Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Selective CO_2 Capture in an Imine Linked Porphyrin Porous Polymer

Venkata S. Pavan K. Neti,[a] Xiaofei Wu,[b] Shuguang Deng,[b] and Luis Echegoyen *[a]

[a] Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States
[b] Department of Chemical Engineering, New Mexico State University, Las Cruces, NM, United States

[a] E-mail: echegoyen@utep.edu, Tel/Fax: +1 (915) 747-7573/(915) 747-8807

Contents

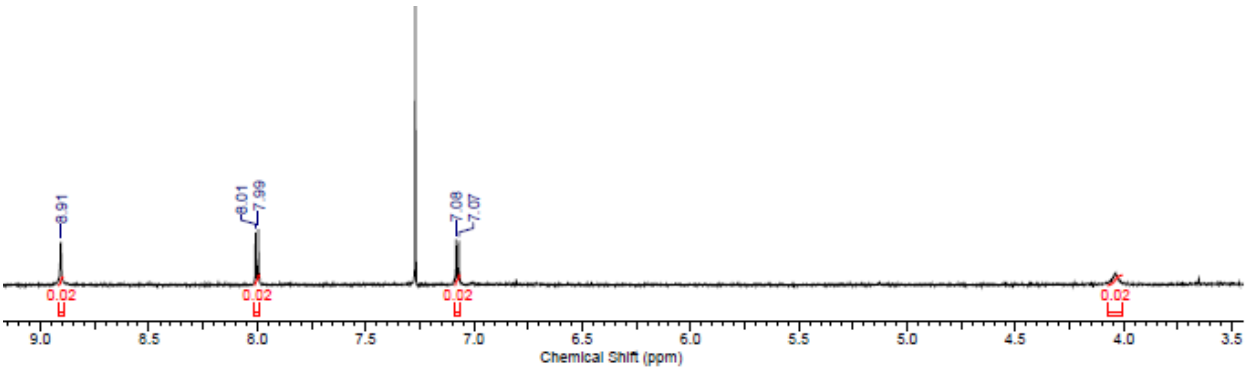
Section A. Materials and methods:

All chemicals and solvents were purchased from Sigma-Aldrich. Fourier transform Infrared (FT-IR) spectra were recorded on a Perkin-Elmer Spectrum one infrared spectrometer (ATR). Field-emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S-4800 fitted with an EDAX energy- dispersive spectrometry system by adhering sample on a sampling platform. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on Bruker benchtop microflex model using matrix trihydroxyanthracene. In order to determine pore textural properties including the specific Brunauer–Emmet–Teller (BET) surface area, pore volume and pore size distribution, nitrogen adsorption and desorption isotherm on CuPor-BPDC sample at 77 K were measured in an ASAP-2020 adsorption apparatus (Micromeritics). The as-synthesized samples were degassed in situ at 150°C with a heating rate of 3°C /min under a vacuum (0.0001 mmHg) for 12 h before nitrogen adsorption measurements in order to ensure the micro-channels in the structure were guest-free. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas by using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. Thermogravimetric analysis from 30-700°C was carried out on a Mettler-Toledo thermogravimetric analyzer in an N_2 atmosphere using a 3°C/min ramp time. Powder X-ray diffraction (PXRD) data were recorded on a Bruker DiscoverD8 model diffractometer by depositing powder on plastic substrate, from $2\theta = 1°$ up to 30° with 0.05° increment.

