Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Synthesis of a benzothiazole nanoporous polymer for selective CO_2 adsorption

Venkata S. Pavan K. Neti,[a] Xiaofei Wu, [b] Ping Peng,[a] 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

Section B. Synthetic procedures

Section C. FT-IR spectral profiles

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

Section E: powder X-ray diffraction profile

Section F. Surface Area Measurements

Section G. Thermogravimetric analysis

Section H: Scanning electron microscope image

Section I: References

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 IBTP 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 1,3,5 tris (4-formylphenyl)-benzene

1,3,5 tris (4-formylphenyl)-benzene was synthesized using a literature procedure,[1] obtained as a white solid. ^{1}H NMR (600 MHz, 298K, $CDCl_3$): δ 10.15 (s, 3H), 8–8.1 (dd, 6H), 7.89 (3H, s), 7.81-7.89 (dd, 6H).

Synthesis of 2,6-diaminobenzo bisthiazole

2,6-diaminobenzo bisthiazole was prepared using a literature procedure,[2] and obtained as a yellow solid. ^{1}H NMR (600 MHz, 298K, DMSO-d_8): δ 7.25 (br, 4H), 7.57 (s, 2H).

Synthesis of IBTP. 5ml of DMSO was added to the mixture of 1,3,5 tris (4-formylphenyl)-benzene (0.2 mmol, 78 mg) and 2,6-diaminobenzo bisthiazole (66 mg, 0.3 mmol) and then refluxed the yellow color homogeneous mixture for 3 days. The dark brown precipitate was filtered and washed with DMSO, dichloromethane, acetone and tetrahydrofuran. The brown powder was dried at 120˚C under vacuum overnight to give the corresponding polymer in 72% yield. Elemental analysis (%) calcd. for IBTP, theory: C, 67.8; H, 2.65; N, 11.40; found C, 69.57; H, 2.43; N, 12.86, respectively.

Section C. FT-IR spectral profiles

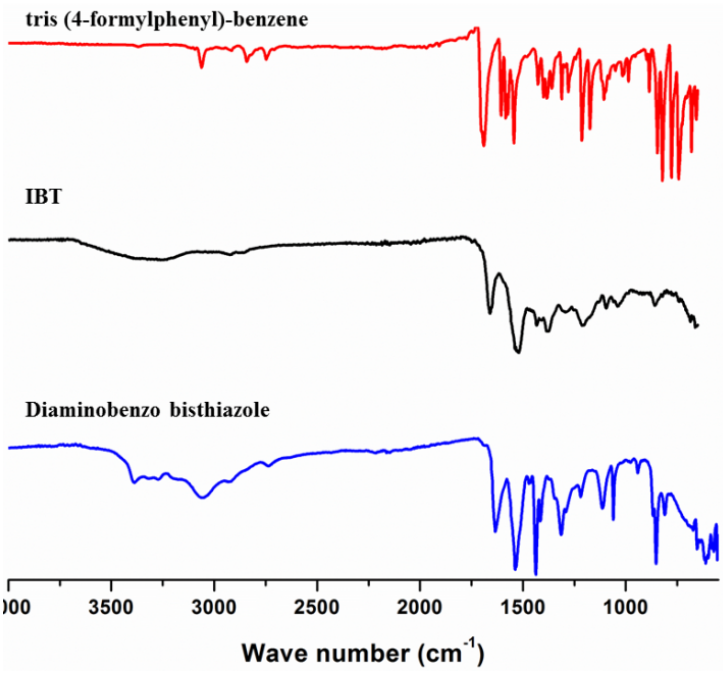

Figure S1. IR spectra of 1,3,5 tris (4-formylphenyl)-benzene and 2,6-diaminobenzo bisthiazole and IBTP.

