

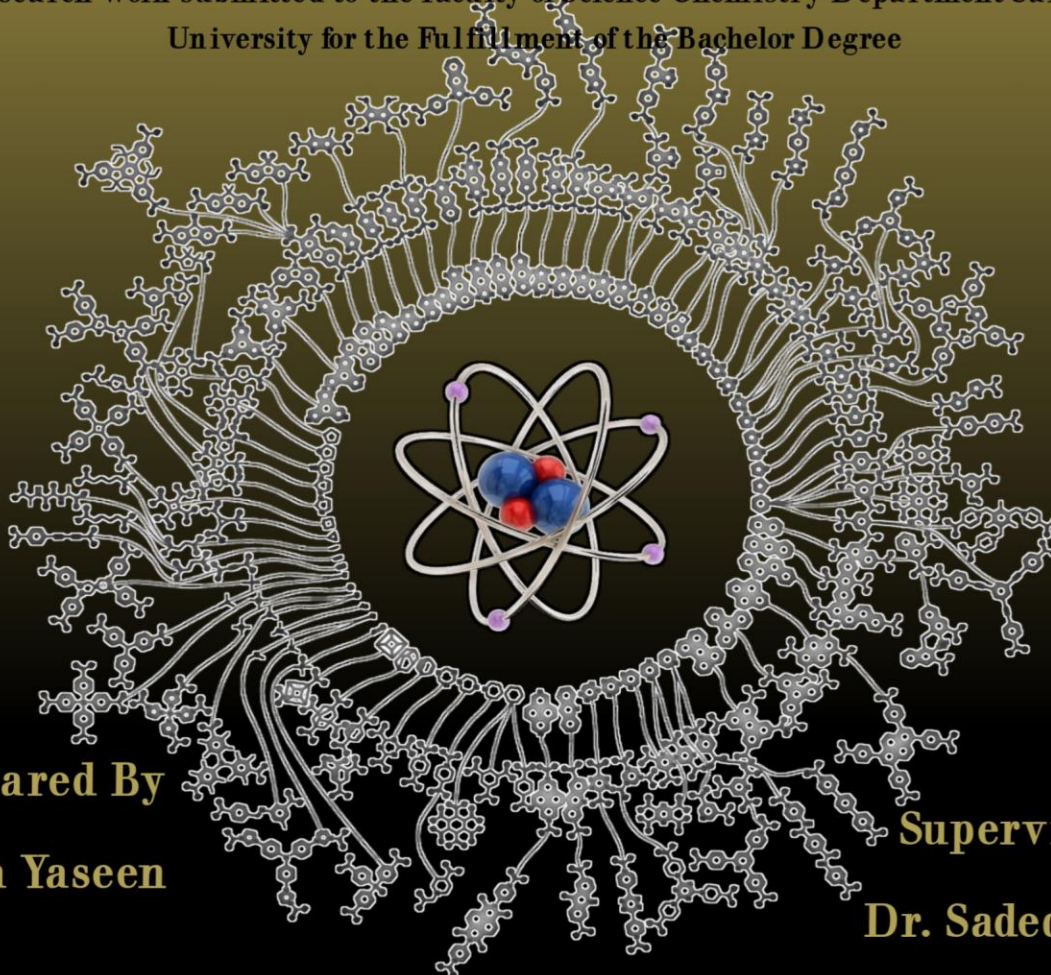


Republic of Yemen
Sana'a University
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Molecular Weaving Of Reticular Chemistry

Research work submitted to the Faculty of Science Chemistry Department Sana'a University for the Fulfillment of the Bachelor Degree



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Abstract

Reticular chemistry, a rapidly evolving field within materials science, focuses on the design, synthesis, and application of metal-organic frameworks (MOFs). These crystalline materials possess intricate three-dimensional structures, composed of metal ions coordinated to organic ligands through strong coordination bonds. This abstract provides an overview of reticular chemistry, highlighting its fundamental principles, synthesis techniques, and promising applications. Reticular Chemistry is the chemistry of assembling predesigned molecular building blocks by strong covalent bonds or non-covalent interactions in order to produce extended two-dimensional or three-dimensional crystalline structures. Metal-organic frameworks and covalent-organic frameworks are the most common examples in reticular chemistry which have been well studied and explored during the last years. Molecular weaving is the last and recent functional solid-state material discovered and synthesized which belongs to reticular chemistry. Until now there are limited strategies developed to synthesize the molecular woven materials; some of these strategies depends on forming covalent bonds during the production of the network and the others targeted to form non-covalent bonds. In this report, the development of molecular woven materials and the different strategies used to synthesize them, will be discussed, as well as their expected applications in different fields. In our live reticular Chemistry is the chemistry of assembling predesigned molecular building blocks by strong covalent bonds or non-covalent interactions in order to produce extended two-dimensional or three-dimensional crystalline structures. Metal-organic frameworks and covalent-organic frameworks are the most common examples in reticular chemistry which have been well studied and explored during the last years. Molecular weaving is the last and recent functional solid-state material discovered and

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Introduction

porous organic frameworks (POFs) have become a highly sought-after research domain that offers a promising avenue for developing cutting-edge nanostructured materials, both in their pristine state and when subjected to various chemical and structural modifications. Metal-organic frameworks, covalent organic frameworks, and hydrogen-bonded organic frameworks are examples of these emerging materials that have gained significant attention due to their unique properties, such as high crystallinity, intrinsic porosity, unique structural regularity, diverse functionality, design flexibility, and outstanding stability. This review provides an overview of the state-of-the-art research on base-stable POFs, emphasizing the distinct pros and cons of reticular framework nanoparticles compared to other types of nanocluster materials. Thereafter, the review highlights the opportunity to produce multifunctional tailored nanoparticles to meet specific application requirements. It is recommended that this potential for creating customized nanoparticles should be the driving force behind future synthesis efforts to tap the full potential of this multifaceted material category.

Reticular chemistry, derived from the Latin term "reticulum" meaning "net-like" involves the connection of individual building units such as molecular and clusters using robust bonding to form extensive and coherent architectures with highly ordered arrangement in a designed manner[1-3]. By combining the best of inorganic chemistry, organic chemistry, and materials science and engineering, reticular chemistry is producing a treasure trove of novel materials with remarkable properties. Considering the number of unique structures catalogued so far in the Cambridge Structural Database surpassing an impressive milestone[4], this field is at the forefront of scientific discovery and innovation[5-9]. Indeed, within the field of reticular chemistry, 2D and 3D porous organic frameworks (POFs) are among the most significant categories of reticular materials (Fig. 1).

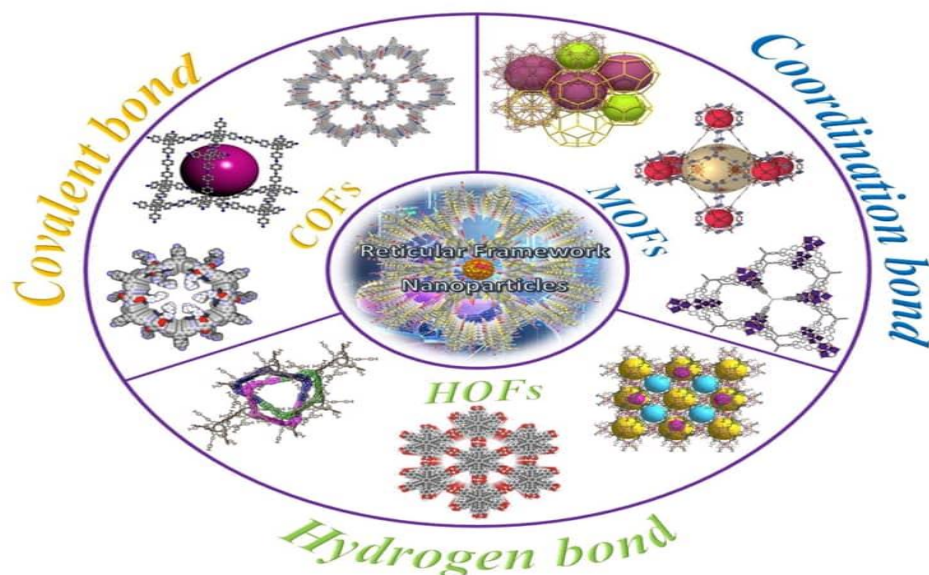


Fig. 1 Classification diagram of POF-derived nanomaterials

These structured materials are characterized by extended crystalline solids which are formed by linking secondary building units (SBUs) joining meta-containing sequences through powerful directional bonds[10-12]. The exceptional capacity of reticular chemistry to create bespoke materials based on POFs structure positions this area as a leading contender for addressing a wide range of issues linked to energy[13-16], separation [17,18] water capture [19,20] catalysis [21,22], gas storage[23,24], sensing[25,26], diagnosis [27,28], and therapy[29,30] (Fig. 2).

