Electronic Supplementary Information for

Quantifying nitrogen effect on CO_2 capture using isoporous network polymers

Thien S. Nguyen and Cafer T. Yavuz

1. Materials and Methods

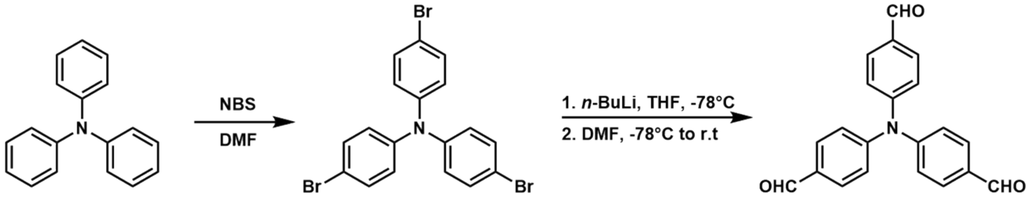
1.1. Materials

Triphenylamine (98%) and N-bromosuccinimide (99%) were obtained from Alfa Aesar, USA. 4'-Bromoacetophenone (98%) and n-butyl lithium (1.6M in hexanes) were purchased from Acros Organic, Belgium. Silicon tetrachloride (99%) and 1,2,4,5-benzenetetraamine tetrahydrochloride (technical grade) were acquired from Sigma-Aldrich, USA. Dimethylformamide (99.5%), tetrahydrofuran (99.8%), and ethanol (99.5%) were from SAMCHUN, South Korea. Other materials were used without further purification.

1.2. Synthetic methods

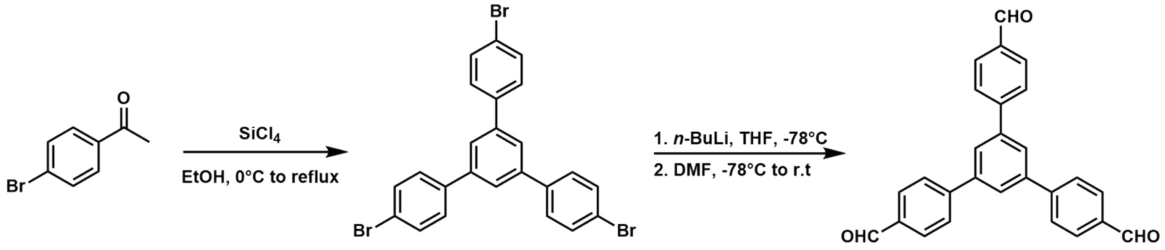
1.2.1. Procedures for the synthesis of trialdehyde monomer

The synthesis of tris(4-formylphenyl)amine.



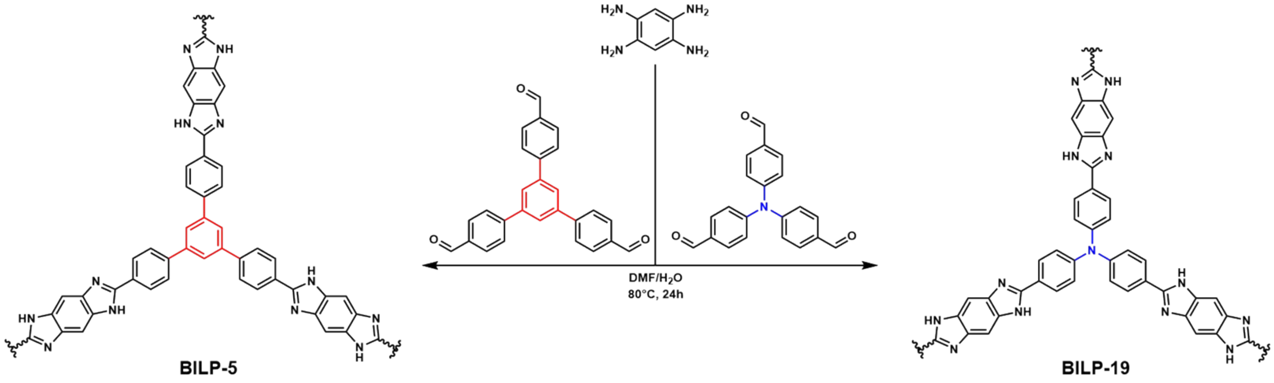
To a solution of triphenylamine (4.9064g, 20 mmol) in DMF (75 mL) at 0 ^{o}C, n-bromosuccinimide (10.6788g, 60 mmol in 25 mL DMF) was added dropwise. The mixture was then stirred for 3h at room temperature. Ice water was subsequently added to the mixture to produce a white solid. The crude product was filtered and washed with excess amount of water and then dried in oven at 60^{o}C for 15h to afford the pure product as a white solid (6.9715g, 72%). The ^{1}H-NMR spectrum matches previously reported data. ^{1}H-NMR ($CDCl_3$, 300 Mhz, ppm): 7.36 (d, 6H, J=9 Hz), 6.93 (d, 6H, J=9Hz). In the next step, the tris(4-bromophenyl)amine (2.651g, 5.5 mmol) was dissolved in 120 mL anhydrous THF under nitrogen atmosphere and the mixture was cooled down to -78^{o}C. *n*-BuLi (1.6M in hexanes, 17.18 mL, 27.5 mmol) was added dropwise and the mixture was allowed to warm up to room temperature and stirred for 30 minutes. The reaction was then cooled back down to -78^{o}C and DMF (2.56 mL, 33 mmol) was added dropwise. The mixture was allowed to gradually warm up to room temperature and stirred for additional 15h. DI water was added to quench the reaction and the organic layer was extracted using a separatory funnel. The aqueous phase was further extracted with DCM and the organic extracts were combined and dried with sodium sulfate. Organic solvent was evaporated under low vaccum to yield the crude product which was subsequently crystallized from ethanol to yield the pure product as a yellow solid (302.4 mg, 17%). The ^{1}H-NMR spectrum matches previously reported data. ^{1}H-NMR ($CDCl_3$, 300 Mhz, ppm): 9.95 (s,3H), 7.85 (d, 6H, J=9 Hz), 7.26 (d, 6H, J=9Hz).