Section B. Synthetic procedures

Synthesis of meso-tetraphenylamino porphyrin Cu(II)

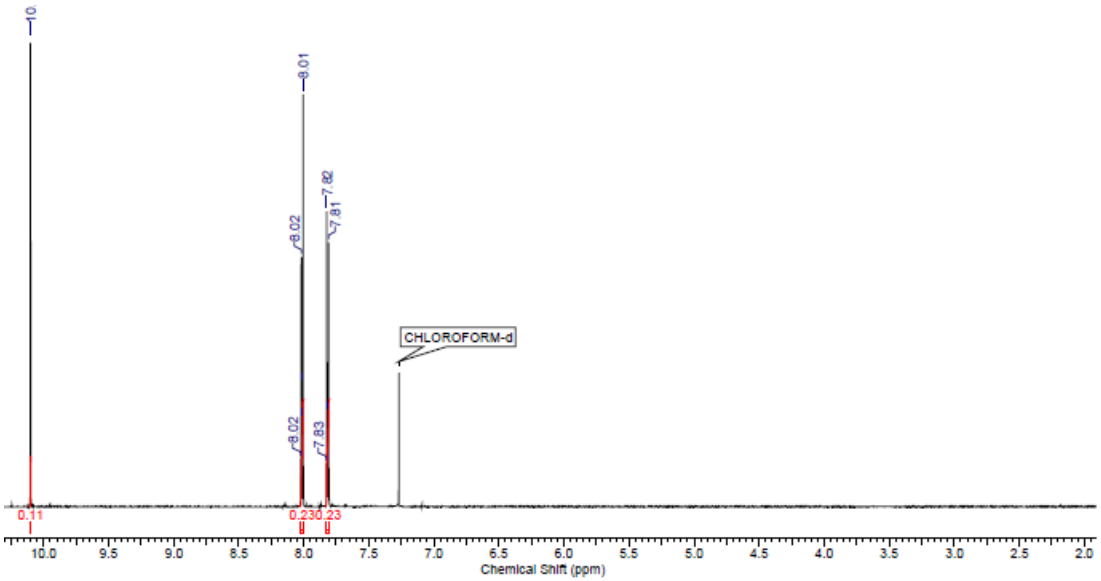
Meso-tetraphenylamino porphyrin was synthesized using a literature procedure,[1,2,3] obtained as a purple solid. MALDI TOF-MS (THA): calcd. (found) for $[M+H]^+$: 735.204 (736.432).



^{1}H NMR spectrum of Meso-tetraphenylamino porphyrin Cu (II) (600 MHz, $CDCl_3$, 298K)

Synthesis of 4, 4'- biphenyl dicarboxaldehyde

4, 4'- biphenyl dicarboxaldehyde was prepared using a literature procedure,[4] and obtained as a white solid.



^{1}H NMR spectrum of 4, 4'- biphenyl dicarboxaldehyde (600 MHz, $CDCl_3$, 298K)

Synthesis of CuPor-BPDC. 0.5ml of Mesitylene/0.5ml of absolute ethanol/0.1 ml of 6 M acetic acid were added to the mixture of CuPor (0.02 mmol, 14.7 mg) and BPDC (8.4 mg, 0.04 mmol), sonicated and degassed in a Pyrex ampoule (5 mL) using liquid N_2 bath. The ampoule was sealed off and heated at 120°C for 3 days. The precipitate at the bottom was filtered and washed with anhydrous dioxane and THF. The purple powder was dried at 100°C under vacuum overnight to give the corresponding partially crystalline polymer in 69% yield. Elemental analysis (%) calcd. for CuPor-BPDC $(C_{116}H_{68}N_{16}Cu)_n$. Theory: C, 76.85; H, 3.78; N, 12.36; found C, 75.95; H, 4.30; N, 11.48, respectively.

