



New Pore Space Partitioning in Metal-Organic Frameworks



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Introduction

Metal-organic frameworks (MOFs) are an emerging group of porous materials that have shown excellent potential for applications in gas adsorption or storage, gas separation, catalysis, and drug delivery. They are crystalline materials composed of metal ions that are coordinated to organic ligands with pores that have the potential to be stable enough to be refilled with other compounds. To further improve their molecular adsorption properties, the process of pore-space partitioning (PSP) has been developed. PSP involves the division of the pore spaces within a MOF in order to refine host-guest interactions and enlarge the density of binding sites, thus enhancing the gas uptake and framework stability of the MOF. Moreover, an appealing feature of MOFs is the ability to influence their physicochemical properties due to a wide range of possible topologies and ligand selection. In fact, properly designed PSP, using the size and the shape of the target guest molecules, allows for more efficient use of the pore space to enhance storage properties for small gas molecules. In particular, the use of tris(pyridin-4-yl)amine (tpa) was considered as this organic ligand is smaller compared to 2,4,6-tri(pyridin-4-yl)-1,3,5-triazine (tpt), which would increase the number of binding sites within the MOF and therefore improve its selectivity. The resulting MOF was made from MgCl_2 , VCl_3 , 1,4-benzenedicarboxylic acid (bdc), tpa, and DMF.

I. Synthesis

The organic ligand used in this synthesis, tpa, was chosen in particular because it is a smaller ligand than tpt. The components were combined and then heated at 120°C for 72 hours. SCXRD measurements were taken to conduct structural analysis, and gas adsorption was measured as well. The full procedure for this project is outlined below:

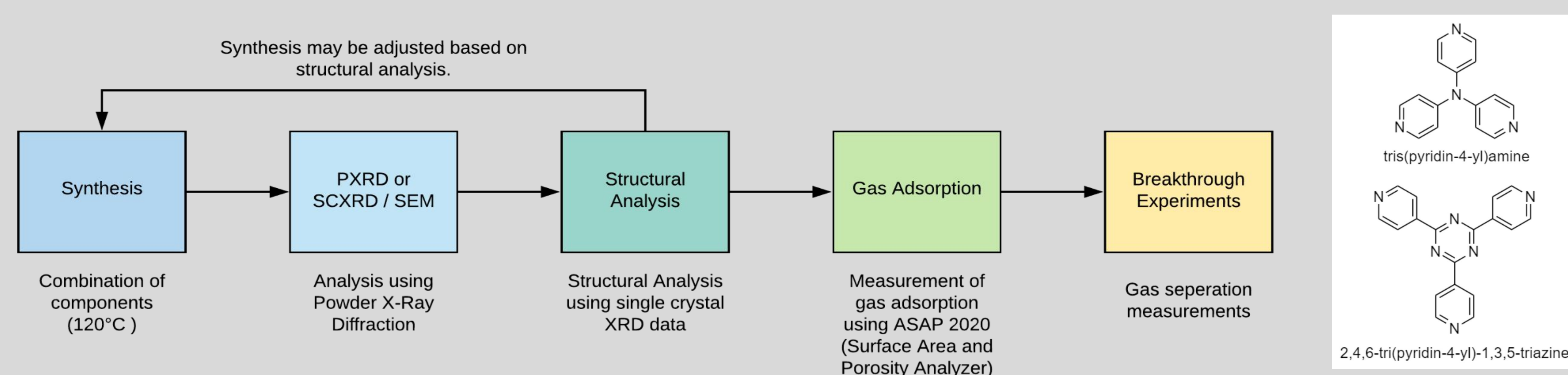


Figure 1. Research Procedure

Figure 2. tpa and tpt Structures

II. Results

This MOF is a partitioned aca-MIL-88 structure with a 9-coordinated partitioned network topology. The net structure has hexagonal shaped channels along the c-axis, as well as trigonal bipyramidal cages. With such geometric attributes, tritopic ligands with C3 symmetry, which can occupy three open metal sites (OMSs) at the same time, can fit within the pore.

