



NAPHTHALENEDIIMIDE-BASED METAL ORGANIC FRAMEWORKS FOR THE CAPTURE OF CARBON DIOXIDE

Gabriela Oliveira¹; José Fernando Queiruga Rey¹; Tatyara Monteiro da Silva¹; Geomar Feitosa da Cruz¹; Caetano Rodrigues Miranda²; Sergio Brochsztain¹

¹ Center for Engineering, Modeling and Applied Social Sciences, Federal University of ABC, Santo André, Brazil, sergio.brochsztain@ufabc.edu.br

² Institute of Physics, University of Sao Paulo, Sao Paulo, Brazil, crmiranda@usp.br

ABSTRACT

We introduce here a novel ligand, N,N'-bis(4-carboxyphenyl)-1,4,5,8-naphthalenediimide (CNDI), which is a suitable compound for the preparation of new materials for the energy sector. The compound was shown to be an excellent ligand for metal organic frameworks (MOFs). The compound was synthesized in a single step and high yields by using molten imidazole as the solvent. Reaction of CNDI with zinc nitrate or zirconium chloride generated the MOFs CNDI/Zn and CNDI/Zr. The MOFs were characterized by x-ray diffraction, nitrogen adsorption isotherms (BET method) and UV-visible spectroscopy. The presence of micropores was evidenced by BET measurements. The MOFs will be incorporated into polymeric membranes, which will be tested for the separation of CO₂ from other gases.

Keywords: Carbon Capture, Naphthalenediimides, Membranes, Metal Organic Frameworks.

Introduction

According to the Intergovernmental Panel on Climate Change of 2021, climate changes caused by human activity are leading to more frequent and extreme weather events. These climate changes have been attributed mainly to an increase in the emissions of CO₂. In this context, it is very important to find new materials for the capture and storage of CO₂. These materials should perform gas separations, such as CO₂/N₂ in the exhaust of thermoelectric stations and should therefore display high selectivity and permeability for gas separations.

Among those materials, metal organic frameworks (MOFs) have been extensively studied [1]. It consists of metallic nodes joined together by organic ligands. The most common ligand is terephthalic acid, also known as 1,4-benzenedicarboxylate (BDC) (Figure 1), a bidentate ligand displaying two carboxylic acid groups at opposite sides. Yaghi et al developed the concept of isorecticular MOFs (IRMOFs), wherein BDC can be replaced by longer molecules with similar structure, giving MOFs with the same structure as formed with BDC, but with increased lattice parameters [1]. A good example is the substitution of BDC by biphenyl dicarboxylate (BPDC) or terphenyl dicarboxylate (TPDC) (Figure 1).

In this context, 1,4,5,8-naphthalenediimides (NDI) are excellent candidates as ligands for MOFs, since they are easily functionalized to have ligand groups at opposite sides of the molecule. The NDI are n-type semiconductors with a variety of applications, such as organic field-effect transistors, light-emitting diodes, electrochromic and photochromic materials, in photocatalysis, lithium ion batteries and gas storage. Furthermore, the NDI have been considered among the best electron transporting layer materials in organic solar cells, only behind the fullerenes [2].

Hupp et al have reported the synthesis of a Zn-based MOF using N,N'-bis-(4-pyridyl)-1,4,5,8-naphthalenediimide (DPNI), a NDI substituted with pyridyl ligands, and shown that the MOF with DPNI was efficient in the separation of CO₂ from CH₄, a process which is very important in the sweetening of natural gas [3]. Following their accomplishment, several authors have reported on NDI-containing MOFs, with a variety of ligand groups attached to the NDI core.



Concerning carboxylate substituted NDI ligands, Hupp's [4] and Wasielewski's [5] groups have introduced *N,N'*-bis(2,6-dimethyl-4-carboxyphenyl)-1,4,5,8-naphthalenediimide (TM-CNDI) (Figure 1), and employed it as a ligand for the synthesis of Zn and Zr MOFs, respectively. Wasielewski et al reasoned that the anion radical $\text{NDI}^{\cdot-}$, the reduced form of NDI, is a powerful reducing agent, reaching the potential needed for CO_2 reduction, opening the doors for using NDI-MOFs for carbon capture and utilization (CCU). The synthesis of tetramethyl-CNDI, however, involves reagents that are not readily available, such as 3,5-dimethyl-4-aminobenzoic acid, which needs to be synthesized, increasing the cost. Hupp et al claimed that the four methyl groups on the benzoic acid rings were essential to obtain crystalline MOFs. They reported that the absence of the methyl groups led only to amorphous compounds, since the methyl groups impose steric hindrance, thus preventing ring-ring π -stacking between the NDI units.

