Ultrapermeable Polymers of Intrinsic Microporosity that redefine the state-of-the-art for CO_2 capture

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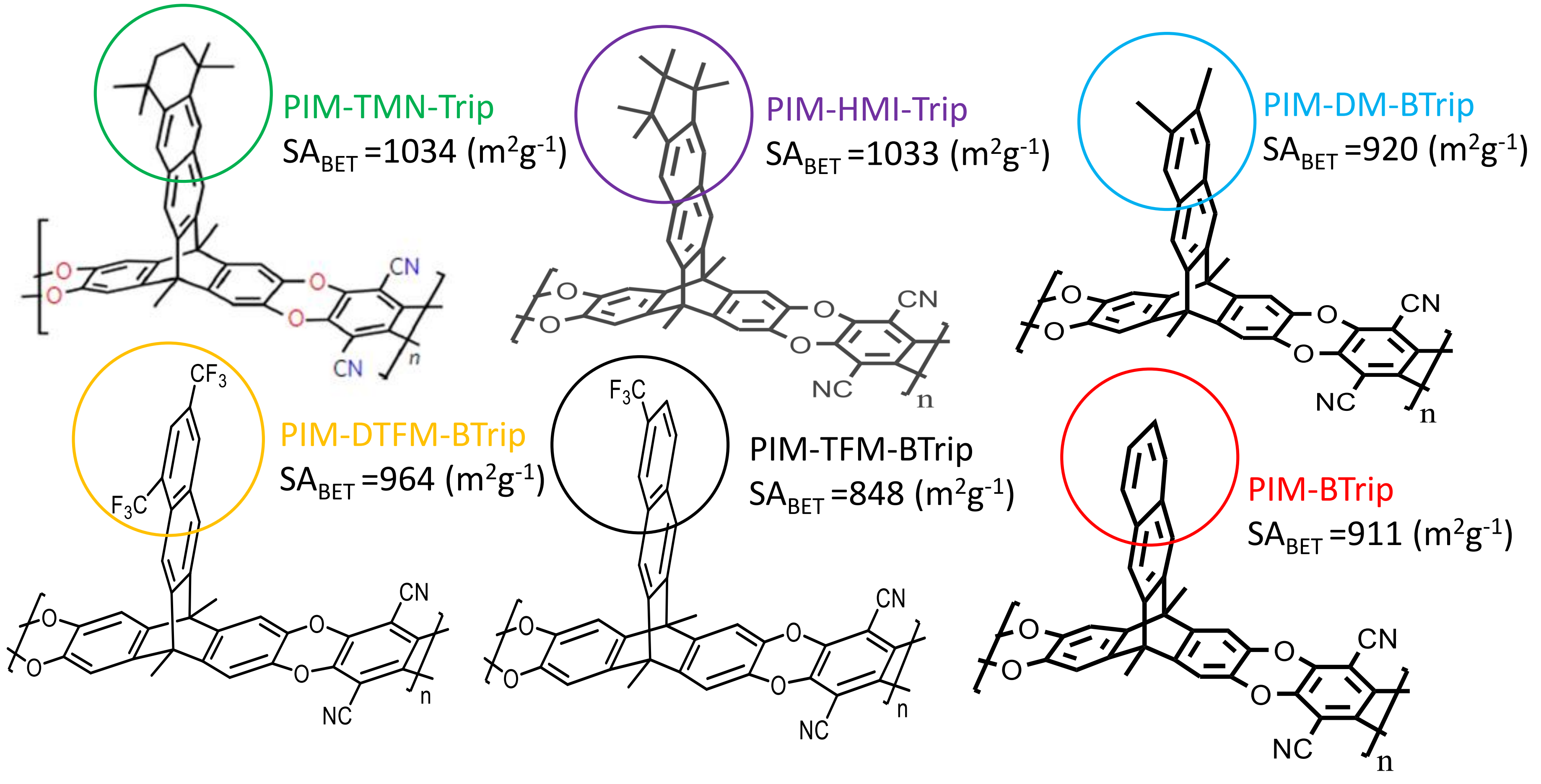
Introduction

Polymers of Intrinsic Microporosity (PIMs) combine the desirable processability of polymers, with a significant degree of microporosity generated from the inefficient packing of their rigid and contorted macromolecular structures. They are attracting attention for a number of industrial gas separation applications, such as oxygen or nitrogen separation from air (separation O_2/N_2) or natural gas treatment and biogas upgrading (separation CO_2/CH_4). A further enhancement of the polymer transport properties is desirable to be cost effective in comparison with the traditional technologies currently applied for CO_2 capture or removal [1].

