Electronic Supplementary Information

Metalloporphyrin-Based Organic Polymer for Carbon Dioxide Fixation to Cyclic Carbonate

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Materials

Unless otherwise stated, all chemicals in this research were commercial available and used without further purification. Propylene oxide (PO), zinc acetate [$Zn(OAc)_2 \cdot 2H_2O$], cobalt acetate [$Co(OAc)_2 \cdot 2H_2O$], propanoic acid (98 wt%), ethanol, methanol, dichloromethane, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P.R. China). Terephthaldehyde, pyrrole, potassium iodide (KI), tetraphenylphosphonium bromide (TPPB), tetrabutylammonium bromide (TBAB), 4-dimethylaminopyridine (DMAP) were purchased from Aladdin Industrial Inc. (Shanghai, P.R. China). Pyrrole was freshly distilled before use. Carbon dioxide ($CO_2 > 99.999\%$) was obtained from Huate Co. Ltd. (Foshan, P.R. China).

Characterization techniques

Fourier transform infrared (FT-IR) spectra of samples with KBr wafers were recorded at room temperature in the 500–4500 cm^{-1} region with a Bruker Tensor 27 spectrotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans.

The surface morphology and structure of Zn(Por)OP was investigated by scanning electron microscopy (SEM) on a FESEM Hitachi-S 4800. The samples were mounted on an aluminum stub using adhesive carbon tape and SEM image were obtained at different magnifications.

The morphological analysis was carried out using transmission electron microscopy (TEM, JEM-2100HR). Samples for TEM studies were prepared by placing a drop of the suspension of Zn(Por)OP sample in ethanol onto a carbon-coated copper grid, followed by evaporating the solvent.

Powder X-ray diffraction (XRD) patterns of (Por)OP, Zn(Por)OP and Co(Por)OP were obtained with a PANalytical X′pert Pro MPD diffractometer operated at 40 KV and 40 mA, using Ni-filtered Cu-Kα radiation.

X-ray photoelectron spectroscopy (XPS) spectra was performed with a Kratos Axis Ultra (DLD) photoelectron spectrometer operated at 15 kV and 10 mA at a pressure of about 5×10^{-9} torr using AlKα as the exciting source ($h\nu = 1486.6$ eV). C 1s photoelectron peak (BE = 284.2 eV) was used for the binding energy calibration.

Metal content in M(Por)OP samples were determined quantitatively by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on an IRIS Advantage 1000 instrument.

Thermogravimetry (TGA) and differential thermal analyses (DTA) of the (Por)OP and M(Por)OP (M = Zn, Co) were carried out in a TGA Instruments thermal analyzer TA-SDT Q-600.

^1H and $^{13}C\{^1H\}$ NMR spectra of (Por)OP were recorded on a Bruker Avance 300 solid-state NMR spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C.

^1H and $^{13}C\{^1H\}$ NMR spectra of propylene carbonate were recorded on Bruker AV III 400 at 25 °C.

Table 1 Properties of (Por)OP, Zn(Por)OP, and Co(Por)OP

Samples	Metal content [a] [mmol g^{-1}]	TGA stability [°C]	XPS binding energy [eV]
(Por)OP	/	up to 301	N(1s) 400.2 (−N=C−), 398.3 (−NH−)
Zn(Por)OP	0.33	up to 300	N(1s) 399.4; Zn($2p_{1/2}$) 1045.3, Zn($2p_{2/3}$) 1022.3
Co(Por)OP	0.51	up to 295	N(1s) 399.5; Co($2p_{1/2}$) 797.3, Co($2p_{2/3}$) 781.3

[a] Based on ICP-AES analysis.