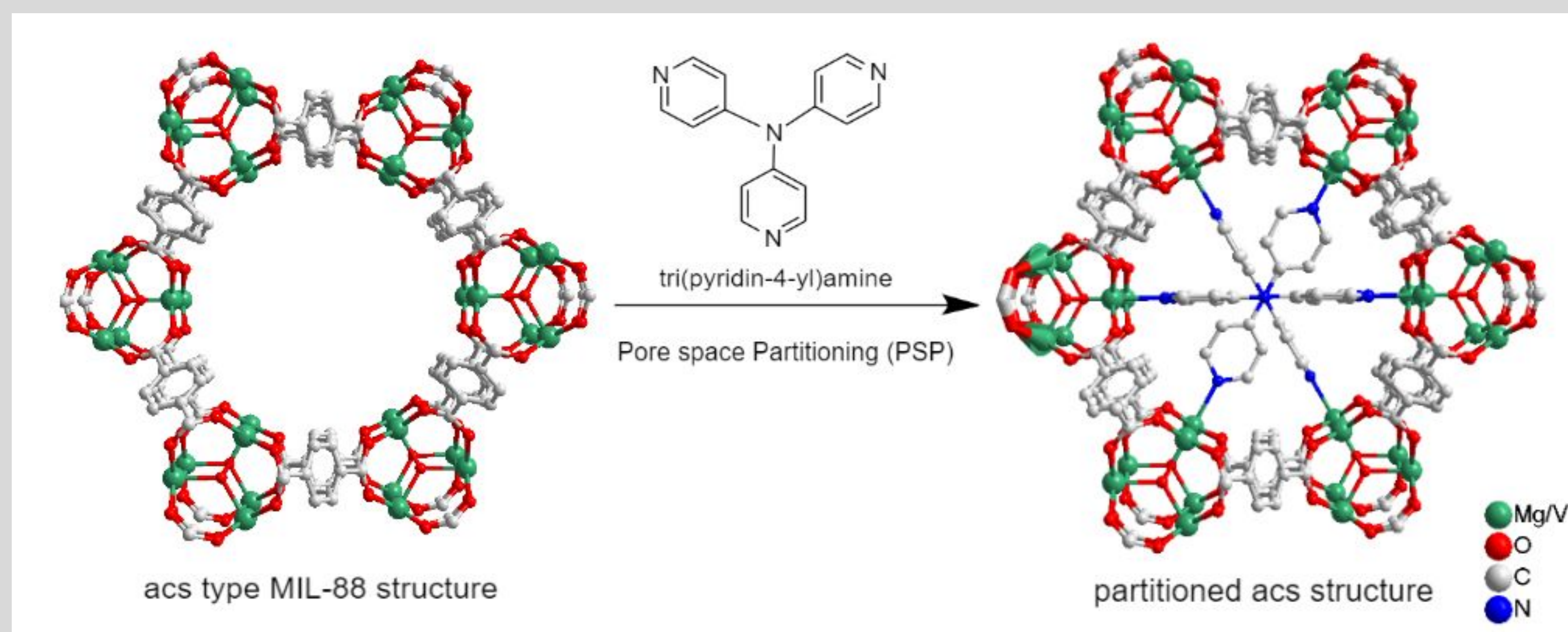


Figure 3. The aca and pacs Structures Viewed Along the c-axis

According to a DFT pore size calculation, pacs-tpa shows a slightly smaller pore size than pacs-tpt (6.5 Å v.s. 6.8 Å).

Identification Code	pacs_tpa	Density (calculated)	1.891 Mg/m ³
Empirical formula	C ₃₉ H ₂₄ Mg ₂ N ₄ O ₁₃ V	Index Ranges	-13<=h<=12, -13<=k<=13, -15<=l<=15
Temperature/ Wavelength	296K / 0.71073 Å	Reflections Collected	11026
Crystal system	Trigonal	Independent Reflections	858 [R(int) = 0.2209]
Space group	P-31c	Completeness to theta = 18.866°	99.99%
Unit cell dimensions	a = 14.685(17) Å α = 90° b = 14.685(17) Å β = 90° c = 17.24(2) Å γ = 120°	Refinement Method	Full-matrix Least Squares on F ²
Volume	3219(8) Å ³	Final R indices	R1 = 0.0741, wR2 = 0.1910
Z	2	R indices (all data)	R1 = 0.1271, wR2 = 0.2308