Ultrapermeable PIMs



PIM-TMN-Trip SA_{BET} =1034 (m^2g^{-1})

PIM-HMI-Trip SA_{BET} =1033 (m^2g^{-1})

PIM-DM-BTrip SA_{BET} =920 (m^2g^{-1})

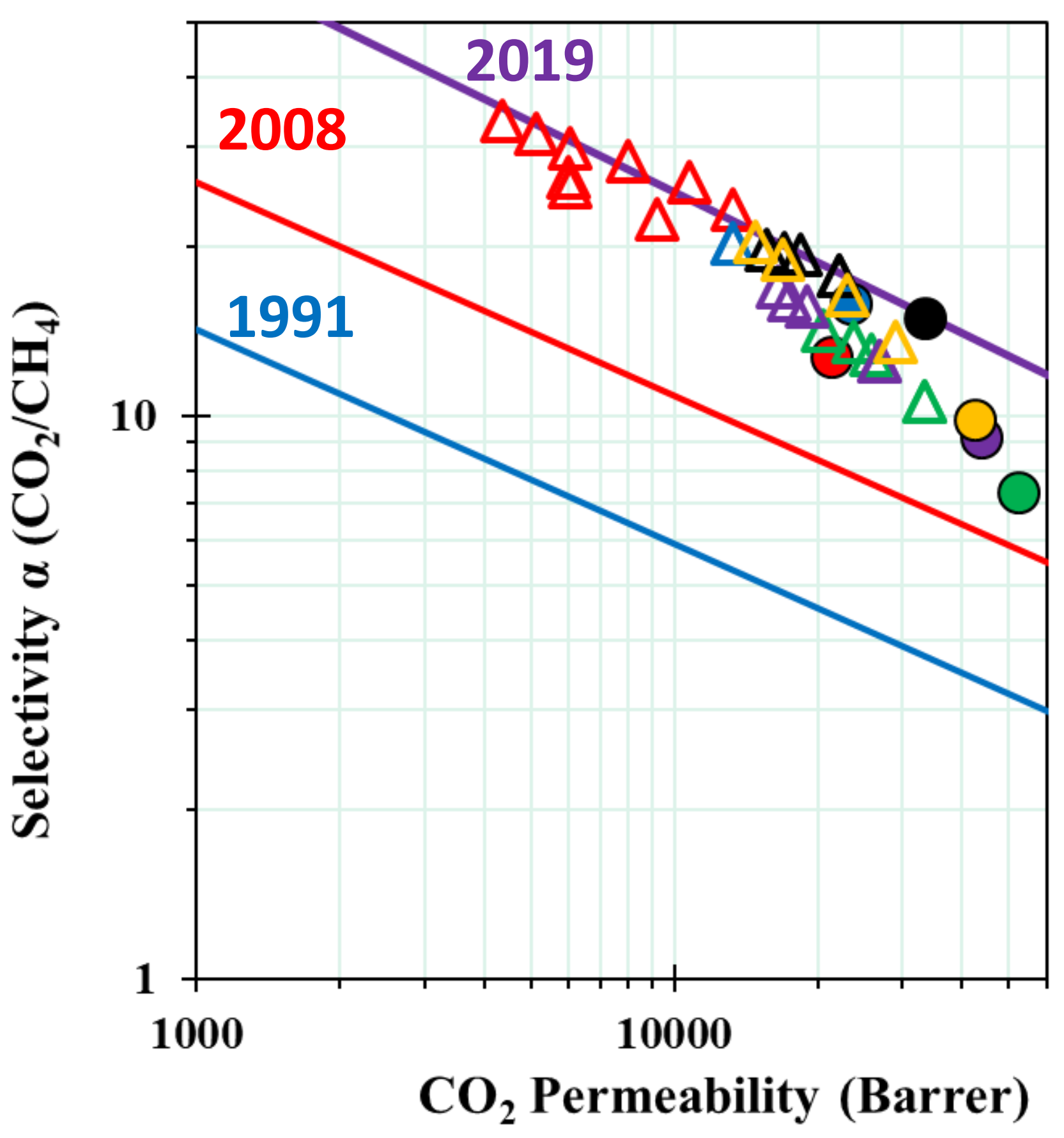
PIM-DTFM-BTrip SA_{BET} =964 (m^2g^{-1})

