Supporting information

Pyridine-Functionalized and Metallized Meso-Macroporous Polymers for Highly Selective Capture and Catalytic Conversion of CO_2 into Cyclic Carbonates

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Table S1 A summary of CO_2 selective capture property on different porous polymers reported in the literature.

Samples	CO_2 capacities at 0 °C (mmol/g) 0.15 bar	References
Co@PDVB-VP-0.25	0.89	**This work**
Co@PDVB-VP-0.5	0.82	**This work**
Co@PDVB-VP-1.0	0.58	**This work**
PINK	1.15	*J. Mater. Chem. A*, **2016**, 4, 2517-2523
CPP	1.50	*J. Mater. Chem. A*, **2015**, 3, 10284-10288
PIN1	0.79	*J. Mater. Chem. A*, **2015**, 3, 18492-18504
TPI-2@IC	0.85	*J Mater. Chem. A*, **2015**, 3, 878-885
PP1-2-tren	1.47	*J. Mater. Chem. A*, **2015**, 3, 16229-16234
A1B1-0.030	1.12	*J. Mater. Chem. A*, **2015**, 3, 10990-10998
NAN-2	0.61	*J. Mater. Chem. A*, **2016**, 4, 8190-8197
PPN-81	1.22	*J. Mater. Chem. A* **2015**, 3,

Table S2 A summary of CO_2/N_2 selectivities on different porous polymers reported in the literature

Porous materials	Temperature (°C)	Method	CO_2/N_2 selectivities	Refs.
Cu/BF_4/BIPLP-1	25	Henry's law	64	*J. Phys. Chem. C* **2015**, *119,* 8174
COP-19	25	IAST	131	*Faraday Discuss.* **2015**, *183,* 401
Azo-COP-2	25	IAST	110	*Nat Commun* **2013**, *4,* 1357
TB-COP-1	25	IAST	69	*J. Mater. Chem. A* **2014**, *2,* 12507
PPN-6-SO_3Li	22	IAST	414	*J. Am. Chem. Soc.* **2011**, *133,* 18126
PPN-6-SO_3NH_4	22	Henry's law	196	*Energ. Environ. Sci.* **2013**, *6,* 3559
PPN-6-DETA	22	IAST	442	*Angew. Chem. Int. Ed.* **2012**, *51,* 7480
PPN-81	25	IAST	4716	*J. Mater. Chem. A* **2015**, *3,* 3252
PFPOP-3	25	IAST	57	*RSC Adv.* **2015**, *5,* 71095
DA-CMP-1	25	IAST	60	*J. Mater. Chem. A* **2015**, *3,* 21185
TB-MOP	25	Henry's law	51	*ACS Macro. Lett.* **2013**, *2,* 660
PAF-3	25	Henry's law	87	*Energ. Environ. Sci* **2011**, *4,* 3991
PAF-33-NH_2	25	Henry's law	80	*Polymer Chem.* **2014**, *5,* 2266
$[HO_2C]_{100\%}$-H_2P-COF	25	IAST	77	*Angew. Chem. Int. Ed.* **2015**, *54,* 2986
CPP	25	Henry's law	94	*J. Mater. Chem. A*

				2015, *3,* 10284
om-ph-MR	25	Henry's law	100	*J. Am. Chem. Soc.* **2015**, *137,* 7210
SNW-1	25	IAST	50	*Adv. Mater.* **2014**, *26,* 3644
TCPF-4	25	Henry's law	56	*Polymer Chem.* **2015**, *6,* 7410
TBMID	25	Henry's law	59	*RSC Adv.* **2015**, *5,* 100322
FCTF-1	25	IAST	31	*Energy Environ. Sci.,* **2013***, 6,* 3684.
$[Cu(tba)_2]_n$	25	IAST	45	*J. Am. Chem. Soc.* **2014**, *136,* 10906.
Co@PDVB-VP-1.0	**25**	**IAST**	**163.5**	**This work**
Co@PDVB-VP-0.5	**25**	**IAST**	**144.5**	**This work**

Table S3 Catalytic activity of different catalysts for cycloaddition of CO_2 to produce propylene carbonate.