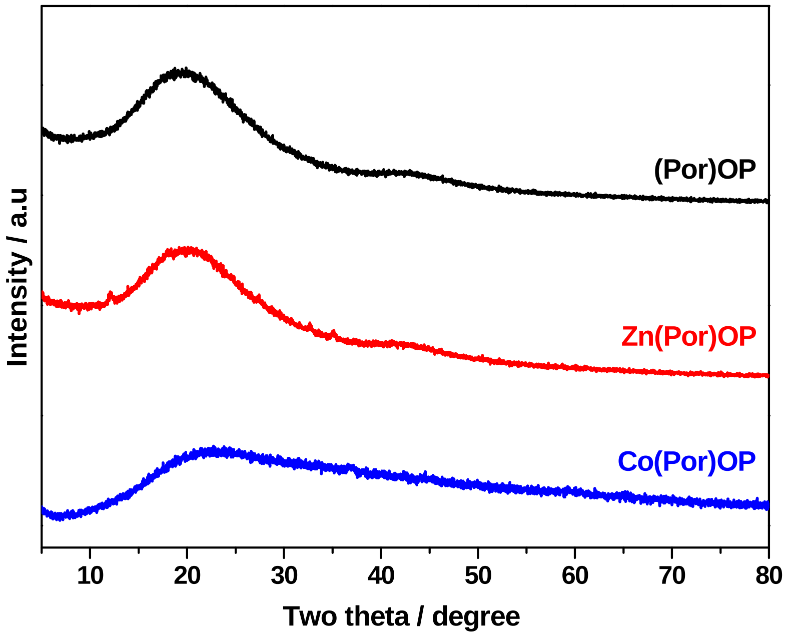

Figure S1 The XRD patterns of (Por)OP, Zn(Por)OP, and Co(Por)OP at wide angel showing broad diffraction for thick amorphous pore wall.

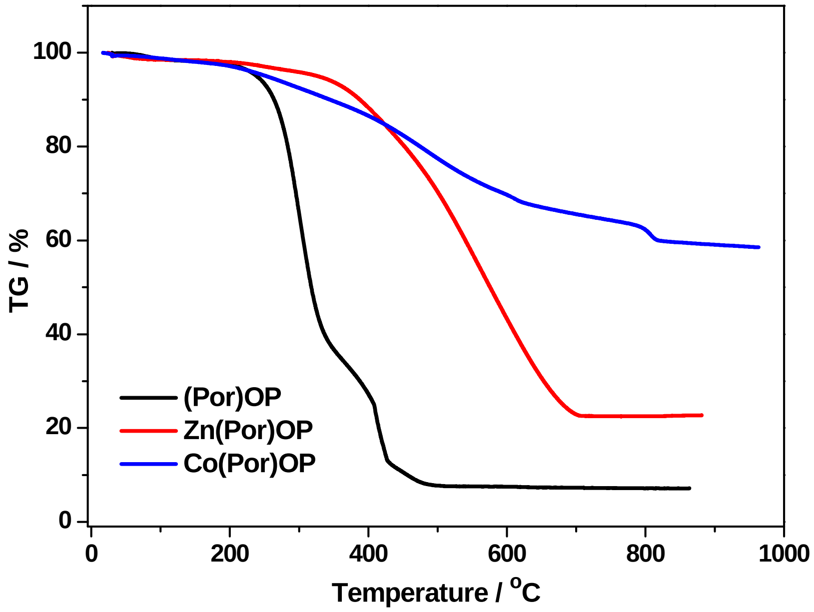

Figure S2. TGA of (Por)OP, Zn(Por)OP, and Co(Por)OP.