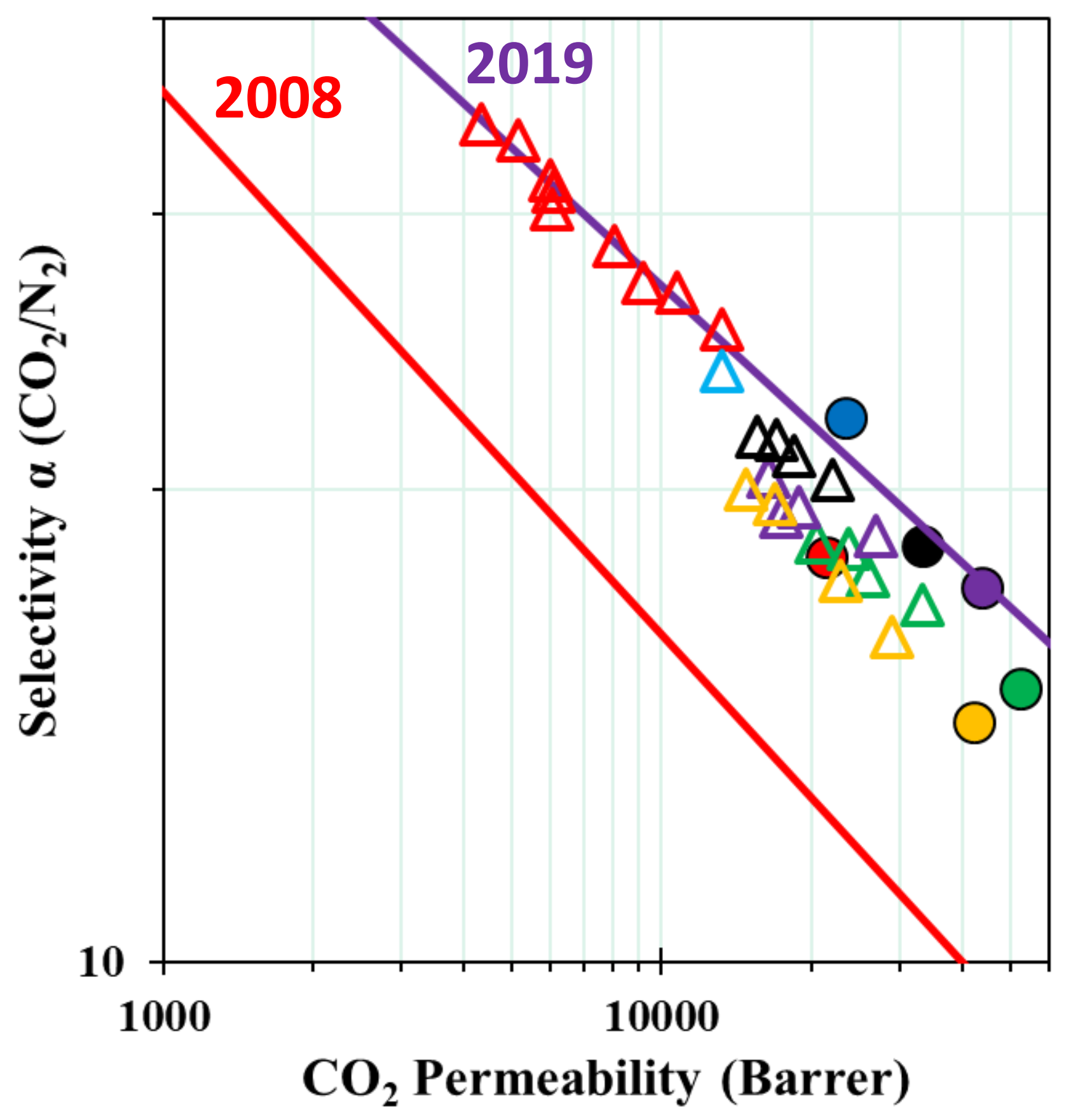
PIM-TFM-BTrip SA_{BET} =848 (m^2g^{-1})

PIM-BTrip SA_{BET} =911 (m^2g^{-1})