Catalyst	CO_2 (MPa)	Co-catalysts	Temp. (°C)	Time (h)	Yield (%)	Refs
Co@PDVB-VP-0.5	1.0(CO_2/N_2= 0.15/0.85)	*n*-Bu_4NBr	30	48	99.2	**This work**
Co@PDVB-VP-0.5	1.0(CO_2/N_2= 0.15/0.85)	*n*-Bu_4NBr	100	0.75	98.9	**This work**
USTC-253-TFA	0.1	*n*-Bu_4NBr	25	72	81.3	*ChemSusChem*, **2015**, *8*, 878-885.
Co-CMP 100	0.1	*n*-Bu_4NBr	25	48	81.5	*Nat. Commun.*, **2014**, *4*, 1960.
Co/POP-TPP	0.1	*n*-Bu_4NBr	29	24	98.5	*J. Catal.,* **2016**, *338*, 202.
Zn/HAzo-POP-1	3.0	*n*-Bu_4NBr	100	0.5	86.0	*Angew. Chem., Int. Ed.,* **2016**, *55*, 9685.
Cu/POP-Bpy	0.1	*n*-Bu_4NBr	29	48	99.0	*ChemSusChem*, **2017**, *10*, 1186.
Silicon-based poly-imidazolium salts	1.0	-	110	2	94.0	*Green Chem.*, **2014**, *16*, 4515
Chitosan	2.0	-	120	4	96.0	*Green Chem.*,

functionalized ionic liquid CS-EMImBr						**2012**, *14*, 654
Co@R/HMTA-0.30	1.0	*n*-Bu_4NBr	100	1.5	97.1	*Adv. Mater.*, **2017**, *29*, 1700445.
TBB-Bpy@Salen-Co	1.0	-	60	6	99.2	*Chem. Eur. J.*, **2016**, *22*, 8368.

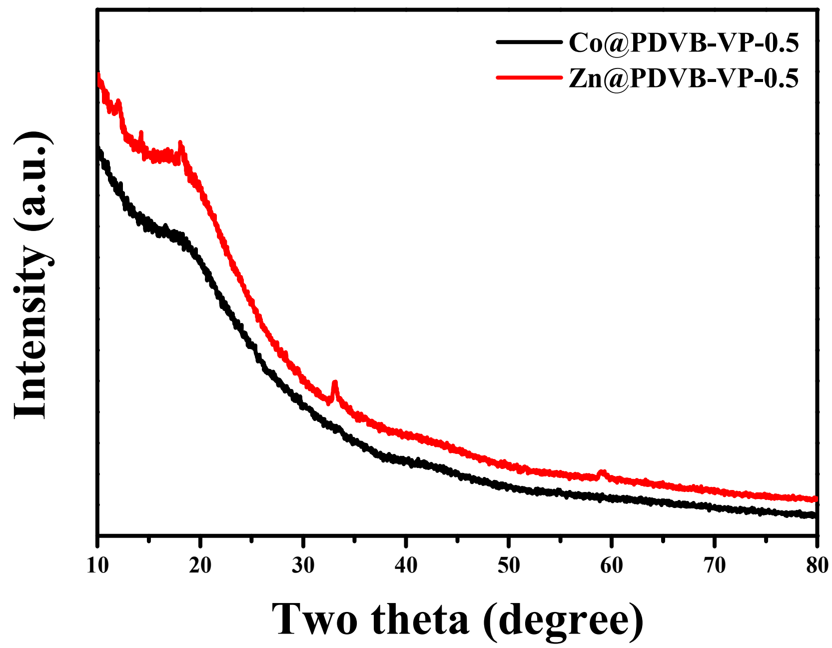

Figure S1 Wide angle XRD patterns of Co@PDVB-VP-0.5 (black) and Zn@PDVB-VP-0.5 (red).

