Electronic Supplementary Information

Bifunctional Catalyst of Metallophthalocyanine-Carbon Nitride Hybrid for Chemical Fixation of CO_2 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.

Powder X-ray diffraction (XRD) patterns of MPc/g-C_3N_4 (M = Co, Cu) and g-C_3N_4 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 of MPc/g-C_3N_4 (M = Co, Cu) were 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 contents in MPc/g-C_3N_4 (M = Co, Cu) samples were determined quantitatively by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on an IRIS Advantage 1000 instrument.

^1H and $^{13}C\{^1H\}$ NMR spectra of 3-chloro-1,2-propylenecarbonate were recorded on Bruker AV III 400 at 25 ℃.

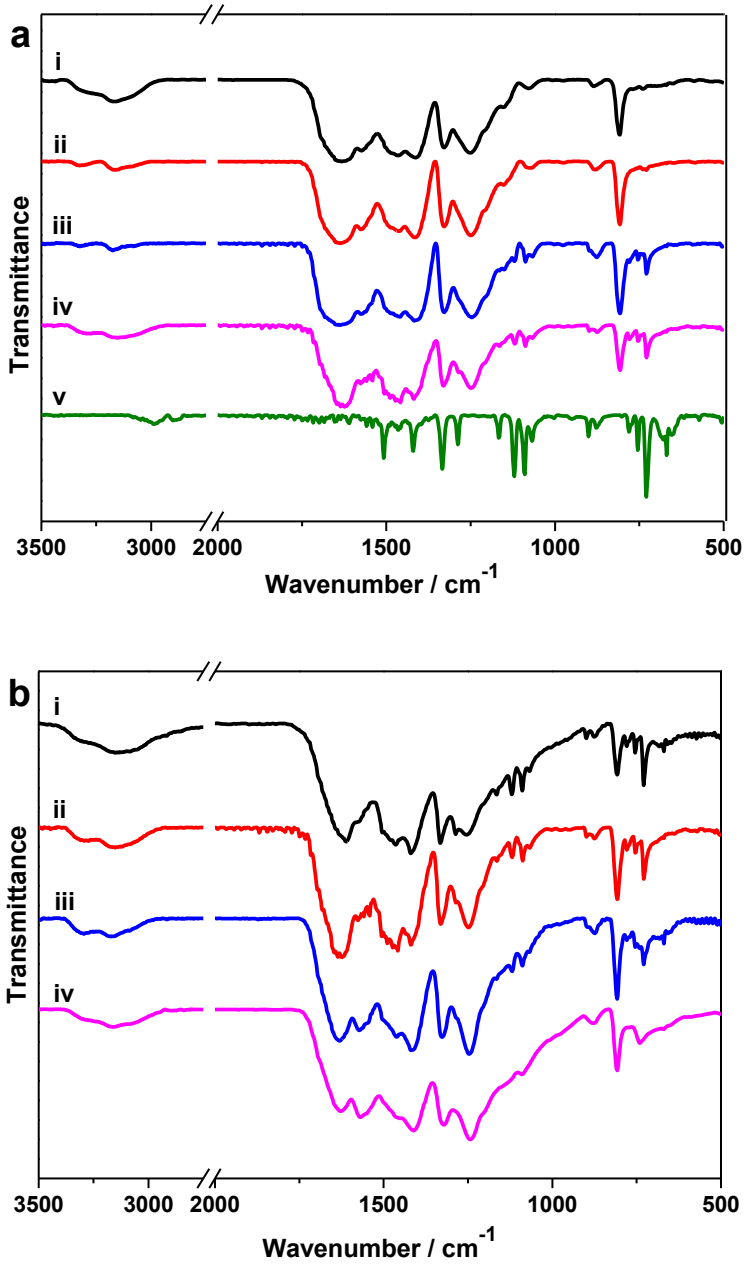

Figure S1. (a) FT-IR spectra of i) g-C_3N_4-480, ii) CuPc/g-C_3N_4-480 (0.15), iii) CuPc/g-C_3N_4-480 (0.39), iv) CuPc/g-C_3N_4-480 (0.78), v) CuPc; (b) FT-IR spectra of i) CuPc/g-C_3N_4-450 (0.72), ii) CuPc/g-C_3N_4-480 (0.80), iii) CuPc/g-C_3N_4-520 (0.74), and iv) CuPc/g-C_3N_4-550 (0.78).