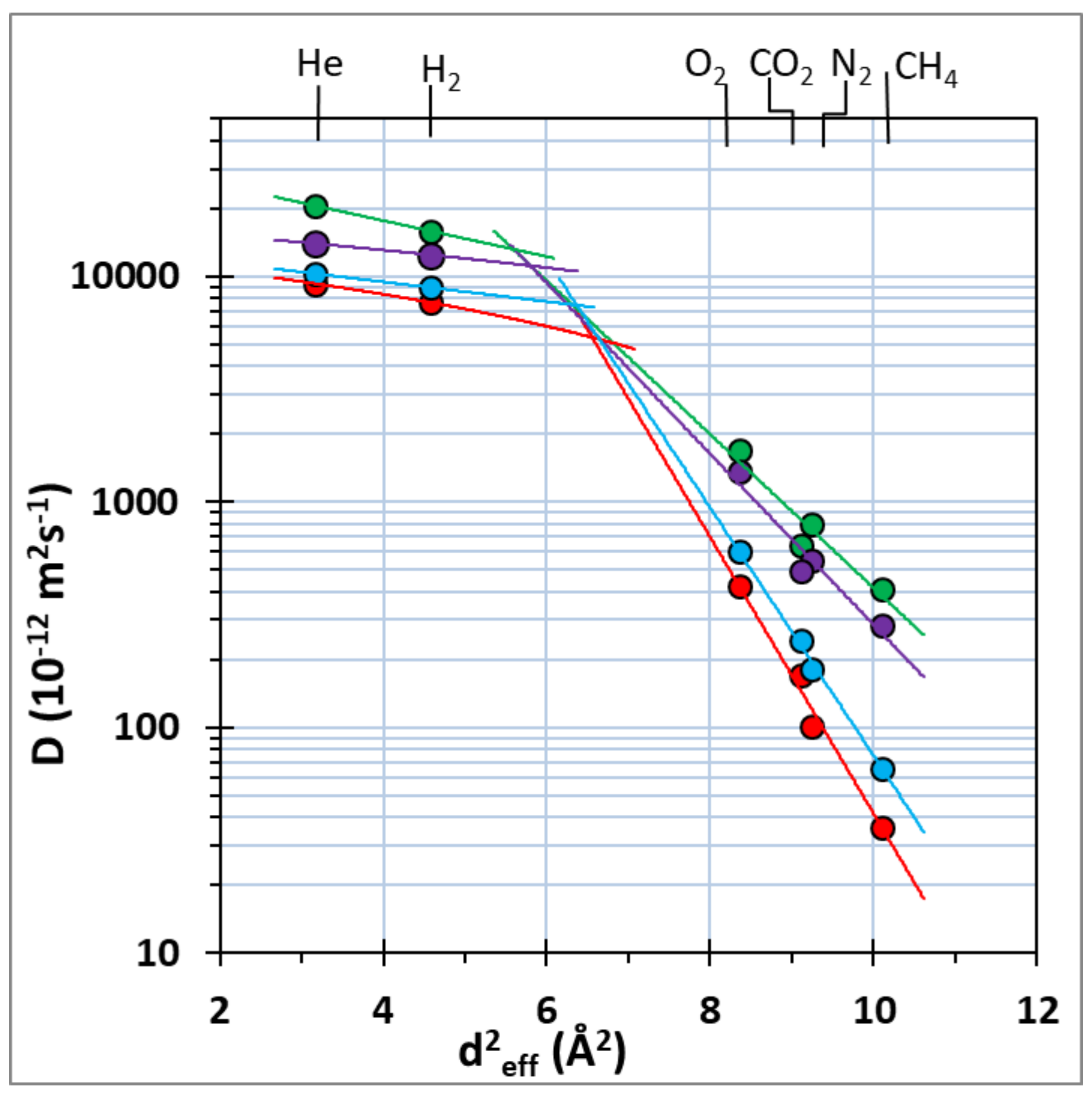
Gas permeability measurements

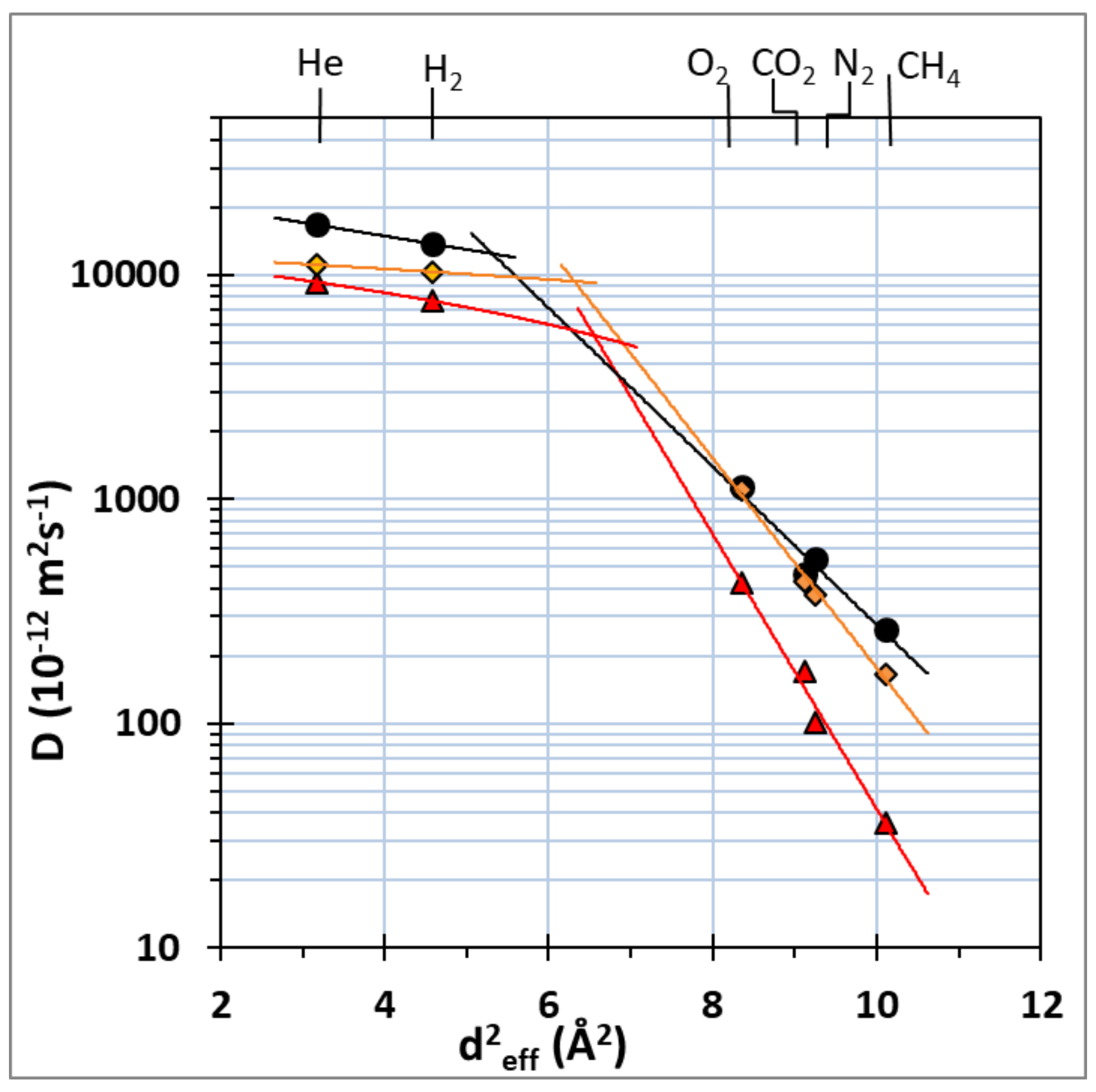
Single gas permeability measurements were carried out with six gases : He, H_2, N_2, CO_2, CH_4, and O_2. The permeability coefficient was calculated from the steady state permeation, while the diffusion coefficient was measured by the well-known time-lag method [2] and S was calculated from S=P/D.





