Supporting Information

Hierarchical mesoporous organic polymer with intercalated metal complex for efficient synthesis of cyclic carbonates from flue gas

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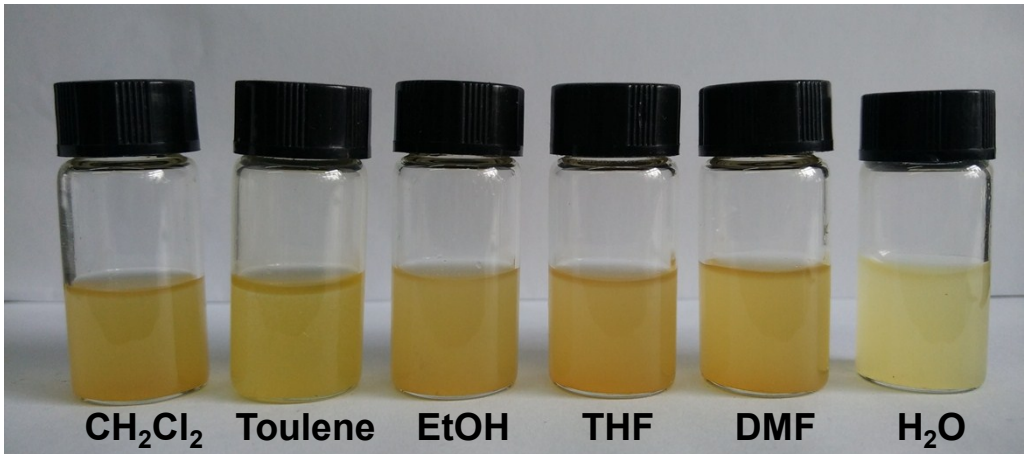

Figure S1. Dispersity of Bp-Zn@MA in common solvents.

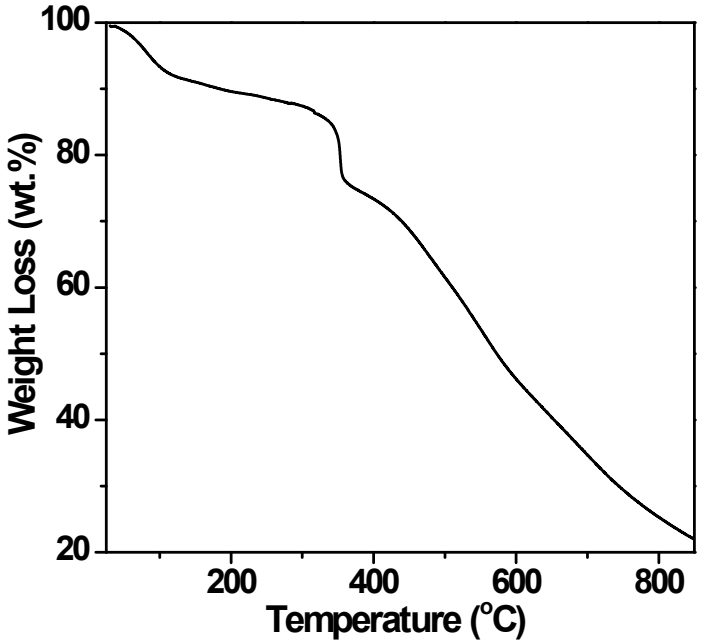

Figure S2. TG curve of Bp-Zn@MA analysed under nitrogen atmosphere.

Calculation of Henry's law selectivity

To calculate the Henry's law selectivity of CO_2 over N_2 at 273 K or 298 K for Bp-Zn@MA, the CO_2 and N_2 isotherms were fitted to a virial-type thermal equation previously used to model gas adsorption on solid adsorbents as literature reported:

$$\ln p = \ln q + \frac{1}{T}\sum_{i=0}^{m} a_i q^i + \sum_{j=0}^{n} b_i q^i$$

p is the pressure, q is the amount of the adsorbed gas (mmol/g), and T is the temperature (K). a_i and b_i are virial coefficients, m and n are the numbers of coefficients required for sufficient description of the isotherms. Then the Henry's constant (K_H) can be obtained:

$$K_H = \exp(-b_0) * \exp(-\frac{a_0}{T})$$

The Henry's law selectivity can be calculated by using the following equation:

$$S_{CO2/N2} = K_H(CO_2)/K_H(N_2)$$

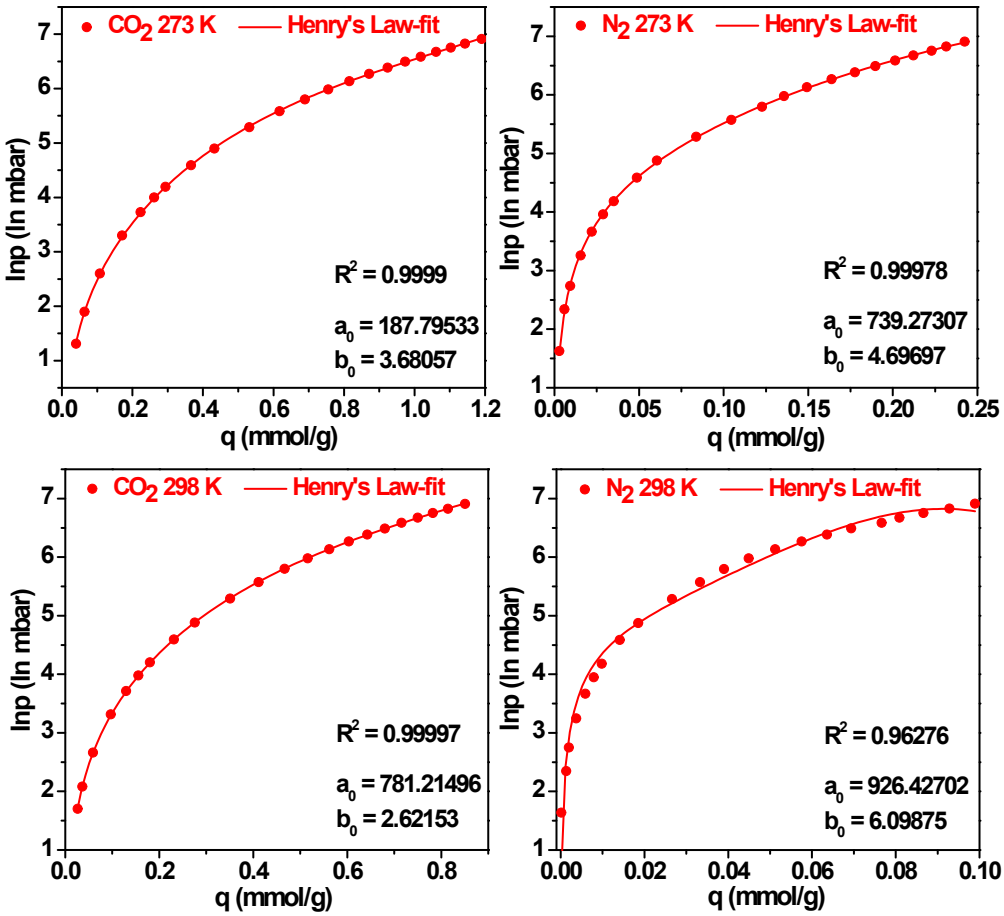

Figure S3. CO_2, N_2 adsorption isotherms and their Henry's law equation fit curves of Bp-Zn@MA.

Calculation of Ideal adsorbed solution theory (IAST) selectivity

To calculate the IAST selectivity of CO_2 over N_2 at 273 K or 298 K for Bp-Zn@MA, the pure component isotherms of CO_2 measured at 273 K or 298 K were fitted with the dual site Langmuir model and the pure component isotherms of N_2 measured at 273 K or 298 K were fitted with the single site Langmuir model as literature reported. The single site Langmuir model is defined as:

$$q = \frac{q_{sat} b p}{1 + bp}$$

The dual site Langmuir model is defined as:

$$q = q_A + q_B = \frac{q_{sat,A} b_A p}{1 + b_A p} + \frac{q_{sat,B} b_B p}{1 + b_B p}$$

q is molar loading of adsorbate; q_{sat} is the saturation loading; b is Langmuir constant; A and B is referring to two distinct adsorption sites.

For the CO_2:N_2 (15:85) gas mixtures, the IAST selectivity can be calculated using the following equation:

