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Covalent and electrostatic incorporation of amines into hypercrosslinked polymers for increased CO$_2$ selectivity

Ammar H. Alahmed,[a, b] Michael E. Briggs,*[a, b] Andrew I. Cooper,[a, b] and Dave J. Adams*[c]

Abstract: Two methods of incorporating functional groups rich in nitrogen into low cost microporous hypercrosslinked polymers (HCPs) have been evaluated and the effects on the CO$_2$/N$_2$ IAST selectivity were measured. Electrostatic incorporation of an ammonium salt into a sulfonic acid-containing HCP polymer afforded a static CO$_2$ uptake of 2.5 mmol/g with a CO$_2$/N$_2$ IAST selectivity of 42:1 at 1 bar and 298 K. Using column breakthrough measurements with a 15:85 CO$_2$/N$_2$ mixture at 298 K and 1 bar a selectivity of 17:1 was obtained. Varying the counter ion however, resulted in polymers with lower CO$_2$/N$_2$ selectivity values. Decoration of the parent polymer with CO$_2$-philic imidazole followed by electrostatic ammonium salt incorporation blocked some of the micropores reducing the selectivity which re-emphasizes the role and importance of pore width for CO$_2$/N$_2$ selectivity.

Introduction

Carbon dioxide (CO$_2$) scrubbing using amine solutions is currently the state-of-the-art technology for post-combustion CO$_2$ capture.[1,2] However, the formation of carbamates caused by the chemisorption nature of the process, coupled with the high specific heat capacity of water, results in a high parasitic energy penalty for regeneration of the scrubbing solution.[3, 4] Solid adsorbents, including metal-organic frameworks (MOFs),[5-9] microporous organic polymers (MOPs),[10-13] and zeolites,[14-18] can bind CO$_2$ either by chemisorption[17] or by physisorption, where the physical interactions are weaker.[18] The isosteric heat of adsorption ($Q_{st}$) indicates how strongly CO$_2$ binds to the adsorbent. The $Q_{st}$ for physisorption is typically below 40-50 kJ mol$^{-1}$, while values over 50 kJ mol$^{-1}$ are usually indicative of chemisorption.[19] For porous adsorbents to compete with amine solutions, certain criteria must be met including low cost of synthesis, moderate to high surface area, high CO$_2$ uptake, and high CO$_2$/N$_2$ selectivity.[20]

Porous organic materials can be further subdivided into crystalline solids[21] (e.g., covalent organic frameworks (COFs)[22-25] and porous organic cages[26,27]) and amorphous solids (e.g., polymers of intrinsic porosity (PIMs)[28,29] conjugated microporous polymers (CMPs)[10,30] and hypercrosslinked polymers (HCPs)[31-35]). HCPs are an interesting platform because they can possess high BET surface areas[32-35] and good thermal and chemical stability while being relatively inexpensive. HCPs are formed by the extensive crosslinking of aromatic monomers, which upon solvent removal affords a strained polymer that is unable to fully collapse to a non-porous state.[11] The diverse nature of the monomers available for the synthesis of HCPs (essentially any aromatic compound that possesses multiple reactive sites for Friedel-Crafts alkylation) offers potential advantages over other classes of microporous materials such as zeolites and MOFs.[9,36-38] HCPs do not require the use of expensive catalysts in their synthesis.[39] They are synthesised by Friedel-Crafts alkylation of activated aromatics in the presence of a Lewis acid catalyst such as iron(III) chloride (FeCl$_3$) using 1,2-dichloroethane (DCE) as a solvent.[11,39,40] However, these polymerisations are known to be hindered by the presence of electron-withdrawing groups such as sulfonic acids, which deactivate the ring.[41-43] This places some limitations on the functionality that can be introduced directly into HCPs. Previously, the post-synthetic introduction of sulfonic acid groups into the porous polymer network PPN-6, followed by neutralization with ammonium hydroxide (NH$_4$OH), was reported to enhance CO$_2$–network interactions.[44,45] However, PPN-6 is synthesised by Yamamoto coupling; this requires the use of expensive catalysts and starting materials under rigorously anhydrous conditions, combined with a multi-step synthesis for the brominated monomer.[46]

Owing to their low cost, ease of synthesis, and high surface area, HCPs are attractive candidates for post-synthetic modification as a strategy to enhance their moderate CO$_2$ uptakes and CO$_2$/N$_2$ selectivities.[35,39] Here, we report the functionalisation of HCP-SC, formed by the self-condensation of 4,4’-bis(chloromethyl)-1,1’-biphenyl (BCMBP) (Scheme 1).[39] Post-synthetic modification of HCP-SC was achieved by stirring the resulting sulfonic acid derivative (HCP-SC-SO$_3$H) with various amines to form the corresponding ammonium salts. The effect of varying the counter-ions on CO$_2$ uptake at 0.15 and 1.0 bar at 298 and 328 K was studied, as well as the effect on CO$_2$/N$_2$ selectivity. We also successfully incorporated imidazole into the HCP by treating the BCMBP monomer with imidazole prior to the crosslinking reaction to afford HCP-SC-IMI (Scheme 2).[19]

Results and Discussion

Analysis of HCP-SC analogues
Due to its ease of synthesis, low cost, and high surface area HCP-SC was chosen as a candidate for post synthetic modification with the aim of producing more CO$_2$-philic materials.