The synthesis of 1,3,5-tris(4-formylphenyl)benzene



$SiCl_4$ (12.9 mL, 112.95 mmol) was added dropwise to a solution of 4'-bromoacetophenone in absolute ethanol at 0°C. A red mixture appeared shortly after the addition was finished. The mixture was then heated to reflux for 24h during which the reaction gradually turn to yellow color. After cooling to room temperature, the reaction was quenched with saturated NH_4Cl (50 mL) and the mixture was further stirred for additional 30 minutes. The crude solid product was filtered and washed with DI H_2O and was finally recrystallized with ethanol to afford the pure product as a pale-white solid (3.6746 g, 81%). The ^{1}H-NMR spectrum matches previously reported data. ^{1}H-NMR ($CDCl_3$, 300 Mhz, ppm): 7.69 (s, 3H), 6.62 (d, 6H, J=9Hz), 7.54 (d, 6H, J=9Hz). In the next step, the 1,3,5-tris(4-bromophenyl)benzene (2.651g, 5.5 mmol) was dissolved in 120 mL anhydrous THF under nitrogen atmosphere and the mixture was cooled down to -78°C. *n*-BuLi (1.6M in hexanes, 17.18 mL, 27.5 mmol) was added dropwise and the mixture was allowed to warm up to room temperature and stirred for 30 minutes. The reaction was then cooled back down to -78°C and DMF (2.56 mL, 33 mmol) was added dropwise. The mixture was allowed to gradually warm up to room temperature and stirred for additional 15h. DI water was added to quench the reaction and the organic layer was extracted using a separatory funnel. The aqueous phase was further extracted with DCM and the organic extracts were combined and dried with sodium sulfate. Organic solvent was evaporated under low vaccum to yield the crude product which was subsequently crystallized from ethanol to yield the pure product as a light yellow solid (486.5 mg, 23%). The ^{1}H-NMR spectrum matches previously reported data. ^{1}H-NMR ($CDCl_3$, 300 Mhz, ppm): 10.11 (s,3H), 8.03 (d, 6H, J=9 Hz), 7.91 (s, 3H), 7.88 (d, 6H, J=9Hz).

1.2.2. General procedure for bisimidazole polymer synthesis



1,2,4,5-Benzenetetraamine tetrahydrochloride (170.4 mg, 0.6 mmol) was first dissolved in DMF (30 mL) at room temperature followed by the slow addition of the monomer aldehyde (0.4 mmol) solution in DMF (6 mL). After the addition was completed, water (4 mL) was then added dropwise and the mixture was heated to 80^{o}C and stirred at this temperature for 24 hours under ambient atmosphere (open flask). The reaction mixture was cooled down to room temperature and the precipitate was filtered and washed successively with water, methanol and acetone before being dried under vacuum at 80^{o}C for 20h.

