



AN OVERVIEW OF DESIGNING POROUS HYDROGEN BONDED ORGANIC FRAMEWORK

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Abstract: Hydrogen-bonded Organic frameworks (HOFs) are new and versatile class of porous materials following the porous crystals (PCs), metal-organic frameworks (MOFs), covalent organic frameworks (COFs), etc. HOFs rely on the assembly of simple organic building blocks. Defining the HOF assembly with new organic building blocks or modules is of high interest, in order to expand this robust family. Hence, we aim to work on newly derived imine based organic modules to form HOF and their detailed characterization to decide its applicability.

Keywords: Bond, Porous, framework, organic, work mater

Review Article: In the last several years, a number of new approaches for the preparation of porous materials have been developed. For a variety of real-time applications, porous materials with predetermined pores and shape are highly desired. The magnitude, organization, and structure of the pores, as well as the porosity and composition of the material itself, influence the characteristics of porous materials. Porous materials are used in applications involving chemical action and chemical separation. It's required in each and every one of biomedical's applications. They're also thermally stable, and they're in high demand as adsorbents, catalytic supports, and catalysts. Mesopores, macropores, and micropores exist in Clay mineral systems. Macropores and mesopores are formed through particle-to-particle interactions, as seen in Figure 1 provided below¹.

Hydrogen-bonded organic frameworks (HOFs)As a unique category of porous crystalline materials, hydrogen-bonded organic frameworks (HOFs), self-assembled from organic or metal–organic building blocks through unit hydrogen-bonding interactions, have attracted additional and additional attention. Designing organic components that can be used to construct porous materials enables the preparation of tailored functionalized materials. Research into porous materials has seen a resurgence in the past decade as a result of finding of self-standing porous molecular crystals (PMCs)².

Over the past decade, variety of porous HOFs are made through discreet choice of H-bonding motifs, that square measure any implemented by alternative weak unit interactions like π - π stacking and van der Waals forces and framework interpenetration. Hydrogen-bonded organic frameworks (HOFs) are a class of porous molecular

materials that rely on the assembly of organic building blocks by means of hydrogen-bonding interactions to form two-dimensional (2D) and three-dimensional (3D) crystalline networks³. A strategy for making molecular networks that are porous and deformable is revealed by the behaviour of compound⁴ the first microporous hydrogen-bonded organic framework with permanent porosity and exhibiting extraordinarily highly selective adsorptive separation of C₂H₂ and C₂H₄ at ambient temperature has been established⁵⁻⁶.

Since the H-bonds square measure weaker than coordinate and Covalent bonds used for the development of metal–organic frameworks (MOFs) and Covalent organic frameworks (COFs), HOFs have some distinctive options like delicate synthesis condition, resolution processability, simple healing, and regeneration. These options modify HOFs to be a tenable platform for the development of useful materials. Here, we have a tendency to review the H-bonding motifs used for constructing porous HOFs and highlight a number of their applications, together with gas separation and storage, chiral separation and structure determination, fluorescent sensing, heterogeneous chemical action, biological applications, proton conductivity, photoluminescent materials, and membrane-based applications⁷. Self-assembled crystalline porous organic salts (CPOSs) formed by an acid-base combination and with one-dimensional polar channels containing water molecules have been synthesized⁸. A robust hydrogen-bonded organic framework with free COOH groups and suitable pore confinement demonstrates excellent performance for the important and challenging C3H6/C3H8 separation. A robust hydrogen-bonded organic framework with free COOH groups and suitable pore confinement demonstrates excellent performance for the important and challenging C3H6/C3H8 separation⁹. Microporous inorganic materials such as zeolites find widespread application in heterogeneous catalysis, adsorption and ion-exchange processes. The rigidity and stability of such frameworks allow for shape- and size-selective inclusion of organic molecules¹⁰.

Imine based mostly H-bonding motifs: The Schiff's base reaction may be a group-specific reaction between aldehydes/ketone and amine. The reaction sometimes happens bellow acidic or basic conditions with aromatic amines to create a Schiff's base. A Schiff's base a compound with the structure $>C=N-R$. These measure the condensation product of primary amines with carbonyl compounds and were initial reported by novelist Schiff. Schiff bases is a most widely used organic compounds. The organic building units synthesized, then processed to create HOF.

Feature of hydrogen bond: 1. Hydrogen bond is weaker than coordinate and covalent bond. 2. Reversible nature of the hydrogen-bond formation provides HOFs with the attributes of resolution processability and normal regeneration. The applications of HOFs are comprehensive, spanning chemical action, energy, and medical specialty product also because the storage and separation of fine chemicals. Advantages of HOF when compared to MOF and COF, Solution processability, Characterization, Easy Purification, Healing by simple crystallization¹¹ for the synthesis of organic building unit Schiff base reaction mechanism is used.

