POMzites a roadmap for inverse design in metal oxide chemistry

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Abstract

Exploring the space generated by the self-assembly of known metal oxides computationally and the ability to predict new architectures is a challenging task. Narrowing it down to a family of all-inorganic porous materials, composed of ring-shaped tungsten oxide building blocks connected with transition metal linkers forming zero to three dimensional frameworks. Structurally like zeolites (213 recognized structures), but an order of magnitude smaller, the POMzite library has only 14 members. Applying the concept of 'materials by design' applied to molecular metal oxide chemistry synthesis, and their assembly into frameworks. Structures with new topologies, but aiming for pure inorganic systems, will be targeted from the beginning.

POMzites a roadmap for inverse design in metal oxide chemistry

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Introduction

Zeolites and metal-organic frameworks (MOFs) are crystalline porous materials that can trap liquid or gas molecules. After intensive research in porous materials, rational design has been achieved and to a broader extent, it is possible to specify the size, shape, and uniformity of the pores in both zeolites and MOFs. Since 2017 there is a new family of all-inorganic porous materials, named 'POMzites', composed of ring-shaped tungsten oxide ($P_8W_{48}O_{184}$) building blocks connected with transition metal linkers forming zero to three dimensional frameworks, see Figure 1.[1] The coined term 'POMzites' reflects their zeolitic nature and their polyoxometalate (POM), or molecular metal oxide, based constituents. Architecturally they appear to be like zeolites (213 recognized structures), but currently the POMzite library is still small, with only 14 members. POMzite 'all-inorganic' frameworks are promising new material able to combine the robustness of inorganic materials with the flexibility of organic frameworks.[2] POMzites are robust porous electrochemically active solids with potential as components in molecular electronics and flex circuits.[3] POMzites are able to uptake small molecules (NH_3, CH_3COH), and structurally change under different humidities with potential applications as small molecule volatile organic compounds (VOCs) and humidity sensors. In solution, POMzites can uptake 3d transition-metal ions, e.g. Cu(II), small organic molecules and aromatic organic amines, making them attractive materials for heavy metal uptake and wastewater remediation.[4]

Technological revolutions and the discovery of new materials go hand in hand, for instance the discovery of tungsten light-bulb filaments, penicillin, Velcro, Teflon, semiconductors, saccharine, etc. have had a huge impact on society. Some these discoveries are the result of goal-oriented lab work and trial and error research, but others are the result of a combination intuition and serendipity. Easy to find materials were found decades ago, now we need to dig deep in the materials space to find compounds with the properties that we are looking for. Material science databases and computations are key to find next generation of materials, we cannot solely

rely on lucky accidents to find new compounds that could transform technology. This perspective presents the recent advances in applying inverse design and high throughput methods for materials discovery. This article is arranged as follows: first overview on POMzite materials, then the current trends in materials discovery and materials, specifically 'inverse design', then the proposed advances in the area presenting inverse design in POMzites and finally an outlook.

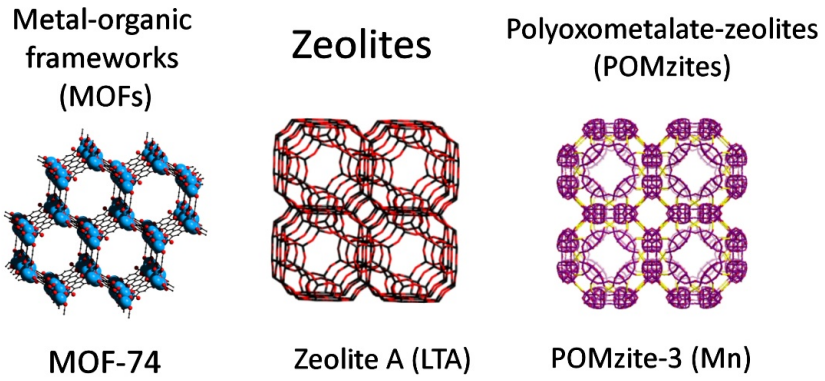


Figure 1. Examples of representative porous materials. Metal-organic frameworks (MOFs), Zeolites and Polyoxometalate-zeolites (POMzites).