HCP-SC was prepared by refluxing BCMBP with iron(III) chloride following the route reported by Wood et al.$^{[47]}$ As shown in Scheme 1, post-synthetic modification of HCP-SC was achieved by stirring in Cl-SO$_3$H at room temperature for 3 days followed by heating the obtained sulfonic acid (HCP-SC-SO$_3$H) under reflux with various amines e.g., NH$_4$OH, to form ammonium salts; in this case, HCP-SC-SO$_3$NH$_4$.

IR spectroscopy obtained for the HCP-SC network (Figure S6, Supporting Information) showed peaks at 1500 and 1600 cm$^{-1}$ corresponding to C=C stretches from the phenylene rings in the network while the two peaks at 2800 and 3000 cm$^{-1}$ occur due to the C–H stretching vibrations of the phenylene rings. Because some of the methyl-chloride terminal groups are not consumed during the crosslinking reaction, a peak occurring at ca. 800 cm$^{-1}$ can be assigned to C–Cl vibrational stretch.$^{[47]}$ This was confirmed by oxygen flask combustion using Cheng’s method, which gave a chlorine content of 2.9 wt% in the polymer. An additional vibrational stretch at ca. 3400 cm$^{-1}$ can be assigned to adsorbed moisture in the network. The adsorbed moisture peak can also be seen in the sulfonated analogue (HCP-SC-SO$_3$H), where it overlaps with O–H vibrational stretch of the sulfonic acid at ca. 3400 cm$^{-1}$. Additional evidence of the presence of sulfonic acid groups is provided by the presence of the vibrational stretch observed at 1345 cm$^{-1}$, which corresponds to O=S=O.$^{[44,48]}$ Neutralisation of the sulfonated analogue with NH$_4$OH resulted in N–H vibrational stretch at ca. 3400 cm$^{-1}$, which also overlaps with the vibrational stretch of the entrapped water.

From CHNS microanalysis, the sulfur and nitrogen loadings in the ammonium salt analogue (HCP-SC-SO$_3$NH$_4$) were found to be 8.8 and 2.2%, respectively (Table 1); lower than the theoretical loading of 11.1 and 4.8% (Table S1, Supporting Information). The theoretical elemental loading of sulfur was calculated by assuming the incorporation of one sulfonic acid group per monomer unit.$^{[44]}$ while nitrogen loading was calculated by assuming full conversion of each sulfonic acid group into the ammonium salt product.$^{[45]}$ The calculated loading of sulfonic acid and ammonia in HCP-SC-SO$_3$NH$_4$ roughly translates to 0.7 and 0.4 units per monomer unit, respectively. It is worth noting that full conversion of the sulfonic acid into the salt was not achieved for any of the polymers, possibly because some of the sulfonic acids are inaccessible to the amine base. Also, discrepancies between calculated and theoretical CHNS microanalyses are often observed in HCPs due to adsorbed water, entrapped catalyst, or deviation from the idealised structure.$^{[40]}$ Similarly, the sulfonated analogue (HCP-SC-SO$_3$H) showed a slightly lower loading of sulfonic acid groups than expected. The calculated loading of sulfur was found to be 9.1% compared to an expected loading of 11.8%, which could be attributed to some of the unsubstituted phenylene rings being inaccessible to the Cl-SO$_3$H or being insufficiently activated to undergo electrophilic substitution. The calculated microanalysis of the parent polymer (HCP-SC) also showed some discrepancies in the carbon and hydrogen content, due to incomplete consumption of methyl-chloride bridges in the crosslinking reaction and physisorption of atmospheric moisture. This former was observed for related self-condensed polymers based on ortho-, meta-, and para-dichloroxylene by Wood et al. and was confirmed here by IR spectroscopy and combustion analysis.$^{[47]}$ We also attempted to react ammonia with the unreacted methyl-chlorides by stirring a suspension of HCP-SC in NH$_4$OH and DCM under reflux. CHN microanalysis of the isolated product indicated no nitrogen was present in the

