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A highly gas permeable polyimide with enhanced selectivity for membrane gas separations†

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Polymers that can be processed from solution to form microporous solids are of growing interest for use as highly permeable membranes for gas separations including O2 or N2 enrichment from air, natural gas upgrading (predominantly removing CO2 from CH4), and hydrogen recovery from ammonia manufacture (separating H2 from N2).1–3 Polymers currently used as membranes for commercial gas separation, such as the polyimide Matrimid,4 generally demonstrate high selectivity but low permeability thus limiting industrial membrane applications to small and medium-scale gas separations. In contrast, highly permeable polymers have potential for large-scale separations but only if selectivity can be enhanced.5 However, for the separation of two gases (x and y), there is a well-established empirical trade-off between permeability (P) and selectivity (αxy = Pxy/Py) that was quantified by Robeson initially in 1991 (ref. 5) and then updated in 2008.6 Based on the permeability data for a large number of polymers, Robeson identified an “upper bound” in plots of log P versus log αxy for each gas pair of interest. The position of a polymer’s gas permeability data relative to the relevant upper bound is used as the universal performance indicator for assessing its potential for the separation of two gases.

Robeson noted that each of the upper bounds are populated by data from glassy polymers with rigid chains that promote diffusivity selectivity – i.e. the preferential transport of lighter gas molecules of smaller kinetic diameters (e.g. He = 2.65; H2 = 2.80; CO2 = 3.3; O2 = 3.45 Å) over that of larger molecules (e.g. N2 = 3.64; CH4 = 3.87 Å). Hence it was predicted that greater size selectivity could be obtained by increasing polymer chain rigidity whereas high gas permeability relies on large inter-chain separation.7 Polymers of Intrinsic Microporosity (PIMs), such as the archetypal PIM-1 (Fig. 1a), fulfill both of these design criteria by possessing a rigid chain structure within which motion is restricted and sites of contortion, often provided by spirobisindan (SBI) units, to prohibit space efficient packing and generate high free volume.7,8,9 Therefore, permeability data for PIMs generally lie over the 1991 upper bound for most gas pairs10,11 and some approach, or even exceed, the 2008 upper bounds (Fig. 2).12,13 Similarly, microporous polyimides based on the SBI unit also demonstrate high permeability with modest selectivity (e.g. PIM-PI-SBI; Fig. 1b).14,15

† Electronic supplementary information (ESI) available: Experimental details for synthesis, characterisation and modeling. Also sorption isotherms for CO2, CH4 and N2 and comparative permeability data for PIM-1, PIM-PI-SBI and PIM-EA-TB. See DOI: 10.1039/c4ta00564c
Recently, we demonstrated that the polymerisation of 2,6(7)-diamino-9,10-dimethylethanoanthracene by the formation of linking groups based on Tröger’s base (TB) provides a highly permeable polymer (PIM-EA-TB; Fig. 1c) with remarkably high gas selectivities so that its data lie well above the 2008 upper bounds for O$_2$–N$_2$ (Fig. 2a), H$_2$–N$_2$ (Fig. 2b), H$_2$–CH$_4$ and H$_2$–CO$_2$.\textsuperscript{16} The exceptional performance of PIM-EA-TB was attributed to enhanced diffusivity selectivity as a result of its highly shape-persistent structure provided by the bridged bicyclic ethanoanthracene (EA) component as compared to the more flexible SBI unit.\textsuperscript{16} Hence it is important to establish whether the exchange of SBI components for EA units in other types of PIMs may also result in enhanced size-selectivity for gas separations and provides a general concept for improving polymers for gas separations.\textsuperscript{17} Here we validate this concept by the synthesis of an EA-based polyimide (PIM-PI-EA; Fig. 1d), which has a structure that allows the direct comparison of its performance with a recently reported highly permeable SBI-based polyimide (PIM-PI-SBI; Fig. 1b).\textsuperscript{14}

The required novel EA-based bisanhydride monomer 1 was prepared from 2,3,6,7,9,10-hexamethylethanoanthracene\textsuperscript{18} and reacted with commercially available 3,3’-dimethylnaphthidine, a monomer of previous utility for preparing highly gas permeable polyimides (Scheme 1 and ESI†).\textsuperscript{14,15} The resulting polymer, PIM-PI-EA, was obtained in 88% yield and proved freely soluble in chloroform and THF, which facilitated its characterisation by $^1$H NMR spectroscopy and Gel permeation chromatography (GPC). The latter indicated that PIM-PI-EA was of very high average molecular mass ($M_w = 340$ 000; $M_n = 110$ 000 g mol$^{-1}$) as calibrated against polystyrene standards. Consequently, cast films of PIM-PI-EA from chloroform solution proved robust and suitable for gas permeability measurements. Nitrogen adsorption
isotherms for a powdered sample of PIM-PI-EA at 77 K showed significant uptake at low relative pressures indicative of intrinsic microporosity and provided an apparent BET surface area of 616 m$^2$ g$^{-1}$, which is lower than that of PIM-PI-SBI (699 m$^2$ g$^{-1}$).

