



## Review

# Potential of metal–organic frameworks for adsorptive separation of industrially and environmentally relevant liquid mixtures

Soumya Mukherjee<sup>a,1</sup>, Aamod V. Desai<sup>a,1</sup>, Sujit K. Ghosh<sup>a,b,\*</sup><sup>a</sup> Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha Road, Pashan, Pune 411008, India<sup>b</sup> Centre for Energy Science, IISER Pune, Pune 411008, India

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## ABSTRACT

Metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are defined as crystalline, open, coordination network architectures with potential voids. They have drawn momentous attention across several crossroads of material chemistry since their discovery, owing to an exciting plethora of application-oriented footprints left by this class of supramolecular network solids. The unmatched aspect of tunable coordination nanospace arising from the countless choice of pre-functionalized organic struts pertaining to varying lengths alongside multivariate coordination geometries/oxidation states of the metal nodes, bestows a distinct chemical tailorability facet to this class of porous materials. Amidst the two-decade long attention dedicated to the adsorption–governed purification of gases, the MOF literature has substantially expanded its horizon into the manifestation of industrially relevant liquid mixtures' adsorptive separation–driven purification. Such chemical separation phenomena categorically encompasses high importance to the manufacturing and processing industry sectors, apart from the fundamental scientific pursuit of discovering novel physicochemical principles. Aimed at the energy-economic preparation of pure industrial feedstocks and their consequent usage as end products, structure–property correlations pursued in the alleys of coordination chemistry has led to major advancements in a number of critical separation frontiers, inclusive of biofuels (alcohol/water), diverse hydrocarbon mixtures, and chiral species. This comprehensive review summarizes the topical developments accrued in the field of MOF based liquid mixtures' adsorptive separation phenomena, structure–selectivity relationships as well as the associated plausible mechanisms substantiating such behavior.

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**Abbreviations:** MOF, metal–organic framework; PCP, porous coordination polymer; PSA, pressure swing adsorption; TSA, temperature swing adsorption; VSA, vacuum swing adsorption; EPA, United States Environmental Protection Agency; EEA, European Environment Agency; SMB, simulated moving bed; Q<sub>st</sub>, isosteric heat of adsorption; MFOF, metal–fluoride–organic framework; MBB, molecular building block; CP, coordination polymer; CB, carbon black; UMC, unsaturated metal center; HUM, hybrid ultramicroporous material; IAST, ideal adsorbed solution theory; S<sub>ads</sub>, selectivity of adsorption/adsorption selectivity; CID, coordination polymer with interdigitated structure; Hip, isophthalic acid; bpy, 4,4'-bipyridine; pcu, primitive cubic; GC, gas chromatography; dabco, 1,4-diazabicyclo[2,2,2]octane; bdp, 1,4-benzenedipyrzolate; Bz, benzene; Cy, cyclohexane; TI, toluene; BTEX, mixtures of benzene, toluene, ethyl benzene and xylene isomers.; nC<sub>6</sub> or n-Hex, n-hexane; FAU, Faujasite; BTC, 1,3,5-benzenetricarboxylate or trimesate; BPz, 3,3',5,5'-tetramethyl-4,4'-bipyrazole; % RH, relative humidity; m, min; HK, Horvath Kawazoe; BTB, 1,3,5-benzenetrisbenzate; ZIFs, zeolitic imidazolate frameworks; BET, Brunauer–Emmett–Teller; QCM, quartz crystal microbalance; Im, imidazole.

\* Corresponding author at: Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha Road, Pashan, Pune 411008, India.

E-mail address: [sghosh@iiserpune.ac.in](mailto:sghosh@iiserpune.ac.in) (S.K. Ghosh).<sup>1</sup> These authors have contributed equally.

