Adjustable Functionalisation of Hypercrosslinked Polymers of Intrinsic Microporosity for Enhanced CO₂ Adsorption and Selectivity over N₂ and CH₄

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1. **General methods and equipment**

Commercially available reagents and gases were used without further purification. All reactions using air/moisture sensitive reagents were performed in oven-dried or flame-dried apparatus, under a nitrogen atmosphere. Low-temperature N\textsubscript{2} (77 K and 298 K), CO\textsubscript{2} (273 K and 298 K) and CH\textsubscript{4} (298 K) adsorption/desorption measurements of PIM powders were made using a Quantachrome Nova-e. Samples were degassed for 800 min at 100 °C under high vacuum prior to analysis. The gases were supplied by BOC and used without any further purification (N\textsubscript{2} purity > 99.999, CO\textsubscript{2} purity > 99.995%). The specimen was measured twice after outgas in two different cells to minimize the error, providing the same results. The data were analysed with the software provided with the instrument. The BET was calculated at a relative pressure $P/P_0 < 0.1$. NLDFT and H-K analysis were performed to calculate the pore size distribution and volume, considering a carbon equilibrium transition kernel at 273 K based on a slit-pore model; the kernel is based on a common, one centre, Lennard-Jones model. To assess the potential chemisorption, heats of adsorption were calculated from the CO\textsubscript{2} curves measured at 237K and 298K. The data were analysed with the QuadraWin software and fitted with the Langmuir-Freundlich equation and calculated via the Clausius-Clapeyron equation. TGAs were performed using the device Thermal Analysis SDT Q600 at a heating rate of 10 °C/min from 30 to 1000 °C. Solid-state $^{13}$C NMR spectra were recorded using a Bruker Avance III spectrometer equipped with a wide-bore 9.4 T magnet (Larmor frequencies of 100.9 MHz for $^{13}$C). Samples were packed into standard zirconia rotors with 4 mm outer diameter and rotated at a magic angle spinning (MAS) rate of 12.5 kHz. Spectra were recorded with cross polarisation (CP) from 1H using a contact pulse (ramped for 1H) of 1.5 ms. High-power ($\nu_1$= 100 kHz) TPPM-15 decoupling of 1H was applied during acquisition to improve resolution. Signal averaging was carried out for 6144 transients with a recycle interval
of 2 s. Chemical shifts are reported in ppm relative to (CH$_3$)$_4$Si (TMS) using the CH$_3$ signal of L-alanine (δ = 20.5 ppm) as a secondary solid reference.

2. IAST Selectivity calculation.

The ideal adsorption solution theory (IAST) of Myers and Prausnitz$^1$ is typically used to the selectivity of binary mixtures of gases from the single isotherms. The isotherms were fitted with Dual-Site Langmuir-Freundlich using the software IAST++$^2$ and the selectivity (S) was calculated according to the formula:

$$S = \frac{Q_{CO_2}}{Q_{N_2}} \times \frac{P_{N_2}}{P_{CO_2}}$$

Where
- $P_{CO_2}$ is the partial pressure of CO$_2$
- $P_{N_2}$ is the partial pressure of N$_2$
- $Q_{N_2}$ is the N$_2$ uptake
- $Q_{CO_2}$ is the CO$_2$ uptake

3. Experimental part

PIM-TPB, PIM-Tript, PIM-TPB-HSO$_3$ and PIM-Tript-HSO$_3$ were synthesised according to our previous paper.$^3$