Polymer	**Yield (%)**	**Calculated elemental composition**			**Found elemental composition**		
		C (%)	**H (%)**	**N (%)**	**C (%)**	**H (%)**	**N (%)**
BILP-5	99	80.42	3.94	15.64	68.16	4.58	10.63
BILP-19	99	75.60	3.82	20.58	62.32	4.16	14.85

Characterizations

Fourier-transform infrared spectroscopy (FT-IR) spectra were collected using a SHIMADZU FT-IR spectrometer IR Trace-100 with single reflection ATR accessory**.** Liquid ^{1}H nuclear magnetic resonance (NMR) was performed by a Bruker NMR spectrometer at 300 MHz. Elemental analysis for C, H, N was carried out using a FLASH 2000 series of Thermo Scientific. For the porosity of samples, nitrogen adsorption-desorption isotherms were measured using a Micromeritics Triflex accelerated surface area and porosimetry analyser at 77 K after the samples had been degassed at 150 °C overnight under vacuum. The specific surface areas of the samples were determined according to the Brunauer-Emmett-Teller (BET) model and the pore size distribution was calculated by the Non-Local Density Functional Theory (NLDFT) method. Thermogravimetric analysis (TGA) was carried out with a differential thermal gravimetry (DTG)-60A of Shimadzu at a heating rate of 10 °C min^{-1} up to 800 °C under air and nitrogen atmosphere, respectively.

2. Supplemental figures

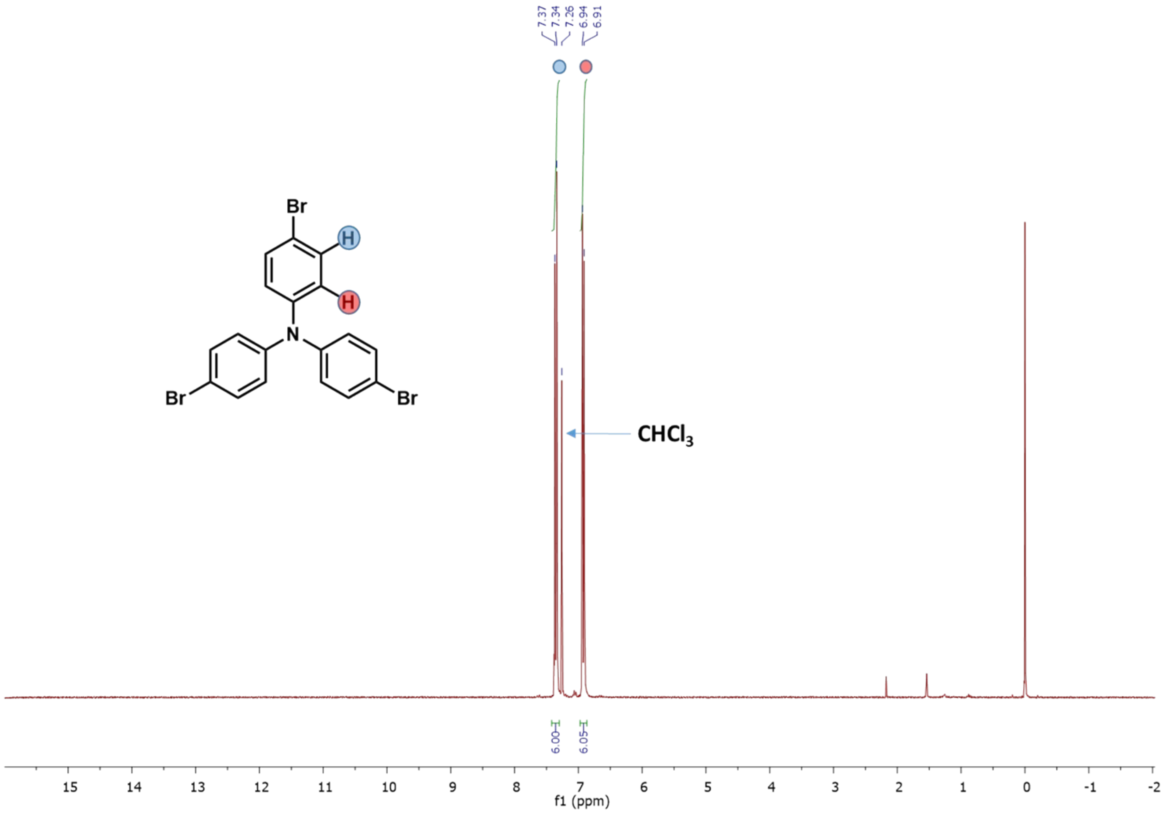


Figure S1. ^{1}H-NMR spectrum of tris(4-bromophenyl)amine.

