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# Interpenetration in coordination polymers: structural diversities toward porous functional materials

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**Interpenetration is a natural phenomenon frequently encountered in porous coordination polymers (PCPs) or metal-organic frameworks (MOFs). Traditionally interpenetration has been considered as a threat to permanent porosity and several strategies have been adopted to control the framework interpenetration. Recent literature reports have unveiled that interpenetration has paramount importance in several material properties particularly in storage and separation of small gas molecules. Such frameworks also show interesting structural flexibility based on shearing or movement of the nets and also reveals guest induced dynamic structural transformation for modulated specific functions. In this review, we will emphasize several interpenetration phenomena observed in coordination polymers, their intriguing structural aspects and fascinating material properties.**

## Introduction

Porous materials are attractive because of their capability to encapsulate various guests (in gas or liquid phase) in high concentrations and homogeneously. The confinement effect in such materials leads to exotic properties such as high gas storage and separation, catalysis, controlled release or delivery of drug molecules etc. [1–5]. The earliest known porous materials are inorganic zeolites, porous carbon and silica. Zeolites are widely used materials in industry for catalysis and water purification while porous carbon and silica materials are also promising for high capacity gas storage and other related properties [6–8]. All these materials do contain enough void space but lack modifiable pore surface and tunable surface area. In this respect, metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are more potent and display outstanding gas adsorption, separation, catalysis and stimuli responsive properties [9–13].

Kitagawa *et al.* first reported gas ($CH_4$, $N_2$ and $O_2$) storage properties in porous coordination polymers $\{[M_2(bpy)_3(NO_3)_4]\cdot xH_2O\}_n$ [M(II) = Zn(II), Co(II) and Ni(II); bpy = 4,4′-bipyridyl] [14]. Followed by this work at late 90s MOF-5 and HKUST-1 have been synthesized having high surface area with different net topology and pore environment [15,16]. Such achievements encouraged researchers to further tune the design strategies and hence achieve an astonishing surface area of ~7140 $m^2/g$ for a PCP NU-110 [17]. The simple ''node-and-linker'' principle originated many isoreticular MOFs (IRMOFs) and further meticulous design of organic linkers lead to mesoporous PCPs with cage like structures [18–20]. In particular, the MIL (Materials of Institut Lavoisier) [21], CID (Coordination polymer interdigitated) [22], CPL (Coordination polymer pillared layer) [23] and ZIF (Zeolitic imidazolate framework) [24] series of frameworks added a different flavor in PCP research due to the structural versatility, tunability, stability and ease of designing highly porous structures. However, the increment in void spaces or surface area through designing long organic linkers has been threatened by the framework interpenetration. Traditionally this phenomenon has been considered as an adverse side of PCP structures and several methodologies have been investigated to avoid interpenetration. But it was also understood that interpenetration is apposite for applications such as separation and storage of different small molecules [25,26]. Though it does reduce the available void space it can create confined narrow pores/channels which permit the trapping of guest molecules in the strong electrostatic potential well. Hence, interpenetration can be vital for PCP design and imperative for specific applications. So far control of interpenetration is one of the research attentions (topics) in PCP chemistry. A literature

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survey would reveal many articles related to ‘‘control over interpenetration’’ which essentially reveals strategies to reduce interpenetration but comparatively fewer reports detail the advantages of interpenetrated frameworks [27–29]. In this review, we will emphasize the interpenetration as an imperious structural feature of PCPs and its outcome in terms of porosity and novel functionality in the frameworks.

It is worth mentioning that apart from simple interpenetration, which is usually observed in PCPs, much more complicated molecular entanglement phenomena have been reported in recent years such as (poly)catenanes, (poly)rotaxanes, polyknotting, polythreading, molecular braids, etc. [30–32]. But the number of such structures is very limited and the properties are yet to be properly explored; hence these are not included in our discussion. We will focus our discussion on the interpenetration in coordination polymer materials of different dimensionalities. To understand the interpenetration phenomenon we will describe several types of interpenetration followed by the classifications of interpenetrated PCPs based on flexibility and rigidity. Concomitantly we will discuss the implications of interpenetration in gas storage and separation, molecular recognition, magnetic and optical properties.

## Definition of interpenetration

Catenation, interlocking, interweaving and entanglement/interpenetration are well-studied phenomena in biology and chemistry. Particularly in biology, examples of interlocked or entangled systems are many; for example the entangled strand in the DNA double helix. Rotaxanes are a slightly different class of entangled structure where disentanglement can be achieved only by breaking the bonds or connections, unlike DNA where such bond breaking is not mandatory [33]. Regardless of the type of entanglement, these are structurally fascinating and can give rise to exotic properties.

