Electronic Supplementary Material (ESI) for Green Chemistry.

A dual-walled cage MOF as an efficient heterogeneous catalyst for the conversion of CO_2 under mild and co-catalyst free conditions

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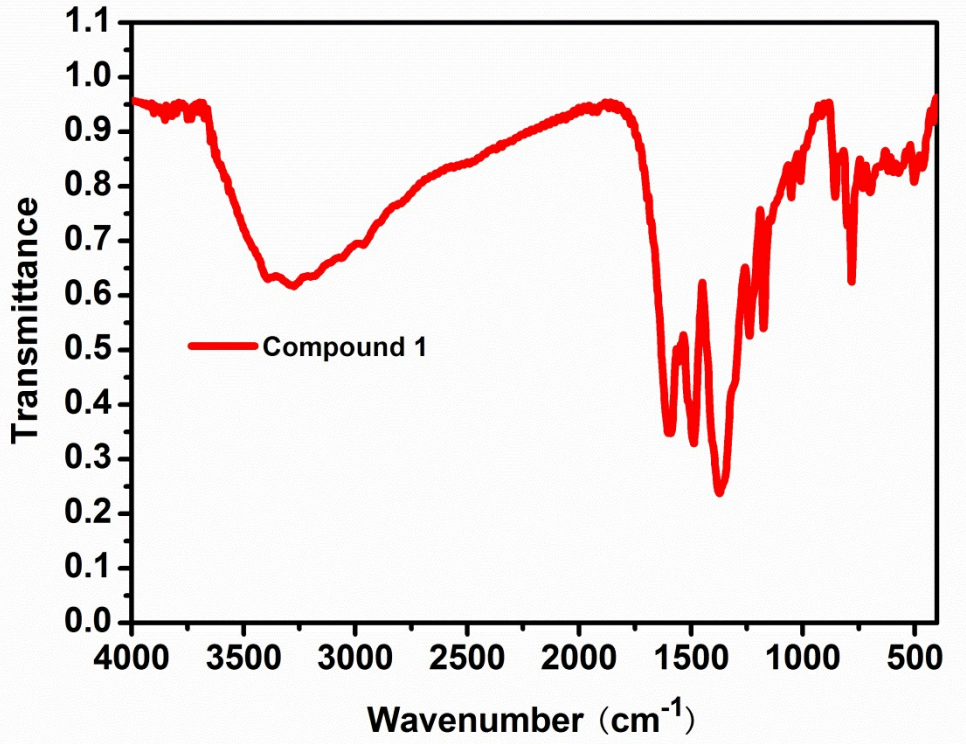

Fig. S1 The IR spectrum of compound **1**.

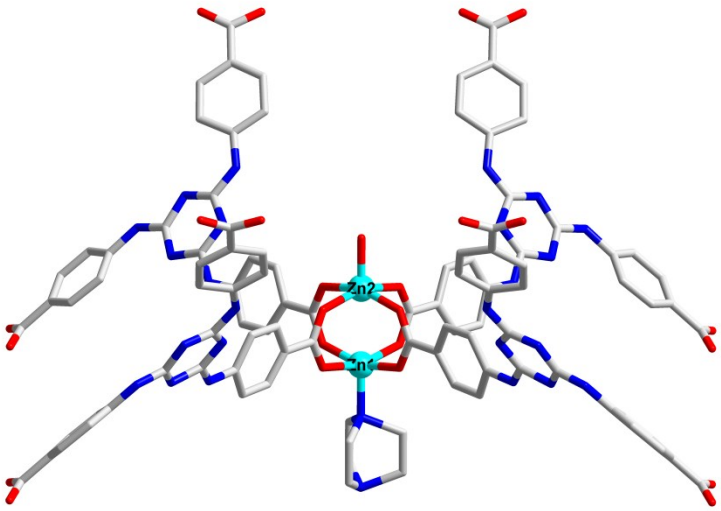

Fig. S2 The environment of the two crystallographic independent Zn^{2+} ions.