Section C. FT-IR spectral profiles

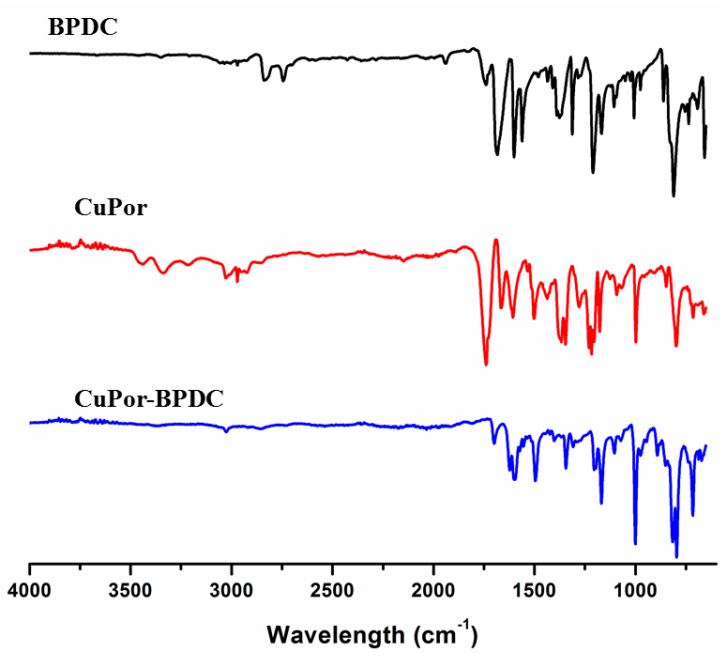


Figure S1. IR spectra of BPDC, meso-tetraphenylamino porphyrin, and CuPor-BPDC.

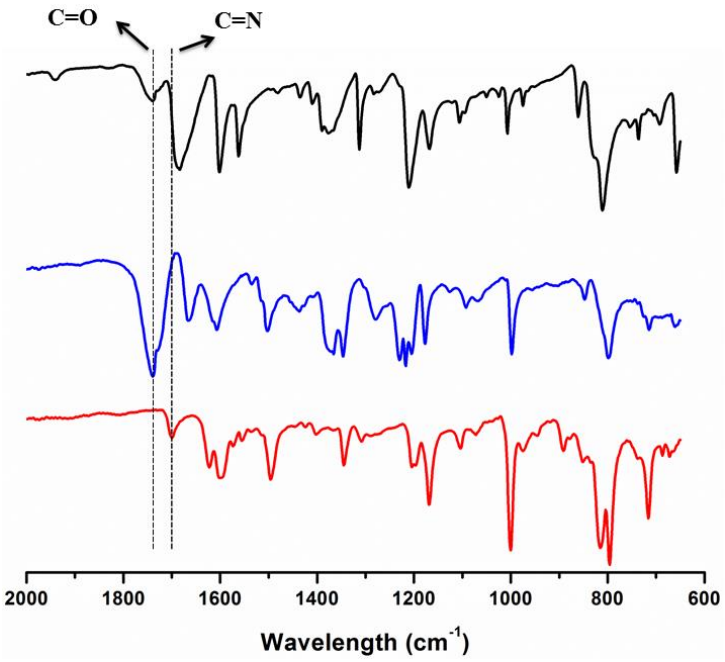


Figure S2. Expanded IR spectra of BPDC (black), meso-tetraphenylamino porphyrin (blue) and CuPor-BPDC (red).