Scheme 2. Synthesis and hypothetical structure of HCP-SC-IMI analogues.
Table 1. Elemental analysis and porosity of HCP-SC, HCP-SC-SO₃H, and HCP-SC-SO₃NH₄.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHNS microanalysis</th>
<th>S_{BET}[^a] [m² g⁻¹]</th>
<th>V_{Total}[^b] [cm³ g⁻¹]</th>
<th>CO₂ uptake[^c] [mmol g⁻¹]</th>
<th>CO₂ uptake[^d] [mmol g⁻¹]</th>
<th>CO₂/N₂ selectivity[^e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP-SC</td>
<td>89.1</td>
<td>5.3</td>
<td>-</td>
<td>1811</td>
<td>3.45</td>
<td>0.26 (0.12)</td>
</tr>
<tr>
<td>HCP-SC-SO₃H</td>
<td>57.6</td>
<td>4.6</td>
<td>9.1</td>
<td>1246</td>
<td>0.94</td>
<td>0.59 (0.23)</td>
</tr>
<tr>
<td>HCP-SC-SO₃NH₄</td>
<td>52.1</td>
<td>4.9</td>
<td>2.2</td>
<td>808</td>
<td>0.59</td>
<td>0.90 (0.36)</td>
</tr>
</tbody>
</table>

[^a] BET surface area calculated from nitrogen isotherms at 77 K. [^b] Total pore volume calculated from nitrogen adsorption isotherm in the range P/P₀=0.94–0.98. [^c] CO₂ uptake at 0.15 bar/298 K (0.15 bar/328 K). [^d] CO₂ total uptake at 1 bar/298 K (1 bar/328 K). [^e] IAST calculated from single and dual-site Langmuir fitting isotherms in a mixture of 15/85 CO₂:N₂ at 1 bar and 298 K.

We therefore hypothesize that the unreacted methyl chloride bridges are inaccessible within the polymer and are unable to undergo substitution reactions with the amines. In addition, the incorporation of the sulfonic acid functional groups further blocks the pore network, most likely increasing their inaccessibility. The chlorine content in HCP-SC-SO₃NH₄ was found to be 2.0 wt% which confirmed that none of the methylenechloride bridges were consumed during the sulfonation and ammonia neutralisation of HCP-SC. ICP-OES analysis of HCP-SC, HCP-SC-SO₃H, and HCP-SC-SO₃NH₄ revealed a residual Fe content of 180, 100, and 148 ppm, respectively.

The apparent Brunauer-Emmett-Teller surface area (S_{BET}) decreased upon functionalisation from 1811 m² g⁻¹ for the parent HCP-SC to 1246 and 808 m² g⁻¹ for HCP-SC-SO₃H and HCP-SC-SO₃NH₄, respectively (Table 1). The parent HCP-SC showed a pronounced hysteresis in the nitrogen adsorption-desorption isotherm at 77.3 K (Figure 1), likely due to swelling, the presence of meso- and macro-pores within the network,[18,40,49] and capillary condensation.[33,50,51] We believe that these factors contribute to the high total pore volume of 3.5 cm³ g⁻¹ observed for HCP-SC (Figure 1). As expected,[44,45] the sulfonated analogue HCP-SC-SO₃H exhibited a lower surface area and pore volume than the parent polymer. However, the presence of the sulfonic acids provide stronger interaction sites for CO₂ with the polymer due to the high quadrupole moment of CO₂ and its amphoteric character.[44] As a result, the CO₂ uptake at 298 K almost doubled to 0.59 mmol g⁻¹ at 0.15 bar and reached 2.2 mmol g⁻¹ at 1 bar. Low pressure CO₂ uptake is more representative of power plant capture conditions, where the partial pressure of CO₂ in flue gas is approximately 0.15 bar.[52] Similarly, the CO₂/N₂ selectivity almost doubled to 19:1 at 298 K in 15/85 CO₂:N₂, due to the favourable interactions of CO₂ with sulfonic acid groups.[44]

The incorporation of ammonia into the polymer reduced the surface area and pore volume to 808 m² g⁻¹ and 0.59 cm³ g⁻¹, respectively. However, CO₂ uptake at 0.15 bar and 298 K increased to 0.90 mmol g⁻¹ (higher than the parent acid), while the uptake at 1 bar increased to 2.5 mmol g⁻¹ (Table 1). The CO₂/N₂ selectivity increased to 42:1 for HCP-SC-SO₃NH₄, which is a promising value for this class of relatively inexpensive polymer.

The higher selectivity observed for HCP-SC-SO₃NH₄ compared to HCP-SC-SO₃H and HCP-SC, is due to the presence of the ammonium salt (–SO₃NH₄) and a narrowing of the micropores, which improve the strength of the polymer-CO₂ interaction (Figure 2 & Figure S1, Supporting Information). The selectivity is similar to that reported for the more expensive nitro-rich (–NO₂) hypercrosslinked triptycene analogue (TPP-4)[53] (42.5:1 at 1 bar and 298 K in 15/85 CO₂:N₂ mixture) but lower than the copper-catalysed azo-linked polymer (ALP-7), which has a selectivity of 56:1 at 1 bar and 298 K in 10/90 CO₂:N₂ mixture.[54] The CO₂/N₂ selectivity for HCP-SC-SO₃NH₄ is significantly lower than the previously reported sulfonated PPN-6 analogue (155:1 at 1 bar and 295 K in 15/85 CO₂:N₂ mixture).[44]

Figure 1. Adsorption-desorption isotherms for HCP-SC, HCP-SC-SO₃H, HCP-SC-SO₃NH₄ at 77.3 K. Adsorption (filled symbols), desorption (hollow symbols).
Table 2. Elemental analysis and porosity of the different counter ion analogues; HCP-SC-SO3TEA, HCP-SC-SO3ETA, HCP-SC-SO3IMI, and HCP-SC-SO3EN.