PIM-SBF$^4$

SBF (1.02 g, 3.22 mmol) and AlCl$_3$ (4.47 g, 33.5 mmol) were added to DCM (60 mL) and stirred at reflux for 24 hours under a nitrogen atmosphere. The solution was filtered, and the obtained powder washed with plenty of water and ethanol. The brown powder was washed sequentially via reflux with ethanol, chloroform, THF, acetone, and methanol, and finally dried in a vacuum oven at 100°C for 20 hours. The SBF-network polymer (1.40 g, 3.80 mmol, 118% yield based on ideal structure. To be considered quantitative but the complete removal of the trapped gases/moisture was impossible) was analysed by IR spectroscopy, thermogravimetric analysis (TGA) and BET. $S_{BET}$= 1604 m$^2$g$^{-1}$, CO$_2$ adsorption at 273 K/1 bar= 3.28 mmol g$^{-1}$, TGA: Thermal degradation commences at 255°C. FTIR-ATR (cm$^{-1}$): 906, 1172, 3060. $^{13}$C NMR SS (101 MHz) δ 147.71, 139.99, 132.26, 127.02, 122.70, 72.66, 66.14, 54.95, 36.46, 16.66, 13.48.
HPB (0.99 g, 1.85 mmol) and AlCl$_3$ (3.28 g, 24.59 mmol) were added to DCM (60 mL) and stirred at reflux for 24 hours under a nitrogen atmosphere. The solution was filtered, and the obtained powder washed with plenty of water and ethanol. The powder was washed sequentially via reflux with ethanol, chloroform, THF, acetone, and methanol, and finally dried in a vacuum oven at 100 °C for 20 hours. The HPB-network polymer (1.30 g, 2.12 mmol, 115% yield based on ideal structure. To be considered quantitative but the complete removal of the trapped gases/moisture was impossible) was analysed by IR spectroscopy, TGA, and BET. SA$_{BET}$ = 1932 m$^2$g$^{-1}$, CO$_2$ adsorption at 273 K/1 bar= 3.12 mmol g$^{-1}$, TGA: Thermal degradation commences at 295 °C. FTIR-ATR (cm$^{-1}$): 1096, 1452, 2978. $^{13}$C NMR SS (101 MHz) δ 136.69, 131.03, 126.72, 82.72, 72.49, 65.76, 54.44, 40.27, 34.15, 13.10.

General procedure for sulfonation of polymers- SBF-SO$_3$H and HPB-SO$_3$H

PIM-SBF (0.51 g, 1.38 mmol) or PIM-HPB (0.49 g, 0.79 mmol) was added to concentrated H$_2$SO$_4$ (20 mL) and stirred for 30 minutes, then warmed to 60 °C and stirred for more 7 hours under a nitrogen atmosphere. The solution was cooled to room temperature and poured over ice, filtered and the obtained solid was washed with plenty of water until a neutral pH of the residue was obtained. The resulting dark powder was refluxed in ethanol and methanol, filtered off and dried in a vacuum oven at 100 °C for 20 hours. The polymers, PIM-SBF-SO$_3$H and PIM-HPB-SO$_3$H, were analysed by IR spectroscopy, TGA, and BET.

PIM-SBF-HSO$_3$ (0.52 g, 0.76 mmol, 64%): SA$_{BET}$ = 1063 m$^2$g$^{-1}$, CO$_2$ adsorption at 273 K/1 bar= 3.47 mmol g$^{-1}$, TGA: Thermal degradation commences at 167 °C. FTIR-ATR (cm$^{-1}$): 1038, 1190, 2980, 3450. $^{13}$C NMR SS (101 MHz) δ 184.97, 140.47, 133.24, 128.25, 66.50, 57.09, 38.78, 19.11.
**PIM-HPB-HSO₃** (0.57 g, 0.52 mmol, 69%): \( \text{SA} = 1390 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar= 2.92 mmol g⁻¹, TGA: Thermal degradation commences at 165 °C. FTIR-ATR \( (\text{cm}^{-1}) \): 1039, 1175, 2980, 3420. \(^{13}\)C NMR SS (101 MHz) \( \delta 255.64, 235.97, 192.27, 135.92, 131.84, 72.44, 55.35, 34.28, 14.61. \)

**General procedure for nitration of polymers - PIM-SBF-NO₂ and PIM-HPB-NO₂**

Under a nitrogen atmosphere, \( \text{H}_2\text{SO}_4 \) (50 mL) was cooled in an ice bath for 20 minutes before PIM-SBF (0.49 g, 1.33 mmol) or PIM-HPB (0.50 g, 0.82 mmol) or PIM-TPB (0.50 g, 1.44 mmol) or PIM-TRIP (0.50 g, 1.70 mmol) were added. Concentrated \( \text{HNO}_3 \) (0.5 mL, 70%) was added dropwise and the solution was then stirred for 2 hours in an ice bath. The resulting solution was poured over ice, stirred for 30 minutes, filtered and the obtained solid was washed with plenty of water until a neutral pH of the residue was obtained. The resulting dark powder was then refluxed in ethanol and methanol, filtered and dried in a vacuum oven at 100 °C for 20 hours. The polymers, PIM-SBF-NO₂ and PIM-HPB-NO₂, were analysed by IR spectroscopy, TGA, and BET.