Section D. Solid-state ^{13}C CP-MAS NMR spectrum

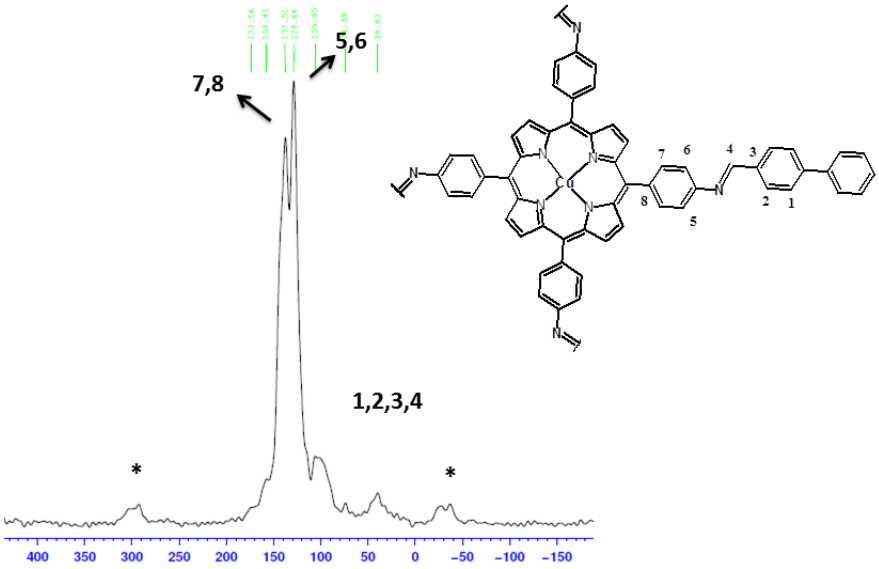


Figure S3. Solid state ^{13}C CP-MAS NMR spectrum of CuPor-BPDC recorded at a MAS rate of 10 kHz. Signals with * are residual solvent and side bands.

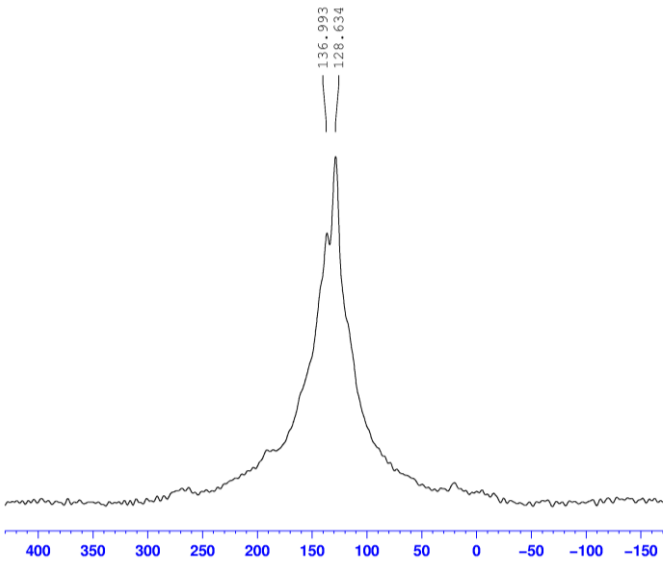


Figure S4. Solid state ^{13}C CP-MAS NMR spectra of meso-tetraphenylamino porphyrin recorded at a MAS rate of 10 kHz.

Section E: UV-Vis absorption spectra

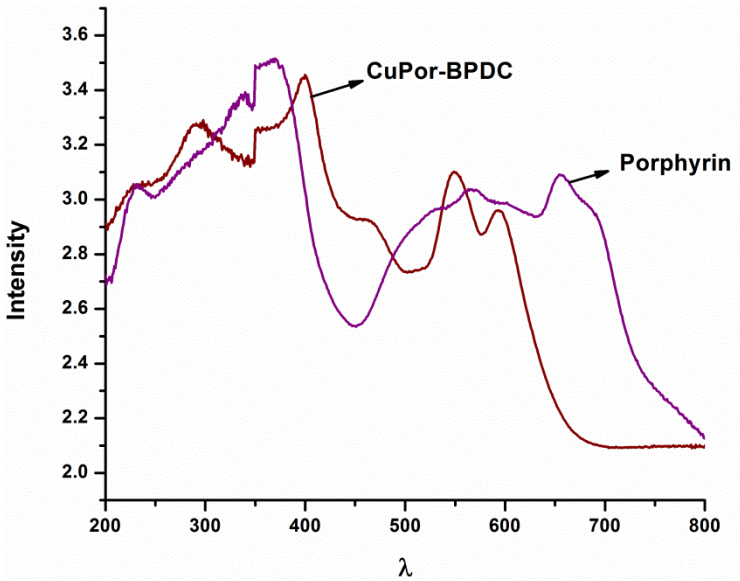


Figure S6: Solid-state absorption spectra CuPor-BPDC (wine), CuPor (purple) as powders using a praying mantis diffuse reflectance accessory. Small, jagged peaks around 340nm are due to instrument lamp shift.