Table 1. Crystal Data and Structure Refinement for pacs_tpa

III. Discussion

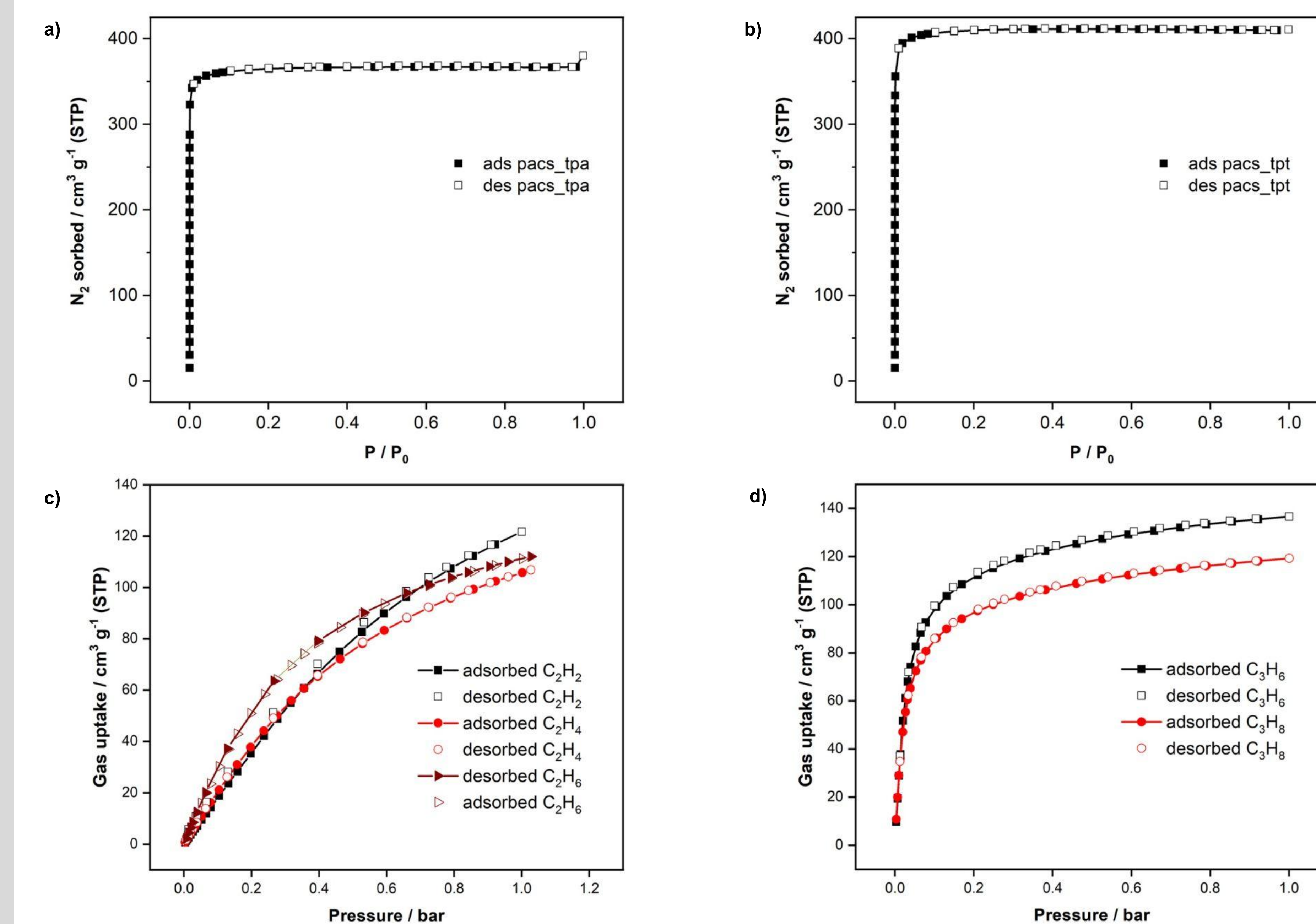


Figure 4. Isotherms a) $\text{Mg}_2\text{V-bdc-tpa}$ N_2 sorption b) $\text{Mg}_2\text{V-bdc-tpt}$ MOFs N_2 sorption c) $\text{Mg}_2\text{V-bdc-tpa}$ C_2H_x adsorption d) $\text{Mg}_2\text{V-bdc-tpa}$ C_3H_x adsorption

Using the adsorption isotherm for N_2 , the surface area of the pacs $\text{Mg}_2\text{V-bdc-tpa}$ MOF was calculated to be 1,161 m^2/g with the BET method and 1,595 m^2/g with the Langmuir method. This is lower than a $\text{Mg}_2\text{V-bdc-tpt}$ MOF whose surface area was calculated to be 1598 m^2/g and 1791 m^2/g . This was expected as tpa is a smaller ligand than tpt. In addition to this, the $\text{Mg}_2\text{V-bdc-tpa}$ MOF has a very high uptake of hydrocarbons due to pore space partitioning (i.e. the uptake for C_2H_4 and C_2H_6 reaches 107 cm^3/g and 111 cm^3/g respectively), even though it does not exhibit high selectivity.

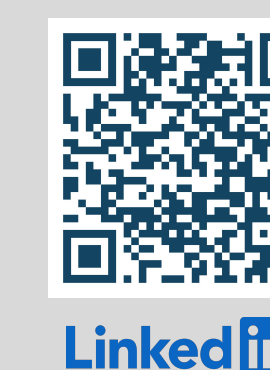
IV. Future Work

Gas adsorption measurements show that the material has low selectivity, therefore, the future steps in this research would include a repetition of the gas adsorption measurements with benzene and cyclohexane gases. It is expected that selectivity might rise since these molecules are larger hydrocarbons than previously examined gases. Then, breakthrough experiments with benzene and cyclohexane would be conducted in order to measure gas separation abilities.

References and Acknowledgements

Huajun Yang, et al. Pore-Space-Partition-Enabled Exceptional Ethane Uptake and Ethane-Selective Ethane-Ethylene Separation, J. Am. Chem. Soc. 2020, 142, 5, 2222–2227.

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