

## Supplementary Information

### **Selective CO<sub>2</sub> adsorption in a porphyrin polymer with benzimidazole linkages**

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## **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 PBILP 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<sub>2</sub> atmosphere using a 3°C/min ramp time.

## Section B. Synthetic procedures

*Meso-tetra-(4-methoxycarbonylphenyl) porphyrin* and *meso-tetra-(4-hydroxymethylphenyl) porphyrin* can be easily obtained following the previous literature procedure (Tetrahedron Letters, 31, 1990, 4739-42). Benzene-1,2,4,5-tetramine (**2**) was purchased from Sigma-Aldrich.

### ***Synthesis of meso-tetra-(4-formylphenyl) porphyrin***

*Meso-tetra-(4-hydroxymethylphenyl) porphyrin* (300 mg, 0.4mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (600 mL) under argon and was added pyridinium chlorochromate (860 mg, 4mmol) and stirred for 3h at room temperature. The mixture was filtered and concentrated, and purified using silica-gel column chromatography to give a purple powder. (190 mg, ~60%). <sup>1</sup>H NMR (600 MHz, 298K, CDCl<sub>3</sub>): δ 10.2 (s, 4H), 8.6–8.5 (d, 8H), 7.9-7.8 (d, 8H), 4.2-4.3 (s, 8H), –2.8 (s, 2H). MALDI TOF-MS (THA): calcd. (found) for [M+H]<sup>+</sup>: 726.23 (727.52).

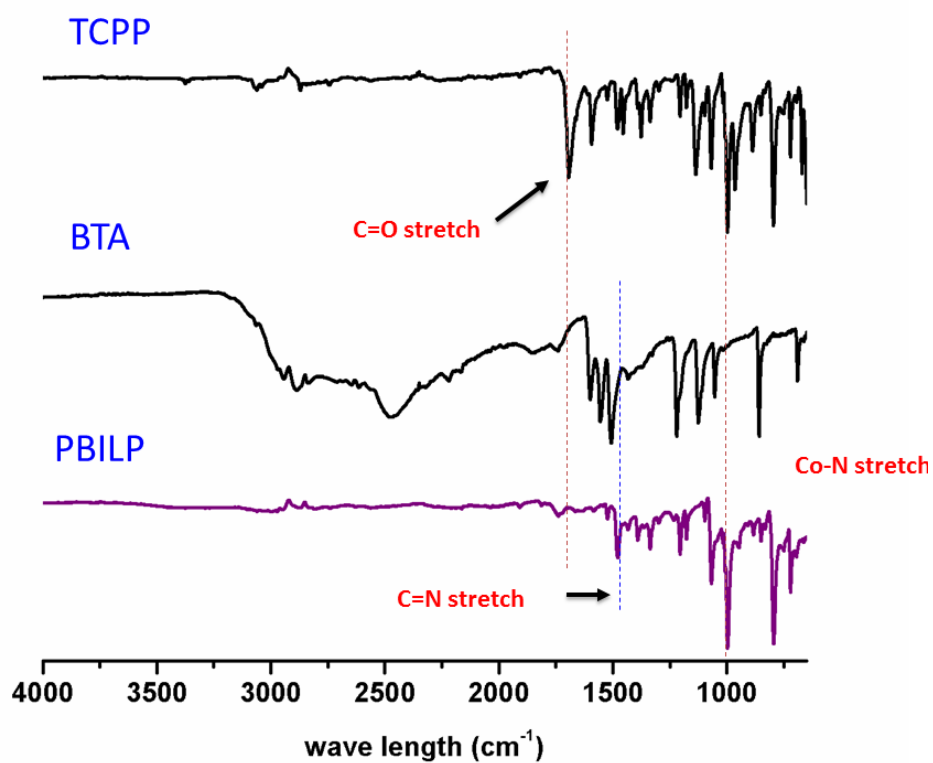
### ***Synthesis of meso-tetra-(4-formylphenyl) porphyrin Co(II) (1)***