Section F: Thermogravimetric Analysis

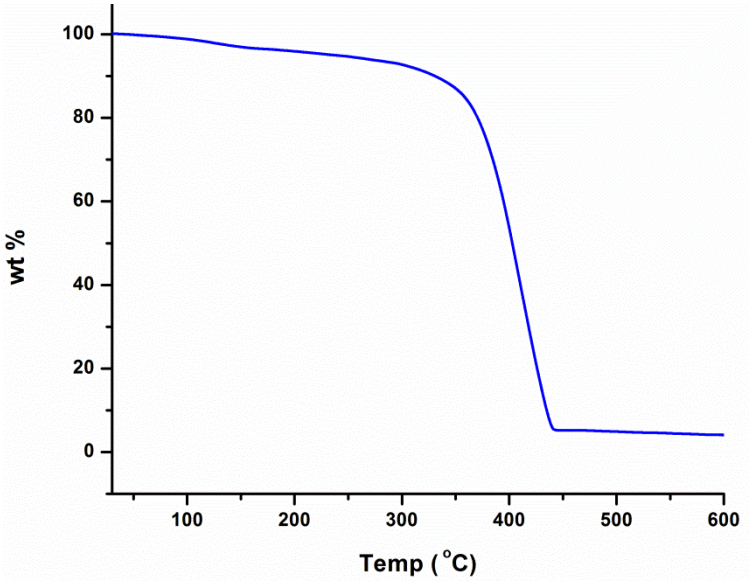


Figure S7. TGA of CuPor-BPDC obtained up to 600°C using a linear 3°C/min ramp method.