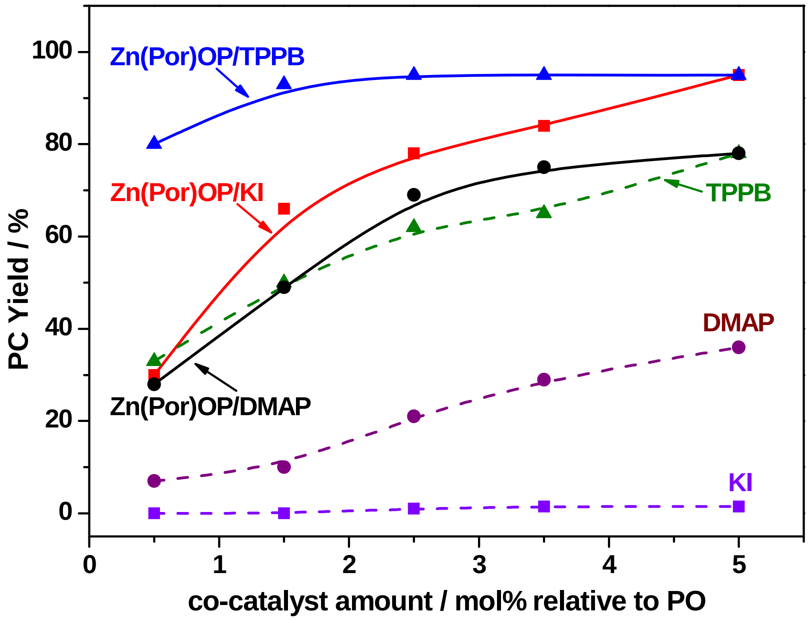

Figure S3. Effect of co-catalyst on the cycloaddition reaction of CO_2 to PO. Reaction conditions: PO (1.162 g, 20.0 mmol), Zn(Por)OP (60 mg, 0.02 mmol Zn, 0.01 mol% Zn relative to PO), co-catalyst [KI, DMAP, or TPPB (0.5−5.0 mol% relative to PO)], CH_2Cl_2 (4.0 mL), CO_2 (3.0 MPa), 120 °C, 2.5 h, in a 25 mL autoclave.

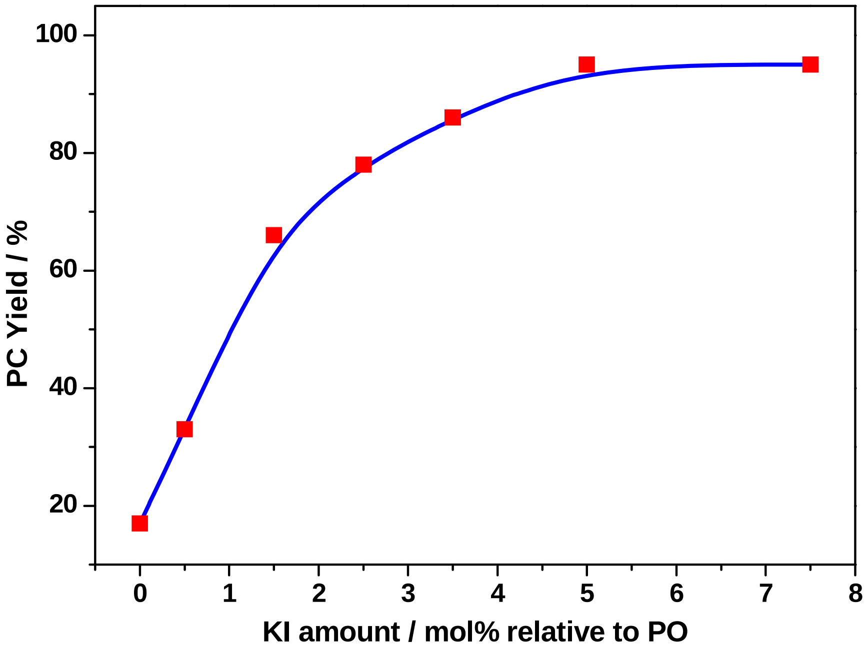

Figure S4. Effect of KI equivalents on the cycloaddition reaction of CO_2 and propylene oxide. Reaction conditions: PO (1.16 g, 20.0 mmol), Zn(Por)OP (60 mg, 0.02 mmol Zn, 0.01 mol% Zn relative to PO), co-catalyst KI (0−7.5 mol% relative to PO)], CH_2Cl_2 (4.0 mL), CO_2 (3.0 MPa), 120 °C, 2.5 h, in a 25 mL autoclave.