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## 1. Introduction

Adsorption represents a rapidly advancing area of separation technologies impacting pharmaceuticals and large-scale production of fine chemicals in the petrochemical industry, promising enough to revolutionize the massive energy footprint associated with. The global market for sorbents (2013–2019) forecasts the market to reach \$11.1 billion by 2019 [1]. An entire miscellany of micro/nanoporous traditional adsorbent materials, viz., zeolites [2,3], aluminophosphates [4,5], carbon molecular sieves [6,7], polymeric or inorganic resins [8–10], and hybrid porous composites [11–13], have already been intensively studied targeted at accomplishing industrially/environmentally critical adsorptive separations. Majority of these physisorbents exhibit reasonably high porosity in addition to different chemical activities, which are necessary for promoting favourable sorbent-sorbate interactions for a range of adsorbates [26–28]. MOFs score over other porous materials such as activated carbons (ACs) or zeolites as they possess wide range of window openings/pore cavities alongside various functionalities, which enable them to include several compounds in their cavities [14]. Most well-studied sorbents, especially the industrially used zeolites and resins typically act as chemisorbing beds, where the key functional groups are either physically or chemically anchored to the sorbent surface. The energy penalty associated with regeneration of such chemisorbent porous polymer network beds is often very high, since elevated temperatures (>100 °C) under reduced pressures are generally required for serving regeneration purpose [15]. With hindsight, in spite of the hydrocarbon species' lower heats of adsorption ( $Q_{st}$ ) encountered for MOF physisorbents when compared to the aforementioned chemisorbent materials, exploiting the former class prevails as a better proposition because of the energy economy factor linked with recyclability, but has so far been impeded by the lack of suitable MOF physisorbents showing inertness to humidity and competing gases/vapors [16]. Needless to reiterate that to manifest the pressing separation demands of today's and rapidly growing industrial manufacturing sectors, superior custom-designed MOF adsorbents are one of the most sought-after and state-of-the-art materials [17].

MOFs, or porous coordination polymers (PCPs) have leaped as one of the most exciting classes of functional materials with enormous promise, owing to their multifarious applications in the realms of gas storage [18–24], separation [25–31], catalysis [32–35], drug delivery [36–39], proton exchange membrane fuel cells [40–43], sensing [44–46], ion-exchange [47–49], water purification [50–53], and photonics [44,54–56]. Albeit the commencement of exploration as early as the 1990s [57–62], research on MOFs in context of their aforementioned application frontiers continues to attract great attention, because of their unique blend of modular nature, chemical tailorability, and permanent porosity. This has led to the recent IUPAC recommendation on nomenclature, which classifies MOFs as coordination polymers (or alterna-

tively coordination networks) bearing open framework architectures with potential voids [63,64]. Judicious selection of molecular building blocks (MBBs) following deft crystal engineering principles can expedite the rational maneuvering of the concerned pore size and pore chemistry attributes in MOFs [65,66], unlike zeolites, aluminophosphates, carbon black, molecular sieves, polymeric or inorganic resins, and hybrid porous composites. In fact, this observed amenability toward crystal engineering principles pursued in the quest of targeted applications further amplifies because of the sheer diversity of miscellaneous combinations presented by a plethora of available organic and inorganic linkers and/or nodes [67].

The synthetically manipulated coordination nanospaces for such varyingly functionalized MOFs have inimitable characteristics: regular nanosized porous channels in void-containing framework structures inclusive of excellent long-range order and rigidity/flexibility of the channels. Additionally, MOFs offer the benefit of synthesizing soft porous solids, which mimic enzymatic behavior without compromising their inherent features [68]. Above all, an appropriately designed pore surface, when amalgamated with these aforesaid attributes can infuse unprecedented porous functionalities, keeping a steady vigil on the targeted separation deliverable in hand. Owing to a facile access to tailor the properties of MOFs via pre- or post-synthetic modifications, the appendage of the desired interacting sites is feasible [69]. Adopting diverse pore surface functionalization rationales bring about a conglomeration of important advantages to this class of coordination framework materials: (a) crystallinity stemming from inherent long-range order; (b) high surface area and large pore size; (c) systematically tunable pores; (d) porous channel surface, replete with multiple functional sites; (e) guest-responsive behavior [70,71]. Typically, modification of the pore surfaces is achieved by pre-synthetic design, post-synthesis reaction or inclusion of secondary functional sites [72]. In addition to these general characteristics, miscellaneous chemical groups/functionalities can be tactfully grafted onto the pore surface of MOFs, by the aid of crystal engineering knowhow: either at the pre-synthesis stage by making correct choices of metal/linker combinations, or via astute adherence to suitable post-synthesis strategies [73]. A number of systematic design principles are often pursued to attain benchmark CO<sub>2</sub> capture (trace and/or bulk) and sequestration deliverables, such as, amine grafting, harnessing coordinatively unsaturated metal centers (UMCs), along with fine-tuning the pore metrics and environments in the heteroatomic hybrid ultramicroporous materials (HUMs) [17,74]. Analogous target-specific rationales hitherto pursued for the separation of industrially important liquid mixtures need to be streamlined in an way to disseminate the key crystal engineering and/or material design factors to be coherently assimilated hereafter (Scheme 1).

Although the design strategies for any MOF primarily relate to the application of interest, some of the associated crucial aspects which pertain to evaluation of these materials include stability

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