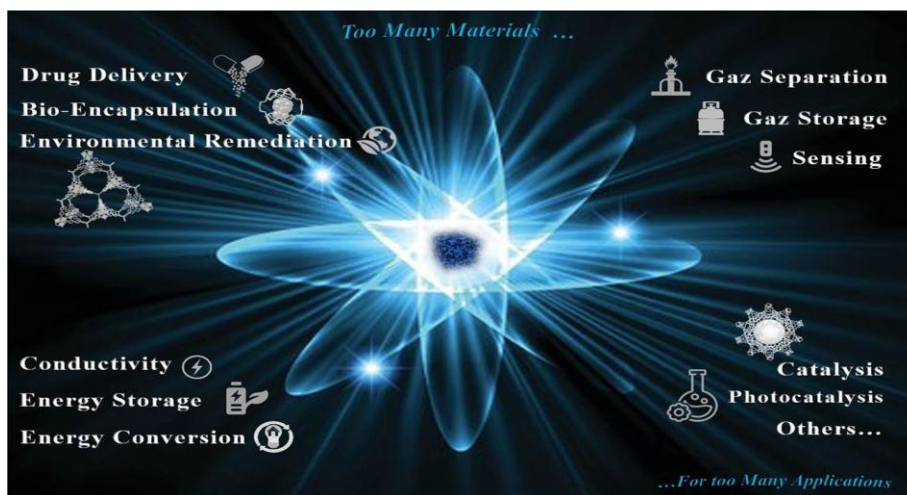


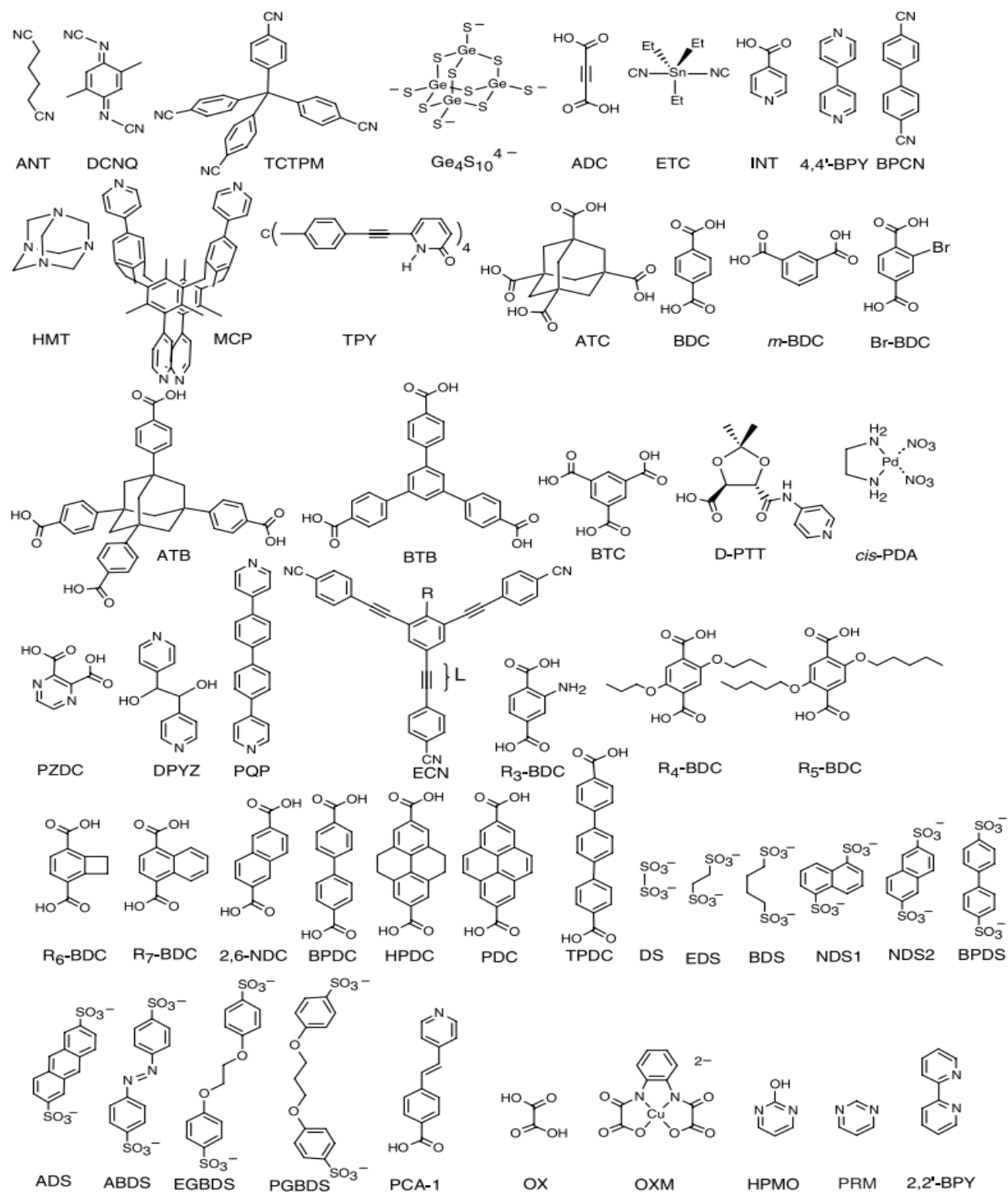
Fig. 2 Overview of the diverse applications of RF-NPs

This outstanding success makes the field a subject of extensive research and development ,with an abundance of scholarly articles dedicated to POFs synthesis, characterization, and prospective practical uses. In this context ,the scientific community is actively engaged in studying various aspects of POFs,leadig to a substantial and continually thriving literat09ure base on this topic.

Recent extensive research into the design and synthesis of metal-organic frameworks (MOFs) has led to numerous practical and conceptual development in that direction.[31-35].Specifically , the chemistry of MOFs has provided an extensive class of crystalline materials with high stability,tunable metrics,organic functionality, and porosity. Here we present some of the important developments that have shaped this rapidly growing field and propose a general conceptual framework, which serves as a useful tool in designing materials constructed from molecular building blocks.

❖ **Definitions and Structures :-**

- **Reticular** :-(adjective) having the form of a (usually periodic) net.
- **Isoreticular**: - Based on the same net (having the same topology).
- **MOF-n:-** Metal-organic framework(with n an integer assigned in roughly chronological order).
- **IRMOF-n:-** isoreticular MOF(with n an integer referring to a member of the series).
- **Interpenetration**: - A term used to describe the mutual intergrowth of two or more networks in a structure where the networks are physically but not chemically linked.
- **Expansion**: - Increasing the spacing between vertices in a network.
- **Decoration**: - Replacing a vertex in a net by a group of vertices.
- **SBU**: - The term 'secondary building unit' has been used for some time to describe conceptual fragments of zeolites; in the context of reticular chemistry it refers to the geometry of the units defined the points of extension (such as the carboxylate C atoms in most carboxylate MOFs).



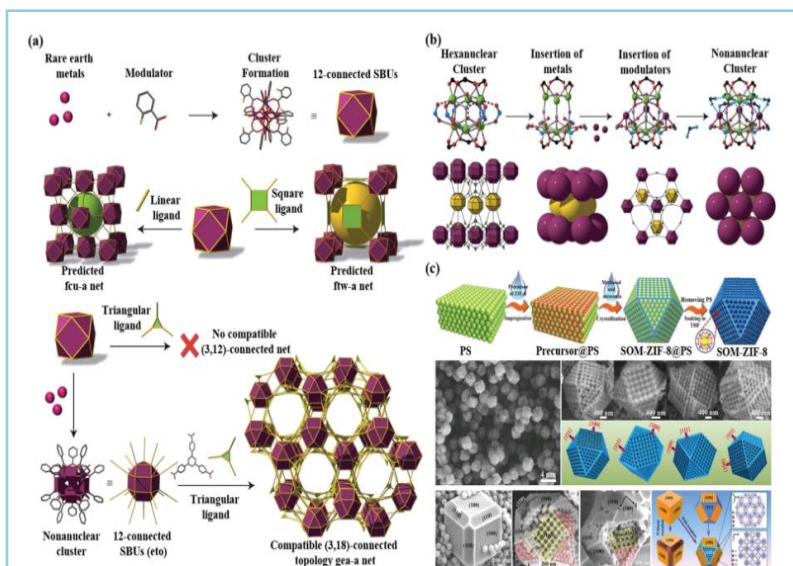


Fig. 9 The role of modulators as a crucial cornerstone in the synthesis of complex systems. **a** Illustrative presentation describes how the incorporation of RE metal ions in combination with Benzoic acid, 2-fluoro as a modulator has been found to promote the formation of a hexanuclear RE cluster. This synergistic combination acts as a facilitator, influencing the self-assembly of the metal ions and ligands into a specific hexanuclear structure. The RE metal ions, known for their unique electronic properties, interact with the fluorobenzoic acid modulator to orchestrate the precise arrangement and coordination of the metal atoms in the cluster. This cooperative effect enables the formation of a stable hexanuclear RE cluster with distinct chemical and structural properties, which holds great potential for various applications in fields such as catalysis, magnetism, and luminescence. **b** A proposed route outlining the development from the hexanuclear to the nonanuclear cluster with their illustrations (bottom) showing the hexagonal close packing of the MBBs in gea-MOF-1. The packing is represented by two layers which are respectively colored in purple and yellow. (reproduced with permission from Ref. [82]. Copyright 2014, Springer Nature). **c** Polystyrene templated technique to create ordered macro-microporous MOF single crystals, which includes the use of a modulator (Adapted with permission from Ref. [90]. Copyright 2018, American Association for the Advancement of Science)