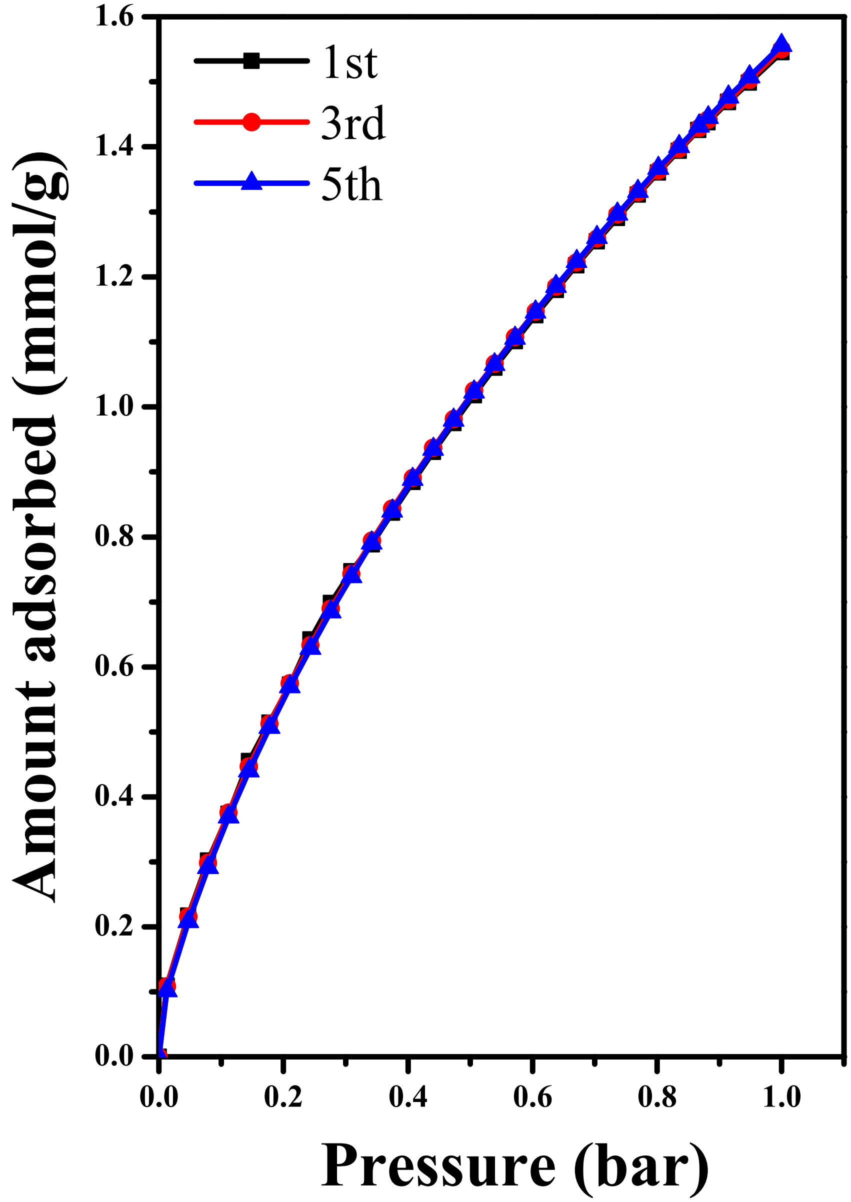

Figure S2 The reuse study of Zn@PDVB-VP-0.5 in the selective capture of CO_2 at 0 °C.

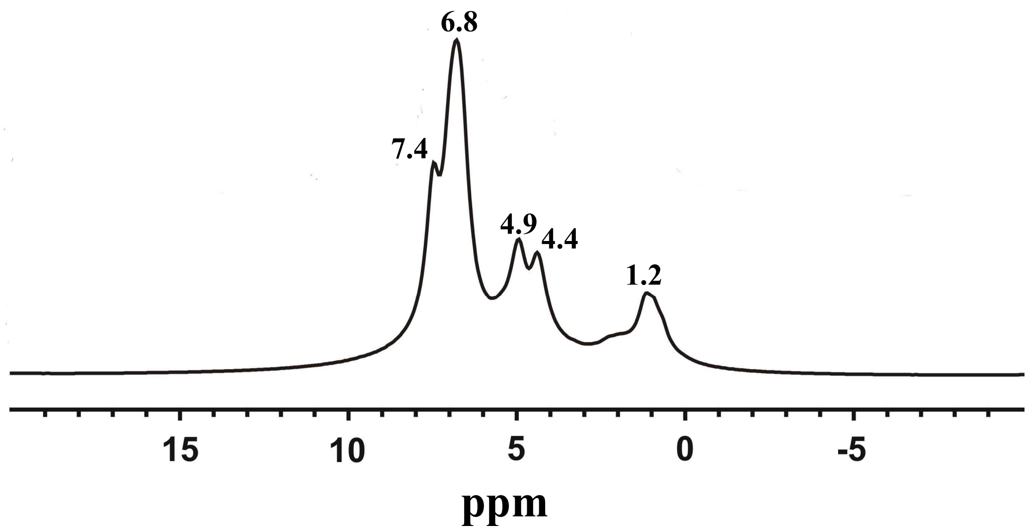

Figure S3 ^{1}H solid state NMR spectra of pyrrole adsorbed on Co@PDVB-VP-0.5.