*Meso-tetra-(4-formylphenyl) porphyrin* (190 mg, 0.26mmol) and cobalt acetate tetrahydrate (75 mg, 0.3mmol) were dissolved in DMF (100 mL), and the solution was refluxed for 2h under argon. The mixture was cooled and solvent was evaporated and the resulting solid was washed with H<sub>2</sub>O and ethanol, and dried under vacuum to yield TCPP (**1**) as a red powder. Yield: 80%. Anal. Calcd for C<sub>48</sub>H<sub>28</sub>CoN<sub>4</sub>O<sub>4</sub>: C, 73.56; H, 3.60; N, 7.15. Found: C, 73.32; H, 3.25; N, 7.22.

### ***Synthesis of PBILP:***

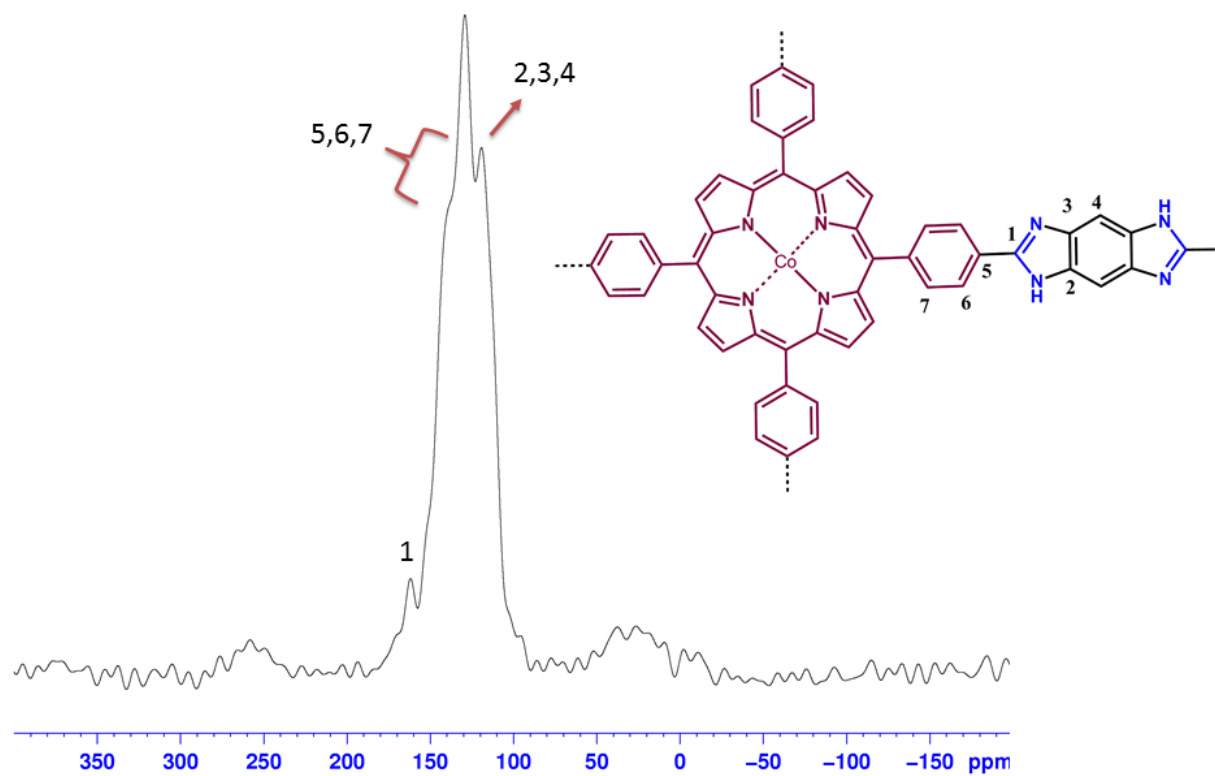
A homogeneous solution of *meso-tetra-(4-formylphenyl) porphyrin Co(II)* (150mg, 0.2mmol) was added drop-wise to the suspension of 1,2,4,5-Benzenetetramine tetra hydrochloride (110mg, 0.4mmol) in *N,N'*-dimethylformamide (20ml+20ml) and stirred for 4h at –30 °C, followed by stirring at room temperature for 12h yielded a purple suspension. The resulting purple suspension was bubbled with O<sub>2</sub>, and heated at 130 °C for 36h. The resulting precipitate was filtered, washed with water and organic solvents and dried under vacuum overnight to give the corresponding polymer in 60% yield. Elemental analysis (%) calcd. for PBILP, theory: C, 73.54; H, 3.29; N, 17.15; found C, 72.69; H, 2.81; N, 17.84, respectively.