$$S = \frac{q_1 / q_2}{p_1 / p_2}$$

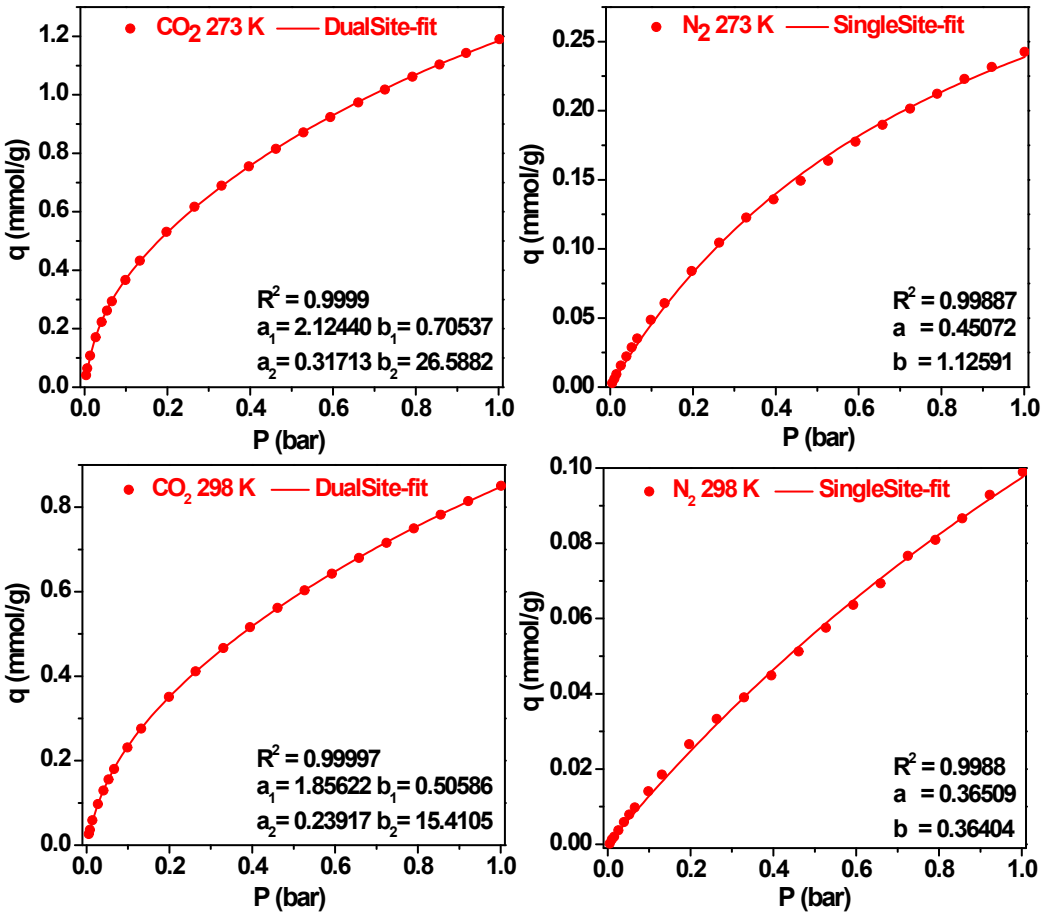

Figure S4. CO_2, N_2 adsorption isotherms and their IAST equation fit curves of Bp-Zn@MA.

Table S1. Comparision of the activity of Bp-Zn@MA in the PO-to-PC conversion reaction with the reported MOFs or POPs catalysts.

Catalyst	S/C	TBAB (x mol%)	T (^{o}C)	Pressure (MPa)	Time (h)	Yield (%)	TOF (h^{-1})	Ref.
Bp-Zn@MA	1160	0.55	100	1	1.5	99	2252	this work
Co-MON	2000	0.15	60	1	12	75	125	1
Co-CMP	205	7.2	100	3	1	98.1	201	2
Zn(Por)OP	1000	5	120	3	2.5	95	1628	3
Al-CMP	2000	0.5	100	3	5	91	364	4
Zn/HAzo-POP	1600	7.2	100	3	0.5	90	2888	5
Zn@SBMMP	250	1.8	80	2	4	97	-	6
In-MOF	770	2.5	80	2	4	57.2	110	7
Zn-CMP	2000	1.25	120	3	1	55.3	1100	8
PSIL-4	148	-	110	6	7	97.4	-	9
T-IM	1540	-	150	1	10	87	134	10
Bp-Zn@MA	1160	0.55	25	0.1	48	99	128	this work
Zn-CMP	500	1.8	25	0.1	48	76.1	8	8
Co-CMP	205	7.2	25	0.1	48	81.5	-	2
MMCF-2	800	1.8	r.t	0.1	48	95.4	-	11
Cu-MOF	500	10	r.t	0.1	48	96	200	12
HKUST-1	500	10	r.t	0.1	48	65	135	12
In-MOF	435	5	r.t	0.1	48	77.9	7.1	7

