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Conjugated microporous polytriphenylamine networks with surface areas of 530 m$^2$/g were synthesized via Buchwald–Hartwig coupling, resulting in high CO$_2$ uptake (up to 6.5 wt%) and CO$_2$/N$_2$ selectivity (75) at 1 bar and 303 K.
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Conjugated microporous polymers (CMPs) with intrinsic properties including small pore sizes (< 2 nm), large specific surface areas (> 6000 m²/g), high chemical stability, low skeleton density and reversible redox properties exhibit great promise for gas storage, separation, sensing, catalysis and battery applications. Versatile CMPs have been obtained readily through template-free chemical processes by careful selection of building blocks and, commonly, suitable C–C or C–N coupling reactions, which show efficient preparation and high flexibility in the molecular design. Typically, Suzuki, Sonogashira–Hagihara and Yamamoto coupling, Schiff-base chemistry, cyclotrimerization and oxidative polymerization reactions have been used to synthesize CMPs. Previous studies demonstrated that control over average micropore size, surface area, and gas uptake of the CMPs was enabled by alternating the strut lengths, rigidities, and functionalities of the building blocks.

Buchwald–Hartwig (BH) coupling is utilized in organic synthesis for the generation of C–N bonds via the palladium-catalysed cross-coupling of amines with aryl halides. The BH coupling approach allows for expansion of the repertoire of possible C–N bond formation through the facile synthesis of aromatic amines. This useful method also provides a simple route to nitrogen-containing redox-active system, as shown in recent work from our laboratories on the synthesis of well-defined symmetrical oligo(amine)s, OANIs. Verification of this approach was achieved by BH cross-coupling of aniline with tris(4-bromophenyl)amine. This resulted in C–N bond formation, affording the fully reduced molecular analogue of the PTPAs, 4,4′,4″-tri(phenylamino)triphenylamine (analogous to the leucoemeraldine base structure found for OANIs, see ESI, Scheme S1). Once verified, BH coupling of diamine species afforded black, blue, brown, and yellow insoluble PTPA-1, 2, 3, 4 powders (Figure S1) with yields of 65–80%. The chemical structures of the PTPAs were confirmed by Fourier transform infrared (FT-IR) and solid-state ¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) investigations. Bands of the primary amine group of the linkers at 3470 and 3420 (–NH deformation) as well as the aryl C–H stretching and 1650 cm⁻¹ (–NH₂ deformation) as well as the aromatic C–Br groups of the tri(4-bromophenylamine) at 1178 cm⁻¹ (aromatic C–Br stretching) are absent or strongly attenuated in the spectra of the PTPAs (Figure S2). The distinct quinoid (Q) and benzenoid (B) bands at 1598 and 1498 cm⁻¹ as well as the aryl C–H band at 820 cm⁻¹ are present in the spectra of the resulting materials. Solid-state ¹³C CP/MAS NMR spectra of all polymers show three main resonances at ~ 141, ~ 127 and ~ 118 ppm, originating from the aryl carbons of both the starting materials (Figure S3). Three additional resonances at 17, 116 and 35 ppm are attributed to the methyl, alkenyl and methylene groups of PTPA-2, 3 and 4, respectively. The ultra-violet/visible near infrared (UV/Vis-NIR) spectra of fully conjugated PTPA-1, PTPA-2, and PTPA-3 exhibit two peaks at 380 and 600 nm, typically attributed to π–π* transition of benzenoid and quinoid rings (Figure 1), respectively, as...
confirmed by recent calculations. Specifically, PTPA-3 displays a broad peak around 1100 nm, attributed to the electron and hole migration found in trans-stilbene. These results confirm the creation of extended conjugated PTPA networks with amine linkages.

**Figure 1** Solid-state UV/Vis-NIR spectra of PTPAs.

As expected, PTPAs displayed amorphous structures, as determined by powder X-ray diffraction (XRD) measurements (broad peaks at 20 = ~12.2°, Figure S4). No π-stacking was evident from these investigations. Scanning electron microscope (SEM) images showed the morphologies of PTPAs consisting of aggregated nanoparticles with diameters of 200-500 nm (Figure 2). This leads to some outer surface area (large meso- and macropores due to interstitial voids), which is highest for PTPA-2 and PTPA-3 as evidenced by cryogenic gas adsorption (see below). The transmission electron microscope (TEM) images indicate the microporous structures of the PTPA nanoparticles (see Figure S5), which are typically found in amorphous CMPs. The materials are thermally stable in N2 up to 300 °C, as revealed by thermal gravimetric analysis (TGA) (see Figure S6). In particular, for PTPA-3 and PTPA-4, ~60 wt% remained after heating to 1000 °C. The excellent thermal stability of PTPAs is ascribed to the nature of their cross-linking networks.