### Section C. FT-IR spectral profiles



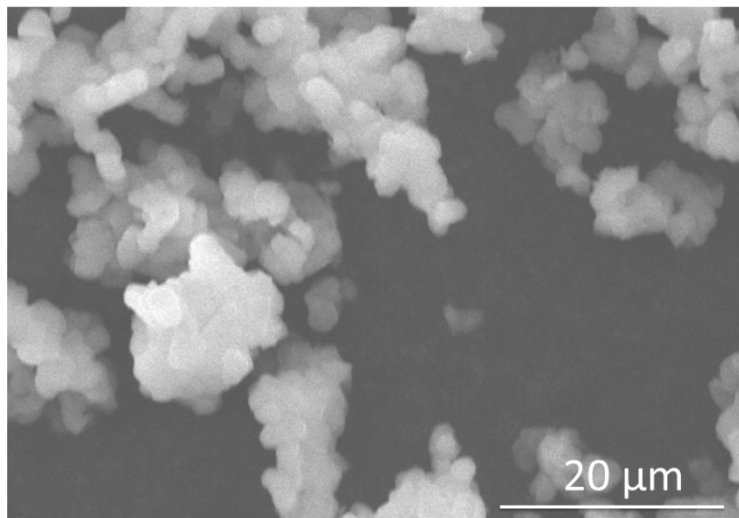
**Figure S1.** IR spectra of TCPP and BTA and PBILP.

## Section D. Solid-state $^{13}\text{C}$ CP-MAS NMR spectrum



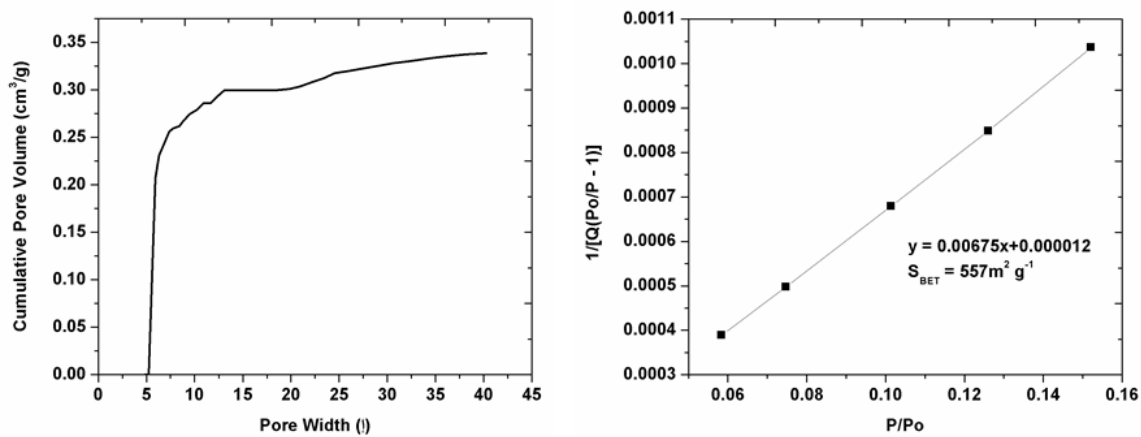
**Figure S2.** Solid state  $^{13}\text{C}$  CP-MAS NMR spectrum of PBILP recorded at a MAS rate of 10 kHz.