POMzites: polyoxometalate based frameworks

Polyoxometalates (POMs) or, molecular metal oxides, are discrete molecular structures composed of metal ions bridged by oxide anions.[5] POMs are primarily constituted of early-transition-metal (*d-block*) elements in their highest oxidation states, a great majority of these structures are anionic and consequently salts with charge balancing cations. They are composed of between 6 to 368 metal ions in a single molecule and are commonly assembled under 'one-pot' reaction conditions. POMs, especially tungsto- and molybdophospates and silicates, are widely used in industry for catalysis.[6] Theoretical estimates for new polyoxometalate (POM) materials and their properties lead to a deeper understanding faster, and more efficiently than with test and experimentation alone. First principles multiscale modelling has allowed a deep understanding of materials by enabling accurate prediction of electronic properties of materials at a low computational cost, for instance, band gaps that are crucial for memory device applications.[7] Computer simulations have represented a breakthrough in materials science and engineering since simulations offer help in directing experimental efforts. POMs are also called molecular metal oxides due to their molecular composition and their position between monomeric entities and bulk oxides. Despite being well known in the literature for over a hundred years, their self-assembly mechanisms remain semi-opaque and controlling the desired output in a reaction is not always possible. This is because POMs are prepared and isolated from both aqueous and non-aqueous solutions whereby-the polymerisation of acidified solutions of Mo^{VI} or W^{VI} yields to a chaotic mixture of materials.[8] Preliminary work,[9] shows that we can obtain information of the building blocks formed in the synthetic mixtures, hence we are closer to the design of new metal-oxide materials with the targeted properties. As happens with zeolites, the preparation of metal oxides can seem like a black art and predicting function and synthesis is notoriously difficult.

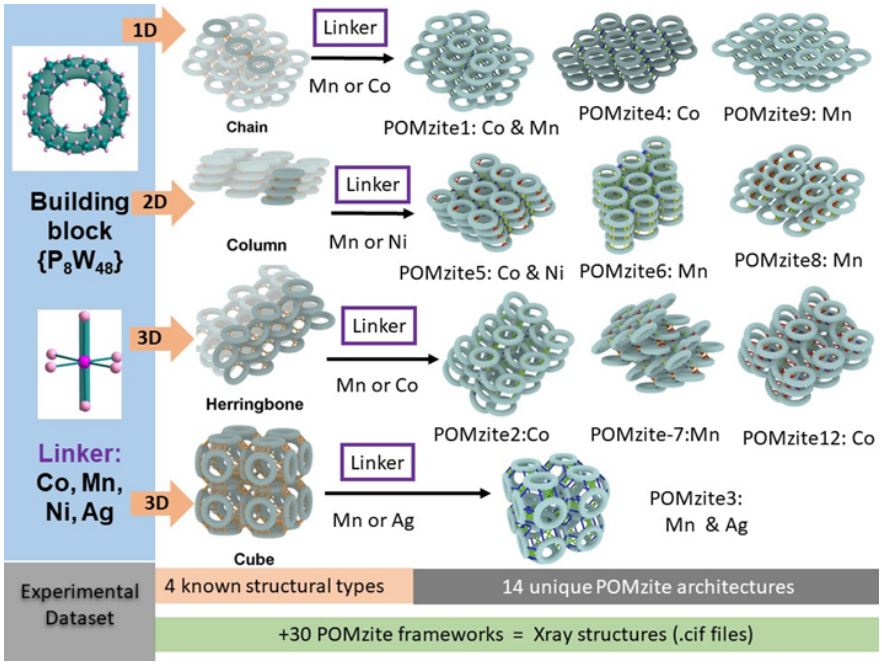


Figure 2. The minimal building block library of $[P_8W_{48}O_{184}]^{40-}$(abbreviated as $\{P_8W_{48}\}$) nodes and transition metal linkers (Co, Mn, Ni, Ag) that forms a family of 14 POM-all inorganic framework architectures (namelly "POMzites"). They all share the $\{P_8W_{48}\}$ building-block, with simplified ring representation green and have the four structural assembly types: chain (POMzite-4, 9,10, 14), column (POMzite-5, 6, 8, 11, 13), herringbone (POMzite-2, 7, 12) and cube (POMzite-3). We have selected 10 representative examples of the 14 POMzite architectures. To date, the explored experimental dataset consists of 30 POMzite frameworks, but the accessible chemical space is vast.