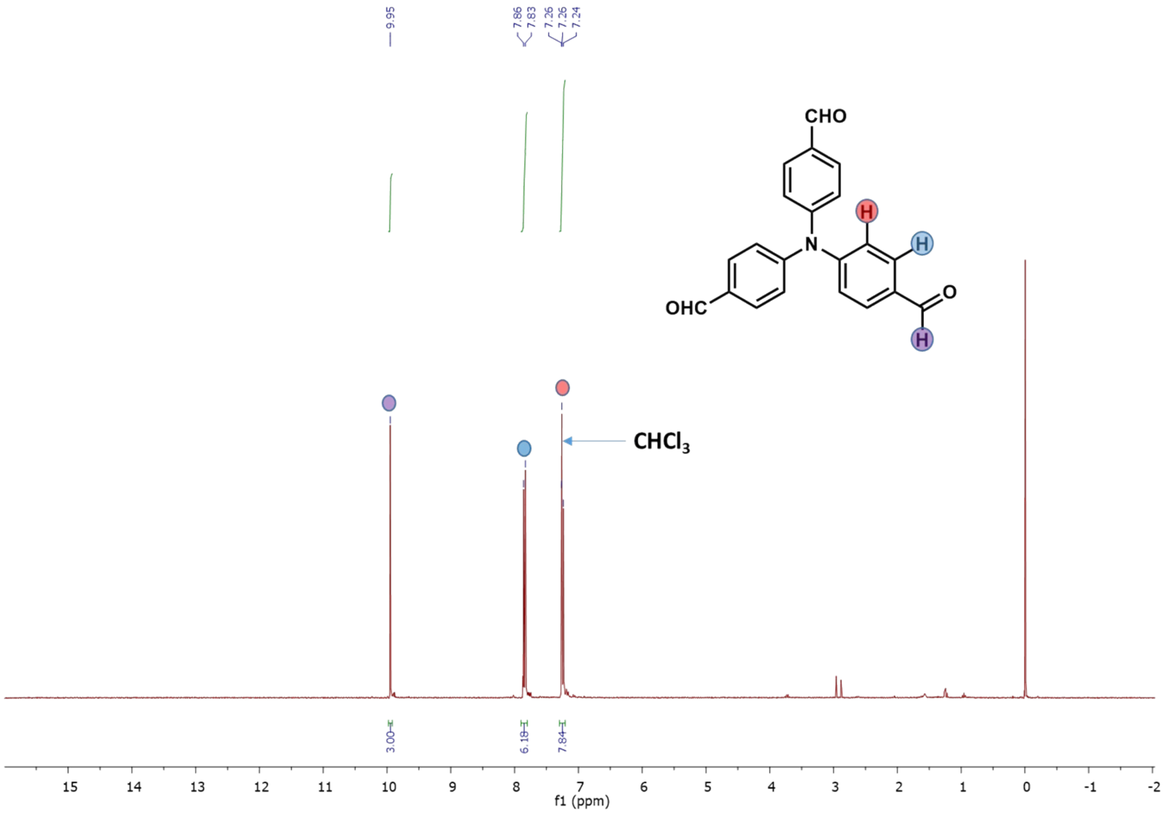


Figure S2. ^{1}H-NMR spectrum of tris(4-formylphenyl)amine.