**Figure 2** SEM images of prepared PTPAs.

The porosity parameters of the polymers were initially studied by gas adsorption analysis using nitrogen as the adsorbate. Nitrogen adsorption/desorption isotherms of PTPAs measured at 77.4 K are shown in Figure 3. All materials showed some outer surface area, most likely originating from interparticulate porosity associated with the meso- and macrostructures of the samples and interparticulate voids. This was evidenced by the steep increase of N2 uptake at relative pressure above 0.9 observed for all materials. It is plausible to expect that precipitation of the growing polymer networks is responsible for the formation of observed macro/mesoporosity.

PTPA-4 does not show any other signs of porosity and consequently shows the lowest N2 uptake. In contrast, PTPA-1 does show some broadly distributed mesoporosity in conjunction with macroporosity, as derived from the hysteresis between the adsorption and desorption curves, which close around p/p0 ~ 0.45.

**Figure 3** (Left) N2 adsorption/desorption isotherms (77.4 K) and (right) CO2 adsorption/desorption isotherm at 273 K.

CO2 adsorption was measured for all PTPA materials at 273 K (see Figure 3) to gain further information on the microporosity. All materials show significant CO2 uptake. The highest uptake was found for PTPA-3 (6.5 wt%), followed by PTPA-2 (5.5 wt%), and PTPA-1 and PTPA-4 (uptake < 4 wt%). The isotherms show only weak hysteresis and were analysed using the commercialized Grand-canonical Monte-Carlo (GCMC) methodology to extract porosity information (see Table 1). All materials show similar broad pore size distributions, which is in line with their amorphous nature. The main fraction of pores have sizes between 0.5 and 1 nm (Figure S7).

Generally, PTPAs prepared from monomers containing longer and more rigid struts should show higher apparent specific surface areas if no interdigitating structures are observed. Shorter linkers might lead to compact structures of low porosity. However, the monomer geometry alone is not decisive in determining final porosity, as the reaction conditions, choice of solvents and solubility of the forming polymeric network phase all contribute to the physical properties of the final CMP. It is nevertheless of worth to discuss the observed porosities with regard to the monomer geometry and rigidity, allowing comparison and conclusions to be drawn for the present systems. The use of the stilbene monomer (L3), which is significantly more rigid compared with its ethylene-bridged counterpart L4, results in the formation of significant microporosity. Interestingly, the very rigid (but shorter) p-phenylenediamine (L1) yields a moderately microporous material. The low microporosity could result from the formation of a more dense structure (PTPA-1), i.e. the conjugated segments are less separated and might adhere to each other, favouring pore closure. The methyl-decorated biphenylene-based linker L2 yields a network of considerable microporosity. The strategy to enhance the free volume of, for
example, membrane polymers using such methyl-decorated monomers is well known, and is effective here as well. In the investigated systems, monomer molecular structures do impact on the observed porosity, thus following commonly known trends. It also shows that our chosen platform is modular and that porosities could be tuned to reach higher values through further exploration and optimization of the reaction conditions.

Table 1 Porosity parameters and CO₂ separation properties of the microporous PTPAs

<table>
<thead>
<tr>
<th>PTPA</th>
<th>S_{BET}^{m} (m²/g)</th>
<th>PV∡ (cm³/g)</th>
<th>MPV (cm³/g)</th>
<th>µ-pore S_{GCMC} (m²/g)</th>
<th>MPV_{GCMC} (cm³/g)</th>
<th>CO₂ uptake at 1.0 bar (w%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>52</td>
<td>0.11</td>
<td>n.a.</td>
<td>195</td>
<td>0.07</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>62/120³</td>
<td>0.06</td>
<td>0.05</td>
<td>292</td>
<td>0.11</td>
<td>5.5</td>
</tr>
<tr>
<td>3</td>
<td>450/530³</td>
<td>0.36</td>
<td>0.18</td>
<td>356</td>
<td>0.13</td>
<td>6.5</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>0.03</td>
<td>n.a.</td>
<td>130</td>
<td>0.05</td>
<td>2.2</td>
</tr>
</tbody>
</table>

