

An entangled flexible MOF for capture of CO₂ and store/separation of (C₁-C₃) hydrocarbons

Globally the swift growth of industrial sectors has immensely shuddered the environmental balance, particularly due to large quantity of greenhouse gas emission from the fossil fuel combustion. Therefore the capture of greenhouse gas, such as CO₂ and also its separation from the gas mixtures at ambient conditions is important. Metal-organic frameworks, a class of crystalline permanently porous material has been found to be a promising candidate to address this issue. By virtue of its periodic well defined structure, it is possible to simulate its porous properties and thus design of suitable porous structure for CO₂ capture and separation is viable. To embark upon we sought for an entangled framework with pore surface carved with polar functional groups and aromatic π clouds. $\{[Zn_2(bdc)_2(bpNDI)] \cdot 4DMF\}_n$ (bdc = 1,4-benzenedicarboxylate, bpNDI = *N,N'*-bis-(4-pyridyl)-1,4,5,8-naphthalenediimide), is such a twofold entangled framework with imide (R₂NC=O) functionalized pore surface (Fig. 1). Most importantly, the 3D framework contains two different adsorption sites created by the entanglement of two different nets. The framework also shows guest specific dynamic structural transformation based on the mutual sliding of the two 3D entangled nets and structural flexibility is comprehended from the powder X-ray diffraction (PXRD) and stepwise adsorption of gases like CO₂ and C₂H₂ at 195 K. At 273 and 298 K, CO₂ uptakmounts are 14.7 wt% and 12.7 wt%, respectively. In contrast, framework reveals little uptake of N₂ and CH₄ at 298 K. Thus it is an ideal system to separate CO₂ from N₂ and CH₄. It is worth mentioning that flue gas (emission from coal-fired power plant) contains ~76% N₂ and ~13 % CO₂ and rests are water vapor (~6%) and oxides of N₂ and sulphur. Similarly natural gas (mainly CH₄) also contains certain amount of non-calorific CO₂. Thus separation of CO₂ from N₂ and CH₄ is of paramount importance. Thus we have tested this framework for CO₂ separation from a binary mixture of CO₂/N₂ (15:85 v/v) and CO₂ /CH₄ (50:50 V/V) by breakthrough column experiments (Fig. 1). Indeed, this dynamic framework showed as an efficient CO₂ separation material at ambient conditions.