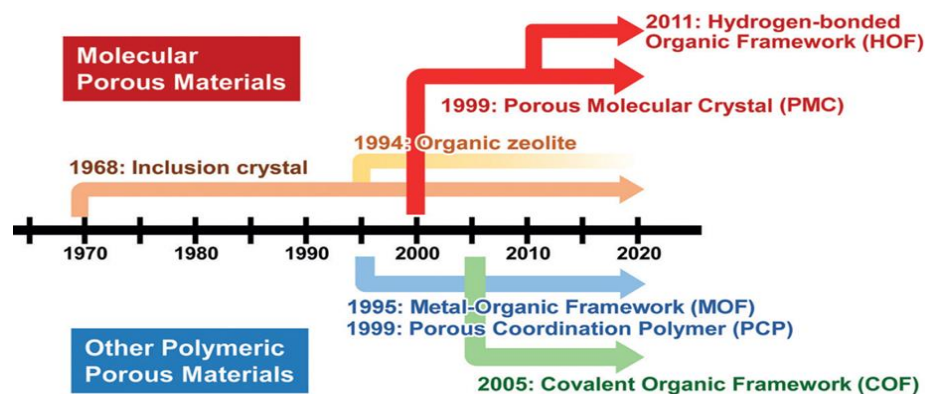
Hydrogen-bonded organic frameworks (HOFs), which are typical molecular materials with easy synthesis and recyclability, are generated via hydrogen bonds, p–p stacking, and even weaker supramolecular interactions. However, because of the poor strength and directionality of the H-bonding motif, HOFs are challenging to construct, especially for extremely porous and symmetric materials. Using highly directed functional groups capable of making numerous hydrogen bonds is the most successful technique for preparing HOFs. As a result, the goal of this research is to create novel imidazole-based H-bonding motifs, characterise them, and then translate them into thin films. Synthesis of large pi-conjugated planar imidazolate H-bonding organic motif which can provide strong intermolecular interactions. b, Characterization of imidazole-based hydrogen bonded organic framework. Preparation of HOF nano-film and defining its formation mechanism.

Porous Materials have long been the leading platform for world scientists and engineers looking to develop new multifunctional materials¹². That are widely used in materials science, engineering, mechanics, geosciences, and medical sciences for filtration, separation, purification, extraction, chilling, drying, and chemical processes. Several common substances, such as charcoal, zeolites, and ceramics, are considered porous media because they include permanent and interconnected voids for gas/liquid permeability.

During the past two decades, porous materials constructed of organic components have attracted much attention. Assembling versatile organic components into a porous framework enables functionalization, such as selective gas storage/separation, catalysis, chemical sensing, and optoelectronics¹³.

Over the last two decades, the use of porous crystalline materials, such as metal–organic frameworks (MOFs)¹⁴, porous coordination polymers (PCPs)¹⁵⁻¹⁶, and covalent+6 organic frameworks (COFs), has increased. MOFs and COFs are crystalline porous materials that are precisely self-assembled from a variety of molecular building pieces using strong coordinative or covalent bonds, resulting in extraordinary consistency, modularity, and utility. Anthracene–monoresorcinol derivative forms hydrogen-bonded poly(resorcinol) 1D chains, which self-assemble via interpenetration or intercalation of the orthogonal anthracene (A) substituents¹⁷. Permeable molecular crystals can be specifically designed to let external agents enter, react, and produce single crystals of new substances with retention of the original crystalline architecture¹⁸. crystals grown from mixtures of hexane with ethyl acrylate, ethyl acetate, THF, or dioxolane all exhibit submaximal 3-fold interpenetration¹⁹. When recrystallized from an appropriate solvent, orthogonal bis (resorcinol)—anthracene compound 1a as host forms molecular sheets involving an extensive hydrogen-bonded network²⁰ the crystal structures of a series of these porphyrins exhibit unique structural features through assembly of porphyrin networks by means of directional hydrogen bonding²¹.

The development of multifunctional porous materials is at the forefront of chemical and materials research aimed at addressing global scientific concerns such as sustainable energy, environmental remediation, and human health. Because of their strong extended structures supported by powerful dative case and covalent bonds, and their high modularity, which allows the functionalization and post functionalization of their frameworks, metal-organic and covalent organic frameworks (MOFs and COFs) represent the key players dominating the sphere of porous materials. Historically, inclusion crystals²² and molecular zeolites²³⁻²⁴ with void spaces capable of accommodating guest molecules (Figure 1) have been explored²⁵. Although hydrogen-bonded organic frameworks (HOFs) have been proposed as potential porous materials and a series of HOFs were structurally characterized about two decades ago,²⁶⁻²⁷.