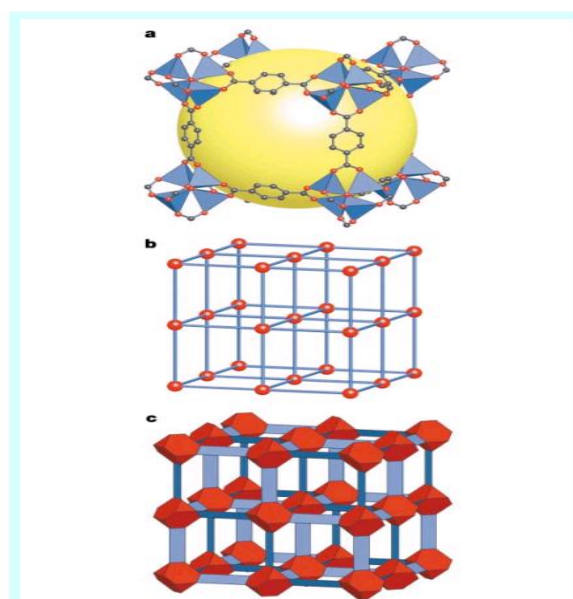
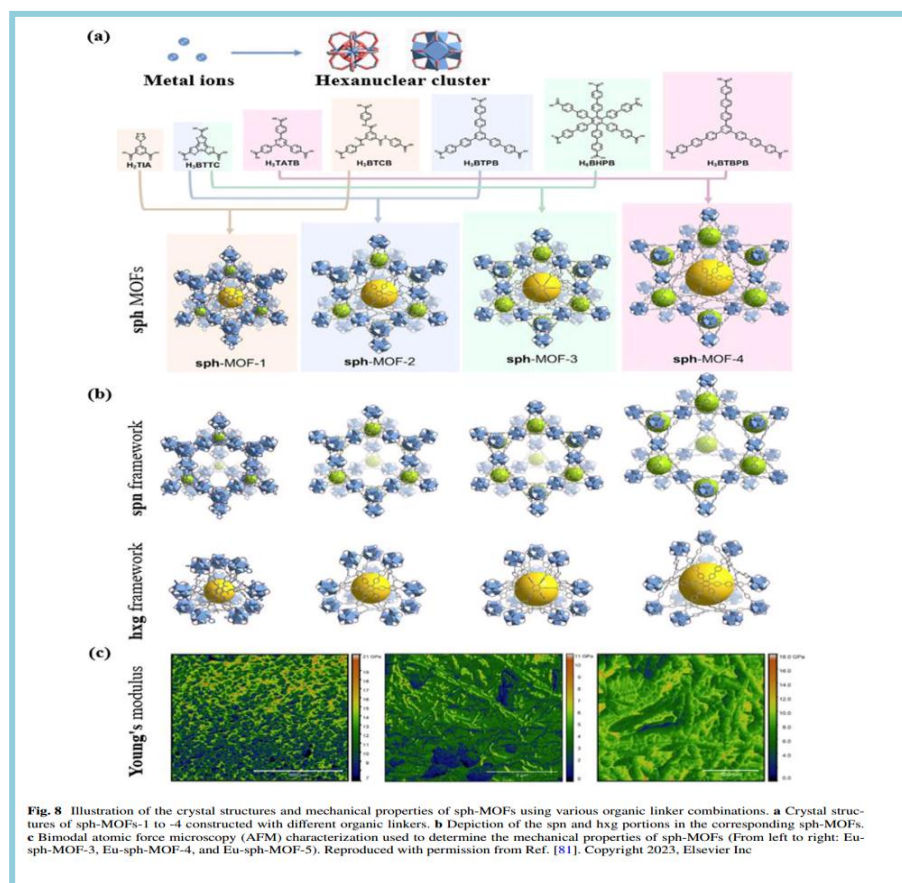


Figure 1 The MOF-5 structure and its topology. **a**, The MOF-5 structure shown as ZnO₄ tetrahedra (blue polyhedra) joined by benzene dicarboxylate linkers (O, red and C, black) to give an extended 3D cubic framework with interconnected pores of 8 Å aperture width and 12 Å pore (yellow sphere) diameter. (Yellow sphere represents the largest sphere that can occupy the pores without coming within the van der Waals size of the framework). **b**, The topology of the structure (primitive cubic net) shown as a ball-and-stick model. **c**, The structure shown as the envelopes of the (OZn₄)O₁₂ cluster (red truncated tetrahedron) and benzene dicarboxylate (BDC) ion (blue slat). Note that opposing slats are all at 90°.

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Reticular materials are crystalline, periodic networks assembled by strong bonds, which have been increasingly studied as a promising class of porous solids due to their high level of control tunability and outstanding performance in many applications pertaining to energy, environment, biomedicine, etc [36-38]. The high scope of their properties relies on a wide catalogue of readily available molecular building blocks (MBBs), either organic or inorganic, that can contribute to the framework's features [39,40]. The simplification of each MBB into their basic geometry, connectivity and directionality features has allowed the rational classification of metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) into underlying nets with various topologies, and probably more importantly, the prediction of their structural features, offering various opportunities for distinct programmed pores or channels. [41-44]

Metal-organic frameworks (MOFs) based on high-connected nets are generally very attractive due to their combined robustness and porosity. Here, we describe the synthesis of BCN-348, a new high-connected Zr-MOF built from an 8-connected (8-c) cubic Zr-oxocluster and an 8-c organic linker. BCN-348 contains a minimal edge-transitive 3,4,8-c eps net, and combines mesoporosity with thermal and hydrolytic stability. Encouraging results from preliminary studies on its use as a catalyst for hydrolysis of a nerve agent simulant suggest its potential as an agent for detoxification of chemical weapons and other pernicious compounds.

Reticular chemistry is widely used for the prediction and design of diverse types of periodic extended structures [45,46,47,48]. During the past two decades of exploration, edge-transitive nets, nets with one type of edge, were found to be ideal targets of simple structures in reticular chemistry [45,49,50]. Recently, we introduced a systematic design principle, named the merged-net strategy, targeting the design of more complex mixed-linker MOFs [51]. The merge of two edge-transitive nets, (3,6)-c spn net (transitivity {21}) and 6-c hxg net (transitivity {11}), will lead to a merged minimal edge-transitive net [49,52]. (3,6,12)-c sph net (transitivity {32}), with a relatively higher complexity (Figure S1). The merged sph net inherited the structural properties from both parent nets and encompassed the ability to be an ideal design target in reticular

chemistry. Based on the sph net, two frameworks can merge through shared inorganic molecular building blocks (MBBs), thus leading to the effective design of intricate mixed-linker MOFs. Practically, utilizing the merged-net approach, we synthesized a series of highly symmetric mixed-linker MOFs, named sph-MOF-1 to - 4, based on the 12-c hexanuclear rare earth (RE) clusters[51].

Access to metal-organic frameworks (MOFs) with enhanced mechanical stability is key to their successful deployment in practical applications. However, the high porosity of the material often affects mechanical stability. In this article, to achieve highly porous MOFs with enhanced mechanical stability, we explored the merged-net approach where two relatively fragile frameworks were merged into a robust MOF structure. We demonstrate the effectiveness of this approach by computationally evaluating mechanical properties of sph-MOFs with varying lengths of linkers. Prominently, we pinpoint the significance of triangular rigidity on the robustness of large-pore MOFs and, subsequently, designed and synthesized a rare earth (RE)-based RE-sph-MOF-5 by the reticulation of hexanuclear RE clusters, tritopic linkers, and unprecedentedly large planar hexatopic linkers containing 19 phenyl rings. The mechanical properties of sph-MOFs were characterized and quantified using amplitude-frequency modulation (AM-FM) bimodal atomic force microscopy (AFM) analyses. Markedly, the mesoporous RE-sph-MOF-5 expresses high mechanical stability despite its large mesoporous cavities. Mechanical stability plays a key role in the practical applications of metal-organic frameworks (MOFs). This study provides new insight into the design of high-mechanical-stability MOFs by merging two mechanically fragile frameworks into a more robust framework. A mesoporous MOF with high mechanical stability was synthesized by combining the topological merged-net approach and the introduction of triangular rigidity.