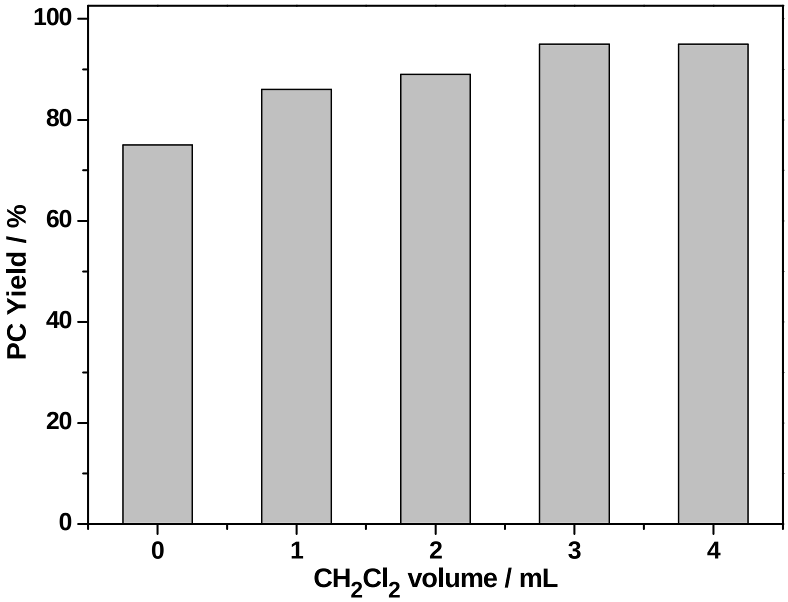

Figure S5. Effect of solvent volume on the cycloaddition reaction of CO_2 to PO. Reaction conditions: PO (1.162 g, 20.0 mmol), Zn(Por)OP (60 mg, 0.02 mmol Zn, 0.01 mol% Zn relative to PO), KI (1.0 mmol), CH_2Cl_2 (0−4.0 mL), CO_2 (3.0 MPa), 120 °C, 2.5 h, in a 25 mL autoclave.