<table>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
<td>%N</td>
<td>%S</td>
<td>[m² g⁻¹]</td>
</tr>
<tr>
<td>HCP-SC-SO3TEA</td>
<td>62.4</td>
<td>5.7</td>
<td>2.2</td>
<td>8.6</td>
<td>582</td>
</tr>
<tr>
<td>HCP-SC-SO3ETA</td>
<td>49.8</td>
<td>5.1</td>
<td>2.8</td>
<td>7.3</td>
<td>546</td>
</tr>
<tr>
<td>HCP-SC-SO3IMI</td>
<td>61.8</td>
<td>4.8</td>
<td>5.8</td>
<td>9.1</td>
<td>657</td>
</tr>
<tr>
<td>HCP-SC-SO3EN</td>
<td>57.6</td>
<td>5.5</td>
<td>5.4</td>
<td>7.9</td>
<td>509</td>
</tr>
</tbody>
</table>

[^a]: BET surface area calculated from nitrogen isotherms at 77 K. [^b]: Total pore volume calculated from nitrogen adsorption isotherm in the range P/P₀=0.94–0.98. [^c]: CO2 uptake at 0.15 bar/298 K (0.15 bar/328 K). [^d]: CO2 total uptake at 1 bar/298 K (1 bar/328 K). [^e]: IAST calculated from single and dual-site Langmuir fitting isotherms in a mixture of 15/85 CO2:N2 at 1 bar and 298 K.

and its ammonium sulfonate salt (796:1 at 1 bar and 313 K in 15/85 CO2:N2 mixture),[^45] but again we would contend that these HCP materials are much more scalable. In addition to IAST selectivity, we collected breakthrough curves for HCP-SC-SO3NH4. Using a binary mixture of CO2 and N2 in 15:85 ratio at 298 K and 1 bar with a helium purge between runs (Figure S20, Supporting Information). A total of 6 breakthrough cycles were run showing no loss in CO2 capacity and selectivity. HCP-SC-SO3NH4 CO2/N2 selectivity was calculated to be 17:1,[^55] lower than IAST value; this may be the result of slower adsorption kinetics of CO2 into the polymer under conditions similar to flue gas streams.[^56]

The Qst of each of the analogues was calculated from three CO2 uptake isotherms at 298, 318, and 328 K. The CO2 Qst for HCP-SC was around 19 kJ mol⁻¹ in the zero-coverage region. This value is relatively low,[^44] as expected due to the lack of CO2 polarizing groups within the network.[^44] Incorporation of sulfonic acids into HCP-SC almost doubled the Qst to ca. 37 kJ mol⁻¹, while the Qst of HCP-SC-SO3NH4 was found to be 36 kJ mol⁻¹ (Figure 3). The reported Qst of the sulfonic acid of PPN-6 and its ammonium salt were ca. 30 and 40 kJ mol⁻¹, respectively,[^45] similar to the values we obtained for these cheaper HCP-SC sulfonated and ammonium salt analogues.

**Analysis of different counterion analogues**

In an attempt to increase the CO2/N2 selectivity in HCP-SC networks through derivatisation to incorporate CO2-philic functional groups, we investigated the variation of the counter ion on CO2 selectivity and uptake. To introduce different counterions, the sulfonic acid, HCP-SC-SO3H, was stirred under reflux for 24 hours in a DCM solution of the specified amine-...
1350 cm⁻¹ and perhaps the sp3 C–H bend in the region of ca. 1300 to 1400 cm⁻¹. As stated previously, theoretical CHNS analysis of HCP-SC-IMI analogues showed the highest loading of nitrogen of 5.4 and 5.8%, respectively, which indicated that conversion of the analogues showed the highest loading of nitrogen of 5.4 and 5.8% across the analogues, with discrepancies observed between the calculated and theoretical values. The lowest nitrogen loading was observed in HCP-SC-SO₃TEA and HCP-SC-SO₃ETA of 2.2 and 2.8%, respectively, which indicated that conversion of the sulfonic acids to the desired salt was not fully achieved (Table S1, Supporting Information). HCP-SC-SO₃EN and HCP-SC-SO₃IMI analogues showed the highest loading of nitrogen of 5.4 and 5.8% mainly due to their higher nitrogen content when compared to triethylamine and ethanolamine.