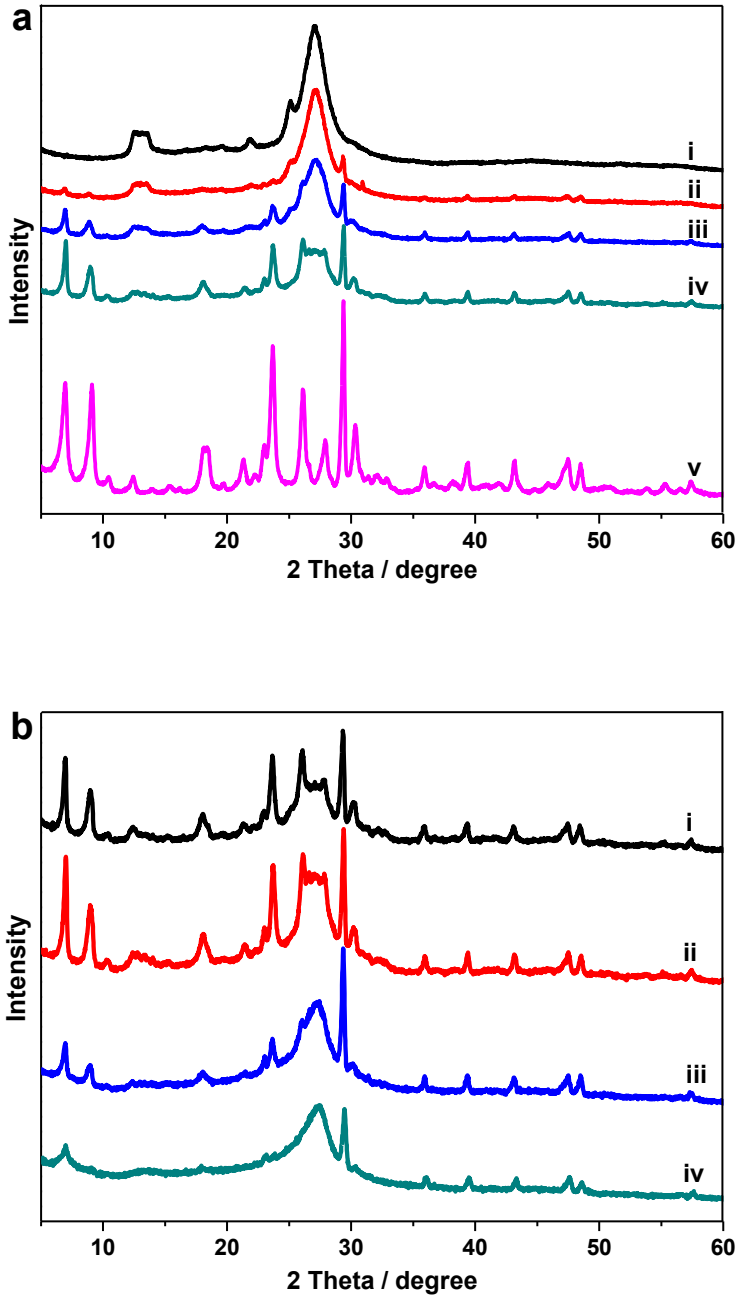

Figure S2. (a) XRD patterns of the i) g-C_3N_4-480, ii) CuPc/g-C_3N_4-480 (0.15), iii) CuPc/g-C_3N_4-480 (0.39), iv) CuPc/g-C_3N_4-480 (0.78), v) CuPc. (b) XRD patterns of i) CuPc/g-C_3N_4-450 (0.72), ii) CuPc/g-C_3N_4-480 (0.80), iii) CuPc/g-C_3N_4-520 (0.74), and iv) CuPc/g-C_3N_4-550 (0.78).

