Chapter 1

Introduction

RETICULAR CHEMISTRY, a field that bridges inorganic and organic chemistry (Yaghi 2020), has emerged from a simple albeit powerful idea: *combining molecular building blocks to form extended crystalline structures* (Yaghi 2019). It all started in 1990s, with the advent of metal-organic frameworks (MOFs), the first "offspring" of reticular chemistry. MOFs, a class of nanoporous materials *composed of metal ions or clusters coordinated to organic ligands aka organic linkers*, possess extraordinary properties, such as ultrahigh porosity and huge surface areas (Farha et al. 2012). To get a sense of how extraordinary these materials are, it is suffice to say that *one gram of such a material can have a surface area as large as a soccer field*. The fact that reticular materials are "brought to life" by combining simple building blocks, allows chemists and material scientists to design materials in a judicious manner. The epitome of design in reticular chemistry is found in the synthesis of a zirconium-based MOF (Alezi et al. 2016), incorporating the polybenzene network or "cubic graphite" structure, predicted about 70 years ago.

1.1 Applications of Reticular Chemistry

Owing to their aforedescribed properties along with their extremely tunable and modular nature, MOFs have been considered prominent solutions for gas-adsorption related problems (Li et al. 2007; Jiang et al. 2022). MOFs find application in fields such as gas storage and separation, catalysis and drug delivery, just to name a few.

Carbon capture is a prime example (An et al. 2009; Sumida et al. 2011; Qazvini et al. 2021), where MOF-based sorbents have been deemed as green, low-cost and energy-efficient solutions. These materials provide versatile solutions to carbon capture, spanning various phases of the capture process, with direct air capture (DAC) being a noteworthy example. DAC includes chemical or physical methods for extracting carbon dioxide directly from the ambient air, with MOF-powered DAC showing great potential as a green and sustainable strategy for reducing carbon dioxide levels, contributing to the combating of climate change (Bose et al. 2023).

Hydrogen storage is one of the greatest challenges of hydrogen economy, currently inhibiting the transition from fossil fuels to hydrogen. Fortunately, characteristics of MOF adsorbents such as fast adsorption/desorption kinetics, low operating pressures and high hydrogen capacities, render them as promising answers to the aforementioned challenge (Suh et al. 2011; Suresh et al. 2021).

Methane is an attractive fuel for vehicular applications, being a relatively clean-burning fuel compared to gasoline. ***Methane storage*** in sorbents known as adsorbed natural gas (ANG) exhibit advantages over compressed natural gas (CNG) and liquefied natural gas (lNG), both in terms of energy-efficiency and vehicular safety. MOFs (Ma et al. 2007; Spanopoulos et al. 2016; Tsangarakis et al.

2023) and their "reticular siblings" covalent organic frameworks (COFs)—composed only of light elements—show great promise as ANG solutions (Furukawa et al. 2009; Mendoza-Cortes et al. 2011; Martin et al. 2014; Tong et al. 2018).

1.2 The Problem

The intrinsic combinatorial character of reticular chemistry, translates to practically an infinite number of realizable structures. Currently, the Cambridge Structural Database (CSD) contains more than 100 000 experimentally synthesized MOFs (Moghadam et al. 2017) while the arrival of in silico designed MOFs (Wilmer et al. 2011; Colón et al. 2017; Boyd et al. 2019; Chung et al. 2019; Lee et al. 2021; Rosen et al. 2021; De Vos et al. 2023) has immensely expanded the available material pool. The huge size of current and future MOF databases (Lee et al. 2021) is both a blessing and a curse for the identification of novel materials. Blessing, since a large number of candidate structures doesn't limit our choices and as such, the chances to find the right material for a given problem. Curse, since the enormous size of MOFs space makes it harder for researchers to efficiently explore it, complicating the tracing of materials with the desired properties. It is therefore crucial to find a way that allows us to efficiently explore such a huge material space. Another way to rephrase our problem is the following: ***Given a large catalog of MOFs, is there a way to efficiently filter out the most promising ones for the application of interest?***

As a first approach to deal with this challenge, one could, in principle experimentally synthesize and characterize each one of the materials listed in the given catalog. Although *experimental synthesis and characterization* is the ultimate way to assess the performance of a material[1], the fact that a single laboratory study can take days or even months, renders experimental techniques impractical. A more refined approach is computational screening based on *molecular simulations*, which for years has served as the principal tool for the discovery of high-performing MOFs (**chong55**; **chong56**; **chong57**; **chong58**; **chong59**). Although computational screening dramatically accelerates the assessment of a single material compared to experimental techniques, brute-force screening of current and upcoming databases is considered suboptimal, given the size of the latter.

Machine learning (ML) aka *data-driven techniques*

1.3 Literature Review

1.4 Objective of Thesis

[1] As Richard Feynmann said: *"The test of all knowledge is experiment. Experiment is the sole judge of scientific truth"*.

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