In the present work, we introduce *N,N'*-bis(4-carboxyphenyl)-1,4,5,8-naphthalenediimide (CNDI) (Figure 1), the parent compound of TM-CNDI, as a ligand for MOFs. Contrary to the suggested by the other authors, crystalline MOFs were obtained from CNDI with both Zr and Zn as the metal cation. CNDI was synthesized in a single step and with high yields, from readily available reagents, especially concerning the primary amine employed in the synthesis of NDIs, *p*-aminobenzoic acid (PABA). It was obtained on a gram scale, providing a good supply of the ligand for MOF synthesis. This is in contrast to TM-CNDI, which requires 3,5-dimethyl-4-aminobenzoic acid as the primary amine, a compound difficult to obtain, has been therefore synthesized in a small scale.

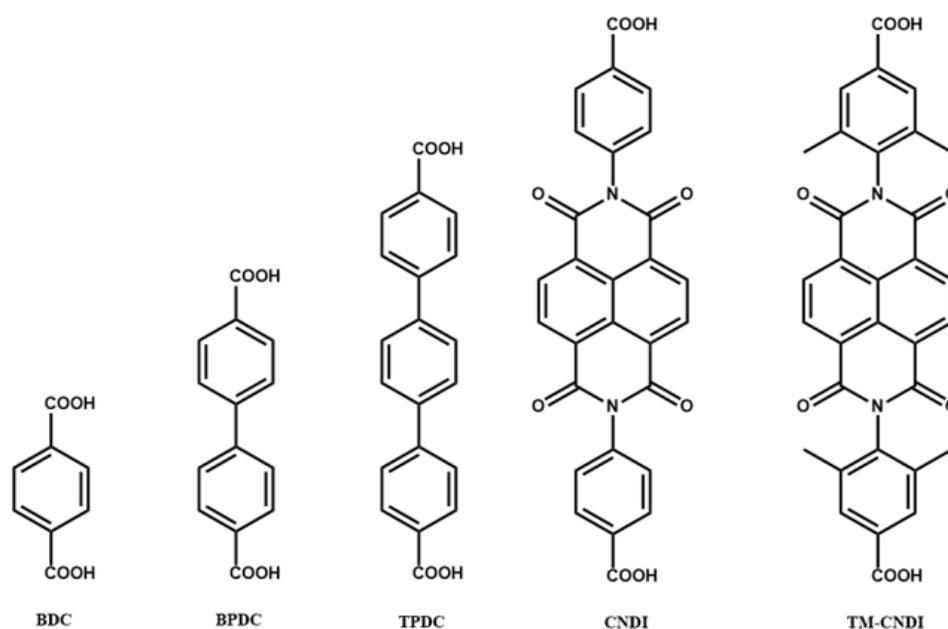


Figure 1 - Structure of ligands homologous to BDC that can be employed for IRMOF synthesis (BPDC: 4,4'-biphenyldicarboxylate; TPDC: 4,4''-terphenyldicarboxylate; CNDI: *N,N'*-bis(4-carboxyphenyl)-1,4,5,8-naphthalenediimide; TM-CNDI: *N,N'*-bis(2,6-dimethyl-4-carboxyphenyl)-1,4,5,8-naphthalenediimide).



Results and Discussion

The ligand CNDI was successfully synthesized through the reaction between 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCA) and p-aminobenzoic acid (PABA). The X-ray powder diffractogram (XRD) of CNDI is seen in Figure 2A. The XRD of the MOF CNDI/Zr is also seen in the figure. It can be noticed a mixing of two phases, one of them being pure CNDI. When the peaks due to CNDI were subtracted, the remaining peaks suggest that the second phase was the desired MOF (Figure 2B). The XRD of the MOF CNDI/Zn is seen in Figure 2C. The peaks at low angles ($2\text{-theta} < 5^\circ$), corresponding to $d > 20 \text{ \AA}$, are indicative of MOF formation. The MOFs were also characterized by Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption isotherms (BET method).