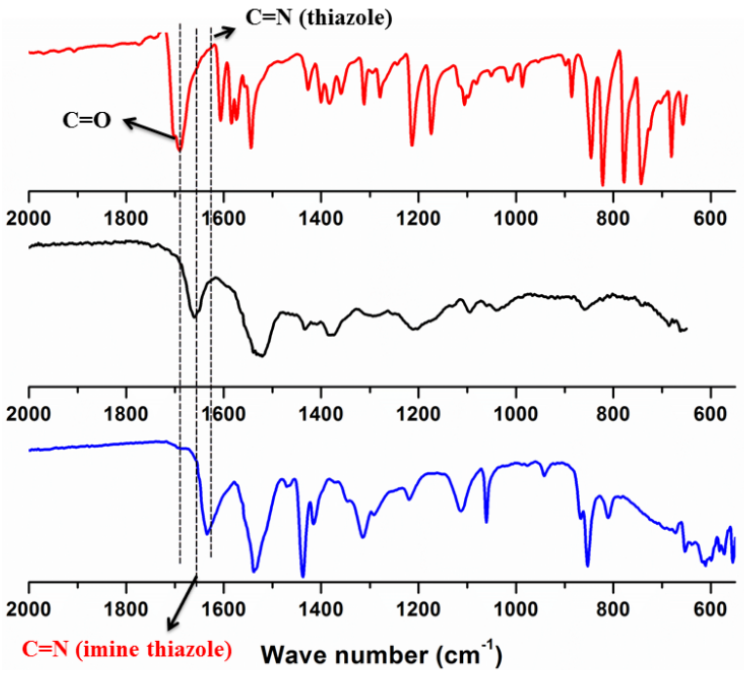

Figure S2. Expanded IR spectra of 1,3,5 tris (4-formylphenyl)-benzene and 2,6-diaminobenzo bisthiazole and IBTP.

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

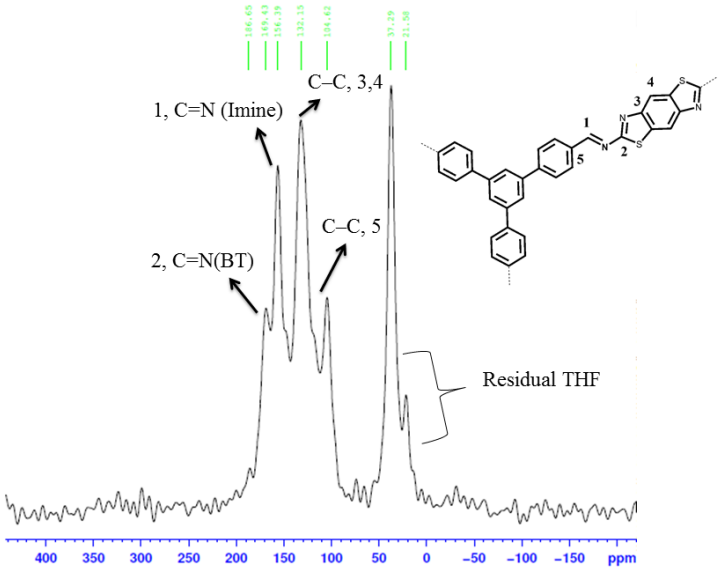

Figure S3. Solid state ^{13}C CP-MAS NMR spectrum of IBTP recorded at a MAS rate of 10 kHz.

Section E. powder X-ray diffraction pattern

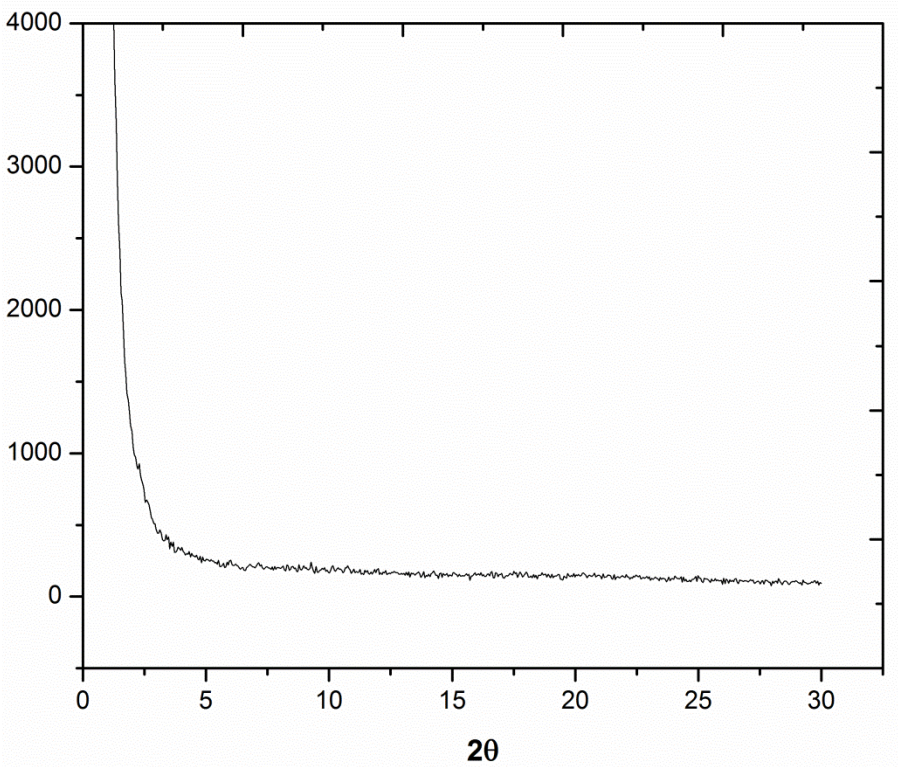

Figure S4. Powder X-ray diffraction pattern of IBTP. No intensive diffraction peaks were observable.