Multifunctional porous materials are being developed at the forefront of chemical and materials research to solve worldwide scientific challenges such as renewable energy, environmental clean-up, and human health. Metal-organic and covalent organic frameworks (MOFs and COFs) are the key players dominating the sphere of porous materials due to their strong extended structures supported by powerful dative case and covalent bonds, and their high modularity, which allows the functionalization and post functionalization of their frameworks.

A variety of crystalline systems with persistent porosity have been produced by self-assembly via chemical element bonding (H-bonding). Chemical element Hydrogen organic frameworks are examples of such systems (HOFs). H-bonding patterns (supramolecular synthons) and molecular structures (tectons) are critical for achieving thermal and chemical stability, a large surface area, and functions such as selective gas natural process and separation, which could provide principles for building HOFs with permanent porosity. Porous materials containing organic elements have been used for a number of decades. Two different porous hydrogen-bonded networks are formed by self-assembly of the radially substituted host²⁸.

Metal-organic frameworks (MOFs)¹ and porous coordination polymers were the initial names for porous lattice frameworks constructed from metal cations and organic ligands, according to Yaghi's and Kitagawa's teams (PCPs) COFs (covalent organic frameworks) were developed later²⁹. Organic molecules were used to create porous molecular crystals (PMCs)³⁰, which were formed by a reversible intermolecular force of attraction. Inclusion crystals and molecular zeolites of various types are used. These spaces are made up of empty areas that can hold guest molecules. When the guest molecule separates from the substance, it collapses. Permanent porosity is sustained by H-bonding in porous molecular crystals [PMCs]. Chen coined the term "hydrogen bonded organic frameworks" (HOFs) to describe these structures. properties of porous molecular crystals (PMCs) constructed through hydrogen-bonding of C_3 -symmetric, rigid, π -conjugated molecular building blocks possessing carboxyaryl groups, which was reported in the last 5 years by the author's group. PMCs with well-defined, self-standing pores have been attracted attention due to various functionalities provided by selective and reversible inclusion of certain chemical species into the pores³¹.

General Features of hydrogen bonded organic frameworks (HOFs)¹. The reversible nature of H-bonding allows for an exceedingly crystalline structure to be created using a simple resolution procedure³². Recrystallization from resolution, for example, yields single crystals that may be used in single-crystal X-ray diffraction (SXRD) to reveal unambiguous structural details³³. 2. No need for a metal element, allowing for the creation of a porous structure that is both light and ecologically beneficial. 3. The ability to reanneal with solvents to restore crystallinity³⁴. Weak chemical element linkages that will cause the framework to collapse after the removal of solvent molecules from voids for activation. 4. In comparison to MOFs and COFs, there is no common style strategy. Even after carefully designating building block molecules, the needed porosity HOFs aren't always created; instead, nonporous materials may arise³⁵. a point at which polar solvent

molecules can capture H-bonding moieties, inhibiting the creation of networked frameworks. Porous solids are important as membranes, adsorbents, catalysts, and in other chemical applications³⁶.

Several molecular moieties, such as carboxylic acid, pyrazole, 2,4-diaminotriazine, amide, benzimidazolone, imide, imidazole, amidinium, boronic acid, resorcinol, pyridine, and 2,6-diaminopurine, are used for H-bonding interactions due to the varied organic teams with H-bonding potential. These organic teams will give large polymorphs via rational assembly in diverse geometries, because to the elastic nature of the H-bond. Only energetically advantageous frames, however, are crystallized. HOFs required slow evaporation from alcohol solution. Even when highly polar solvents, such as DMF, were necessary for crystallization, network structures have been formed by slow evaporation of a mixed solvent with an apolar template solvent at high temperatures³⁷. Tectons are molecules whose interactions are dominated by specific attractive forces that induce the assembly of aggregates with controlled geometries, and molecular tectonics is the art and science of supramolecular construction using tectonic subunits³⁸.