The enhancement of mechanical stability was studied by computational force field calculation and experimental AFM characterization. Reticular chemistry is the study of linking molecular building blocks by strong to make crystalline extended structures.

❖ MOF AND COF Structures :

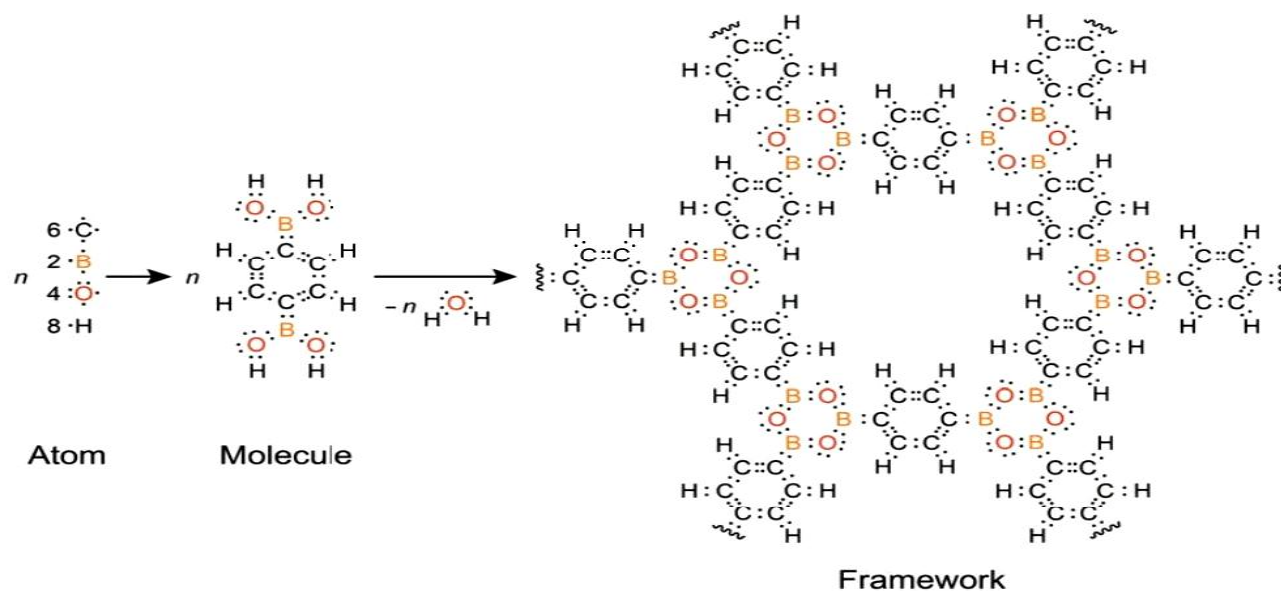
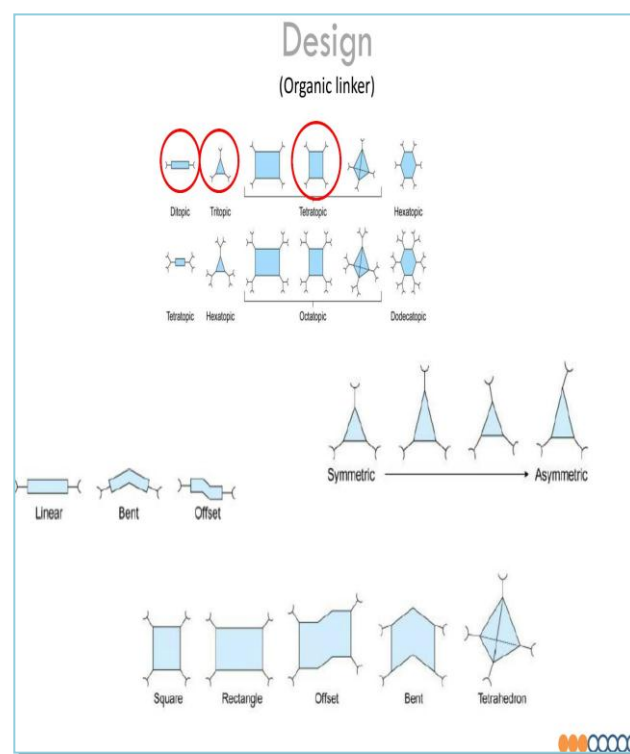
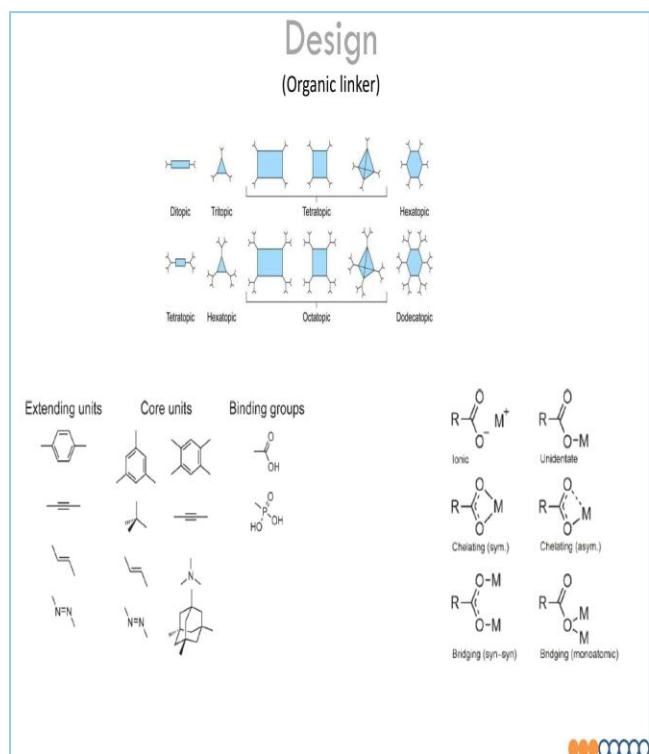
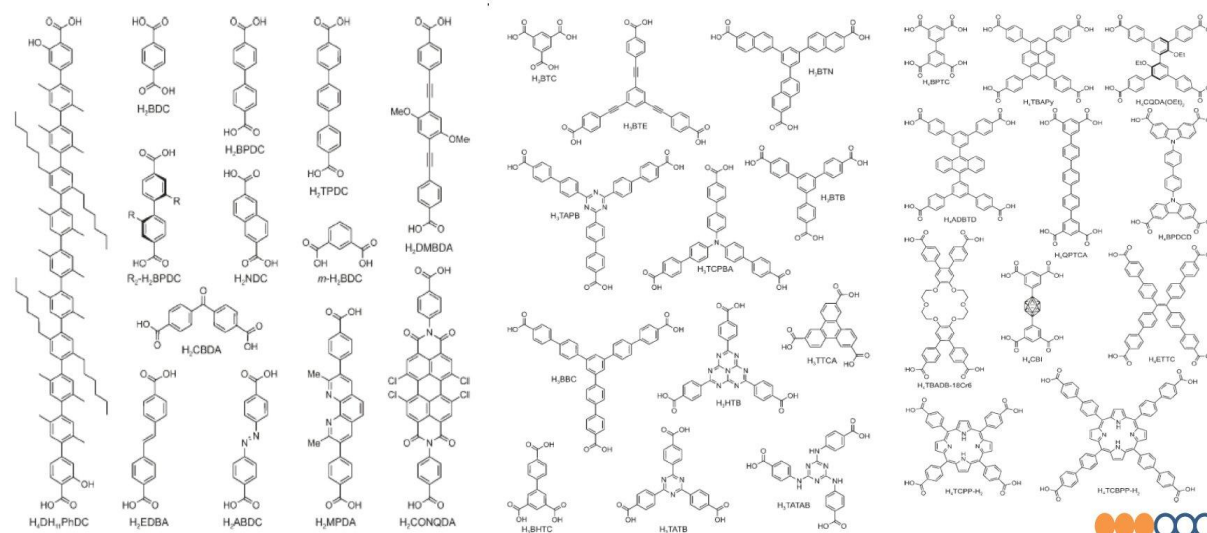
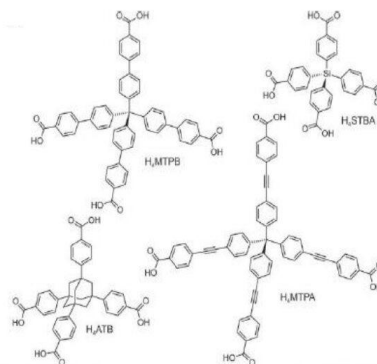
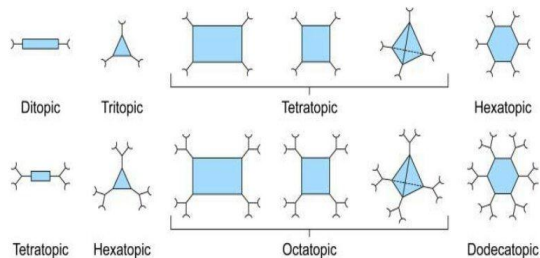


Fig. 12. The atom, the molecule, and the covalent organic framework. This progression indicates how the molecule fixes atoms in specific geometry, connectivity, and spatial arrangement, and with reticular chemistry, the framework fixes molecules in specific geometry, connectivity, spatial arrangement. However, unlike the molecule, the framework encompasses space into which matter can be further manipulated and controlled.