**PIM-SBF-NO₂** (0.55 g, 1.00 mmol, 83%): \( \text{SA} = 909 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar= 3.32 mmol g⁻¹, TGA: Thermal degradation commences at 230 °C. FTIR-ATR \( (\text{cm}^{-1}) \): 1344, 1538, 3051. \(^{13}\)C NMR SS (101 MHz) \( \delta 192.17, 182.57, 145.51, 134.90, 125.58, 66.61, 56.04, 53.18, 36.63, 14.21. \)

**PIM-HPB-NO₂** (0.58 g, 0.66 mmol, 69%): \( \text{SA} = 1286 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar= 3.12 mmol g⁻¹, TGA: Thermal degradation commences at 216 °C. FTIR-ATR \( (\text{cm}^{-1}) \): 1349, 1536, 3023. \(^{13}\)C NMR SS (101 MHz) \( \delta 186.18, 133.90, 70.27, 57.00, 34.32, 14.75. \)
PIM-TPB-NO$_2$ (0.60 g, 1.15 mmol, 80%). $S_{\text{BET}}$ = 950 m$^2$g$^{-1}$, CO$_2$ adsorption at 273 K/1 bar = 5.13 mmol g$^{-1}$, TGA: Thermal degradation commences at 180 °C. FTIR-ATR (cm$^{-1}$): 1048, 1298, 1676, 2972. $^{13}$C NMR SS (101 MHz) δ 182.79, 162.93, 133.65, 72.66, 55.09, 35.12, 30.24, 16.50.

PIM-TRIP-NO$_2$ (0.62, 1.45 mmol, 85%) $S_{\text{BET}}$ = 975 m$^2$g$^{-1}$, CO$_2$ adsorption at 273 K/1 bar = 4.87 mmol g$^{-1}$, TGA: Thermal degradation commences at 195 °C. FTIR-ATR (cm$^{-1}$): 1046, 1295, 1675, 2992. $^{13}$C NMR SS (101 MHz) δ 182.37, 163.14, 145.72, 132.16, 73.49, 49.61, 35.59, 30.45, 14.82.

**General procedure for amination of polymers: SBF-NH$_2$ and HPB-NH$_2$**

PIM-SBF-NO$_2$ (0.30 g, 0.61 mmol) or PIM-HPB-NO$_2$ (0.30 g, 0.42 mmol) or PIM-TPB-NO$_2$ (0.30 g, 0.625 mmol) or PIM-TRIP-NO$_2$ (0.30 g, 0.701 mmol) were added to a solution of methanol and water (30 mL each), and the solution was degassed by a flow of nitrogen for 20 minutes. Sodium dithionite (4.01 g, 23 mmol) was added, and the solution stirred for 24 hours at 75 °C under a nitrogen atmosphere. The solution was filtered, and the resulting powder was washed with hot water. The powder was dispersed in 75 °C water (60 mL) and stirred for 30 minutes, then filtered and washed again with hot water. After being dried under reduced pressure, the powder was suspended in 4M HCl (60 mL) and stirred for 1 hour, then filtered and washed with plenty of water until a neutral pH of the residue was obtained. The resulting powder was refluxed in methanol, filtered and dried in a vacuum oven at 100 °C for 20 hours. The polymers, PIM-SBF-NH$_2$ and PIM-HPB-NH$_2$, were analysed by IR spectroscopy, TGA, and BET.
**PIM-SBF-NH₂** (0.15 g, 0.40 mmol, 64%): \( \text{SA}_{\text{BET}} = 669 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar = 2.9 mmol g\(^{-1}\), TGA: Thermal degradation commences at 190 °C. FTIR-ATR (cm\(^{-1}\))：1080, 1595, 3000, 3264. \(^{13}\)C NMR SS (101 MHz) \( \delta \) 254.48, 182.63, 170.09, 140.98, 134.43, 126.43, 66.62, 53.60, 31.37, 31.37.

![Chemical structure of PIM-SBF-NH₂](image1)

**PIM-HPB-NH₂** (0.22 g, 0.37 mmol, 88%): \( \text{SA}_{\text{BET}} = 997 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar = 2.80 mmol g\(^{-1}\), TGA: Thermal degradation commences at 161 °C. FTIR-ATR (cm\(^{-1}\))：1074, 1196, 1602, 2950, 3348. \(^{13}\)C NMR SS (101 MHz) \( \delta \) 226.7, 186.88, 133.37, 71.30, 53.53, 34.06, 14.87.