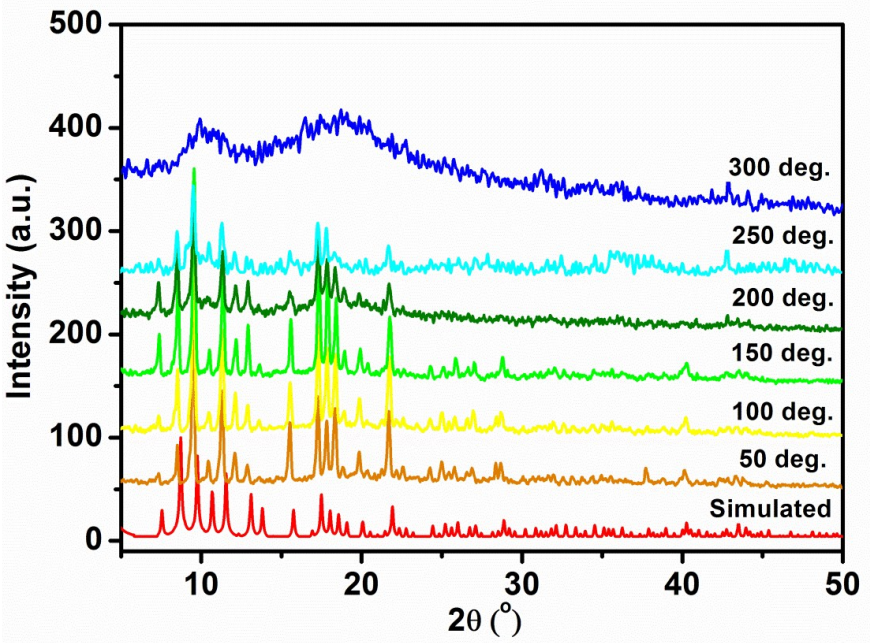

Fig. S3 The PXRD patterns of **1** recorded at different temperatures.

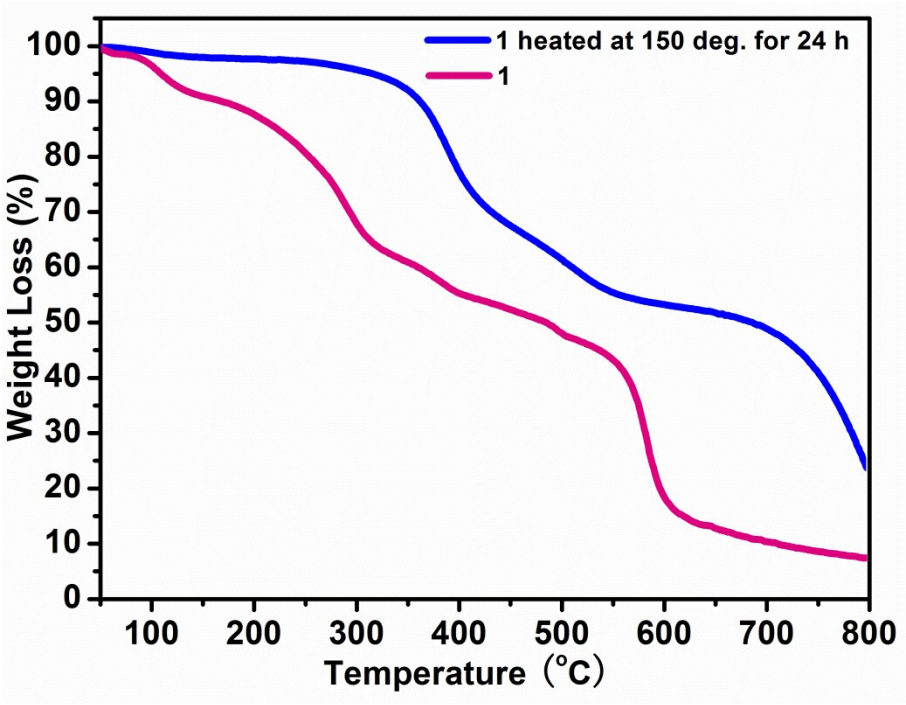

Fig. S4 The TGA curves of compound **1**.