The SA_BET of these salts decreased with respect to the parent acid polymer to values of between 509 and 657 m² g⁻¹ (Tables 1 and 2). We anticipated that the various counterions might interact differently with CO₂, thus resulting in different CO₂/N₂ selectivity values. For instance, the delocalized positive charge over imidazolium might result in weaker interactions with CO₂ when compared to HCP-SC-SO₃EN.

The highest CO₂/N₂ selectivity among these analogues was 18:1, as obtained for the imidazolium salt, HCP-SC-SO₃IMI. We ascribe this to a combination of the CO₂–imidazolium salt interactions and the narrower pores present in the imidazolium analogue compared to the other three alkylammonium analogues (Figure 2). However, the selectivity for HCP-SC-SO₃IMI is lower than that observed for the ammonium salt, above, which has a CO₂/N₂ selectivity of 42:1; this is probably because of its high localized positive charge density, which results in stronger CO₂ interactions. As a result, the uptake of CO₂ in the low pressure region was measured to be 0.90 vs 0.43 mmol g⁻¹ for the ammonium and imidazolium salts, respectively. Similarly, the total uptake of CO₂ at 1 bar was higher for the ammonium salt as a result of its higher surface area of 808 m² g⁻¹ compared to 657 m² g⁻¹ for the imidazolium salt (Tables 1 and 2). Hence, alkylated amines did not provide a selectivity or CO₂ capacity benefit with respect to the ammonium salt, HCP-SC-SO₃NH₄.

The presence of nitrogen in the polymer increases the number of preferential CO₂ binding sites. This can be seen in the case of the ethylenediamine-containing salt. Despite HCP-SC-SO₃EN having a pore volume of only 0.34 cm³ g⁻¹ and a SA_BET of 509 m² g⁻¹ its CO₂/N₂ selectivity was calculated to be 12:1. Although the HCP-SC-SO₃ETA analogue has a similar pore volume of 0.34 cm³ g⁻¹ and a slightly higher SA_BET of 546 m² g⁻¹, its CO₂/N₂ selectivity decreased to 8:1. We ascribe the drop in selectivity to the blocking of the narrower micropores (<1.0 nm) in the case of the ethylenediamine-containing salt. Despite HCP-SC-SO₃ETA in addition to its lower nitrogen content compared to HCP-SC-SO₃EN (Figure 2), its CO₂/N₂ selectivity was lowest for HCP-SC-SO₃TEA, where blocking of the narrower micropores and steric hindrance around the nitrogen lowered its selectivity to 6:1. Although nitrogen loading provides stronger binding sites for CO₂, pore width also plays an important role.

Varying the counter ions also has an impact on Q_st values and how strongly the CO₂ interacts with the polymers. The imidazolium salt showed the highest Q_st of 45 kJ mol⁻¹ in the zero-coverage region, which is higher than the ammonium salt, HCP-SC-SO₃NH₄ (Figure 3). Ethylenediamine and ethanolamine analogues showed Q_st of 31 and 32 kJ mol⁻¹, respectively in the zero-coverage region while the triethylamine analogue was slightly higher with a value around 36 kJ mol⁻¹ in the zero-coverage region. The Q_st values of the different salts all fall within physisorption range.

Analysis of HCP-SC-IMI analogues

Full conversion of the sulfonic acid to the salt was not achieved for any of these polymers, most likely due to some of the sulfonic acids being inaccessible to the amine bases. We therefore...
decided to covalently attach imidazole to BCMBP prior to the crosslinking reaction, and to study the effect on the CO₂ uptake and CO₂/N₂ selectivity. The BCMBP monomer was reacted with imidazole (6:1 ratio) in DCE under reflux and nitrogen. The crosslinking reaction was then induced by the addition of FeCl₃ and heating under reflux to yield HCP-SC-IMI (Scheme 2). Similar to HCP-SC, HCP-SC-IMI was also derivatised to yield the corresponding sulfonated and ammonium salt analogues; HCP-SC-IMI-SO₃H and HCP-SC-IMI-SO₃NH₄.

₁H NMR spectra of BCMBP-IMI in the reaction mixture (Figure S19, Supporting Information) confirmed the attachment of imidazole to BCMBP through the appearance of three singlet peaks between 5.48–5.54 ppm, suggesting the presence of three new methylene environments. These correspond to methylene protons adjacent to an imidazole, which is formed by the displacement of the chloride at one or both ends of the BCMBP. It is also possible for an imidazole to act as a bridge between two molecules of BCMBP. Protonation of any mono-substituted imidazole by the HCl generated in the reaction is also a possibility and might explain the presence of peaks between 9.11 and 9.57 ppm in the ¹H NMR. The peak at 4.8 ppm corresponds to the methyl-chloride; since imidazole was reacted in limitation, the higher intensity of this peak when compared to the methyl-imidazole resonance was anticipated. Due to the lower intensity of the methyl-imidazole in BCMBP-IMI, ¹³C NMR signal of the methyl carbon was below the level that could be detected.