³ Surface area calculated from nitrogen adsorption isotherms using the BET equation. ² Surface area calculated from the desorption branch of the N₂ isotherms using the BET equation. ¹ Porosity volume calculated from nitrogen adsorption at p/ₚ₀ = 0.95. ⁴ Micropore volume calculated from QSDFT (slit pore model, desorption branch) analysis of N₂ data. ⁵ Micropore surface area determined from GCMC analysis of the CO₂ adsorption data at 273 K. n.a. not applicable; n.d. not determined.

The presence of fairly small pores with a uniform distribution of polar amine units is expected to result in favourable interactions between specific adsorbate molecules and the polymeric adsorbent. We analysed the potential of PTPA-3 for gas separation, exemplified by the CO₂/N₂ gas pair. The separation of CO₂ from, for example, flue gas (post-combustion) is of current interest with regard to the capture of CO₂ for environmental (greenhouse gas) or economic reasons (CO₂ as alternative feedstock for new polymers). There are various other applications, such as cryogenic spray-freezing and food preservation that would benefit from CO₂ recycling and food separation. CO₂ adsorption on PTPA-3 at 30°C (303 K) was 0.765 mmol/g (3.4 wt%) at 1.0 bar, lower compared with some standard materials (zeolites, activated carbon). The N₂ adsorption on PTPA-3 at 30°C was found to be 0.022 mmol/g at 1.0 bar, resulting in an equilibrium selectivity of α (CO₂/N₂)eq ∼ 35. Further analysis was performed by calculating the IAST selectivity at 30°C based on the assumption of a gas composition of 15% (v/v) CO₂. The necessity description of the isotherm was achieved by fitting the experimental data points by either a simple Langmuir (N₂) or a dual-site Langmuir fit (CO₂). It should however be noted that the CO₂ data could also be described very well by a simple Langmuir fit (see Figure S8). The IAST selectivity of CO₂ over N₂ is calculated to be 75 at ambient pressure (1.0 bar, 30°C). This value compares very favourably with most reported results for microporous organic polymers, usually with selectivities in the range 20 to 50.¹⁷ The predicted adsorption isotherms from the gas mixture are shown in Figure 4.

Figure 4 CO₂ and N₂ adsorption/desorption isotherms (single gas) at 303 K (symbol+line) with predicted adsorption isotherms (line only) from a 0.15/0.85 v/v gas mixture of CO₂ and N₂ at 303 K (based on IAST methodology).

The fact that the CO₂ adsorption isotherm could also be represented by a simple Langmuir approach indicates that the surface area of PTPA-3 is very homogenous. This is indeed supported by first estimation of the isosteric heat of adsorption qst based on the CO₂ isotherms measured at 273 and 303 K. The qst remained almost constant over the whole coverage range (values between 27 and 28 kJ/mol) indicating a very stable operation regime. The qst values are somewhat higher than values commonly found for activated carbons or other polymers, but low enough for adsorbent regeneration without too high an energetic penalty.

In summary, we have successfully synthesized a series of conjugated microporous polytriphenylamine (PTPAs) based on a triphenylene core motif using Buchwald–Hartwig (BH) cross-coupling. The BET surface area of these conjugated microporous polymers is up to 530 m²/g. Owing to the microporosity and the homogenously electron-rich and polar pore surface, they exhibit high CO₂ uptakes of up to 6.5 wt% and good CO₂/N₂ adsorption ideal selectivities of up to 75 at 303 K and 1.0 bar. The overall porosity and the corresponding gas adsorption properties strongly depend on the building block size, molecular architectures and functionalities. BH coupling exhibits a promising approach for large-scale manufacturing of conjugated microporous polymers and provides a high conversion of functional monomers used. Post-synthesis treatment of the tertiary and secondary amines resulting in permanent quarterisation and careful choice of corresponding counterions may enable tuning of gas uptake and selectivity. Continued investigation into the design, synthesis and characterisation of related materials is on-going in our laboratories.

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Notes and references

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† Electronic Supplementary Information (ESI) available: studies on the synthesis, characterization, morphology, and gas adsorption/desorption of the PTPAs. See DOI: 10.1039/c000000x/