All data for the benzotriptycene PIMs are above the 2008 upper bound for CO_2/CH_4 and CO_2/N_2. The exceptional performance in CO_2/CH_4 separation appears due to a combination of both high diffusivity selectivity, with D_{CO2}/D_{CH4} in the range of 5.7–9.5 for aged films, and good solubility selectivity ($S_{CO2}/S_{CH4} > 3$). They also provide state-of-the-art data for materials to be used for CO_2 removal from flue gas. In particular, the unsubstituted PIM-BTrip ($PCO_2 > 4000$ Barrer and $PCO_2/PN_2 > 30$) is promising for its unusually high D_{CO2}/D_{N2} of 2, whereas the substituted members of the series rely on a greater number of CO_2 adsorption sites [3].



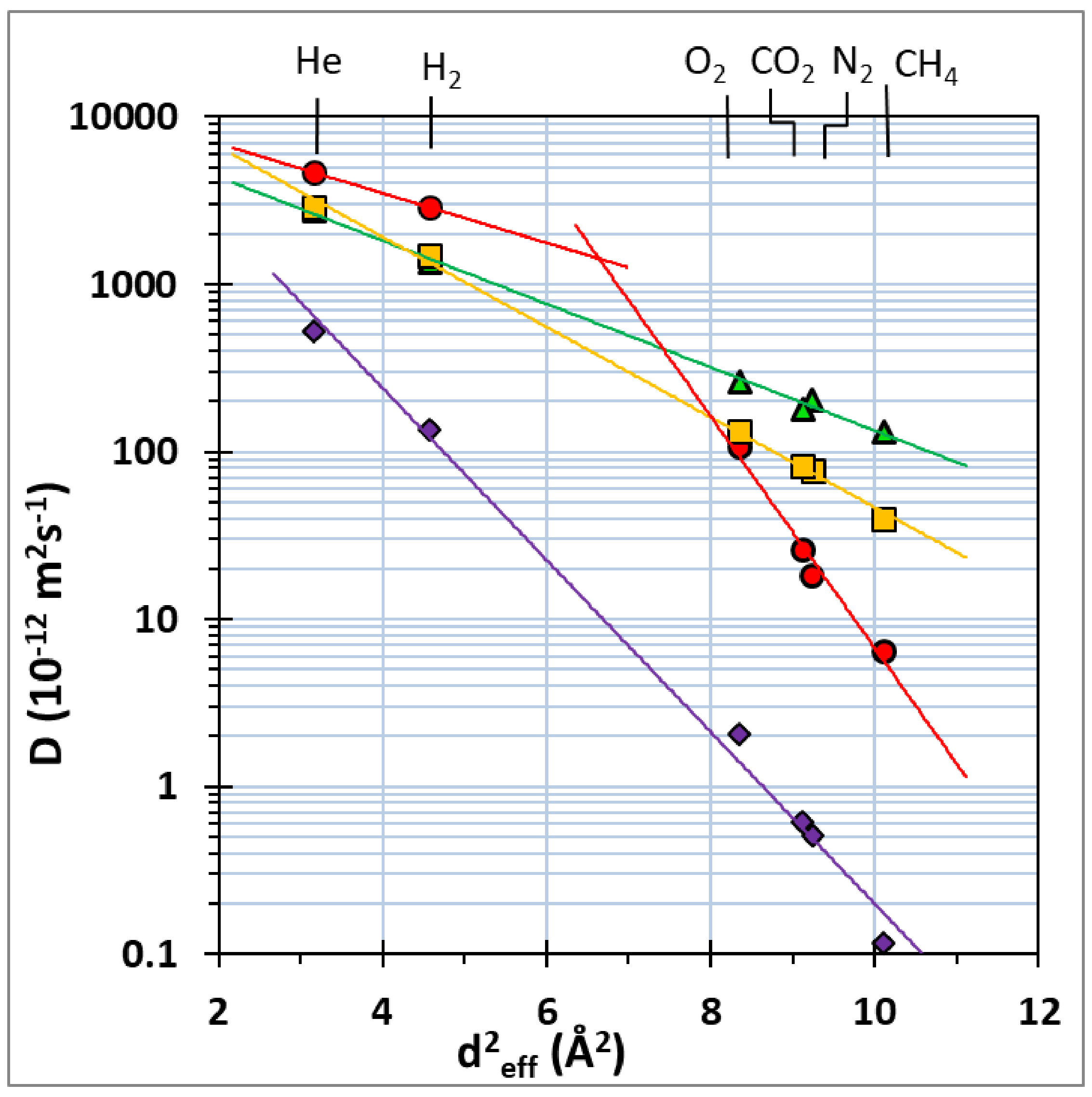


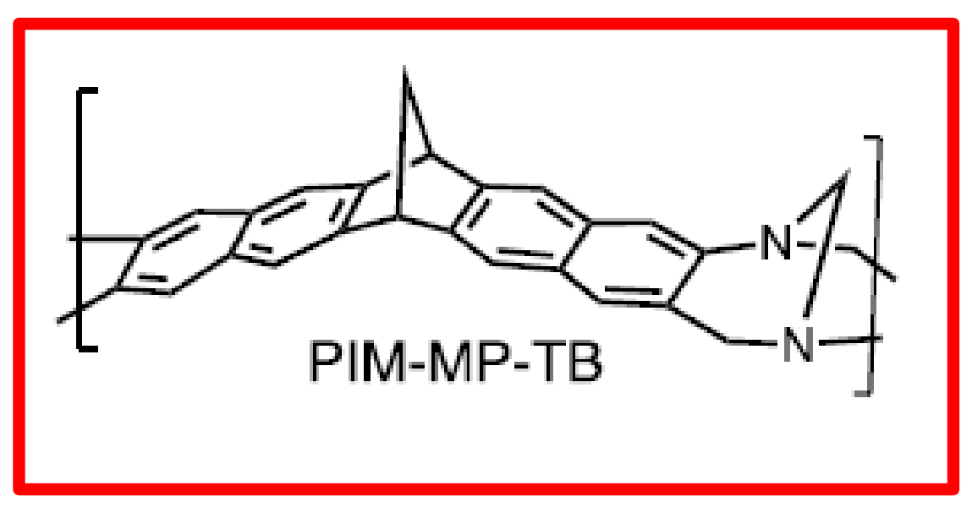
The remarkable positions of the benzotriptycene-PIMs data on the Robeson plots are due to their very high diffusivity selectivity, originating from the size-sieving behaviour of the polymers, which differentiates between gas molecules of differing effective diameters (d_x). This is