## Section E. SEM

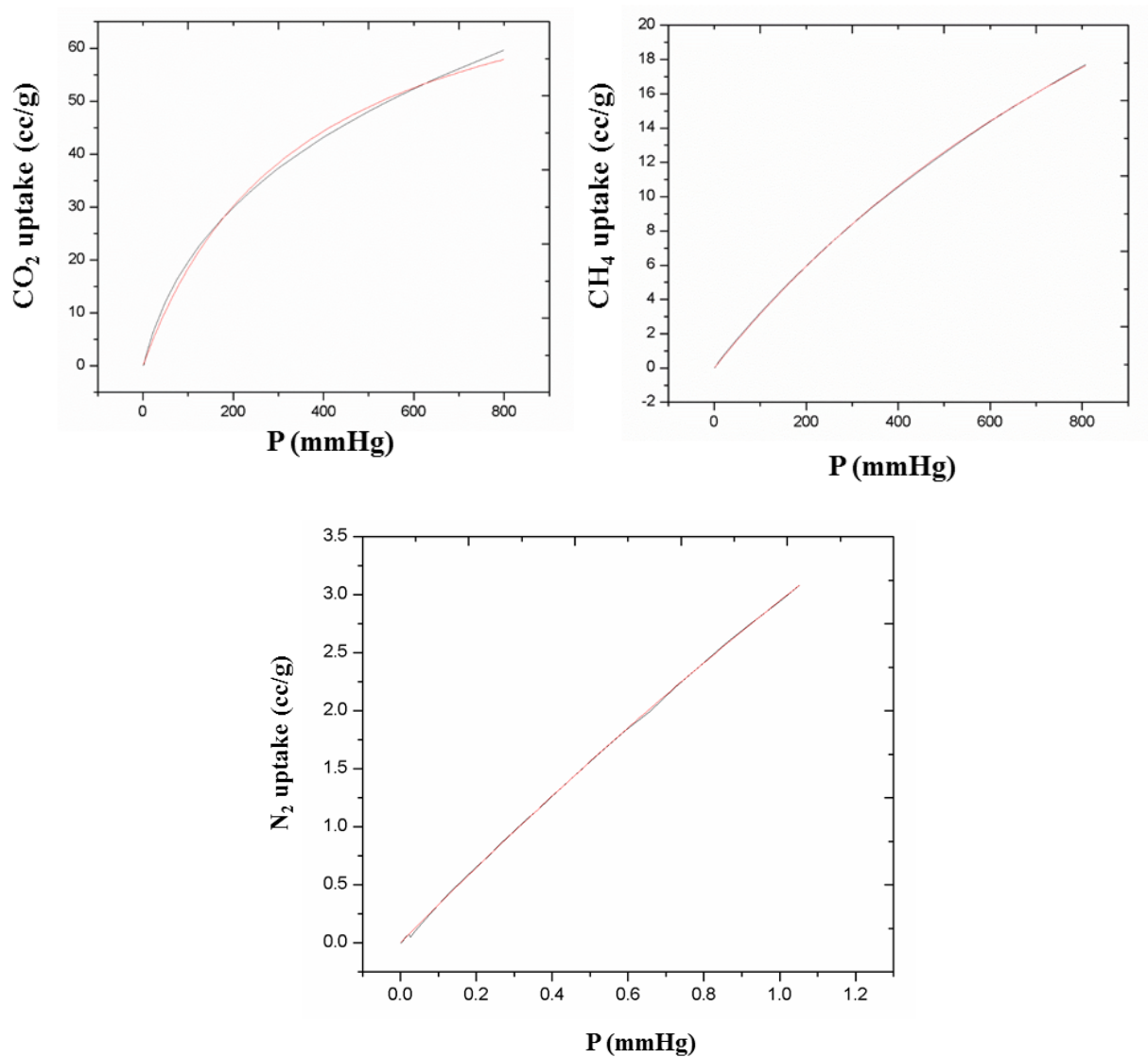


**Figure S3.** Scanning Electron Microscope image of PBILP.

## Section F. Surface Area Measurements

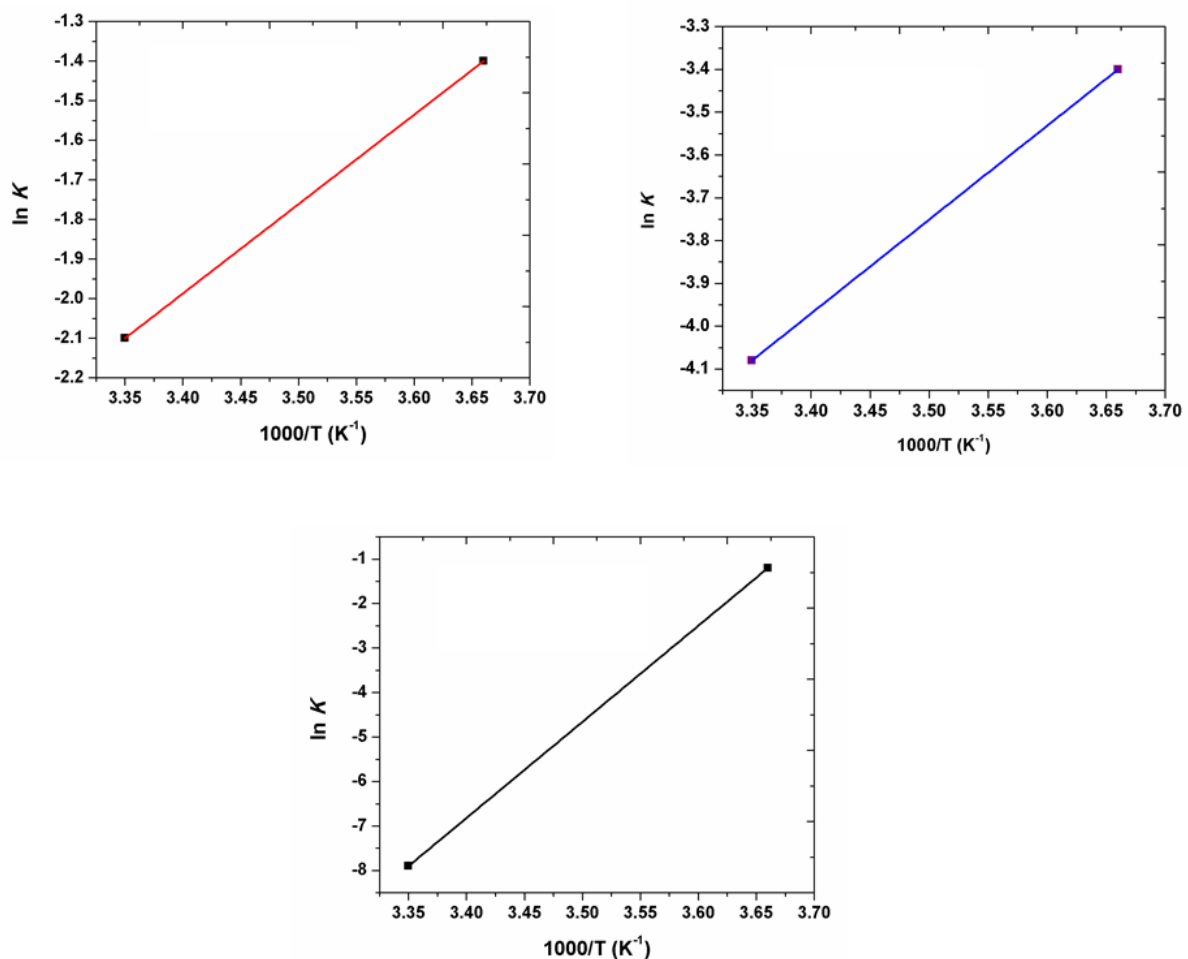


**Figure S4.** Cumulative (left) pore size distribution plot of PBILP from the application of the NLDFIT model to the N<sub>2</sub> isotherm. BET plot (right) for PBILP calculated from isotherm data.