Current trends in materials design

Materials discovery and design efforts ideally involve a close coupling between materials prediction, synthesis, and characterization. We need to speed up and lower the cost in the discovery of materials able to adapt to the needs of a much more demanding technology. The increased use of computational tools, the generation of materials databases, and advances in experimental methods have substantially accelerated these activities.[10] Amongst the numerous solutions that have been proposed for this challenge high-throughput experimental (HTE) methodologies,[11] stand out since they are able to establish quickly relationships between composition, structure and functional properties. Over the past 10 years,[12] HTE methodology has been adopted by material chemists in order to create large libraries of compounds allowing a rapid and systematic investigation of new materials. Success examples of this methodology include the search for materials for Li–batteries,[13] for hydrogen storage,[14]scintillators,[15]electrocatalysts,[16] 2D materials for electronics[17] or to accelerate the discovery of light-absorbing materials.[18] HTE methods are a powerful tool for exploring materials space and for screening materials without having to synthesize them first. Other solutions in the field of materials by design include: directed simulation,[19] pathway assembly[20] and inverse design.[21] All the methodologies address similar challenges using large data sets and aim to accelerate the discovery of new materials with targeted properties. In practice, the design of complex materials from the bottom up is very demanding computationally as the number of parameters increases with the complexity of the desired material. In molecular metal oxides the current understanding of self-assembly is limited to low nuclearity clusters, and the design of new systems is almost impossible at nuclearities greater than $\{M_{12}\}$, due to a combinatorial explosion. Furthermore, unlike in fullerenes,[22] or gold clusters,[23] no topological principles that allow prediction have been found. In my previous research we have identified common motifs in many

clusters synthesis and we have been able to manipulate them as a function of the pH, the template and the linker heteroatom to generate a promising cross-shaped nano-molecular structure.[24] This represents a game changer in POM chemistry since trapping reactive POM building blocks is the first step into generating libraries with the desired properties that will later assemble into the desired material.

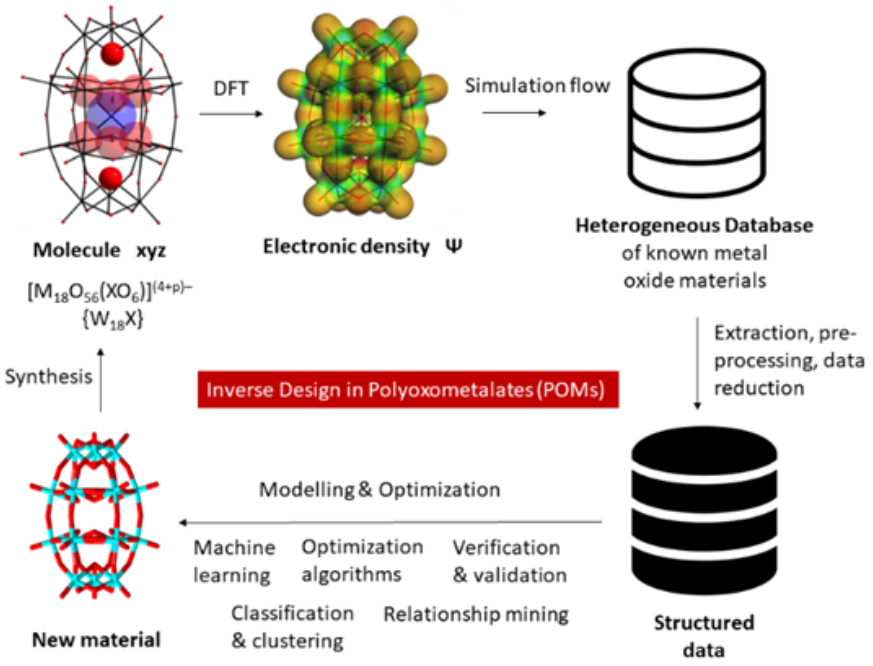
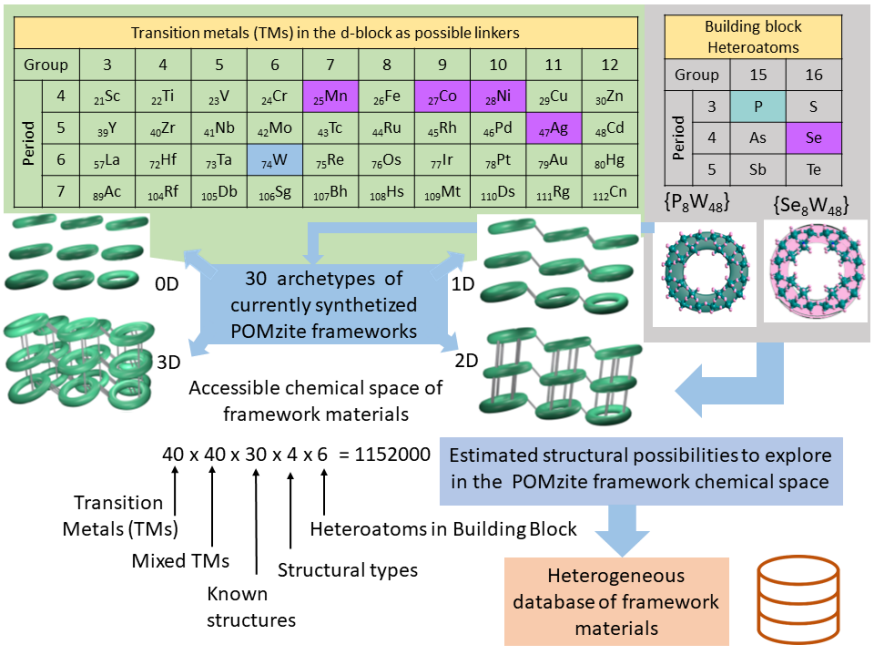