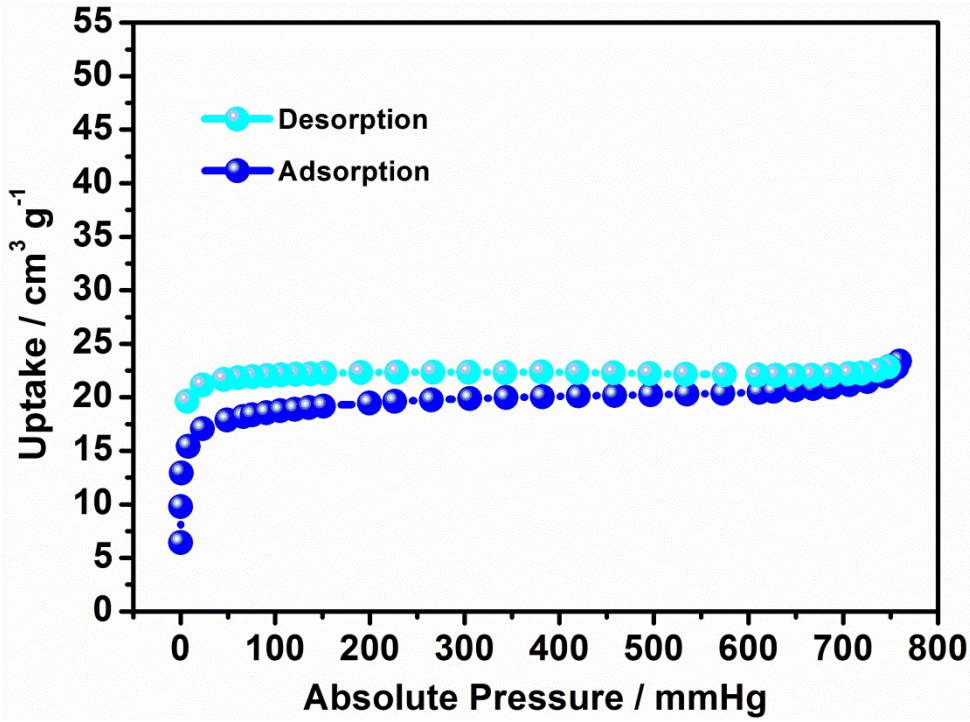

Fig. S5 The Gas sorption isotherm of **1** for N_2 measured at 77 K.

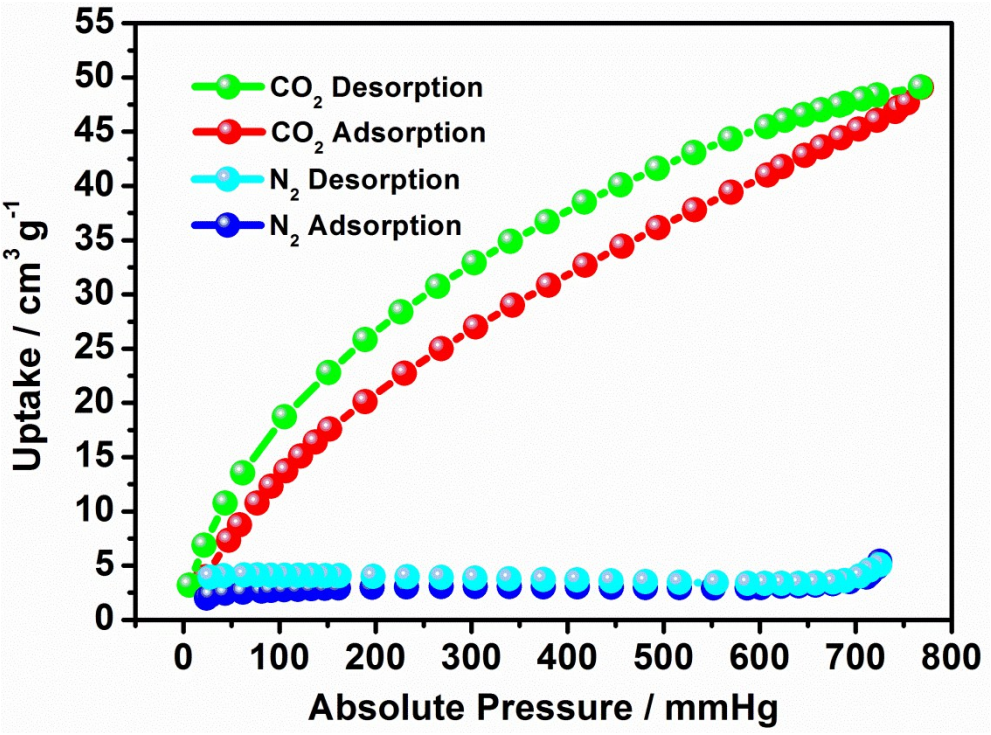

Fig. S6 The Gas sorption isotherms of **1** for CO_2 and N_2 measured at 273 K.