The basic strength of Co@PDVB-VP-0.5 was investigated by using solid-state ^{1}H NMR technique involving pyrrole as the probe molecule (Figure S3), which is frequently used to investigate the basic properties of solid catalysts, mainly because of the hydrogen-bonding interaction between the NH group of pyrrole and the basic sites in catalysts. The solid-state ^{1}H NMR technique is a reliable and *state-of-the-art* approach to determine the basic strength of various kinds of solid base catalysts [S1-S4]. Notably, Co@PDVB-VP-0.5 shows multiple ^{1}H resonance peaks centered at around 1.2, 4.4, 4.9, 6.8 and 7.4 ppm, which indicates the presence of variously basic sites with different basic strength in the sample. The peak at around 1.2 ppm may be assigned to the signals of physical absorbed pyrrole in Co@PDVB-VP-0.5. The resonances at around 4.4 and 4.9 ppm can be attributed to absorbed pyrrole on the pyridinic sites, which partially coordinate with Co^{2+}, further resulting in relatively weak basic strength. The strong peaks at around 6.8 and 7.4 ppm should be attributed to the absorbed pyrrole on exposed pyridinic sites, which show relatively strong basic strength and confined inside different environments. The base property of Co@PDVB-VP-0.5 was in the range of medium strength [S1-S6], which results in its competitive property for the selective capture of CO_2.

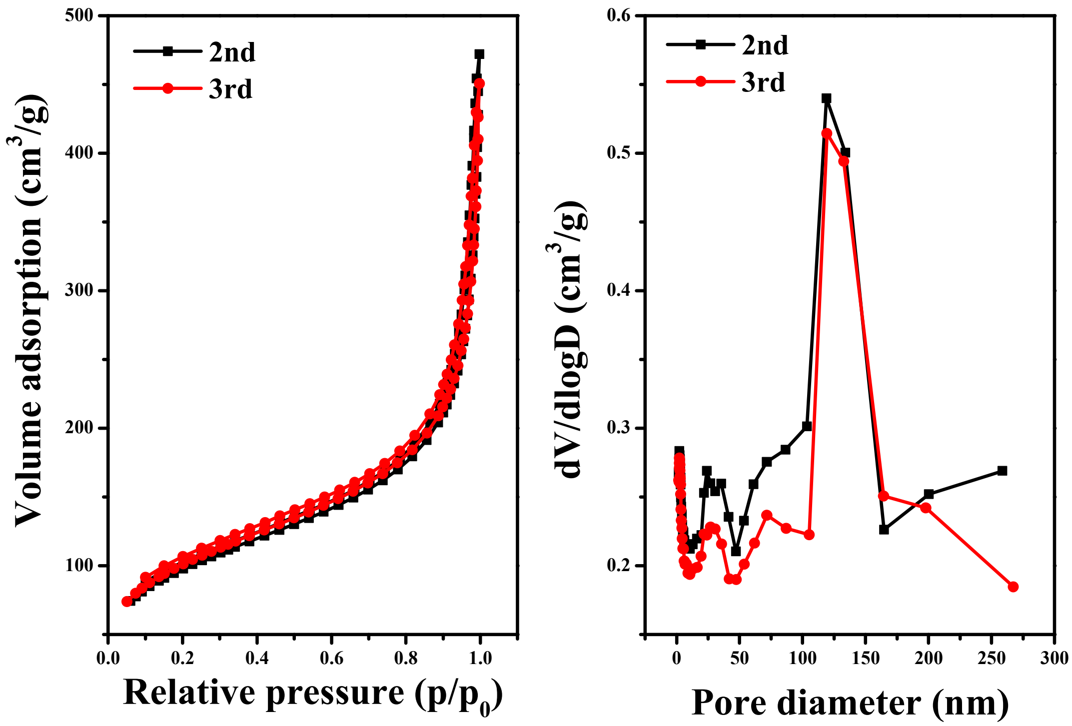

Figure S4 N_2 isotherms and pore size distribution of recycled Co@PDVB-VP-0.5 for (black) two and (red) three times.

Figure S4 showed N_2 isotherms and pore size distribution of recycled Co@PDVB-VP-0.5 (two and three times recycling) in catalyzing conversion of CO_2. Compared with fresh Co@PDVB-VP-0.5, the obvious changes of isotherms and nanopore sizes of recycled Co@PDVB-VP-0.5 can not be observed (Figure 1). In addition, fresh Co@PDVB-VP-0.5 shows the BET surface area and pore volume at 479 m^2/g and 0.61 cm^3/g, and nearly no decreasing of BET surface areas and pore volumes for the 2nd (482 m^2/g, 0.63 cm^3/g) and 3rd (476 m^2/g, 0.60 cm^3/g) recycled Co@PDVB-VP-0.5. The above results confirm very stable porous structure of Co@PDVB-VP-0.5, which was very important for it used as stable and reusable catalysts for the capture and conversion of CO_2.

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