It is quite important to understand the reason or origin of such complex characteristics of polymeric nets before we move onto a much more rigorous discussion of the structures. To be precise, interpenetration is a natural phenomenon to reduce the void space, as nature always prefers high entropy, in other words a dense system. In most cases, void space of PCP is occupied by the additional template molecules such as solvent, cation or anion. But in some cases to fill the large void, secondary net(s) growth seems to be essential and thus interpenetration occurs. Two polymeric nets that are not tethered or connected by any covalent interaction but cannot be separated without breaking any bond;

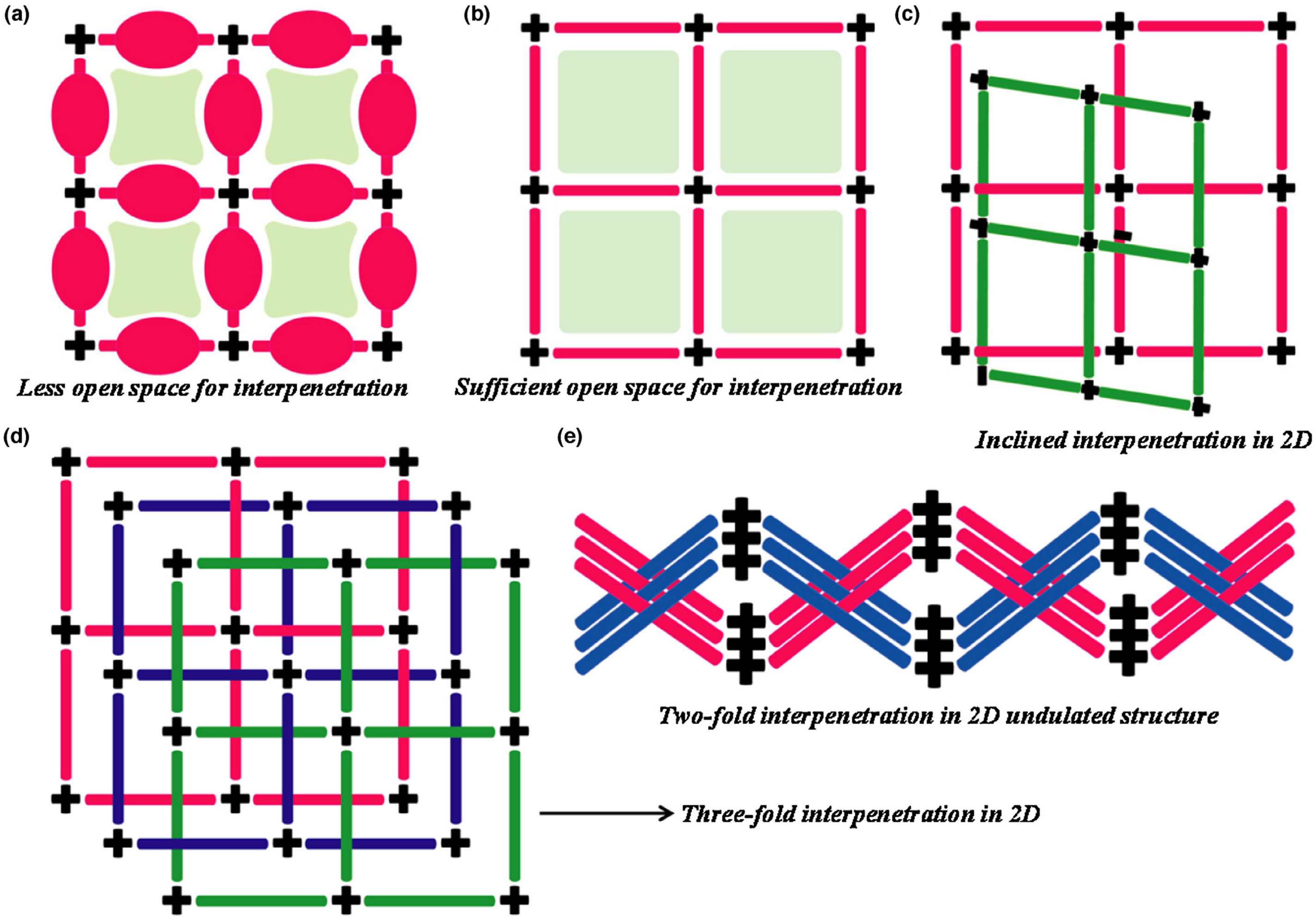

**FIGURE 1**

Representation of 2D nets with varying different void spaces that direct the interpenetration phenomenon: (a) 2D network with no interpenetration, (b) A 2D network with sufficient two dimensional open space, (c, d, e) Different types of interpenetration in 2D networks.