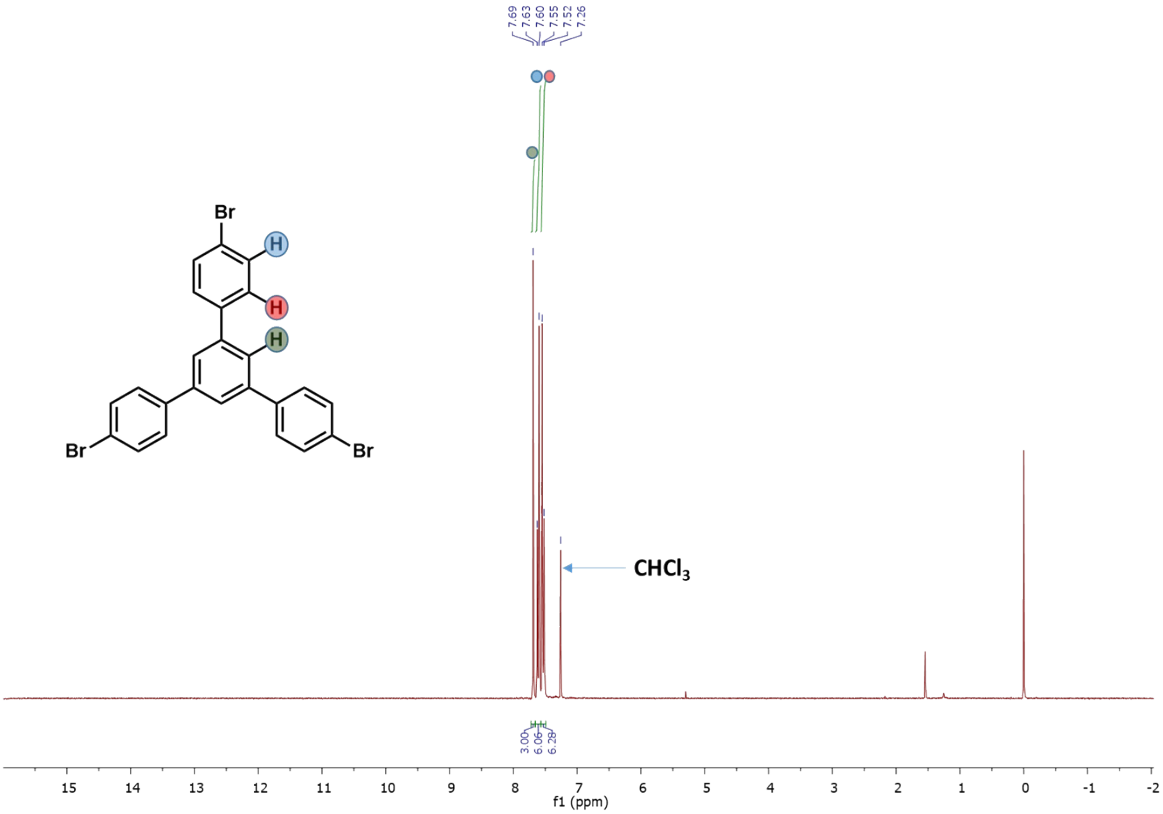


Figure S3. ^{1}H-NMR spectrum of 1,3,5-tris(4-bromophenyl)benzene.

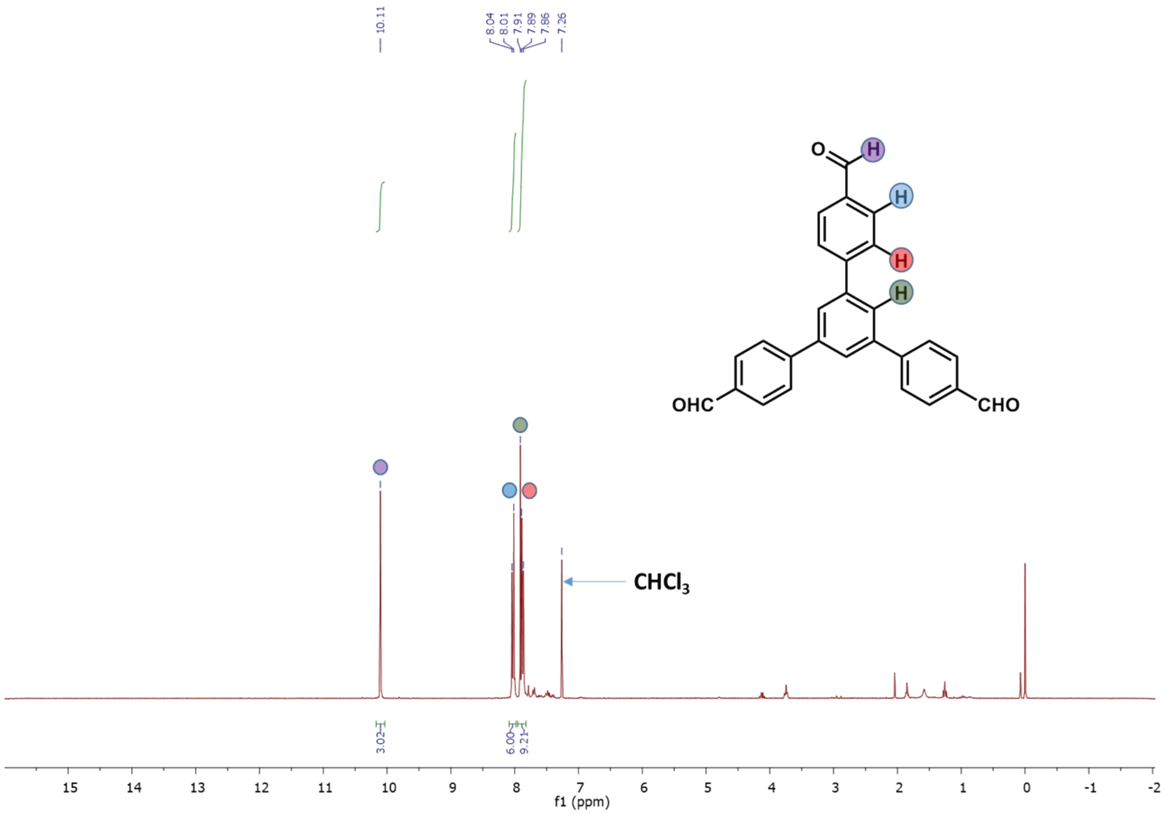
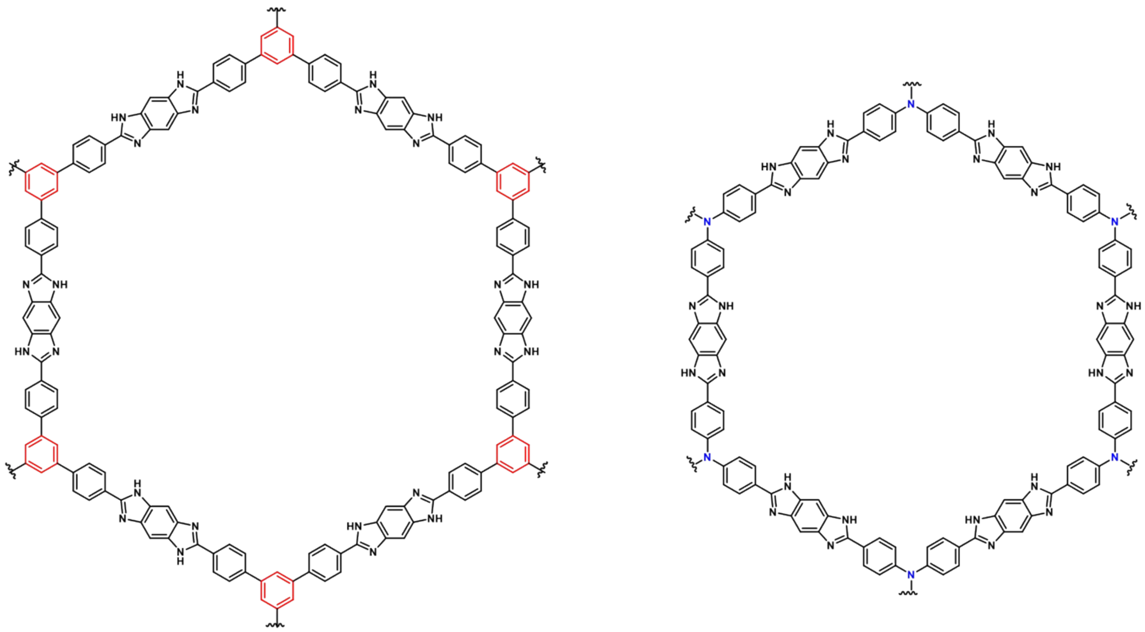