Section F. Surface Area Measurements

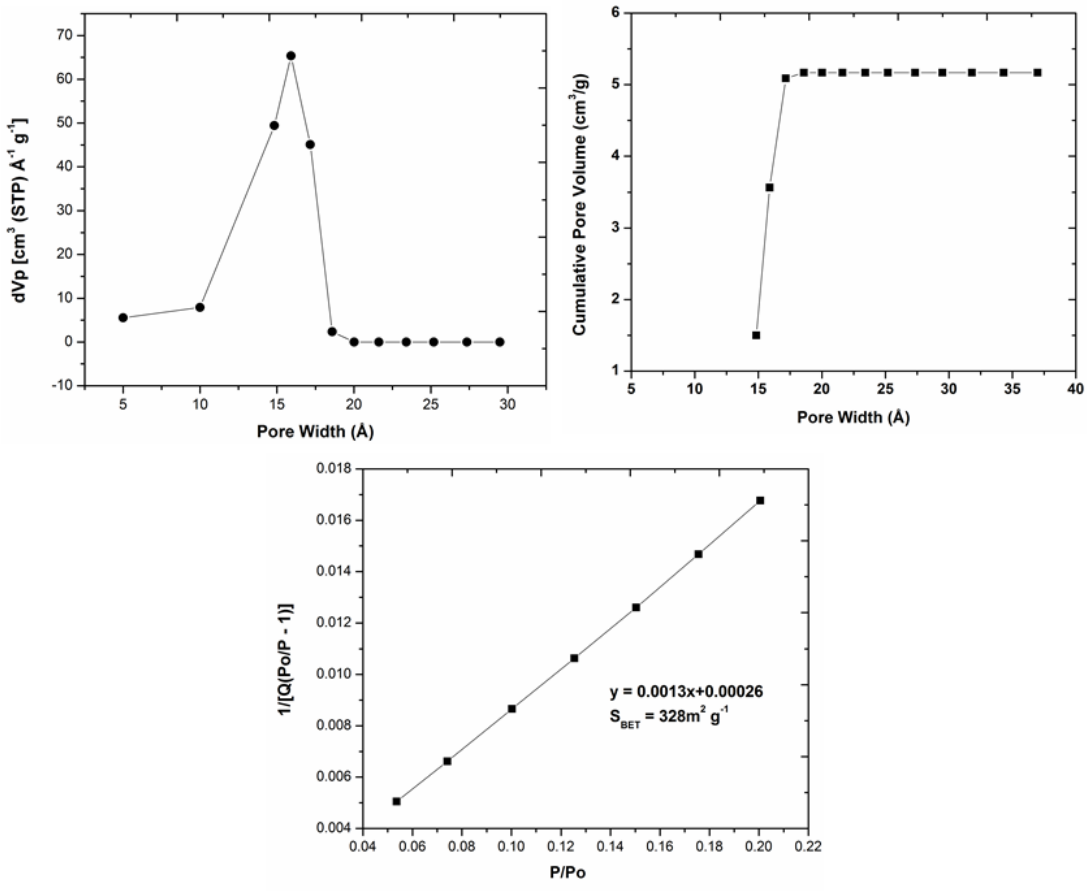

Figure S5. Differential (top left) and cumulative (top right) pore size distribution plot of IBTP from the application of the NLDFT model to the N_2 isotherm. BET plot (below) for IBTP calculated from isotherm data.