![Chemical structure of PIM-HPB-NH₂](image2)

**PIM-TPB-NH₂** (0.21 g, 0.53 mmol, 86%): \( \text{SA}_{\text{BET}} = 710 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar = 4.45 mmol g\(^{-1}\), TGA: Thermal degradation commences at 200 °C. FTIR-ATR (cm\(^{-1}\))：1035, 1280, 1610, 2980, 3436. \(^{13}\)C NMR SS (101 MHz) \( \delta \) 184.28, 164.95, 133.26, 73.97, 51.34, 34.87, 15.58.

![Chemical structure of PIM-TPB-NH₂](image3)

**PIM-TRIP-NH₂** (0.18 g, 0.53 mmol, 76%): \( \text{SA}_{\text{BET}} = 997 \text{ m}^2\text{g}^{-1} \), \( \text{CO}_2 \) adsorption at 273 K/1 bar = 2.80 mmol g\(^{-1}\), TGA: Thermal degradation commences at 221 °C. FTIR-ATR (cm\(^{-1}\))：1046, 1200, 1594, 2950, 3405. \(^{13}\)C NMR SS (101 MHz) \( \delta \) 183.69, 163.22, 131.93, 72.26, 47.55, 35.46, 30.47, 14.62.
4. Selectivity CO₂/N₂

**Figure SI1.** Selectivity CO₂/N₂
5. Selectivity CO₂/CH₄

Figure SI2. Selectivity CO₂/CH₄
6. Isotherms

**Figure SI3.** Nitrogen adsorption isotherms for HPB-PIMs
Figure S14. CO₂ adsorption isotherms for HPB-PIMs and NLDFT pore size distributions
**Figure SI5.** Nitrogen adsorption isotherms for SBF-PIMs
Figure SI6. CO$_2$ adsorption isotherms for SBF-PIMs and NLDFT pore size distributions.
**Figure SI7.** Nitrogen adsorption isotherms for TPB-PIMs
Figure S18. CO\textsubscript{2} adsorption isotherms for TPB-PIMs and NLDFT pore size distributions.
Figure SI9. Nitrogen adsorption isotherms for TRIP-PIMs
Figure SI10. CO$_2$ adsorption isotherms for TRIP-PIMs and NLDFT pore size distributions
7. Heats of adsorption

![Graphs of Qst for different PIMs](Figures/SI11.png)

**Figure SI11.** Heats of adsorption for PIMs.
8. FT-IRs

Figure SI12. FT-IR spectra of HPB-PIMs polymers. A- HC, B- HSO₃, C- NO₂, D- NH₂.

Figure SI13. FT-IR spectra of SBF-PIMs polymers. A- HC, B- HSO₃, C- NO₂, D- NH₂.
Figure SI14. FT-IR spectra of TRIP-PIMs polymers. A- HC, B- HSO₃, C- NO₂, D- NH₂.

Figure SI15. FT-IR spectra of TPB-PIMs polymers. A- HC, B- HSO₃, C- NO₂, D- NH₂.
9. Solid state $^{13}$C NMRs

Figure SI16. $^{13}$C solid state NMR for HPB-HC

Figure SI17. $^{13}$C solid state NMR for SBF-HC
Figure SI18. $^{13}$C solid state NMR for TPB-HC

Figure SI19. $^{13}$C solid state NMR for TRIP-HC
Figure SI20. $^{13}$C solid state NMR for HPB-NO$_2$

Figure SI21. $^{13}$C solid state NMR for SBF-NO$_2$
Figure SI22. $^{13}$C solid state NMR for TPB-NO$_2$

Figure SI23. $^{13}$C solid state NMR for TRIP-NO$_2$
Figure SI24. $^{13}$C solid state NMR for HPB-$\text{NH}_2$

Figure SI25. $^{13}$C solid state NMR for SBF-$\text{NH}_2$
Figure SI26. $^{13}$C solid state NMR for TPB-NH$_2$

Figure SI27. $^{13}$C solid state NMR for TRIP-NH$_2$
Figure SI28. $^{13}$C solid state NMR for HPB-HSO$_3$.

Figure SI29. $^{13}$C solid state NMR for SBF-HSO$_3$. 
Figure SI30. $^{13}$C solid state NMR for TPB-HSO$_3$.

Figure SI31. $^{13}$C solid state NMR for TRIP-HSO$_3$. 

SO$_3$H

SO$_3$H

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Figure SI32. TGA overlay of HPB-PIMs

Figure SI33. TGA overlay of SBF-PIMs
**Figure SI34.** TGA overlay of TPB-PIMs

**Figure SI35.** TGA overlay of TRIP-PIMs
11. References

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