Figure S4. ^{1}H-NMR spectrum of 1,3,5-tris(4-formylphenyl)benzene.



BILP-5 **BILP-19**

Figure S5. Pore structure of BILP-5 and BILP-19

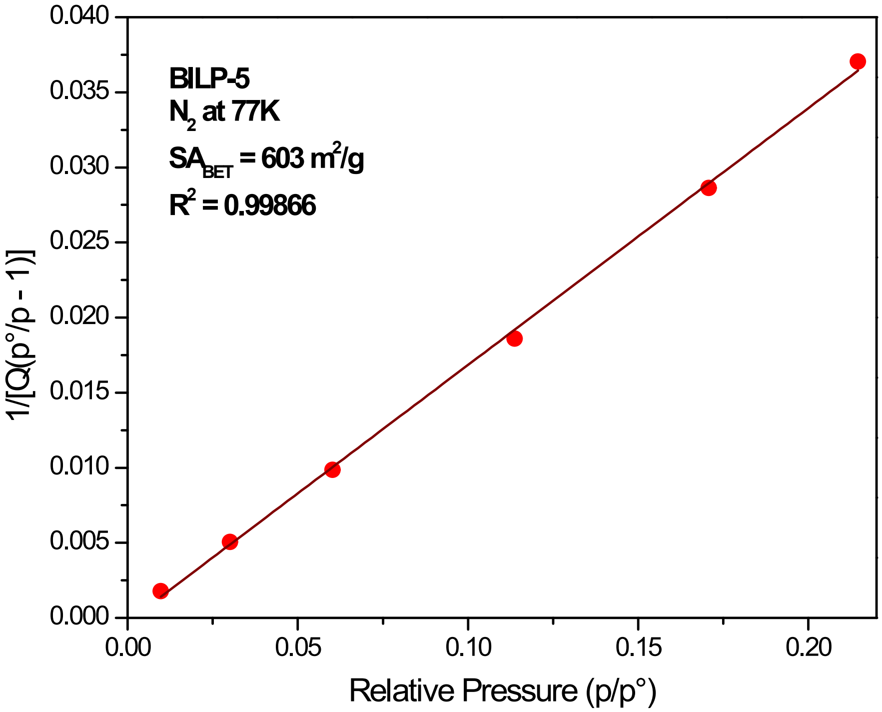


Figure S6. BET plot for BILP-5 calculated from the N_2 adsorption isotherm at 77K.