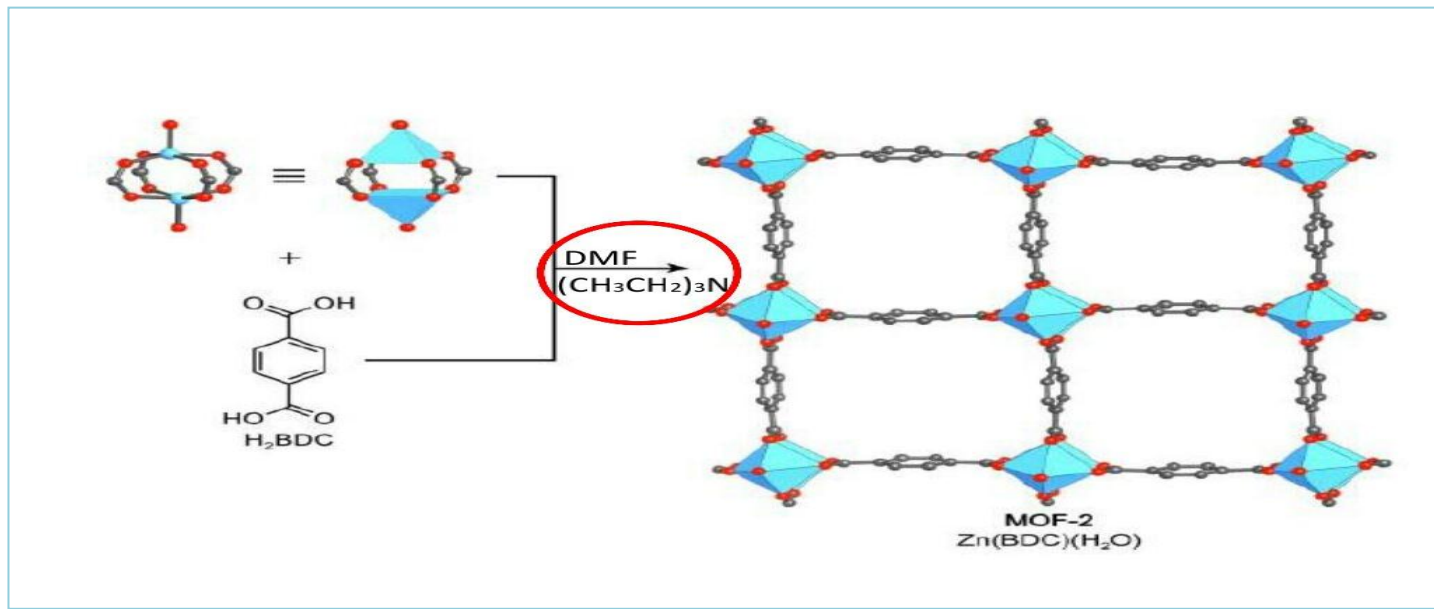




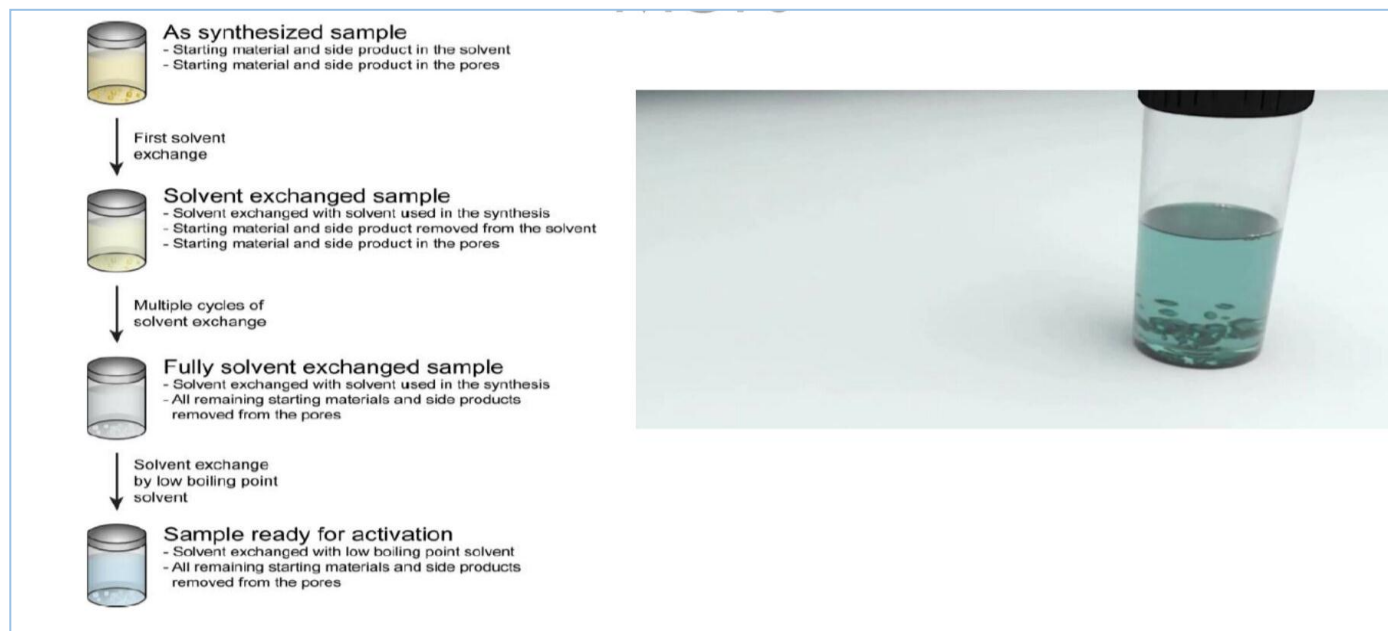
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2.MOF-2

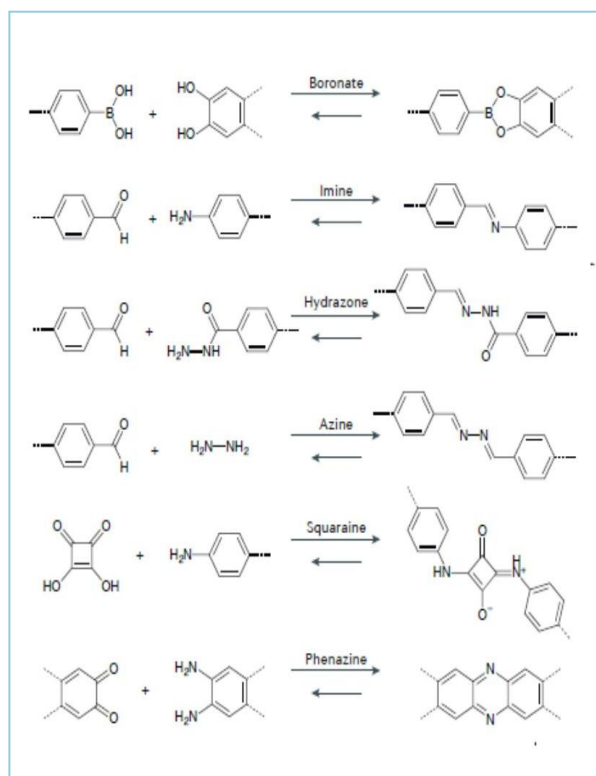
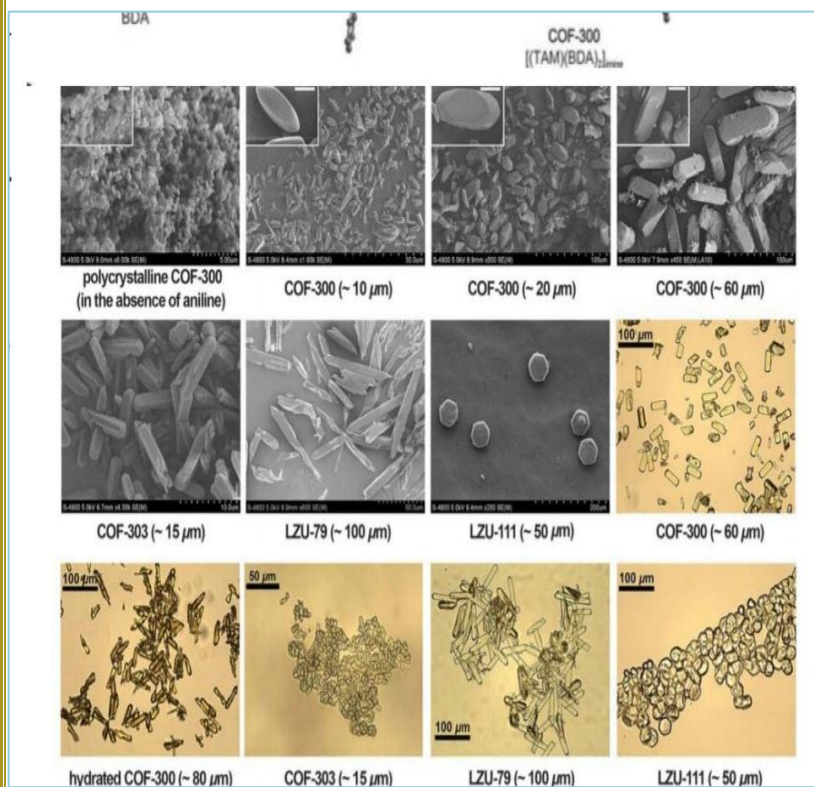
. (Introduction of SBUs and charged linkers) for the link of ions. [54]



Synthesis-Activation of MOFs. [55]



Covalent Organic Frameworks(COFs) (64)



Synthesis Strates:-

I. Covalent Molecular weaves:-

1) Metal complexes as crossing points.