IR spectroscopy obtained for HCP-SC-IMI analogue (Figure S8, Supporting Information) showed a stronger intensity at ca. 3450 cm⁻¹ compared to HCP-SC. However, the overlap of the N–H stretch with the O–H vibrational stretch makes it difficult to assign the protonated imidazole vibrational stretch. The appearance of O–S–O stretch at ca. 1250 cm⁻¹ in the IR spectra of HCP-SC-IMI-SO₃H confirmed the presence of the sulfonic acid.

**Table 3.** Elemental analysis and porosity of HCP-SC-IMI, HCP-SC-IMI-SO₃H, and HCP-SC-IMI-SO₃NH₄.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHNS microanalysis</th>
<th>SÀET[a]</th>
<th>VTotal[b]</th>
<th>CO₂ uptake[c]</th>
<th>CO₂ uptake[d]</th>
<th>CO₂/N₂ selectivity[e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCP-SC-IMI</td>
<td>84.0 5.4 1.5</td>
<td>0.36</td>
<td>0.36 (0.11) 1.7 (0.8)</td>
<td>14:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCP-SC-IMI-SO₃H</td>
<td>58.2 4.6 0</td>
<td>0.72</td>
<td>0.54 (0.24) 1.7 (1.1)</td>
<td>29:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCP-SC-IMI-SO₃NH₄</td>
<td>53.9 4.8 3.0</td>
<td>0.54</td>
<td>0.79 (0.35) 2.1 (1.3)</td>
<td>30:1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] BET surface area calculated from nitrogen isotherms at 77 K. [b] Total pore volume calculated from nitrogen adsorption isotherm in the range P/P₀=0.94–0.98. [c] CO₂ uptake at 0.15 bar/298 K (0.15 bar/328 K). [d] CO₂ total uptake at 1 bar/298 K (1 bar/328 K). [e] IAST calculated from single and dual-site Langmuir-fitting isotherms in a mixture of 15/85 CO₂:N₂ at 1 bar and 298 K.

**Figure 4.** Top) Pore-size distribution for HCP-SC-IMI analogues calculated using pillared clay model of NL-DFT method assuming cylindrical pores. Bottom) Nitrogen isotherms of HCP-SC-IMI analogues at 77.3 K. Adsorption (filled symbols), desorption (hollow symbols).
difficult due to overlapping with the O–H of the trapped moisture and the sulfonic acid groups (Figure S8, Supporting Information).

Due to the incorporation of the imidazole and the fewer methyl-chloride groups being available for crosslinking, the $S_{A\text{BET}}$ and pore volume of HCP-SC-IMI decreased to $1049 \text{ m}^2 \text{ g}^{-1}$ and $0.95 \text{ cm}^3 \text{ g}^{-1}$, respectively, when compared to HCP-SC (Tables 1 and 3). The nitrogen sorption isotherm of HCP-SC-IMI at 77.3 K showed less hysteresis than for HCP-SC due to less inner-ster within the network as a result of the fewer crosslinking bridges (Figure 4).$^{[34,66]}$ The $CO_2$ uptake at 0.15 bar and 298 K, increased by around 40%, from 0.26 mmol g$^{-1}$ in HCP-SC to 0.36 mmol g$^{-1}$ in HCP-SC-IMI, while the uptake at 1 bar and 298 K was 1.7 mmol g$^{-1}$ for HCP-SC-IMI compared to 1.4 mmol g$^{-1}$ for HCP-SC under similar conditions (Tables 1 and 3). The increase in $CO_2$ capacity is likely due to the presence of the Lewis basic nitrogen in HCP-SC-IMI,$^{[82,65]}$ which would also explain the high $Q_{st}$ of 45 kJ mol$^{-1}$ (Figure S5, Supporting Information). The $Q_{C}$ value falls near the chemisorption region of 50 kJ mol$^{-1}$, but the reversibility of $CO_2$ isotherms suggests that the polymer maintains a physisorption adsorption mechanism.