best illustrated by the correlation between d_x^2 and the diffusion coefficient (D_x), which is steepest for PIM-BTrip and less steep for benzotriptycene PIMs that possess a substituent, for which the absolute value of the diffusion coefficient is larger.

The extraordinary performance of PIM-BTrip can be attributed to its ultramicroporosity, which facilitates the diffusivity of small gas molecules, together with very high chain rigidity, which hinders the activated transport of larger gas molecules by reducing thermal motions needed to form gaps between the existing voids. The extreme rigidity of PIM-BTrip accounts for the very high activation energy reported for the diffusion of larger gases such as N_2 and CH_4 [4].

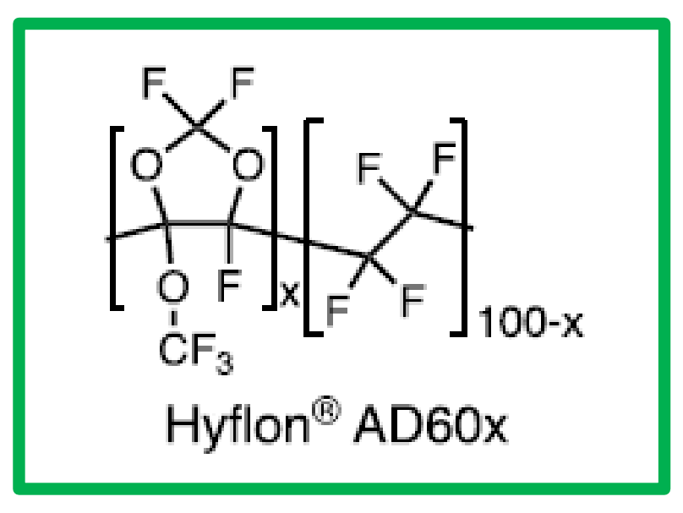
Molecular modelling

The physical properties of the packed polymer were characterized by Molecular Dynamics on four different polymers. For each of the models, the free volume was characterized for three probes: one small H_2 molecule and two bigger gases, N_2 and CH_4.





