns of compounds **1-3**.



Scheme S1 The cleavage of the N-O bond in ligands mpca upon heating. The N-O bond of isoxazole in mpca cleaved and generated a diradical structure **I** upon heating. But the diradical structure **I** was not stable and further generated the vinyl nitrene type reactive structure **II**.