Encouraged by these results, we hypothesised that further post-synthetic modification of HCP-SC-IMI to introduce the ammonium salt could result in an increase in $CO_2/N_2$ selectivity. Sulfonation was carried out in a similar manner to the HCP-SC network (Scheme 2). HCP-SC-IMI-SO$_3$H had a sulfur content of 9.5% (Table 3) and a $S_{A\text{BET}}$ of 745 m$^2$ g$^{-1}$. The $CO_2$ uptake at 1 bar and 298 K did not change when compared to the parent polymer, but the $CO_2/N_2$ selectivity almost doubled to 29:1 because of an increase in $CO_2$ uptake at low pressure. Stirring the sulfonated analogue in ammonium hydroxide afforded HCP-SC-IMI-SO$_3$NH$_4$, which has the lowest $S_{A\text{BET}}$ amongst HCP-SC-IMI analogues of 642 m$^2$ g$^{-1}$. The $CO_2$ uptake at 1 bar and 298 K, however, increased to 2.1 mmol g$^{-1}$ despite the total pore volume decreasing to 0.54 cm$^3$ g$^{-1}$. The corresponding selectivity value was 30:1; lower than the 42:1 value that was obtained for HCP-SC-SO$_3$NH$_4$ both at 1 bar and 298 K in 15/85 $CO_2/N_2$ mixture. This loss of selectivity is attributed to the loss of some micropores in HCP-SC-IMI-SO$_3$NH$_4$ that are present in HCP-SC-SO$_3$NH$_4$ (Figures 2 and 4). This result emphasizes the important role pore size distribution plays in obtaining high $CO_2/N_2$ selectivity.$^{[38,64,65]}$

Finally, the $Q_{C}$ of the sulfonated analogue (HCP-SC-IMI-SO$_3$H) dropped to 36 kJ mol$^{-1}$ compared to HCP-SC-IMI but the selectivity almost doubled. The ammonium salt analogue showed a slightly lower $Q_{C}$ value of 35 kJ mol$^{-1}$, but due to the loss of some of the narrower micropores, the $CO_3/N_2$ selectivity has not improved compared to the sulfonated analogue (Figure S5, Supporting Information).

**Conclusions**

In conclusion, we have combined two approaches—electrostatic and covalent attachment—to maximise amine loading in BCMBP-derived HCPs in an attempt to increase $CO_2/N_2$ selectivity. After screening a range of amines, we found that ammonium salts afforded the highest $CO_2$ uptakes and selectivities for HCP-SC-SO$_3$NH$_4$ and HCP-SC-IMI-SO$_3$NH$_4$, respectively. The presence of additional micropores in the HCP-SC-SO$_3$NH$_4$ afforded the highest selectivity of $CO_2$ over nitrogen for all the materials tested. Finding the right tradeoff between nitrogen loading and pore diameter is important to achieve high $CO_2/N_2$ selectivity.

**Experimental Section**

**Materials and methods:** 4,4’-Bis(chloromethyl)-1,1’-biphenyl was obtained from TCI chemicals, UK. All other reagents were purchased from Sigma-Aldrich and used as received.

**Synthesis of HCP-SC:** To a solution of BCMBP (2.14 g, 8.52 mmol) in anhydrous DCE (20 mL), was added FeCl$_3$ (1.38 g, 8.52 mmol) under a nitrogen atmosphere. The resulting mixture was heated under reflux for 18 hours. The brown precipitate was washed with water (50 mL), methanol (3 x 50 mL), and with diethyl ether (30 mL), followed by drying for 24 hours at 60 °C under vacuum to produce HCP-SC (yield = 1.52 g) (Scheme 1).

**Derivatisation of BCMBP with imidazole:** Under a nitrogen atmosphere, a solution of BCMBP (1.38 g, 5.49 mmol) and imidazole (0.06 g, 0.88 mmol) in DCE (40 mL) was heated under reflux overnight, at which time the imidazole was consumed (monitored by TLC) to produce BCMBP-IMI (Scheme 2).

**Synthesis of HCP-SC-IMI:** FeCl$_3$ (0.89 g, 5.49 mmol) was added to the above mixture of BCMBP-IMI then the reaction was heated under reflux overnight. After cooling, the precipitate was collected by filtration and washed with water (50 mL) and methanol (3 x 50 mL). The solid was further purified by Soxhlet extraction in methanol for 24 hours, then dried in a vacuum oven at 60 °C for 24 hours to produce HCP-SC-IMI (yield = 1.27 g) (Scheme 2).

**General procedure for sulfonation of HCP-SC and HCP-SC-IMI:** An ice-bath-cooled suspension of HCP-SC (200 mg) in DCM (20 mL) was stirred and allowed to swell for a few hours. To this was added Si-SC-OH (6 mL, 90 mmol) drop-wise. The resulting mixture was stirred at room temperature for three days then poured into ice. The solid was collected, thoroughly washed with methanol and water, then dried at 60 °C under vacuum to produce HCP-SC-SO$_3$H (yield = 262 mg) (Scheme 1). The same procedure was followed using HCP-SC-IMI to produce HCP-SC-IMI-SO$_3$H (yield = 278 mg) (Scheme 2).

**General procedure for ammonium salt formation with HCP-SC-SO$_3$H and HCP-SC-SO$_3$IMI:** A suspension of HCP-SC-SO$_3$H (150 mg) in 10 mL DCM was allowed to swell for a few hours. Na$_2$OEt solution (20 mL) was added and the mixture was washed with methanol and water, then washed with water (50 mL) and methanol (3 x 50 mL) and dried at 60 °C. The resulting mixture was stirred at room temperature for three days then poured into ice. The solid was collected, thoroughly washed with methanol and water, then filtered and dried at 60 °C under vacuum to produce HCP-SC-SO$_3$NH$_4$ (yield = 195 mg) (Scheme 2).