Figure 3. Description of the workflow proposed for achieving inverse design in metal oxides.

Inverse design in POMzites



Here, we propose a suite of 'top-down' design and 'bottom-up' discovery of porous metal oxides metal oxides and anticipate the formation of extended materials based upon these molecular building blocks, see Figure 4. Leveraging the decades-long expertise of the broad computational material science community and the large amount of data available at Density Functional Theory (DFT) level will be beneficial to obtain reliable description of POMs electronic structure, which can be used to generate the database obtained by exploring the chemical space of POMzite materials.[25] This initial database will be explored and refined using principal component analysis that will be used to establish a new bottom-up method. Top-down methods will rely on analysis of the structural database, and the development of deep neural network produce new synthetic routes by developing theory from aggregated observations using Reinforced Learning (RL) algorithms.

Figure 4. The estimated accessible chemical space generated by expanding the POMzite family.

The general objective is to develop a new conceptual approach for the fabrication of functional nano-molecules and adaptive materials. Proposing to explore the hypothesis of first predicting and then synthesizing new POMzite materials. The ideal outcome of the research proposed here is to predict new POM all-inorganic framework materials, followed by experimental realization by our collaborators. By theoretically expanding the acessible chemical space generated by the derivatization of polyoxometalate (POM) clusters, which enables their assembly into a range of frameworks by use of inorganic linkers.[2] These robust all-inorganic frameworks are made using metal-ion linkers (Co, Mn, Ni, Ag), which combine molecular synthetic control without the need for organic components.[1] Later generating the heterogeneous database of POMzite materials, 1.6 10^7 estimated structures, see Figure 4. For instance, so far we have just explored 4 transition metals as linkers, out of 30 possibilites

We have the tools to understand POMzites at a molecular level and understand the interactions between the electrons of atoms bound in molecules using 'first principle' techniques DFT algorithms. By mapping their electronic structure by modelling, using an *ab init* o packages with basis sets and functionals for transition metal clusters. The cyclic heteropolyanion $[P_8W_{48}O_{184}]^{40-}$(abbreviated as $\{P_8W_{48}\}$) is the current building block for the construction of porous framework materials. Preliminary gas-phase calculations confirmed the stability of $\{P_8W_{48}\}$ as an initial structural motif, [26] derivatives such as the Se equivalent are also stable. Theoretically derivate other cyclic POMs with different heteroatoms (As, Sb, S, Te) and asses their potential to aggregate into porous structures. We are also interested in understanding the binding sites of the POMzite materials, this will only be possible by describing their molecular structure. This basic computational setup will provide with data (e.g. molecular charge, optimized geometry, HLgaps, etc.) to start the initial layer of a neural network.

Given the size and the characteristics of their unique porous environment, we will need macroscale modelling of the POMzite architectures. To advance this area, we need to combine experimental input with computational modelling to imagine a wide range of different rearrangements, and to create a blueprint for building these materials.[27] Aiming to understand the connectivity and the stability of $\{P_8W_{48}\}$ rings in POMzite structures and predict new motifs from the results, as well as being able to anticipate new favourable structures with different linker modes. Given the fact that some POMzites have just been observed with Co or Ni, e.g. POMzite-5, by modelling we will be able to substitute those linkers with another TM. We use simple topological methods such as stochastic modelling to make predictions of the different binding sites.[28] We will be able to predict new bulk physical properties from assemblies of these building blocks e.g. electropotential, acidity, optical properties, electronic storage. Once we have fully understood the chemical system and created a database of all the molecular architectures, we would like to predict their physical properties.