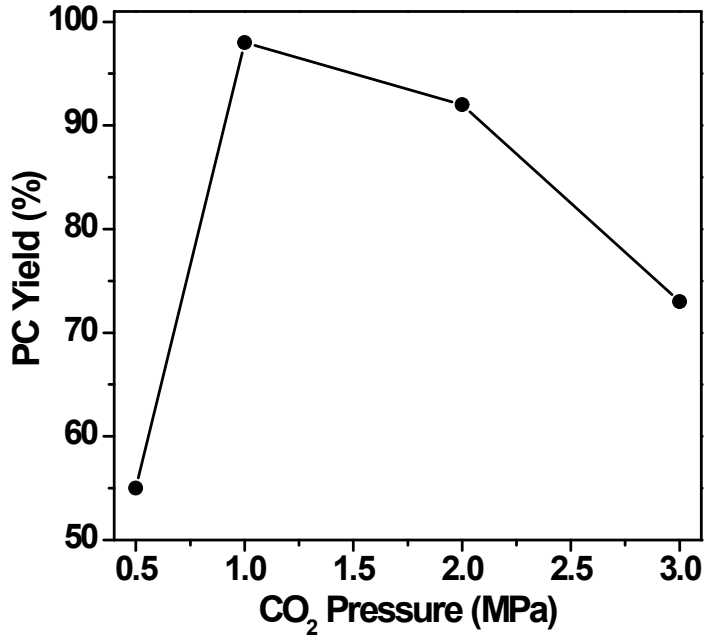

Figure S5. Dependence of PC yields on the pressure (pure CO_2). Reaction conditions: PO (390 mg), Bp-Zn@MA (20 mg, 5.8 μmol) and TBAB (12 mg, 37 μmol), 100 °C, 1.5 h.

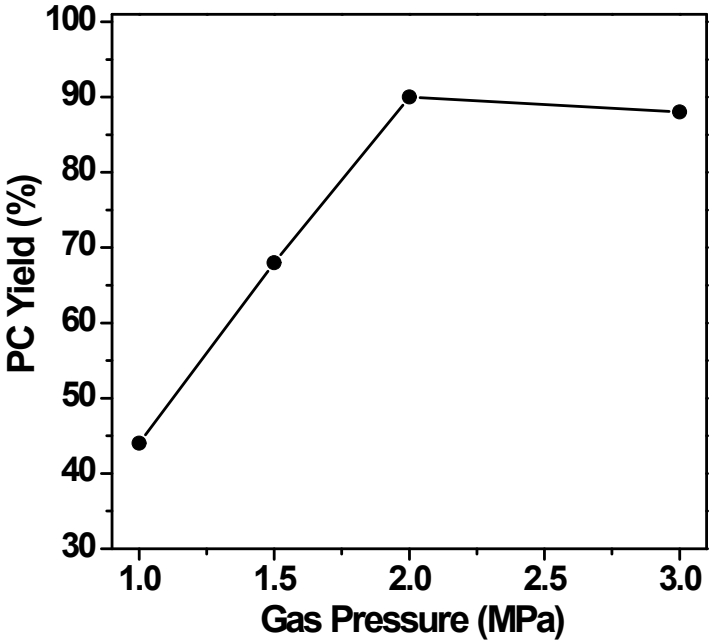

Figure S6. Dependence of PC yields on the pressure (diluted CO_2, 20% CO_2 in N_2). Reaction conditions: PO (390 mg), Bp-Zn@MA (20 mg, 5.8 μmol) and TBAB (12 mg, 37 μmol), 100 °C, 4 h.

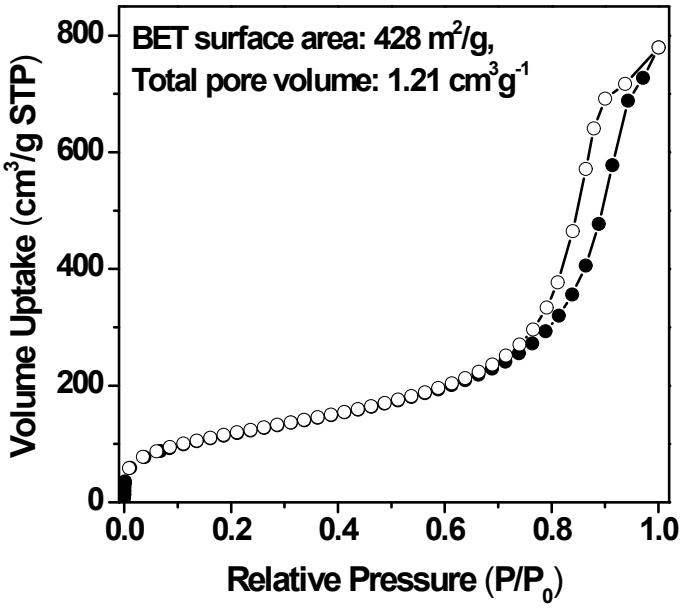

Figure S7. N_2 sorption isotherms of Bp-Zn@MA after 5th catalytic cycle measure at 77 K.

