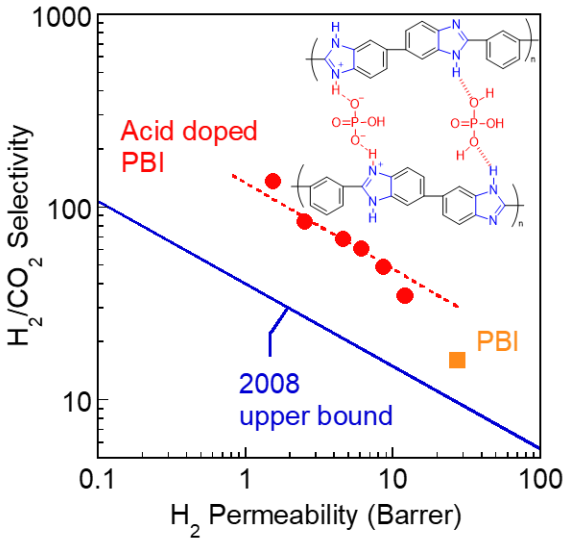
Unprecedented Size-Sieving Ability in Polybenzimidazole Doped with Polyprotic Acids for Membrane H_2/CO_2 Separation

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Polymers with efficient and tight chain-packing and thus strong size-sieving ability are of great interest for H_2/CO_2 separation. Herein, for the first time, we demonstrate a new approach to manipulating polymer structure by acid doping, leading to superior H_2/CO_2 separation performance. We have doped polybenzimidazole (PBI) with polyprotic acids, specifically H_3PO_4 and H_2SO_4. These acids cross-link PBI chains and drastically decrease free volume, improving the material's H_2/CO_2 selectivity to far surpass the Robeson's 2008 upper bound for membrane performance. For example, PBI doped with H_3PO_4 at a molar ratio of 1:1 exhibits an unprecedented H_2/CO_2 selectivity of 140 at 150 °C, which exceeds that of previously known polymeric materials and is superior or comparable to that of state-of-the-art 2D materials with sharp size separation, such as graphene oxide, MoS_2, and metal-organic frameworks. This presentation will discuss the effect of acid doping on gas sorption, diffusion and permeation. A free volume model is used to correlate the gas transport and structural changes induced by acid doping. The facile acid doping approach to enhancing polymer chain-packing efficiency opens up a new avenue for designing strong size-sieving polymers for membrane gas separations.