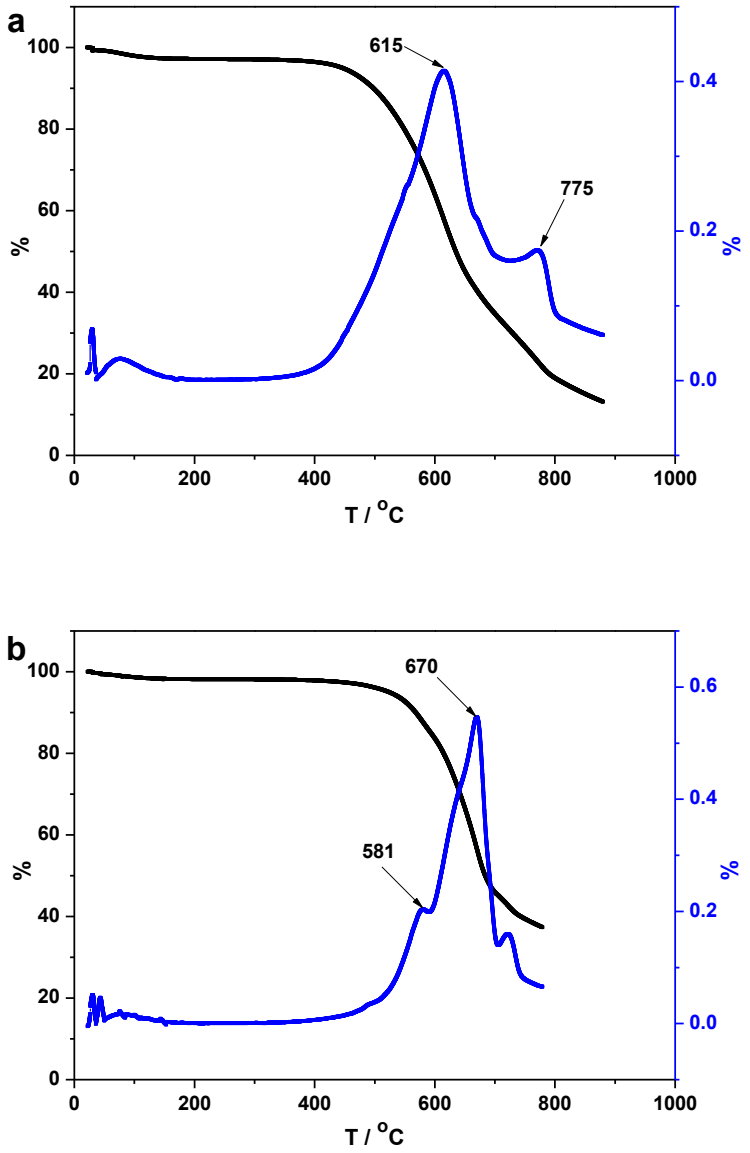

Figure S3. TGA of (a) CoPc/g-C_3N_4-480 (0.66) and (b) CuPc/g-C_3N_4-480 (0.75).