PIM-MP-TB



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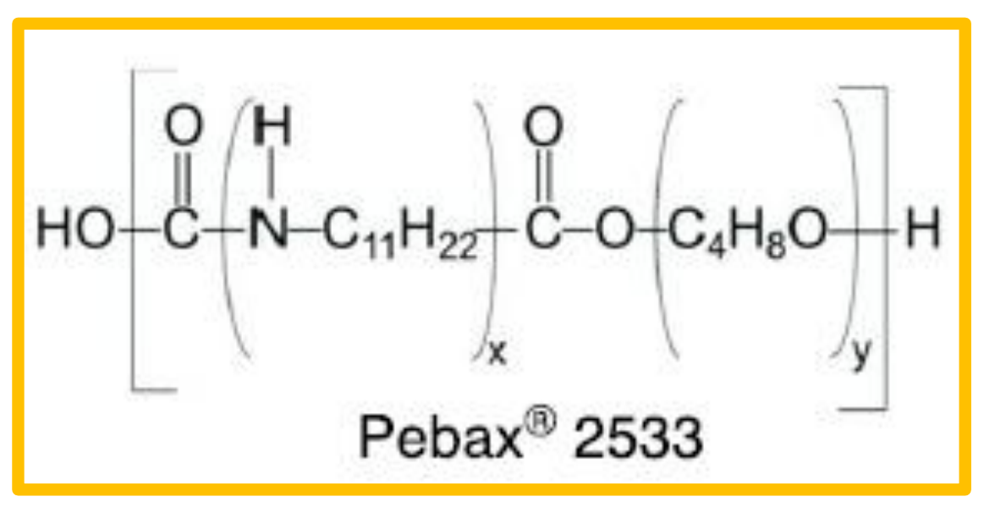