The data generated in this project will provide a greater insight in the binding site and the resulting in the crude heteregoneous framework materials database, with an estimate of 1.6 10^7structures. The curation of this database will require initial data pre-processing of the POMzite geometries, checking its format and presenting them in an understandable format. This will be the ideal training set to use an end-to-end Reniforcement Learning (RL) approach to investigate whether is possible to predict new and stable POMzite materials. We propose to use a modular behaviour-based reinforcement architecture that will start training neural networks with a known solution,[29] leveraging on knowledge of known, and/or predicted to be stable,

POMzite materials. Classically a learning algorithm training will split the dataset into 3 sets: training, validation, and testing datasets. The first one is used in the learning process, where the model parameters are obtained. Once we obtain an optimal set of parameters, the test set is used to assess the performance of the model. If the obtained model is unsuccessful, the previous steps are repeated with improved data selection, representation, transformation, sampling, and removing outliers, or by changing the algorithm altogether.[10]

Outlook

Our technology landscape and research methodologies need to change to solve the access to clean water along with sustainable energy and the protection of the environment. DFT-based simulations will be key to develop a new conceptual approach for the fabrication of functional nano-molecules and adaptive materials. Inverse design is a more advanced approach than simply using optimization algorithms and automating the search for a structure. The goal is to have a chemical property input its desired performance metrics and allow for the algorithm to generate the best possible structure. The ultimate test for inverse design methodologies in chemistry is the synthesis, characterization, and evaluate the properties of a new material. None of what we do is in a vacuum, the era of relying on serendipity to advance in materials discovery is coming to an end. Given the current challenges already faced by chemistry, we added the 2020 global pandemic. To thrive during this uncertain period we may need to adapt human labor to stricter shifts, increase PPE, etc. Furthermore, materials scarcity will require a greater planning and a goal-oriented search to new materials. Inverse design in metal oxides has the promise to answer the 200-year-old question of the self-assembly mechanisms in polyoxometalates but has a lot more to offer. Inverse design can help in finding a specific catalyst for a zero-carbon fertilizer fuel and energy store; or in obtaining a material for a new memory device able to write data more efficiently to reduce wear associated with read/write cycles and increase its lifetime. This quarantine and reflecting time have been a wake-up call, we need to adapt our research methodologies to be more effective. Chemists will raise again to this challenge and as a community we will offer a new generation of materials.

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Keywords: metal oxides, polyoxometalates, computational chemistry, inverse design, porous materials

About the author: Dr Vilà-Nadal coursed a M.Sc. in Theoretical and Computational Chemistry at the Rovira i Virgili University (Spain). In 2011 she awarded a PhD in the same university under supervision of Prof. J.M. Poblet and Dr. Rodríguez-Fortea, in her thesis she studied the step-by-step building-block mechanisms for small, 6 to 12 metal clusters, tungsten, and molybdenum oxides. The same year moved to the University of Glasgow (UK) working with Prof Lee Cronin in a project that found a new memory device based on a W-Se molecular metal oxide. In 2019 she was appointed as a Lecturer (PI). In her first independent academic position, she stablished the *Laia Vilà-Nadal group*(LVN-group) to explore the broad topic of self-assembly in metal oxides and study their properties as porous materials, memory devices and energy storage.

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GRAPHICAL ABSTRACT

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TITLE: POMzites a roadmap for inverse design in metal oxide chemistry

TEXT: Recent advancements in computational inverse-design approaches, algorithmic techniques for discovering materials based on desired properties, have reshaped the landscape of porous materials research. Computationally exploring a new family of all-inorganic porous materials, composed of ring-shaped tungsten oxide building blocks connected with transition metal linkers forming zero to three dimensional frameworks, named '*POMzites* '. This is a new class of all-inorganic metal oxide frameworks that combine the robustness of inorganic materials with the flexibility of organic frameworks.

GRAPHICAL ABSTRACT FIGURE ((Please provide a square image to be produced at 50 mm wide by 50 mm high. Please avoid graphs and other figures with fine detail due to the relatively small size of this image.))