Section G. Surface Area Measurements

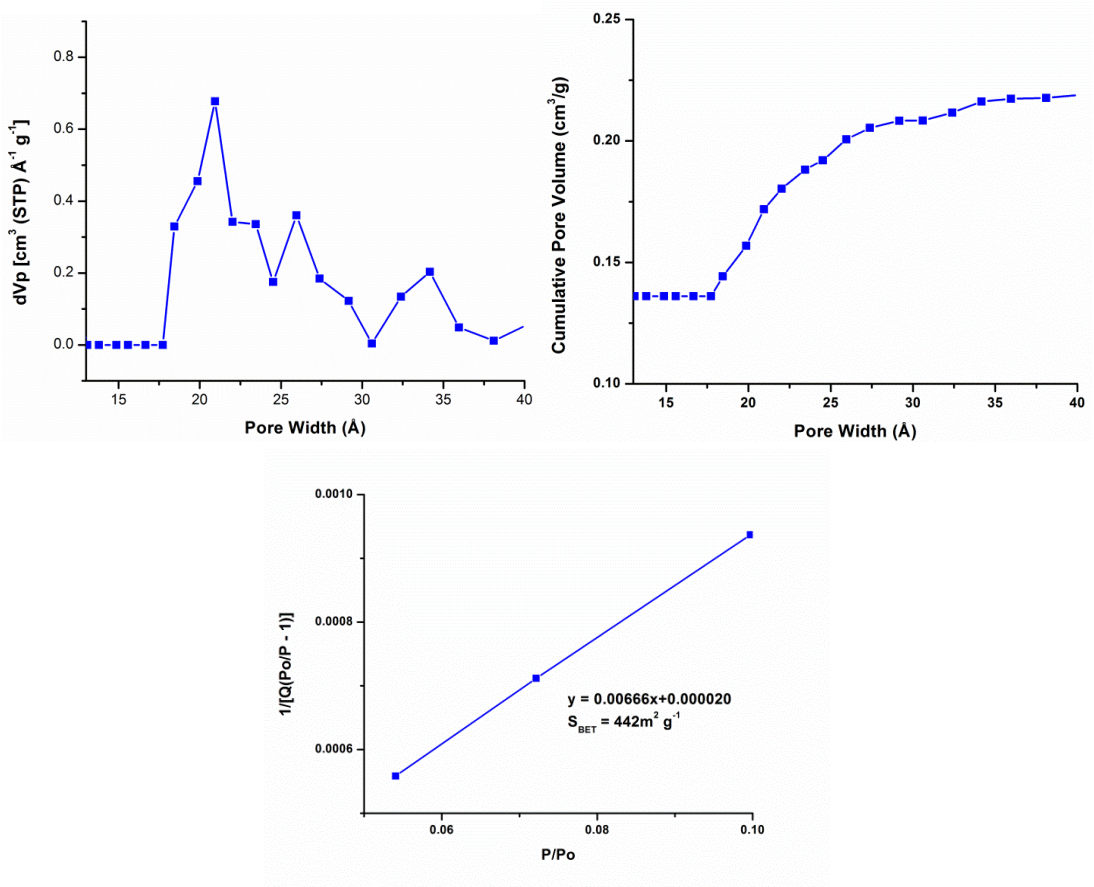


Figure S8. Differential (top left) and cumulative (top right) pore size distribution plot of CuPor-BPDC from the application of the NLDFT model to the N_2 isotherm. BET plot (below) for CuPor-BPDC calculated from isotherm data.

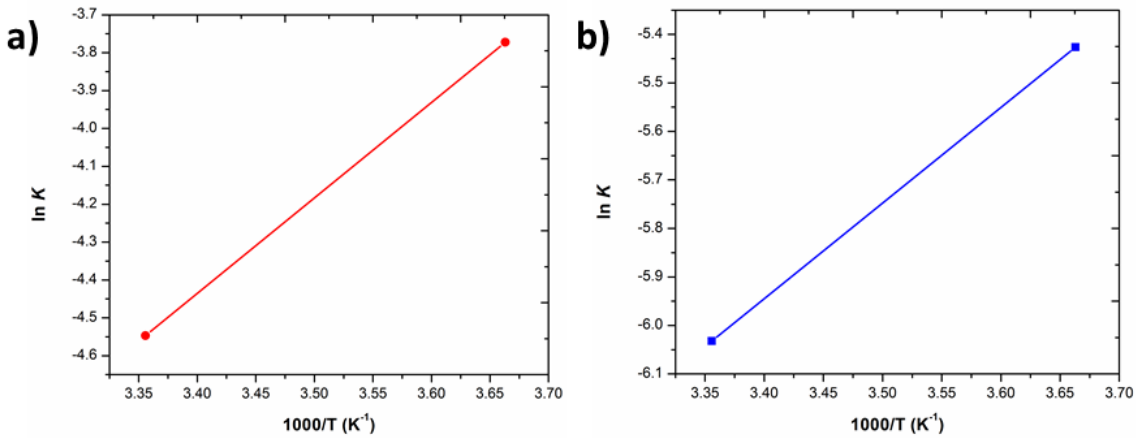


Figure S9. Van't Hoff plots of CO_2 (red) and CH_4 (blue).

Calculation of isosteric heat of adsorption

The adsorption enthalpy at zero coverage was calculated from Henry constant using the Van't Hoff equation as

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

K is Henry constant, T is temperature, plotting ln *K* v.s. 1000/T

Section H: Supporting References

1) A. Bettelheim, *et al. Inorg. Chem.,* **26**, 1987, 1009.

2) M. Yuasa, *et al. J. Am. Chem. Soc.*, **126**, 2004.

3) A. Tsuda, *et al. Angew. Chem., Int. Ed.* **43**, 2004, 6327.

4) Kunpeng Guo, *et al. Org. Lett*, 14, 2012, 2214.