**Figure S5.** Langmuir model fits for CO<sub>2</sub> (top left), CH<sub>4</sub> (top left) and N<sub>2</sub> adsorption (below) of PBILP 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 S6.** Van't Hoff plots of isosteric heat of adsorption for  $CO_2$  (red),  $CH_4$  (blue), and  $N_2$  (black).

### Calculation of isosteric heat of adsorption

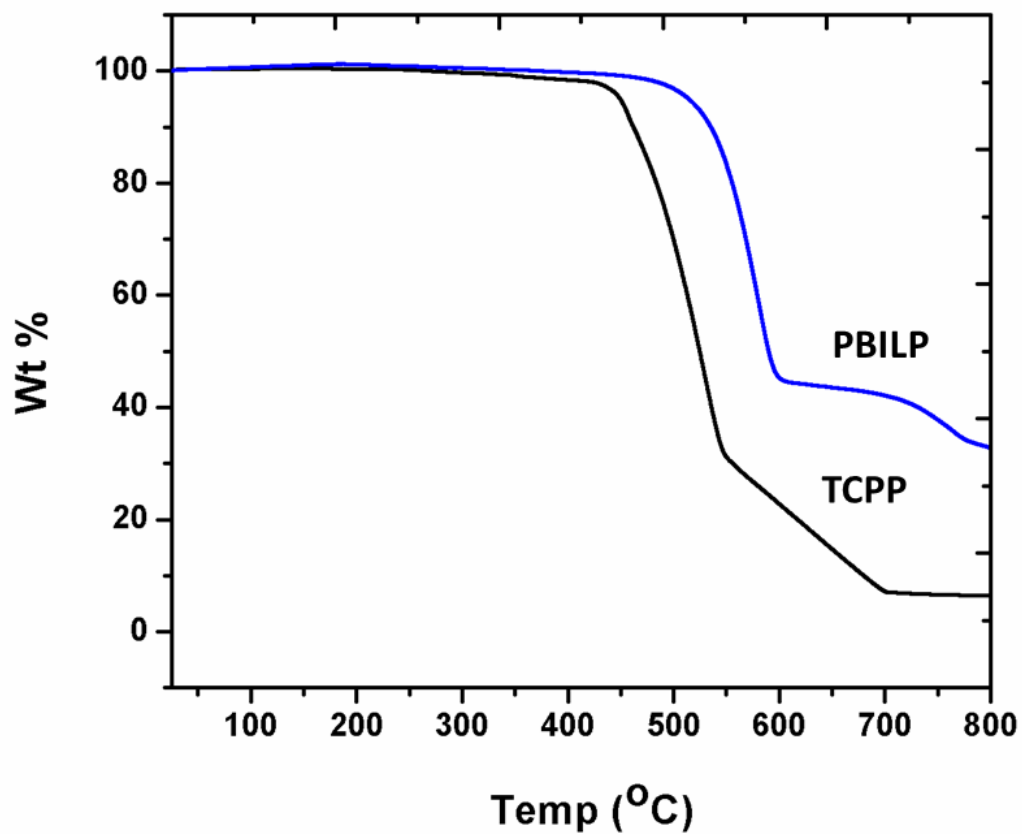
The adsorption enthalpy at zero coverage was calculated from Henry's constant using the Van't Hoff equation as

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

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



## Section G: Thermogravimetric Analysis



**Figure S7.** TGA of PBILP and TCPP obtained up to 800°C using a linear 5°C/min ramp method.