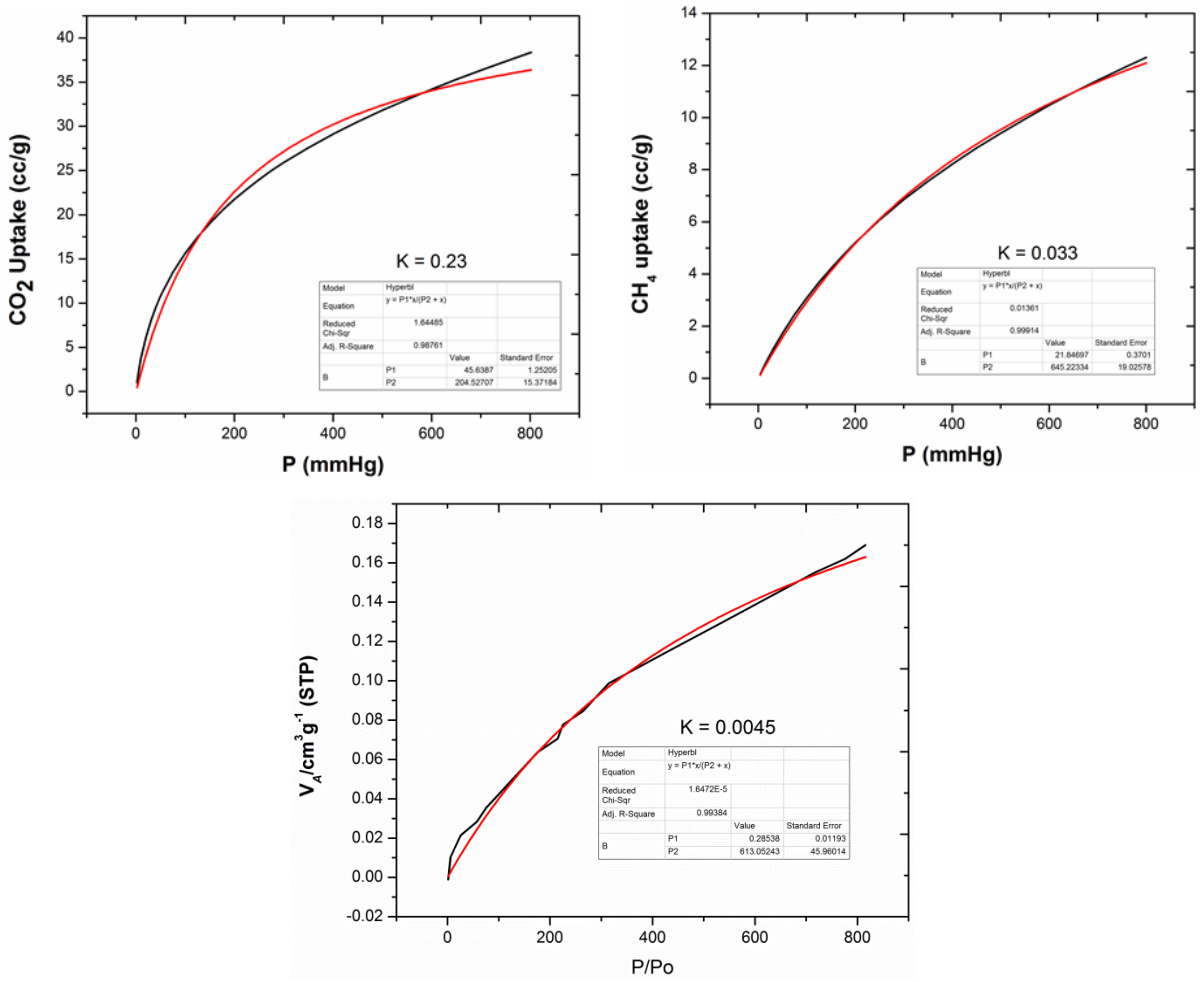

Figure S6. Langmuir model fits for CO_2, CH_4 and N_2 adsorption of IBTP at 273K.

Henry's constant by the product of Langmuir constants, that is K=a*b. K1 (273K) and K2 (298K), *ln* K vs 1/T (below). Van't Hoff equation is used to get Q_{st} at zero coverage.