**Synthesis of HCP-SC-SO$_3$NH$_4$ and TEA, ETA, IMI, and EN:** (a) Synthesis of HCP-SC-SO$_3$TEA: An ice-bath-cooled mixture of HCP-SC-SO$_3$H (150 mg) in DCM (10 mL) was allowed to swell for few hours. To this, was added trimethylamine (TEA) (20 mL) and the mixture was heated under nitrogen and reflux overnight. The solid was collected, thoroughly washed with water and methanol, and then dried at 60 °C under vacuum to produce HCP-SC-SO$_3$NH$_4$ (yield = 195 mg) (Scheme 2). (b) Synthesis of HCP-SC-SO$_3$IMI: An ice-bath-cooled mixture of HCP-SC-SO$_3$H (150 mg) in DCM (20 mL) was allowed to swell for few hours. To this, was added imidazole (IMI) (2.0 g, 0.05 mol) and the mixture was heated under reflux overnight. The solid was collected, thoroughly washed with water and methanol, and then dried at 60 °C under vacuum to produce HCP-SC-SO$_3$IMI (yield = 195 mg) (Scheme 2). (c) Synthesis of HCP-SC-SO$_3$IMI: An ice-bath-cooled mixture of HCP-SC-SO$_3$H (100 mg) in DCM (10 mL) was allowed to swell for few hours. To this, was added ethylenediamine (EN) (10 mL) and the mixture...
The sample was heated under reflux overnight. The solid was collected, thoroughly washed with water and methanol, and then dried at 60 °C under vacuum for 24 hours to produce HCP-SC-SO₃EN (yield = 112 mg).

**Fourier transform infrared (FTIR):** IR spectra for HCP analogues were collected on a Bruker Tensor 27 using KBr disks.

**Elemental analysis:** CHN elemental analysis was carried out using a Thermo FlashEA 1112 Elemental Analyser and CHNS elemental analysis was carried out using an Elementar vario MICRO cube.

**nuclear magnetic resonance (1H NMR):** Solution 1H NMR was carried out on a Bruker 400MHz Advance spectrometer.

**Gas sorption.** Nitrogen adsorption and desorption isotherms of the HCP analogues were collected at 77.3 K using an ASAP2420 volumetric adsorption analyser (Micrometrics Instrument Corporation). Brunauer-Emmett-Teller surface area (S_{BET}) was calculated in the relative pressure (P/P₀) range of 0.05–0.25 and total pore volume (V_{total}) was calculated at P/P₀ = ca. 0.89–0.99. The pillared clay method of non-local density functional theory (NL-DFT) was used to determine the pore size distribution assuming cylindrical pore geometry. Carbon dioxide and nitrogen isotherms were collected up to a pressure of 1 bar on a Micromeritics ASAP2020 at 298 K for nitrogen and 298, 318, and 328 K for carbon dioxide. HCP analogues were degassed at 120 °C for 90 minutes under dynamic vacuum (10⁻⁵ bar) before analysis.

**Scanning electron microscopy (SEM):** A Hitachi S 4800 cold field emission scanning electron microscope (FE SEM) was used to collect high resolution imaging of the polymer morphology. The samples were loaded 1 to 600 °C under nitrogen followed by switching to air at 600 °C.

**Thermogravimetric analysis (TGA):** TGA was carried out in aluminium pans using a Q5000IR analyser (TA instruments) with an automated vertical overhead thermostable. The samples were heated at 20 °C min⁻¹ to 600 °C under nitrogen followed by switching to air at 600 °C.

**Breakthrough measurements:** Hiden Iso-chroma Automated Breakthrough Analyzer (ABR) was used to carry out breakthrough measurements for HCP-SC-SO₃NH₄. The measurements were run at 1 bar in a 15:85 CO₂/N₂ mixture at 298 K and a total flow rate of 8 mL min⁻¹.

**Chlorine analysis:*** The analysis of chlorine was performed by Exter Analytical, UK. The polymers were combusted in a microwave prior to analysis.

**Inductively coupled plasma optical emission spectrometry (ICP-OES):** ICP-OES analysis was performed by Exter Analytical, UK, using a Thermo iCap 7000; samples were digested with nitric acid and hydrogen peroxide in a microwave prior to analysis.

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**Keywords:** Hypercrosslinked polymers • CO₂ capture • microporous materials • increased selectivity • cost efficiency

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Reducing the cost of carbon dioxide capture applications is crucial for future commercial applications of porous adsorbents. A relatively cheap hypercrosslinked polymer grafted electrostatically with ammonium salt showed an appropriate narrow pore size distribution leading to a high CO₂/N₂ selectivity.