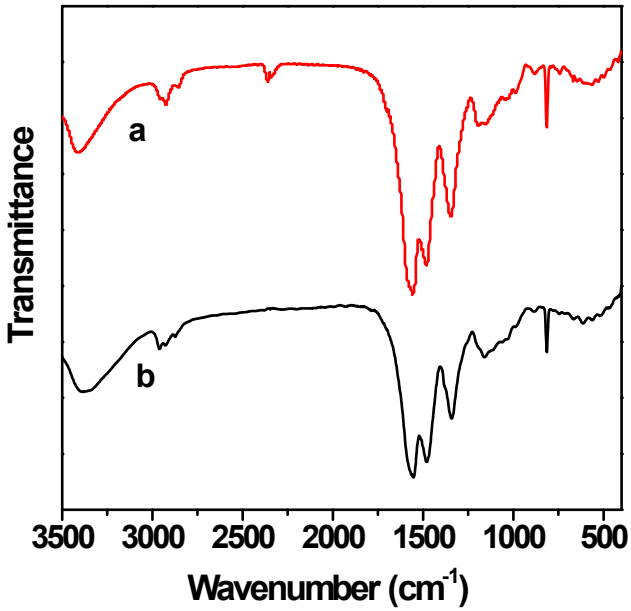

Figure S8. FT-IR spectra of (a) the fresh Bp-Zn@MA and (b) Bp-Zn@MA after 5th catalytic cycle.

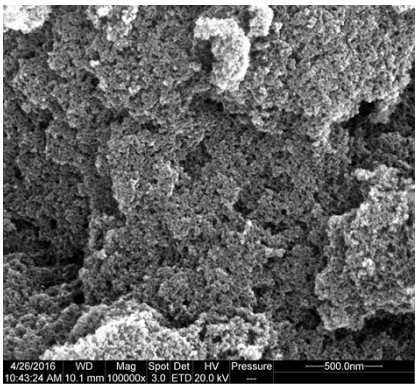

Figure S9. SEM image of the Bp-Zn@MA after 5th catalytic cycle.

Table S2. CHN Elemental analysis and ICP result of zinc for the fresh and reused Bp-Zn@MA.

Sample	CHN elemental analysis			Zn content (wt%)
	C (wt%)	H (wt%)	N (wt%)	
Bp-Zn@MA	32.2	4.54	40.6	1.9
Bp-Zn@MA after 5 cycles	34.2	4.17	41.1	1.8

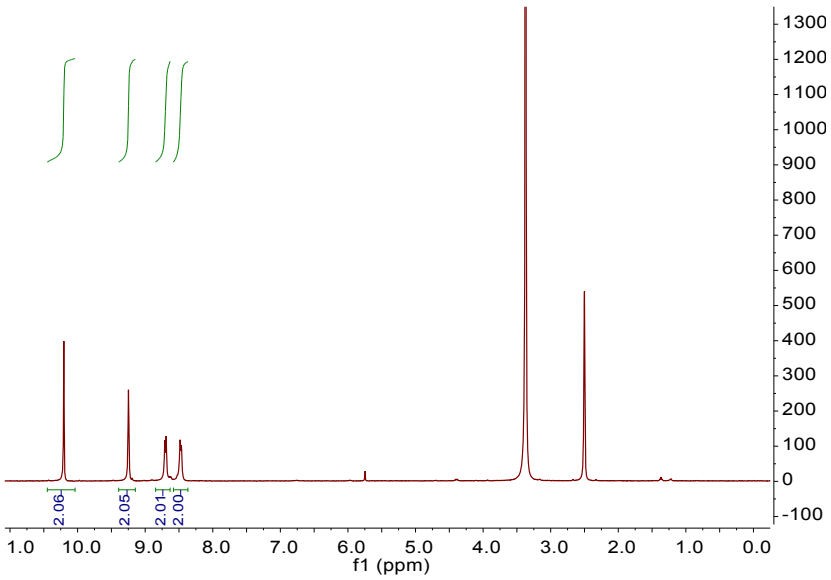

Figure S10. [1]H-NMR spectrum of 2,2'-bipyridine-5,5'-dicarboxaldehyde zinc bromide.

References of Supporting Information.

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