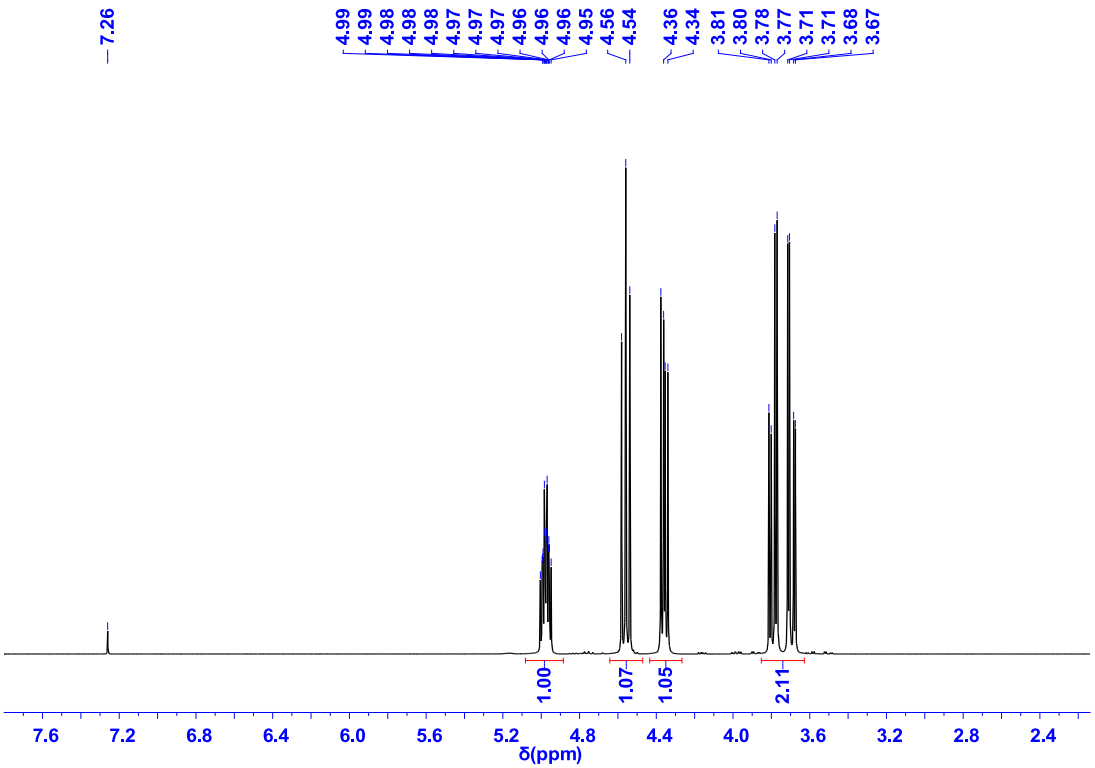

Figure S4. ^{1}H NMR of 3-chloro-1,2-propylenecarbonate in $CDCl_3$.

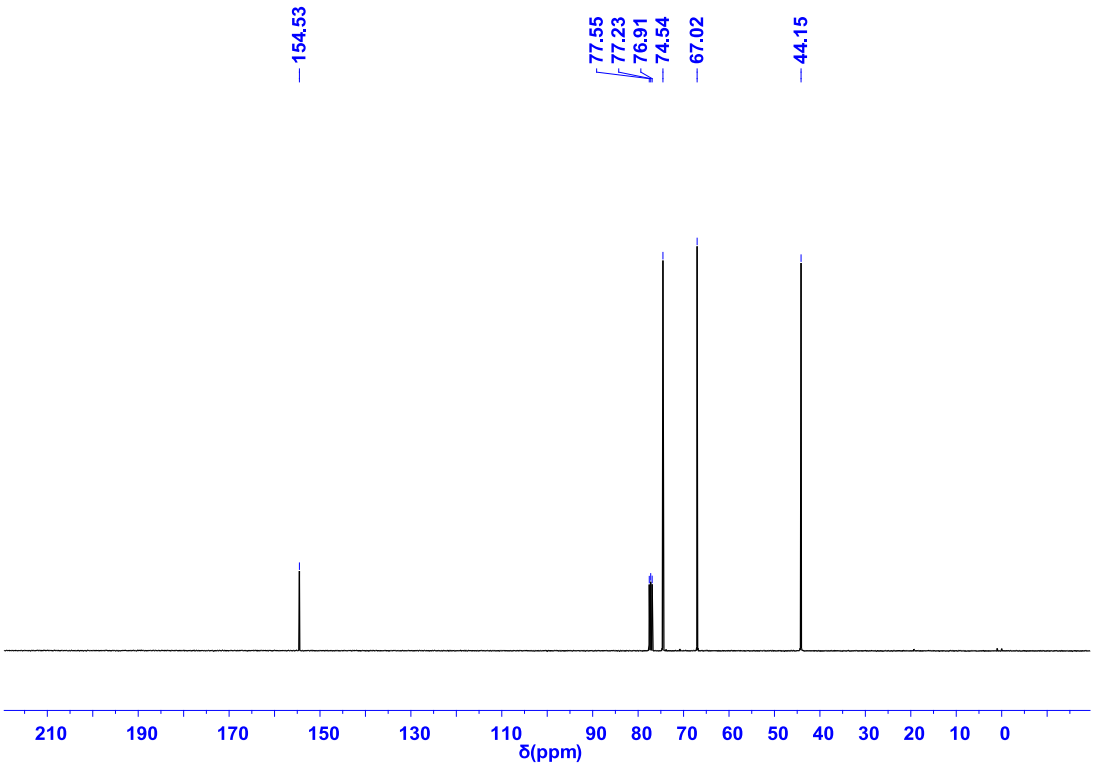

Figure S5. ^{13}C {^{1}H} NMR of 3-chloro-1,2-propylenecarbonate in $CDCl_3$.

CPC: ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$) δ 4.98 (dddd, *J* = 8.4, 5.7, 4.8, 3.7 Hz, 1H), 4.64–4.47 (m, 1H), 4.36 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.74 (ddd, *J* = 16.0, 12.3, 4.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, 25 °C, $CDCl_3$) δ 154.5, 74.5, 67.0, 44.1.