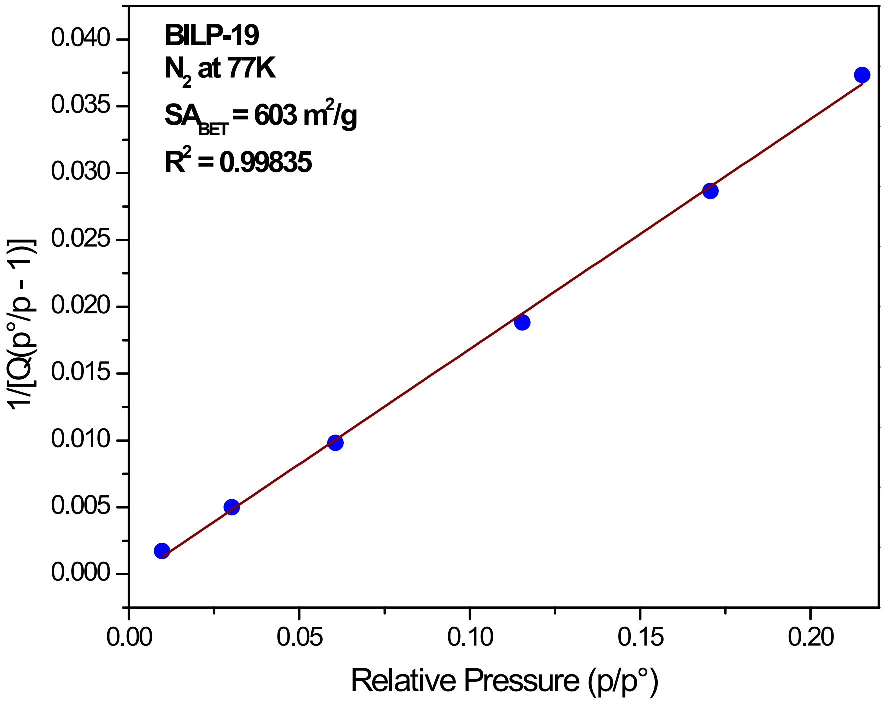


Figure S6. BET plot for BILP-19 calculated from the N_2 adsorption isotherm at 77K.