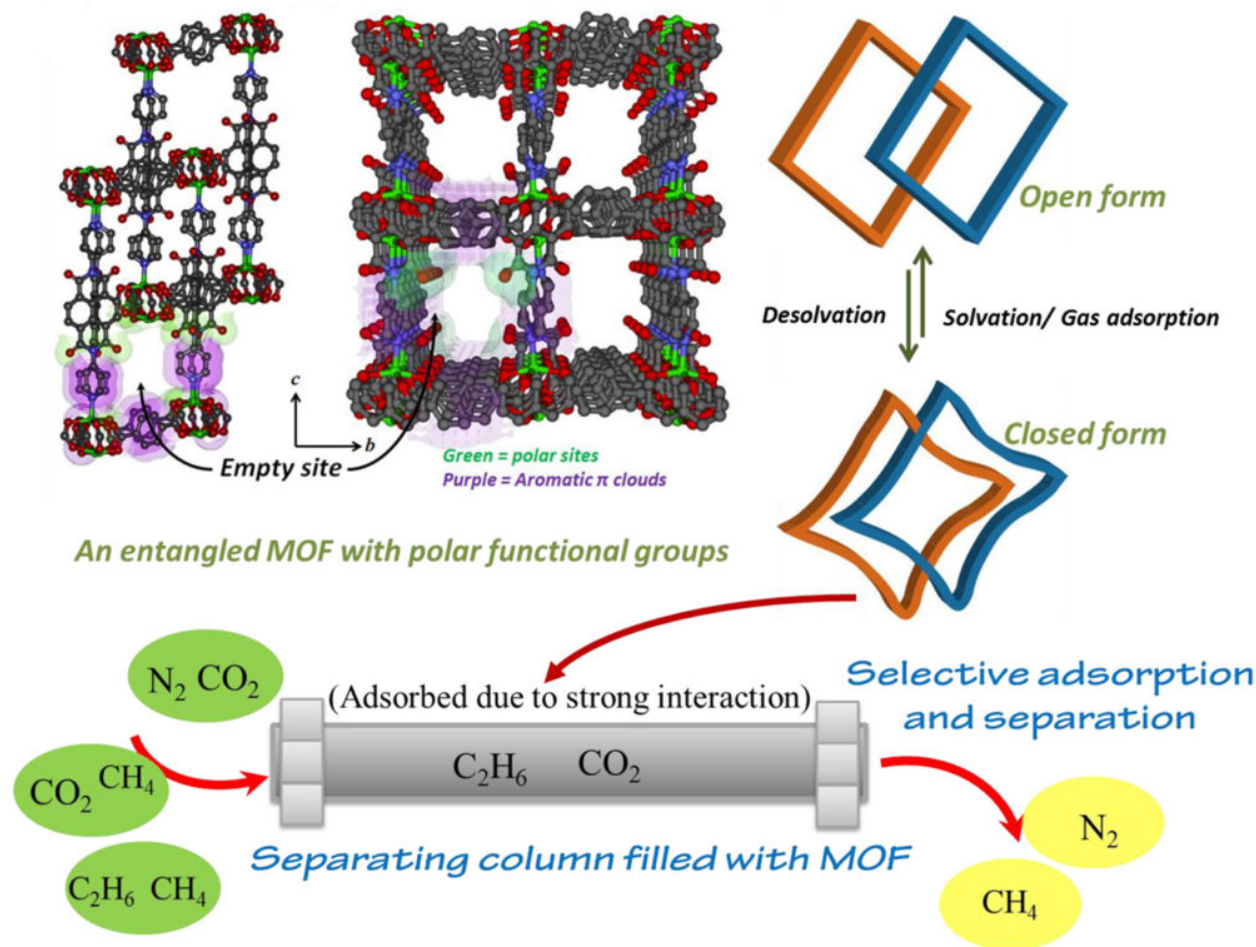


Fig. 1. Two-fold interpenetrated dynamic porous metal-organic framework. The framework showed selective CO_2 capture and potential for separation of CO_2 from N_2 and CH_4 gas mixture. The framework also adsorb significant amount of different C2-C3 hydrocarbons and potential for separation of C_2H_6 from CH_4 as realized by breakthrough column experiments.

In addition to the above described applications, this framework can also adsorb different C2-C3 hydrocarbons. As mentioned before, the rapid growth of industrialization also demands continuous supply of energy and hence searches for alternative fuel source and their storage is in high demand. Light hydrocarbons such as CH_4 (methane), C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), C_3H_6 (propene), and C_3H_8 (propane) are known to be used as feedstock for numerous industrially important materials and also can serve as resource of energy as a fuel. At 298 K, the activated framework can adsorb 81, 44, 49 and 43 cc/g of C_2H_2 , C_2H_4 , C_2H_6 and C_3H_8 , respectively. The adsorption capacity is in accordance to the kinetic diameter and adsorbent-adsorbate interactions in the hydrophobic pore surface. Using IAST calculations and breakthrough measurements of the gas mixtures ($\text{C}_2\text{H}_6/\text{CH}_4$, 50:50 V/V) we could also confirm the selective

capture of ethane (C₂H₆) in this porous functionalized framework (Fig. 1).

In brief, the entangled functionalized porous framework showed as a potential material for CO₂ capture and also revealed its potential to separate hydrocarbons and CO₂ from mixture of gases at ambient condition. In absence of unsaturated metal sites, such prolific efficiency to selectively capture and separate gases is rarely achieved.

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