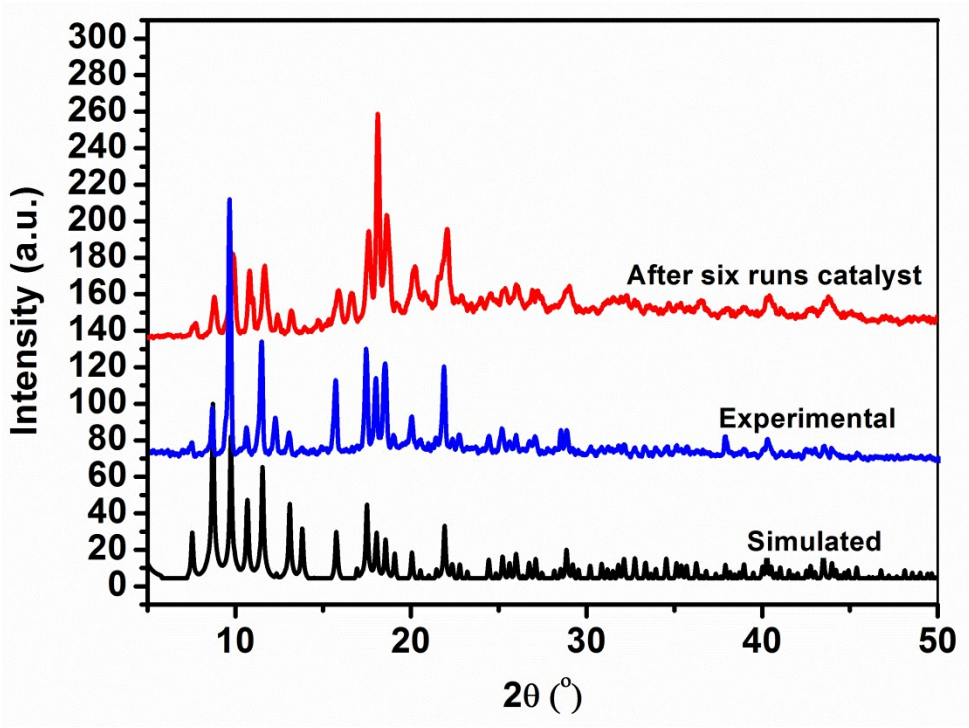

Fig. S7 The PXRD patterns of **1** after six runs for the cycloaddition of CO_2 with propylene oxide.