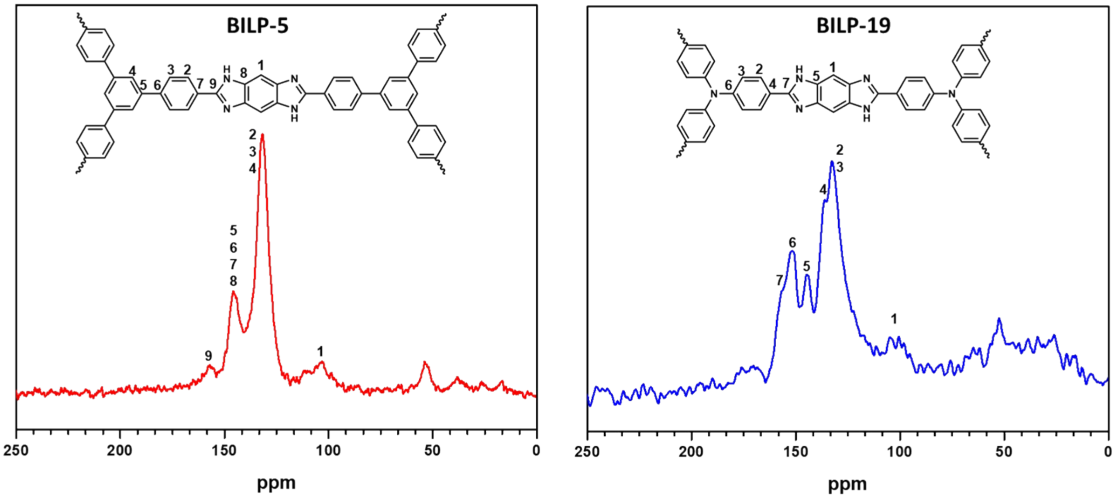


Figure S7. Solid state ^{13}C CP-MAS NMR spectra of BILP-5 and BILP-19

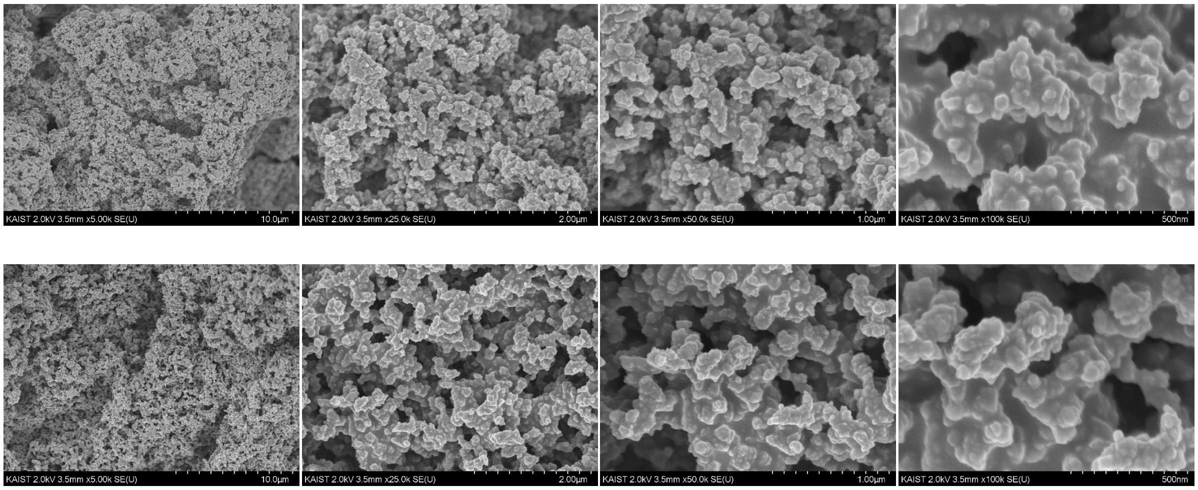


Figure S8. SEM images of BILP-5 (top) and BILP-19 (bottom).

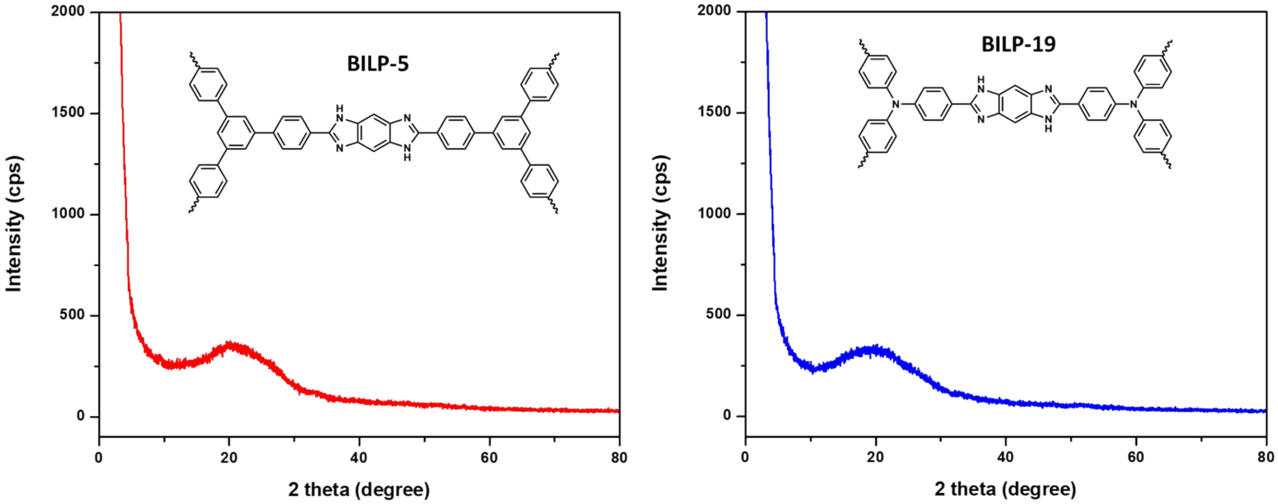


Figure S9. PXRD spectra of BILP-5 and BILP-19

Table S1. Comparison table of analogous bisimidazole polymers

Polymer	SA_{BET} (m^2/g)	CO_2 at 1bar (mmol/g)	CO_2/N_2 selectivity (mol/mol)
BILP-101[1]	536	2.43 (298K)	71 (298K, CO_2/N_2 (10/90))
BILP-16(AC)[2]	643	3.46 (273K) 2.32 (298K)	49 (273K, CO_2/N_2 (10/90)) 61 (298K, CO_2/N_2 (10/90))
BILP-19 (Senker group)[3]	1325	5.97 (273K) 5.2 (298K)	60 (298K, CO_2/N_2 (15/85))
BILP-5 (El-Kaderi group)[4]	599	2.9 (273K) 1.98 (298K)	95 (273K, CO_2/N_2 (10/90)) 36 (298K, CO_2/N_2 (10/90))
BILP-2[4]	708	3.38 (273K) 2.36 (298K)	113 (273K, CO_2/N_2 (10/90)) 71 (298K, CO_2/N_2 (10/90))
TPILP-1[5]	330	2.66 (273K) 1.77 (298K)	62 (298K, CO_2/N_2 (10/90))
BILP-5 (this work)	603	2.29 (273K) 1.47 (298K)	63 (298K, CO_2/N_2 (15/85))
BILP-19 (this work)	603	2.62 (273K) 1.57 (298K)	117 (298K, CO_2/N_2 (15/85))

References

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