The gas permeability data for a 72 µm thick film of PIM-PI-EA are provided in Table 1 and the equivalent data for PIM-PI-SBI, PIM-1 and PIM-EA-TB are given in the ESI.† Prior to analysis the film of PIM-PI-EA was treated by immersion in methanol as this is known to reverse the effects of physical ageing for glassy polymers and also removes the last residues of the casting solvent.9,10,19 Hence, this treatment allows a direct comparison between the gas permeabilities of different polymers.

The order of gas permeabilities for the freshly methanol treated film of PIM-PI-EA is CO$_2$ > H$_2$ > He > O$_2$ > CH$_4$ > N$_2$. This differs from most other PIMs including PIM-1 and PIM-SBI in that He is faster than O$_2$. It is notable that the value for N$_2$ permeability through PIM-PI-EA is very similar to that of PIM-PI-SBI, whereas gases composed of smaller molecules (He, H$_2$, CO$_2$ and O$_2$) are transported faster and CH$_4$, composed of larger molecules, is transported significantly slower through PIM-PI-EA relative to PIM-PI-SBI. These results validate the enhanced permeability of CO$_2$ through PIM-PI-EA as compared to PIM-PI-SBI for a value of $\text{PIM-PI-SBI}$ Fig. 1a†), as demonstrated by CO$_2$ sorption isotherms measured at 298 K. (ESI Fig. 1a†). The solubility of CH$_4$ within PIM-PI-EA and PIM-PI-SBI (ESI Fig. 1b†) is very similar. Therefore, the impressive potential of PIM-PI-EA for the commercially important CO$_2$–CH$_4$ separation is due to both enhanced diffusivity selectivity and solubility selectivity. CO$_2$ sorption is higher in PIM-PI-SBI than in PIM-1, but not as high as in PIM-EA-TB, where the tertiary amine groups of the Tröger’s base appear to contribute to the affinity for CO$_2$ (ESI Fig. 1a†).21

Molecular modelling, which is the only technique which can visualize the free volume distribution, supports these findings.22–24 The high rigidity of the polymer structure is reflected in the difficulty to pack the polymer models. Fig. 3 shows the free volume in a PIM-PI-EA model, packed and equilibrated at the measured film density of 1.1 g cm$^{-3}$. The small o-positronium probe gains access to the highly interconnected void structure. The H$_2$ molecule is able to access more free volume than the larger N$_2$. For H$_2$ the FV is also more interconnected than for the N$_2$ probe. This explains the higher diffusivity of H$_2$ as compared to N$_2$ found experimentally (Table 1).

From a fundamental perspective, this study provides a direct comparison between structurally related polyimides PIM-PI-EA and PIM-PI-SBI and demonstrates the advantage of the rigid bridged bicyclic ethanoanthracene over the more flexible and often used spirobisindane for enhancing diffusivity selectivity.19,22 In this regard, the results of Table 1 suggest that the PIM-PI-EA model is the one that most closely resembles the experimental polymer film.

Table 1 The gas permeabilities $\text{P}_{x}^*$, diffusivity $D_x$, solubility coefficient $S_x$ and ideal selectivities $\alpha(P_x/P_{N_x})$ for a methanol treated film of PIM-PI-EA of thickness $= 72$ µm with comparable data for a the same film obtained after 273 days given in parentheses

<table>
<thead>
<tr>
<th>$N_x$</th>
<th>$O_2$</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>H$_2$</th>
<th>He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_x^*$</td>
<td>369 (131)</td>
<td>1380 (659)</td>
<td>7340 (3230)</td>
<td>457 (156)</td>
<td>4230 (2860)</td>
</tr>
<tr>
<td>$D_x^*$</td>
<td>— (—)</td>
<td>3.7 (5.0)</td>
<td>19.9 (24.6)</td>
<td>1.2 (1.2)</td>
<td>11.5 (21.8)</td>
</tr>
<tr>
<td>$D_x/D_{N_x}$</td>
<td>84 (32)</td>
<td>270 (144)</td>
<td>95 (48)</td>
<td>24 (8.4)</td>
<td>3.2 (4.8)</td>
</tr>
<tr>
<td>$S_x$</td>
<td>3.29 (3.3)</td>
<td>3.83 (3.4)</td>
<td>57.8 (50.1)</td>
<td>14.2 (13.5)</td>
<td>0.29 (0.18)</td>
</tr>
<tr>
<td>$S_x/S_{N_x}$</td>
<td>3.29 (3.3)</td>
<td>3.83 (3.4)</td>
<td>57.8 (50.1)</td>
<td>14.2 (13.5)</td>
<td>0.29 (0.18)</td>
</tr>
</tbody>
</table>

$a$ Units = barrer. $b$ $\alpha = (P_x/P_{N_x})$. $c$ Units = 10$^{-12}$ m$^2$ s$^{-1}$. $d$ Units = cm$^3$ cm$^{-3}$ bar$^{-1}$. $e$ For He and H$_2$ the time lag is too short (<1 s) for determination of $D$ with error <10%, and the value of $D$ is the minimum limit.
addition, PIM-PI-EA has gas permeability data that lie well above the Robeson upper bounds for important gas pairs including CO$_2$–CH$_4$, of interest for natural gas upgrading, and CO$_2$–N$_2$, of interest for post-combustion carbon capture applications. Therefore, methodologies that have been developed for polyimide membrane technology (e.g. cross-linking strategies) can also be applied to PIM-PI-EA, thus making it a strong candidate for exploitation as a membrane material.

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