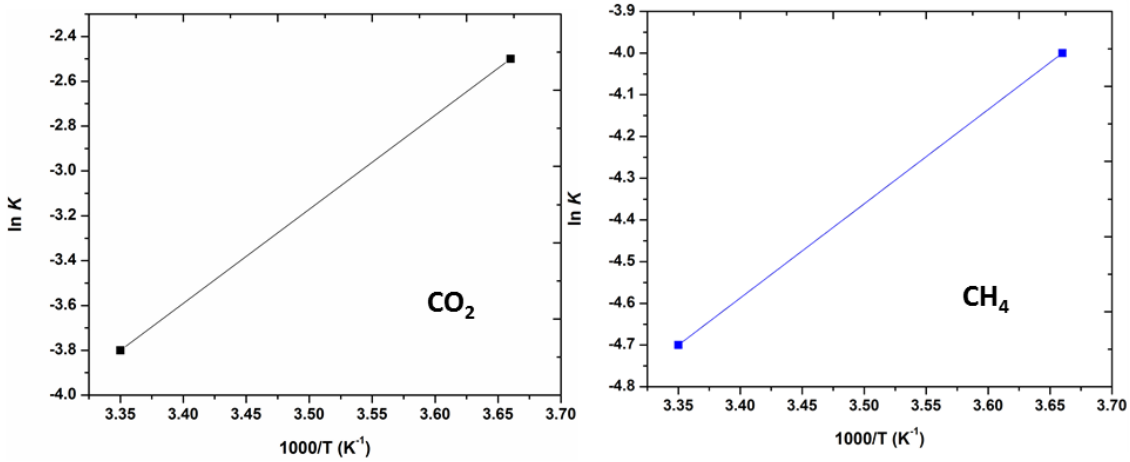

Figure S7. Van't Hoff plots of isosteric heat of adsorption for CO_2 (black) and CH_4 (blue).

Calculation of isosteric heat of adsorption

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

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

K is the Henry's constant, T is the temperature, plotting *ln K* vs. 1000/T

Section G: Thermogravimetric Analysis

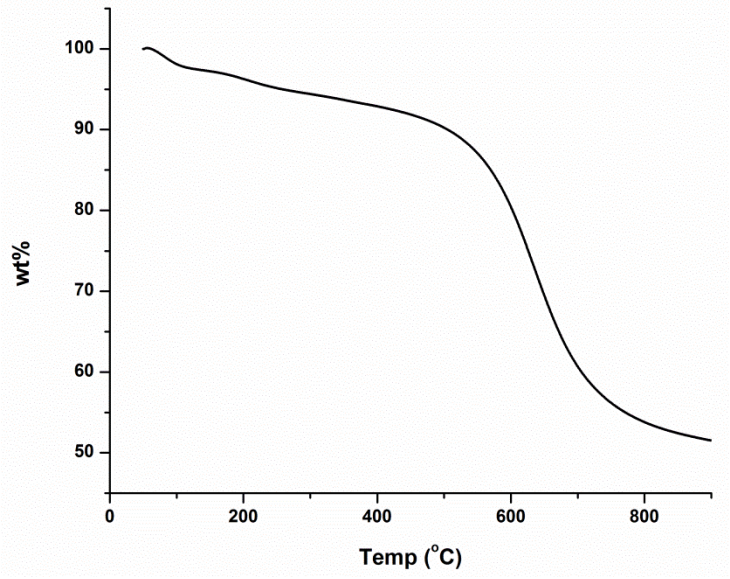

Figure S8. TGA of IBTP obtained up to 900°C using a linear 5°C/min ramp method.

Section H: Scanning electron microscope image

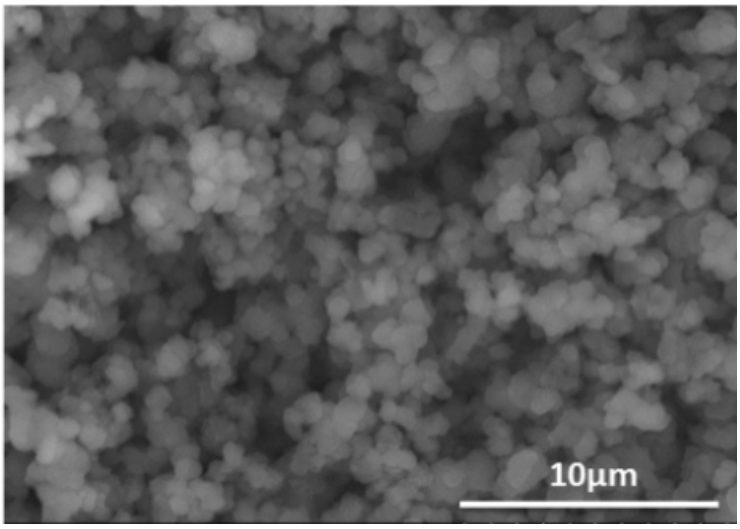

Figure S8. Scanning electron microscope image of the IBTP.

Section H: Supporting References

1) E. Weber *et al. J. Chem. Soc.,* Perkin Transactions 2: Physical Organic Chemistry, 1988, **7**, 1251-7.

2) J. F. Wolfe *et al. Macromolecules,* 1981**, 14,** 915-920.