The first molecular weave form by using metal complexes as templates for the formation of crossing points, was achieved by Yaghi and coworkers, in 2016. This molecular weave consists of two interlaced threads (Figure 2.1). To produce this molecular weave, bidentate phenanthroline equipped by two aldehyde moieties was used as ligand to complex with Cu(I) ion in a nearly tetrahedral geometry. [56-63]

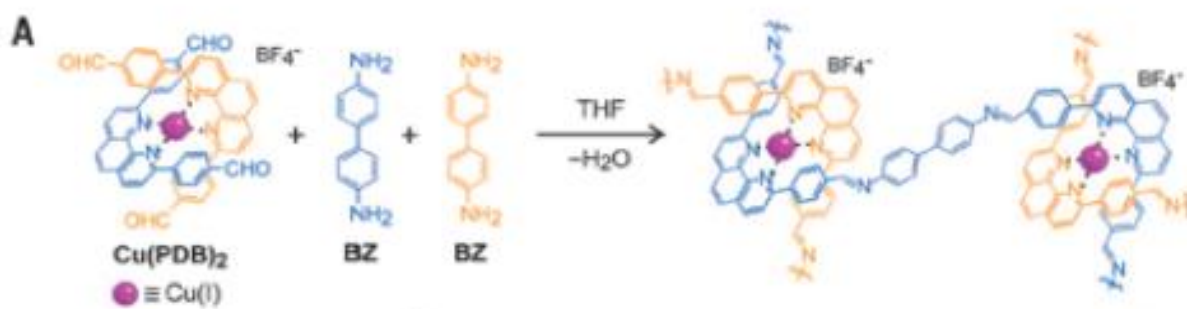
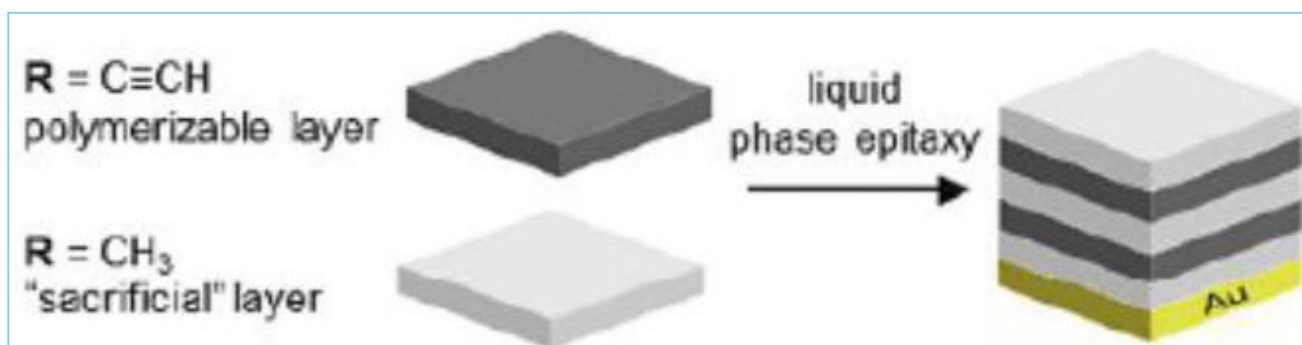


Figure 2.1: Molecular weave was constructed from organic threads using copper(I) as a template (A) to make an extended weaving structure.

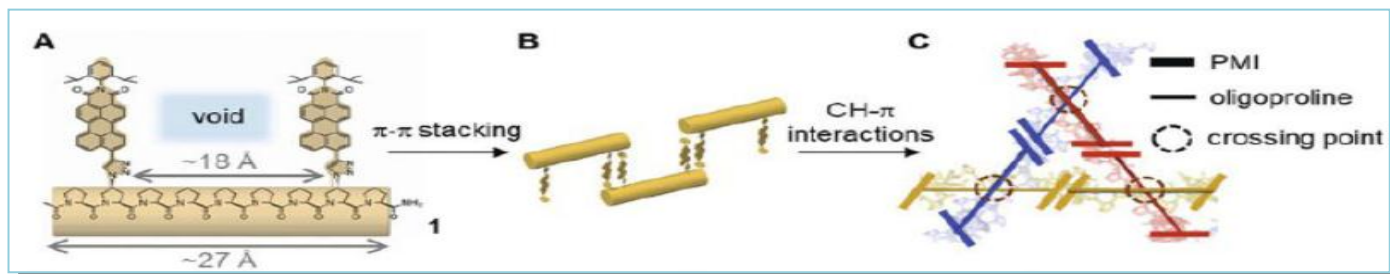
2) Layered Metal Organic Frameworks:-

The synthesis of quadritopic cross-shaped building blocks that equipped by carboxylic acid moieties at two opposite sites and at the other two sites alkyne moieties as reactive groups for Glaser coupling reactions, was used (Figure 2.4). Square planar complexes formed between the carboxylic groups of four building blocks and Cu(I) ions, which resulted in a regular grid-like 2D metal-organic framework (MOF) layer.[\[56-63\]](#)



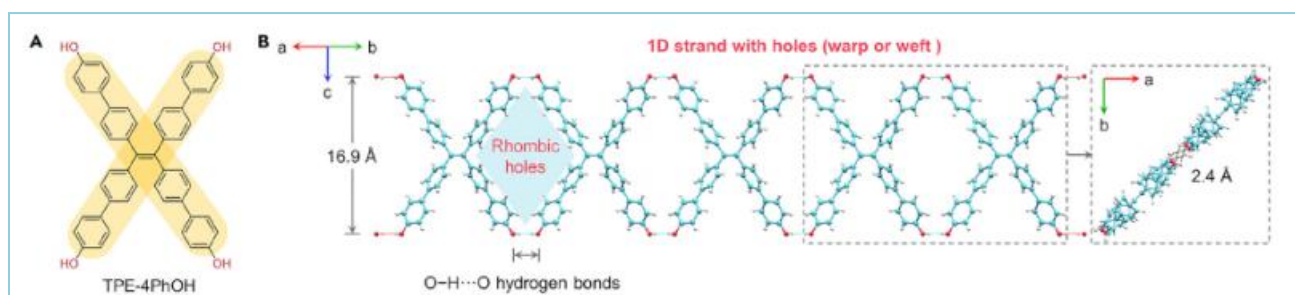
II . Non-Covalent Molecular

1) . π - π and CH- π Interactions: In this method, perylene monoimide (PMI) moieties were installed in the same direction via triazole linkages at the two penultimate positions of a rigidoligoproline.[56-63].



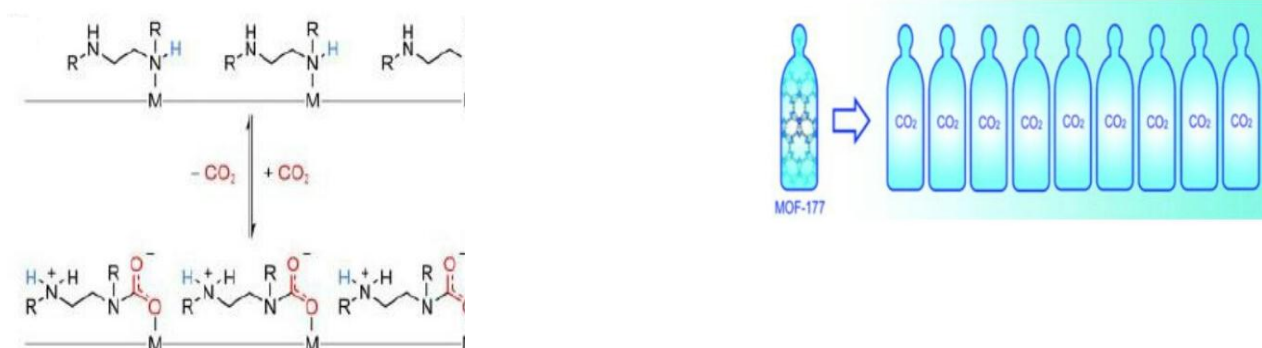
2) Hydrogen-Bonded Organic Frameworks:-

It is known that the hydrogen bonds are quite weaker than covalent bonds, but hydrogen bonds distinguished by their ability to produce bicentric linkages; a single proton can hydrogen-bond to multiple centers in some cases. Tetrasubstituted tetraphenylethene (TPE) derivative equipped by four phenyl-hydroxy (PhOH) groups was synthesized and used as a raw material for weaving structures.[56-63].