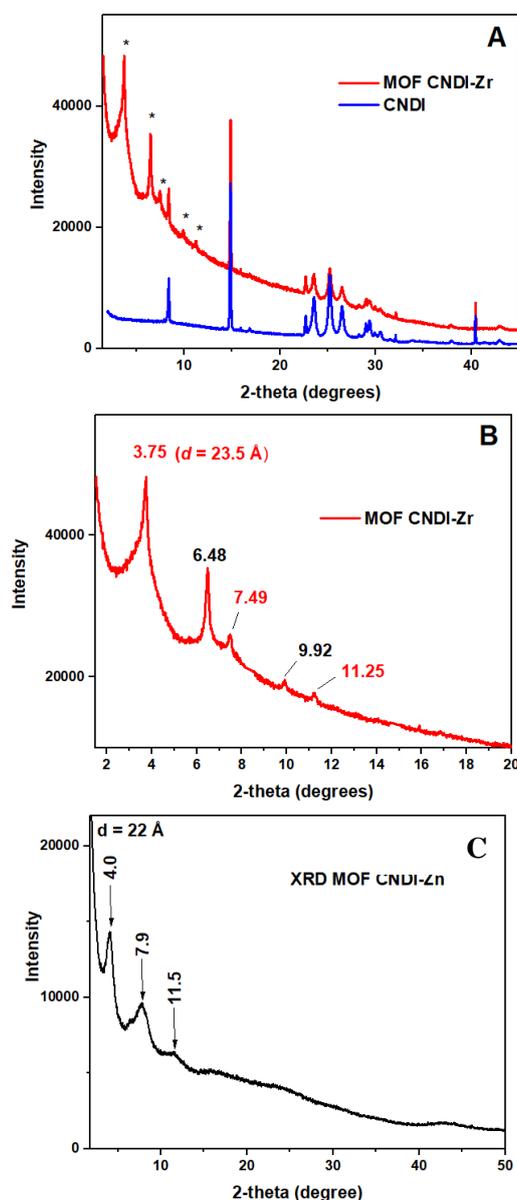


Figure 2 – (A) XRD of CNDI (blue) and MOF CNDI/Zr (red). (B) Difference XRD from part A. (C) XRD of the MOF CNDI/Zn.



The membranes were prepared from either poly ether sulfone (PES) or polysulfone (PS) by the phase inversion method. Figure 3 shows the photograph of one of the produced membranes. We are presently trying to incorporate the MOFs in one such membrane. The next step is to measure the permeability of the membranes towards CO₂ and N₂ gases, and then to calculate the CO₂/N₂ selectivity, what will be performed with a device specially constructed for the purpose (Figure 3).

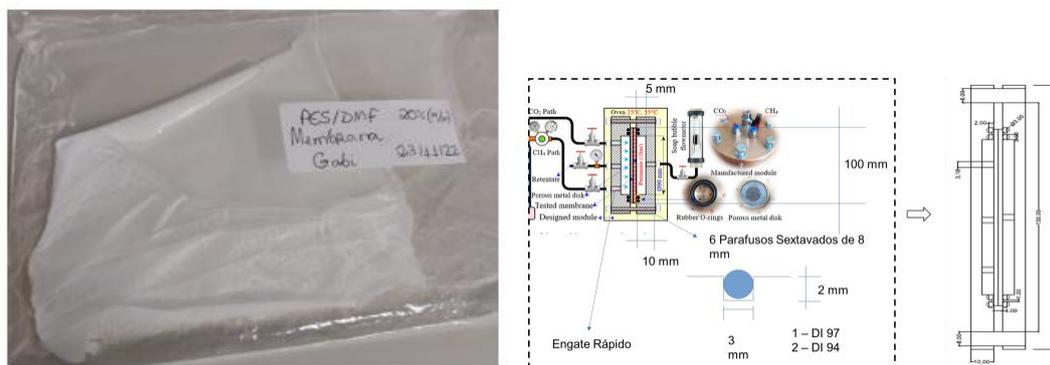


Figure 3 – Membrane prepared with the polymer PES (left) and device to measure the permeability of the membranes towards different gases (right).

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