Ultrapermeable Polymers of Intrinsic Microporosity (PIMs) based on Benzotriptycene

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Polymers of Intrinsic Microporosity (PIMs) are being investigated as materials for gas separation membranes due to their combination of high permeability and moderate selectivity for several gas pairs of importance. Over the past few years we have engaged in a research programme to understand the structure-property relationships of PIMs in order to optimise their performance. It has been established that highly rigid bridged bicyclic structural units such as triptycene and Tröger's base enhance the gas selectivity of the polymer[1]. Here we report our findings on attempts to increase intrinsic microporosity by extending the rigid structure of the triptycene unit that is used to introduce non-linearity into the PIM structure. The synthesis and properties of PIMs containing the Benzotriptycene unit will be described and their remarkably high gas permeabilities reported.

Results and discussion

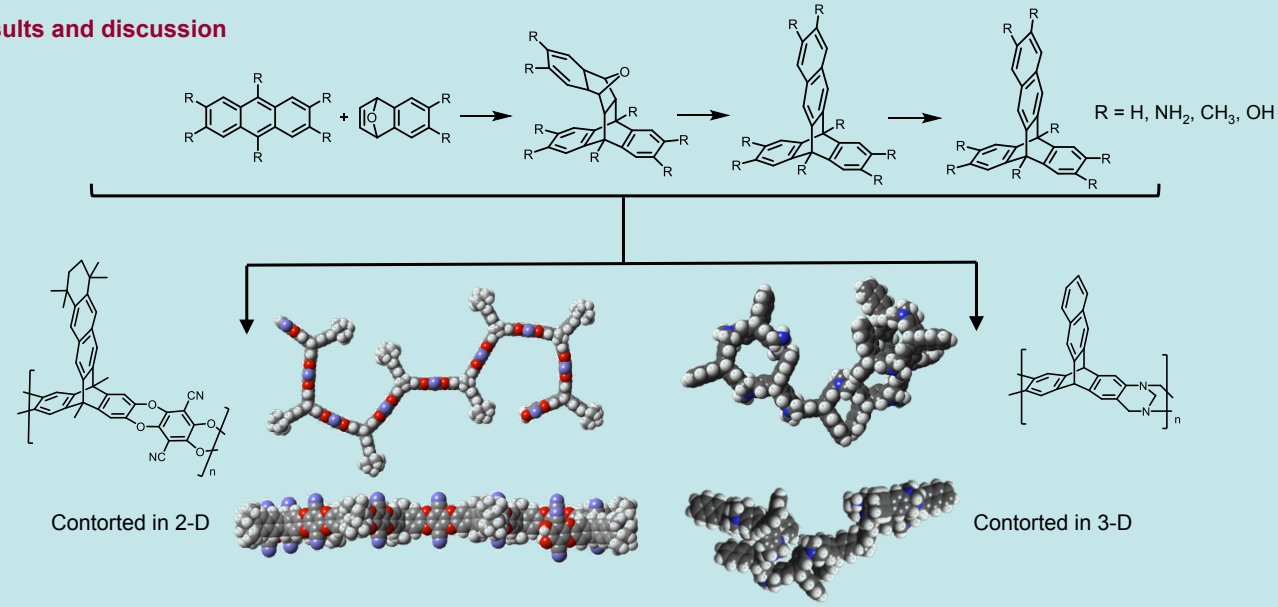

Figure 1. Molecular model of PIM-BenzoTrip(cy-6) and Molecular model of PIM-BenzoTrip-TB (made with Spartan 10 Version 1.1.0; Wavefunction Inc.Irvine, CA, USA)[2].

From the general synthesis of benzotriptycene, two different polymerisations can be attempted. Following the preparation of diaminobenzotriptycene, the subsequent Tröger's Base polymer can be synthesised. The synthesis of benzotriptycene biscatechol, instead, followed by its reaction with the commercially available 2,3,5,6-tetrafluoroterephthalonitrile, leads to the formation of a polybenzodioxane based polymer. The superior properties of the two polymers shown arise from their rigid and contorted structures.

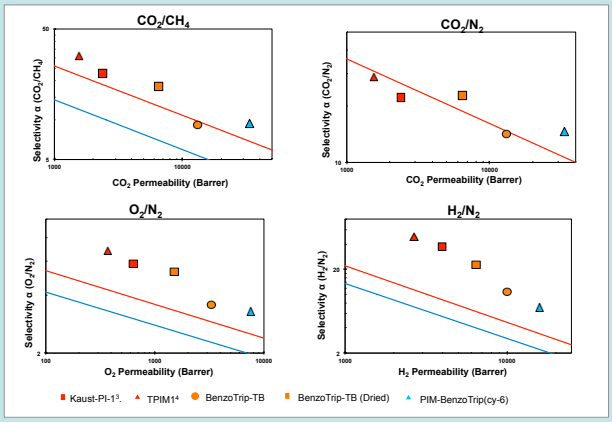

Figure 2. Robeson plots for the O_2/N_2, CO_2/N_2, CO_2/CH_4 and H_2/N_2 gas pairs showing the data

Robeson plots are a universal method to evaluate the performance of membranes for gas separation. For the plots shown (Figure 2), both polymers surpass the 2008 upper bound, which means they possess an excellent compromise between permeability (X axis) and selectivity (Y axis). The structure of PIM-BenzoTrip(cy-6) demonstrates higher surface area (Figure 3) and improved permeabilities, possibly due to its 2-D layered arrangement, compared with the 3-D contortion for PIM-BenzoTrip-TB, as predicted by the model in Figure 1.

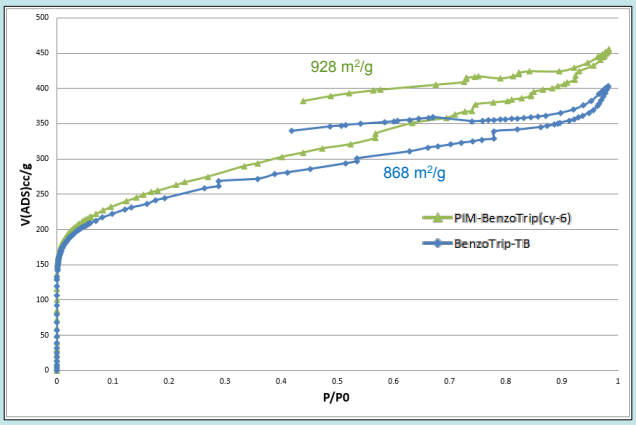

Figure 3. Nitrogen adsorption isotherms at 77 K for PIM-BenzoTrip-TB and PIM-BenzoTrip(cy-6)

Conclusions

Robust films were prepared by casting from solution that enabled gas permeability measurements. The results showed that PIM-BenzoTrip-TB exceeds the overall gas permeability performance of previously reported PIM-TBs apparently due to the additional free volume generated by the benzotriptycene component. The results also show that PIM-BenzoTrip(cy-6) exceeds the Robeson 2008 upper bound which has extremely high permeabilities for the gas pairs shown.

References

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2. Rose, I.; Carta, M.; Malpass-Evans, R.; Bernardo, P.; Clarizia, G.; Jansen, J. C.; McKeown, N. B., **2015**. (Submitted).
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