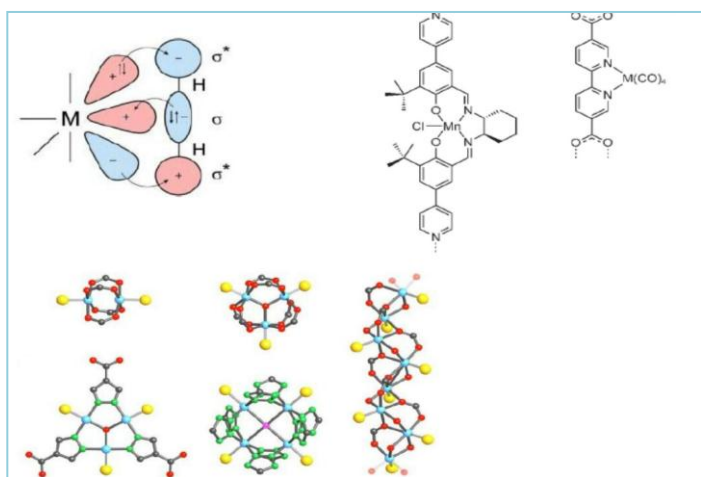


❖ Application of MOFs:

1. CO_2 capture/separation
 - Open metal sites
 - Amine groups [65]

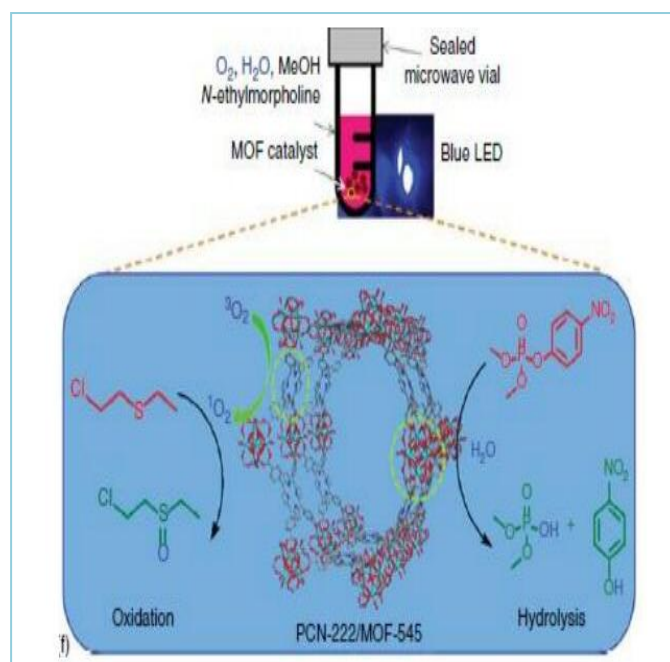
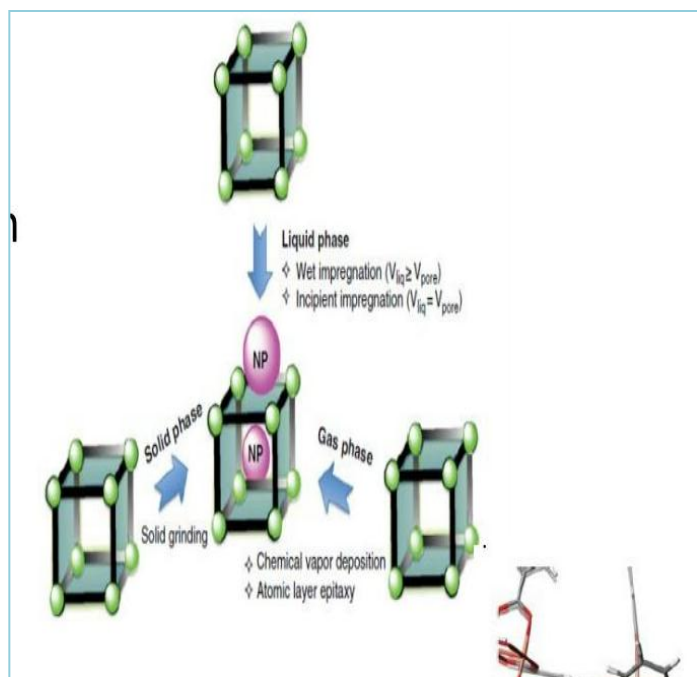


2. H_2 and CH_4 storage
 - Open metal sites
 - high surface areas



❖ -Other applications of MOFs

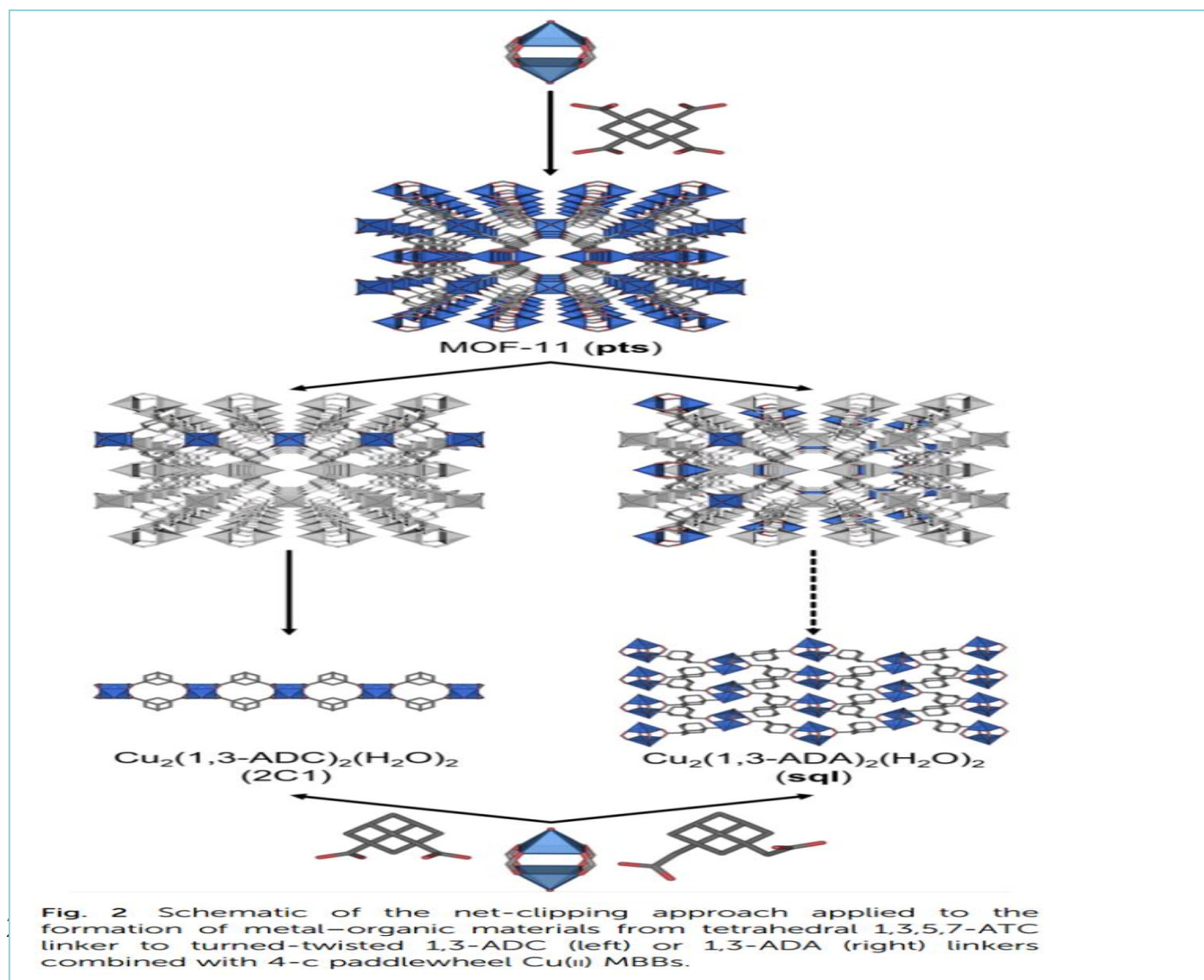
1. Liquid and Gas Phase separations.
2. Capture and Degradation of Chemical Warfare Agents.
3. Catalysis.
4. Drug Delivery.
5. Sensing.
6. Air purification.