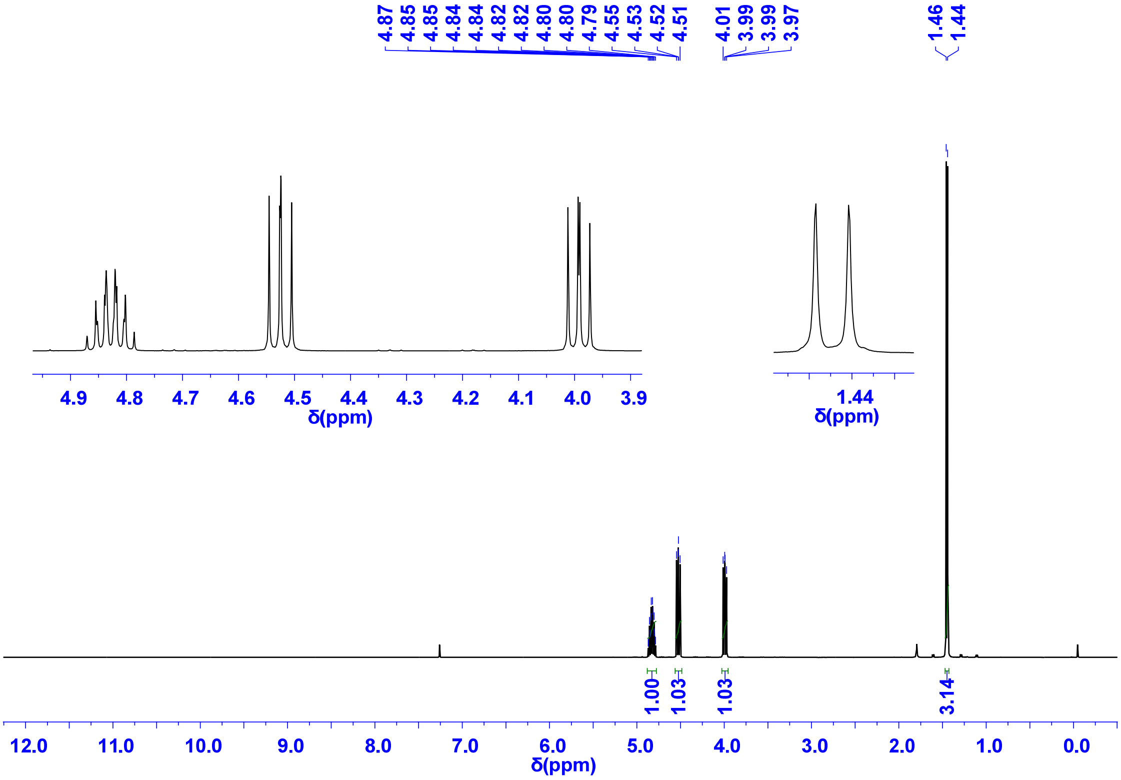

Figure S6. ^{1}H NMR of propylene carbonate in $CDCl_3$.

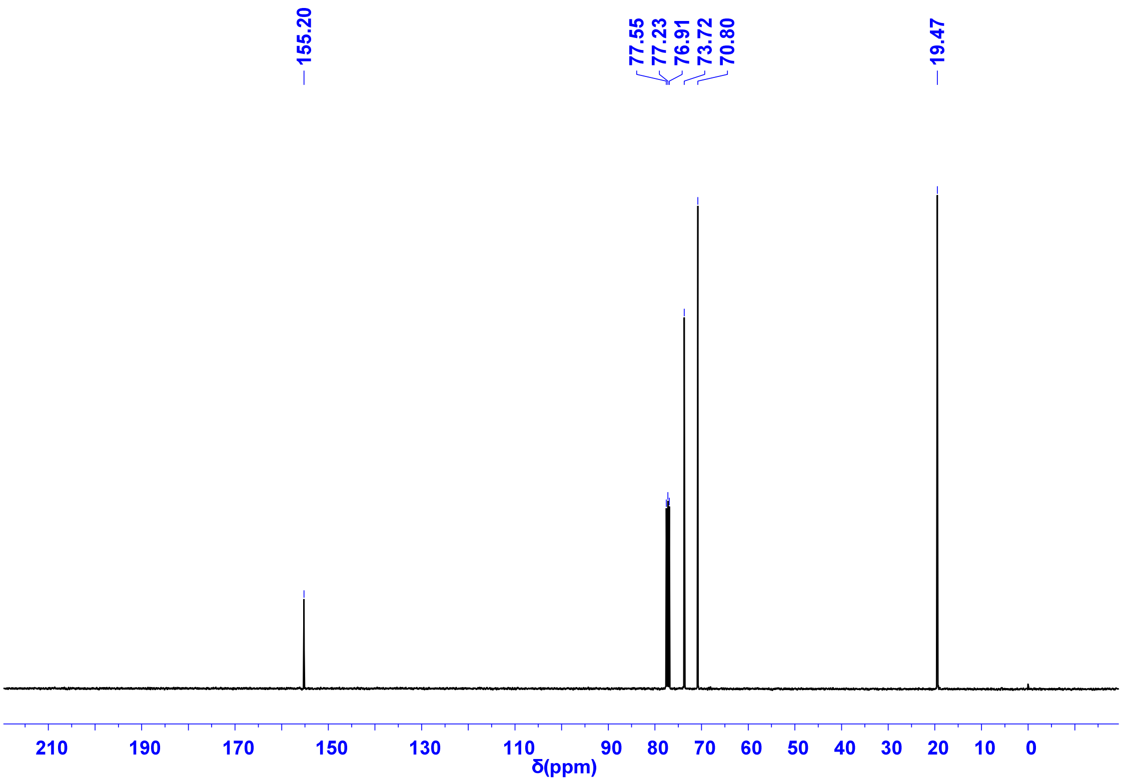

Figure S7. ^{13}C {^{1}H} NMR of propylene carbonate in $CDCl_3$.