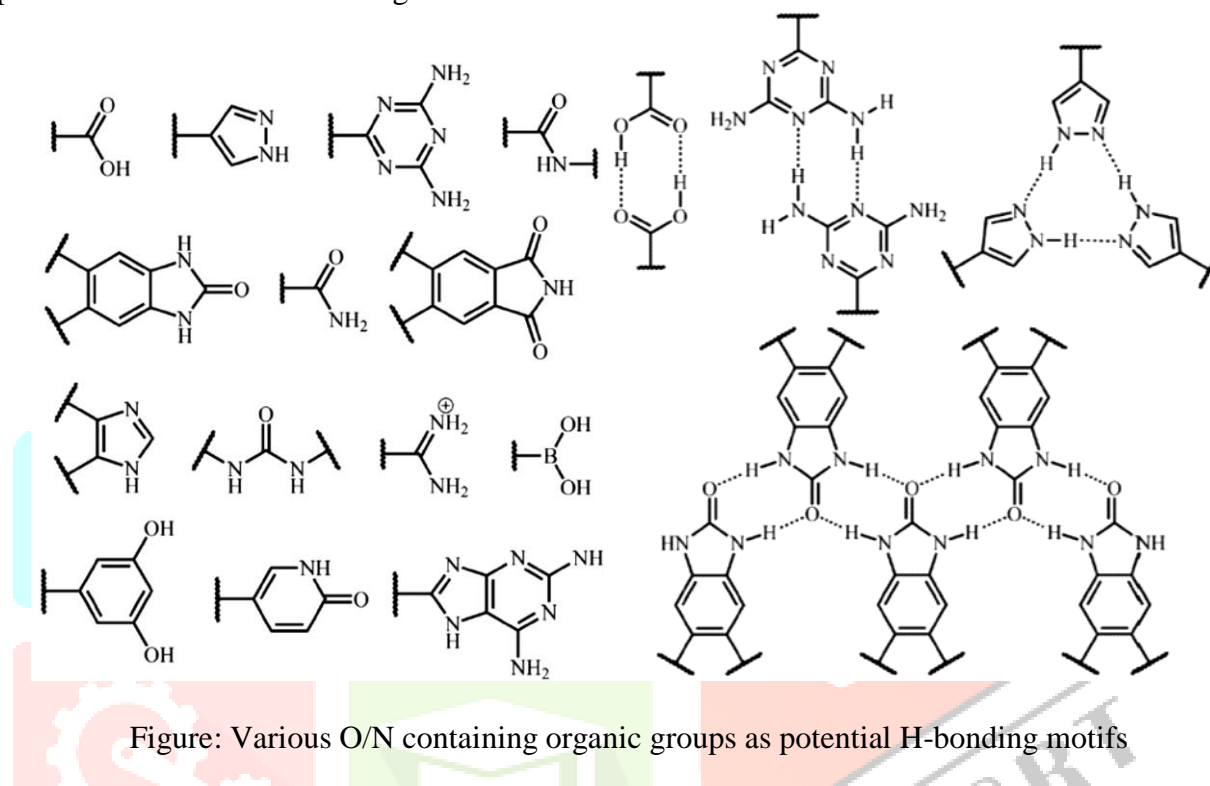


Figure: Various O/N containing organic groups as potential H-bonding motifs

micro porous solids have focused largely on inorganic materials such as zeolites³⁹. The tetrahedral centres of the 10 tectons in the drawing define a distorted adamantane, shown at the right at one-half scale. Non-hydrogen atoms are represented by ellipsoids corresponding to 50% probability⁴⁰. We have defined a tecton as a molecule whose interactions are dominated by specific attractive forces that induce the assembly of aggregates with controlled geometries; molecular tectonics is then the art and science of supramolecular construction using tectonic subunits⁴¹. Tecton yields an HOF with an interpenetrated (10,3)-b network (referred to as HOF-11⁴² or IISERP-HOF1⁴³. The CPHAT-1 a retained single crystallinity⁴⁴. The HOF showed acid-responsive color changes due to nitrogen atoms in the conjugated p-system⁴⁵. Bucky-Bowl 15 formed both single and double-layered HOFs⁴⁶. Upon applying various tectons with DAT groups, they constructed a series of HOFs HOF-2⁴⁷, HOF-5⁴⁸, HOF-7⁴⁹ with different crystal structures.

Conclusion: Organic teams with an equal number of H-bonding donors and acceptors are more suitable for HOF creation in principle, because these H-bonding donors/acceptors will clearly sort bonded intrinsic H-bonding units, which might be dimers, trimers, or even chain structures. H-bond building units appear to be stiffer and more directed than single H-bonding donor/acceptor pairs, which aids in the formation of HOFs. Expanded frameworks with a variety of topologies and pore architectures are created by combining H-bond building units with suitable organic backbones. It's worth noting that the concept of H-bonding units is critical for the construction of higher-porosity HOFs, since their pure mathematics is communicated into net when the length of organic backbones occasionally dominates the pore size.

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