❖ Applications of reticular chemistry :-

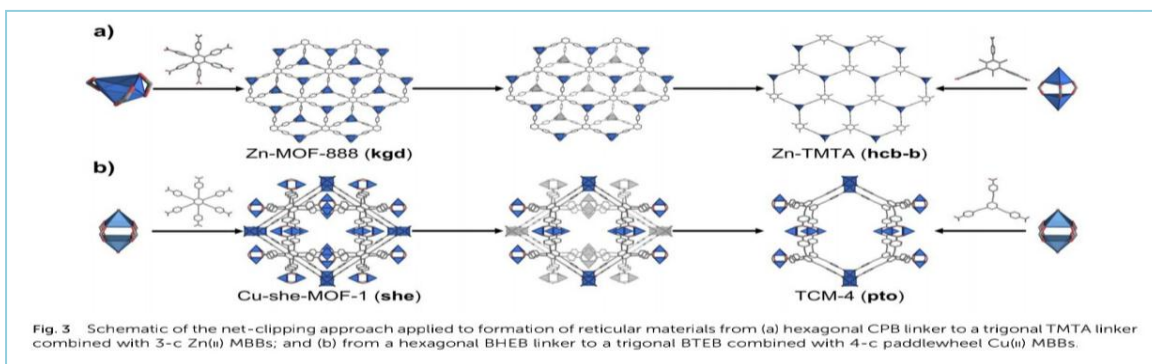
1. Net-clipping of 4-c tetrahedra :-

We began by selecting the 17 edge-transitive nets assembled by the combination of 4-c tetrahedral MBBs with other polygonal and polyhedral MBBs. Among the six uninodal nets, five (dia, sod, lcs, qtz, ana) were considered to be in their binary form (net-b), to allow for selective splitting.



2- Net- Clipping of 6-c hexagons:

There are five edge-transitive nets constructed with hexagons: the 2D kgd and hxl topologies; and the 3D she, hxg-b and mgc nets. Among these, we excluded the hxl topology, due to the unfeasibility to generate a binodal net due to the presence of odd cycles, as for the aforementioned tetrahedral lcs net (Fig. S4). In the remaining four nets (kgd, she, hxg-b, and mgc).



3- Reticular chemistry and harvesting water from desert air: -[66]

All the advantages imparted by the use of clusters as building units did not at this point include the ability to functionalize what eventually would be open pores in such frameworks. Accordingly, attention was focused on the incorporation of organic molecules as building units and these would preferably be charged in order to enhance the bonding strength with metal ions. However, first it was useful to demonstrate that crystalline materials can be made by combining transition metal ions with charged organic linkers. Indeed, in a 1995 report, [67] carboxylate organic molecules (1,3,5-benzenetricarboxylate). An important illustration of the SBU approach came in 1998 when 1,4-benzenedicarboxylate was linked by zinc ions to make what is known as MOF-2 (Figure 3) whose structure is composed of di-nuclear metal nodes linked into a layered structure with pores filled with N,N-dimethylformamide molecules [68].

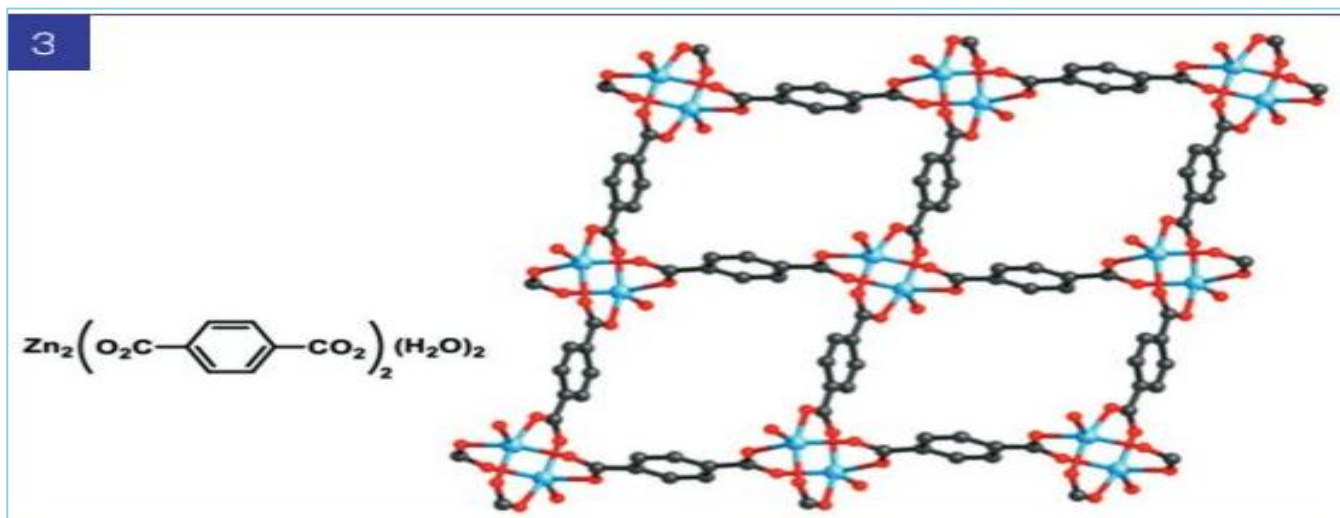


Figure 3: The carboxylate linkers form di-metallic units (secondary building units, SBUs), to make architecturally robust, porous MOFs.

At this juncture, it is useful to mention that the SBU approach, the strong metal ion charged linker bonds, the gas adsorption measurements to prove permanent porosity, and the ultrahigh porosity of these early MOFs became the preferred methods and strategies for the further development of MOF chemistry. Today, nearly all MOFs reported use (a) the same or similar synthesis and crystallization conditions to those used for these early MOFs, (b) the SBU approach outlined above, and (c) the same gas adsorption measurements to evaluate and study their porosity. On a foundational level, the success of the building block approach was extended from the very early examples of all inorganic metal-sulfide frameworks to metal-organic frameworks where the latter combined two fields of chemistry inorganic and organic into one, and extended molecular metal-organic chemistry into infinite 2D and 3D structures.[\[69\]](#)

❖ potential Applications :-

Adaptive Guest Inclusion:

The introducing of motions into solids has become possible by using flexible building blocks and dangling switchable or mechanically interlocked units into the pores, After the discovery of reticular chemistry. There are four modes of dynamics in Solids (Figure 3.1):-

- a) flexible constituents yield frameworks that distort in response to external stimuli.
- b) mechanically Interlocked molecules appended onto the struts move within the constraints imposed by their interlocking.
- c) switchable units dangling in the pores respond to external stimuli by conformational changes.
- d) woven frameworks where large degrees of freedom of the threads allow for adaptive inclusion of guests[56-63].

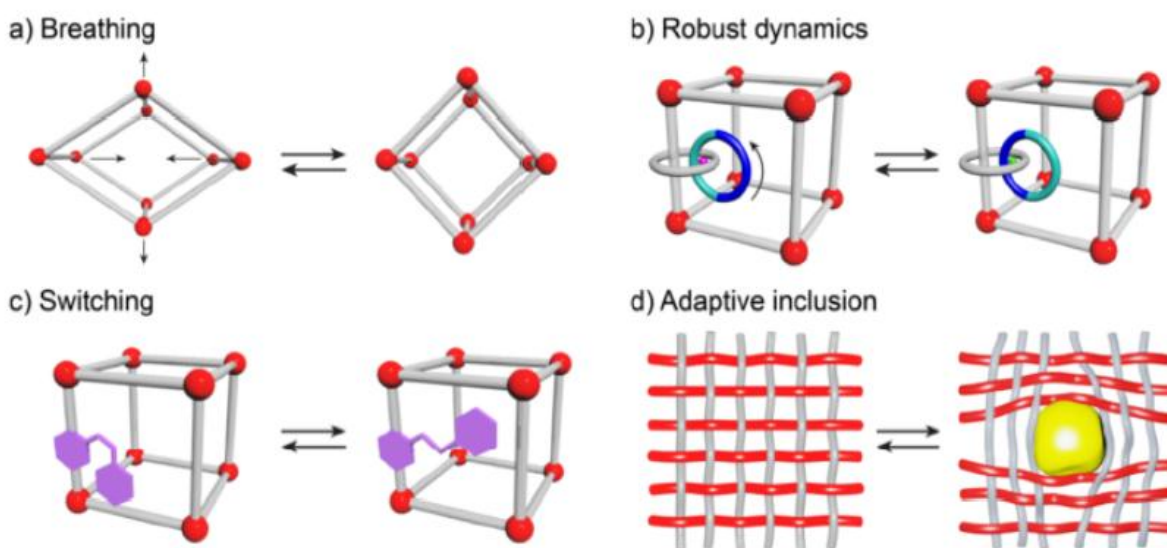


Figure 3.1: Modes of dynamics in solids.

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