Electronic Supplementary Information

Bifunctional Catalyst of Metallophthalocyanine-Carbon Nitride Hybrid for Chemical Fixation of CO$_2$ to Cyclic Carbonate

Ting Zhang,$^{a,b}$ Xuefeng Wang,$^a$ Xueli Huang,$^a$ Yinnian Liao$^a$ and Jinzhu Chen$^{a,b}$

$^a$ Key Laboratory of Xinjiang Coal Clean Conversion and Chemical Process, College of Chemistry and Chemical Engineering, Xinjiang University. Urumqi, Xinjiang 830046 (PR China).

$^b$ CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. Guangzhou 510640 (PR China).

* Corresponding author, Tel./Fax: (+86)-20-3722-3380, E-mail address: chenjz@ms.giec.ac.cn (J. Chen)
Materials

Unless otherwise stated, all chemicals in this research were commercial available and used without further purification. Propylene oxide (PO), zinc acetate [Zn(OAc)$_2$·2H$_2$O], cobalt acetate [Co(OAc)$_2$·2H$_2$O], 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$_3$N$_4$ (M = Co, Cu) and g-C$_3$N$_4$ were obtained with a PANalytical X’pert Pro MPD diffractometer operated at 40 KV and 40 mA, using Ni-filtered Cu-K$\alpha$ radiation.

X-ray photoelectron spectroscopy (XPS) spectra of MPc/g-C$_3$N$_4$ (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 AlK$\alpha$ 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$_3$N$_4$ (M = Co, Cu) samples were determined quantitatively by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis on an IRIS Advantage 1000 instrument.

$^1$H and $^{13}$C$\{^1$H$\}$ NMR spectra of 3-chloro-1,2-propylene carbonate were recorded on Bruker AV III 400 at 25 °C.
Figure S1. (a) FT-IR spectra of i) g-C₃N₄-480, ii) CuPc/g-C₃N₄-480 (0.15), iii) CuPc/g-C₃N₄-480 (0.39), iv) CuPc/g-C₃N₄-480 (0.78), v) CuPc; (b) FT-IR spectra of i) CuPc/g-C₃N₄-450 (0.72), ii) CuPc/g-C₃N₄-480 (0.80), iii) CuPc/g-C₃N₄-520 (0.74), and iv) CuPc/g-C₃N₄-550 (0.78).
Figure S2. (a) XRD patterns of the i) g-C₃N₄-480, ii) CuPc/g-C₃N₄-480 (0.15), iii) CuPc/g-C₃N₄-480 (0.39), iv) CuPc/g-C₃N₄-480 (0.78), v) CuPc. (b) XRD patterns of i) CuPc/g-C₃N₄-450 (0.72), ii) CuPc/g-C₃N₄-480 (0.80), iii) CuPc/g-C₃N₄-520 (0.74), and iv) CuPc/g-C₃N₄-550 (0.78).
Figure S3. TGA of (a) CoPc/g-C₃N₄-480 (0.66) and (b) CuPc/g-C₃N₄-480 (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$_3$) $\delta$ 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$_3$) $\delta$ 154.5, 74.5, 67.0, 44.1.