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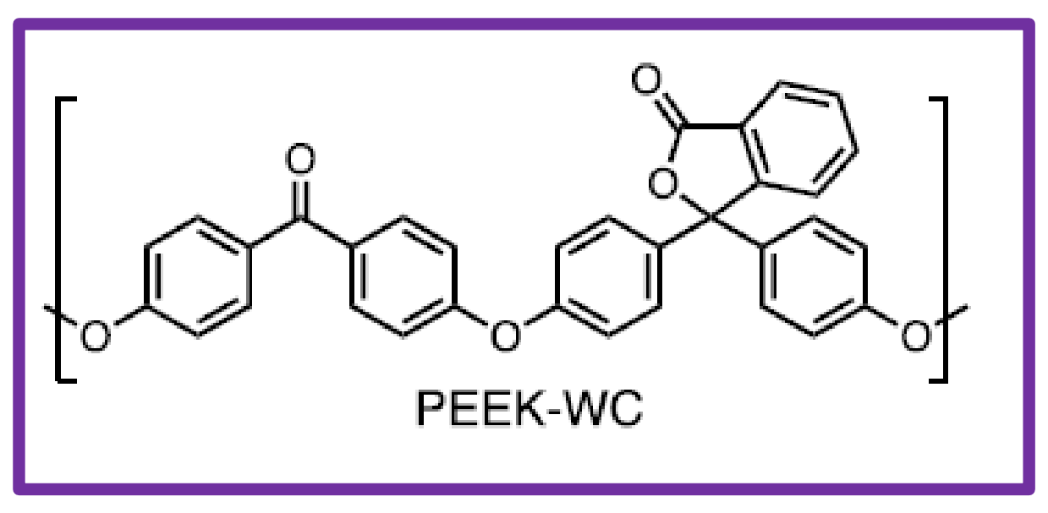
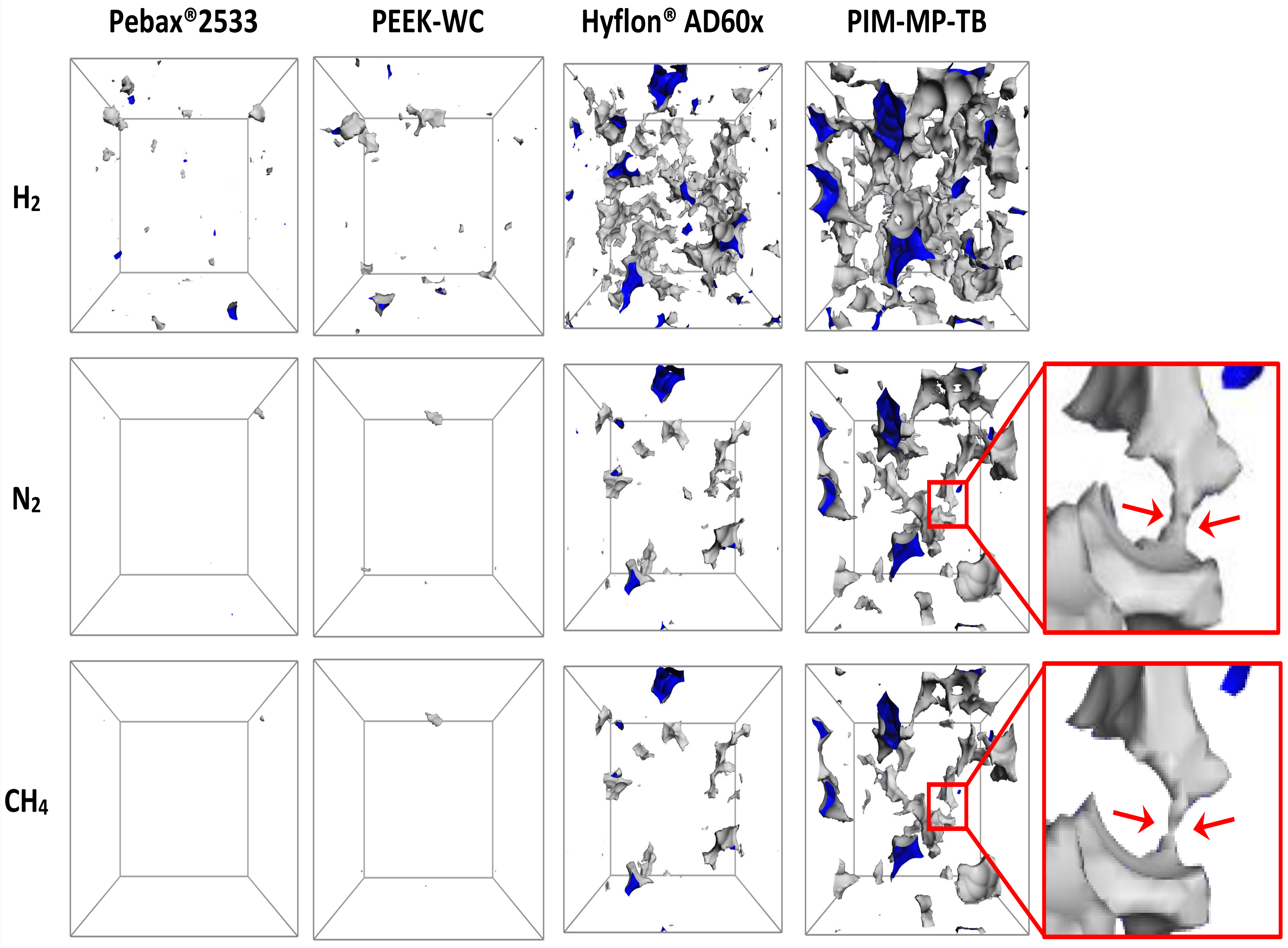


PEEK-WC

The smaller H_2 and He gas molecules permeate via a transport mechanism that is similar to that in porous materials, whereas larger gas molecules, CH_4, N_2, O_2 and CO_2, show activated transport similar to that in conventional dense polymers. A typical and *defining* feature of PIMs, which differentiate their properties from other high free volume polymers, and common glassy polymers and rubbers, is the change in slope of the plot of the diffusion coefficient as a function of the gas diameter, with a stronger size-selective trend for the larger gas molecules than for He and H_2. Molecular modelling shows that the size selectivity in PIMs originates from the presence of tight bottlenecks between the individual free volume elements [5].



Molecular models showing the accessible fractional free volume for H_2, N_2 and CH_4 in four polymers. The inserts are zoom-ins of the connection between two free volume elements for N_2 and CH_4. Grey shading indicates the free volume elements seen from the outside, facing the polymer; blue shading indicates the inside of the free volume elements.

Conclusions

The benzotriptycene-based PIMs exhibit exceptional gas permeability for most important gas pairs and allow for the redefinition of the CO_2/CH_4 and CO_2/N_2 Robeson upper bounds. This is important in order to set aspirational targets for chemists in the design and synthesis of novel polymers. Further analysis of the correlation of the diffusion coefficient and the effective diameter of gases for PIMs provides insight into the underlying mechanism of their gas separation properties. It reveals that small molecules such as He and H_2 experience the fractional free volume as interconnected and these molecules therefore permeate predominantly via the pore diffusion mechanism rather than the 'normal' activated solution-diffusion mechanism. This leads to a non-linearity that appears to be general and, together with their solution processability, a *defining* feature of PIMs.

The resulting improved credibility of polymer membranes for these crucial separations will stimulate research activity in this technological area of prime importance to energy and the environment.

References:

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[3] B. Comesana-Gandara *et al.*, *Energy Environ. Sci.*, 2019, **12**, 2733-2740
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