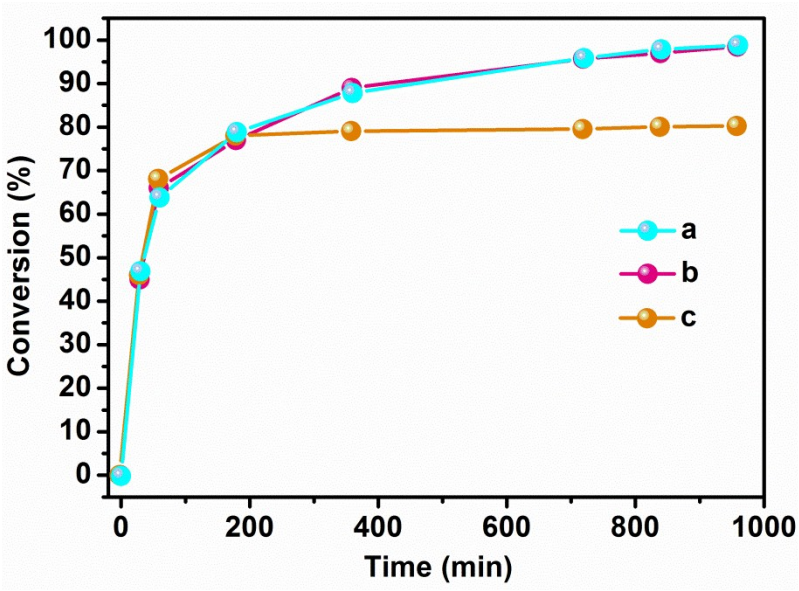

Fig. S8 Recycle reaction kinetics for the formation of propylene carbonate catalysed by **1** at 100°C and 1 atm (a) cycle 1, (b) cycle 2 and (c) after the reaction was performed for 3 hours, **1** was removed from the mixture and the reaction was continued for another 13 hours.

Table S1 Conversion of propylene epoxide into propylene carbonate with CO_2 catalysed by different MOF-based systems

Entry	Catalyst	Co-Catalyst	Solv.	T (°C)	P (atm)	t (h)	Yield (%)	TON	Ref.
1	1	**No**	No	100	**1**	**12**	**98.5**	246.3	This work
2	MMCF-2[a]	TBAB	No	R.T.	1	48	95.4	254.4	1
3	MMCF-9[b]	TBAB	No	R.T.	1	48	87.4	--	2
4	BIT-103[c]	No	No	160	30	24	95.2	230.2	3
5	BIT-102[c]	No	No	160	30	24	89.4	216.2	3
6	BIT-101[c]	No	No	160	30	24	84.7	174.9	3
7	MOF-5[d]	TBAB	No	50	60	6	97.6	68.8	4
8	ZIF-8[e]	No	No	80	7	4	43.7	18.1	5
9	ZIF-8-f[e]	No	No	80	7	4	73.1	32.3	5
10	CHB(M)[f]	No	No	120	12	6	62	--	6
11	Co-CMP 100[g]	TBAB	No	100	30	1	98.1	201	7
12	Mg-MOF-74[h]	No	chlorobenzene	100	20	4	95	28.5	8
13	BIT-C[i]	TBAB	No	60	4	10	95	--	9
14	MIL-101-N(n-Bu)$_3$Br[j]	No	No	80	20	8	99.1	110.1	10
15	MIL-101-P(n-Bu)$_3$Br[j]	No	No	80	20	8	98.6	109.6	10
16	Ni−TCPE1[k]	TBAB	No	100	10	12	99	2000	11

Reaction Conditions: [a] epoxide (25.0 mmol) with catalyst (0.125 mol% per paddlewheel units), nBu$_4$NBr (0.58 g); [b] epoxide (25 mmol) with MMPF-9 (0.03125 mmol), nBu$_4$NBr (0.58 g); [c] epoxides (20 mmol), BIT-103 (3.76 mmol); [d] epoxide 20 mmol with 2.5 mol% nBu$_4$NBr, 0.1 g MOF-5; [e] Catalytic performance of ZIF-8 and Functionalized ZIF-8 in the cycloaddition of CO_2 to epichlorohydrin Reaction, ZIF-8-f stands for functionalized ZIF-8; [f] 0.3 mmol CHB(M), 18.6 mmol epoxide; [g] propylene oxide (25mmol), Co-CMP (100mg, Co: 0.122mmol), TBAB (1.8 mmol); [h] substrate : catalyst = 30 : 1; [i] Epoxide 20 mmol, BIT-C 1 mol% (based on Cu^{2+}), Bu$_4$NBr 5 mol% as the co-catalyst; [j] PO (30 mmol), catalyst (0.27 mmol); [k] epoxide (20 mmol), catalyst (10 μmol, based on Ni), and TBAB (0.3 mmol).

Table S2 Crystallographic data and structure refinement details for compound **1**

Compound	Compound 1
Formula	$C_{150}H_{204}N_{42}O_{48}Zn_6$
Fw	3755.79
Cryst. Syst.	Cubic
space group	*Im-3*
***a*, Å** ***α*, °**	28.6573(3) 90.00
***V*, Å^3**	23534.5 (4)
Z	12
***μ*, mm^{-1}**	0.670
***D*$_{calcd}$,g cm^{-3}**	1.060
GOF	1.302
$^aR_1$	0.0726
***wR*$_2$**	0.2349

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

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