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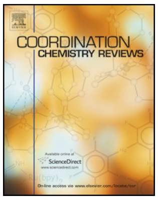

Review

Ionic metal-organic frameworks (iMOFs): Design principles and applications

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Abbreviations: MOF, metal-organic framework; PCP, porous coordination polymer; CP, coordination polymer; 3D, 3 dimensional; DMF, dimethylformamide; DEF, diethylformamide; BDC, benzene-1,4-dicarboxylic acid; BTC, 1,3,5-benzenetricarboxylate; DMA, dimethyl ammonium system; SBU, secondary building unit; ZMOF, zeolite-like metal-organic frameworks; BPTC, biphenyltetracarboxylic acid; TMA, tetramethylammonium cation; TEA, tetraethylammonium cation; TBA, tetrabutylammonium cation; TCPT, 2,4,6-tris-(4-carboxyphenoxy)-1,3,5 triazine; Q_{st}, isosteric heat of adsorption; CCS, carbon capture and sequestration; H_2ppz^{2+}, piperazinium cation; DMNB, 2,3-dimethyl-2,3-dinitrobutane; Bpp, 1,3-bis(4-pyridyl)propane; Btapa, 1,3,5-benzene tricarboxylic acid tris[N-(4-pyridyl)amide]; EDTPN, ethylenediaminetetrapropionitrile; Mtpm, mtpm=tetrakis(m-pyridyloxy methylene)methane; tatrz, 1-(9-(1H-1,2,4-triazol-1-yl)anthracen-10-yl)-1H-1,2,4-triazole; dpzm, di-2-pyrazinylmethane; bpe, 1,2-bis(4-pyridyl)ethane; bipy, 4-4′-bipyridine; POM, polyoxometalates; RH, relative humidity; DFT, density functional theory; RTMPyP, 5,10,15,20-tetrakis(1-methyl-4 pyridinio)porphyrin; COD, 1,5-cyclooctadiene; Bpy, 4-4′-bipyridine; Dppe, 1,2-bis(diphenylphosphino)ethane; NLO, non-linear optics; SHG, second harmonic generation; DPASM, 4-(4-(diphenylamino)styryl)-1-methylpyridinium; DPASB, 1-butyl-4-(4-(diphenylamino)styryl)pyridinium; DPASN, 4-(4-(diphenylamino)styryl)-1-nonylpyridinium; DPASD, 4-(4-(diphenylamino)styryl)-1-dodecylpyridinium; PBS, phosphate-buffered saline; TNP, 2,4,6-trinitrophenol; TNT, 2,4,6-trinitrotoluene; DMNB, 2,3-dimethyl-2,3-dinitrobutane; 2,6-DNT, 2,4-dinitrotoluene; 2,4-DNT, 2,4-dinitrotoluene; NM, nitromethane; p-XBP4, N,N′-p-phenylenedimethylenebis(pyridin-4-one); LDH, layered double hydroxides; EDS, 1,2-ethanedisulfonate; Btr, 4,4′-bis(1,2,4-triazole); CD, cicular dichroism; MTT, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide; Imid, 3-bis(4-carboxy-2,6-dimethylphenyl)-1*H*-imidazolium; NHC, N-heterocycliccarbenes; NOTT, University of Nottingham; PC, proton conduction; OG, orange gelb.

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A B S T R A C T

Metal-organic frameworks (MOFs) have commanded significant attention in recent years on account of the applicability of these materials across several disciplines in material chemistry. The liberty of tuning the coordination nanospaces owing to the infinite choice of organic linkers and multivariate oxidation states of the metal nodes bestows a distinguished advantage of designable architectures to this class of materials. Majority of the reported MOFs comprise of neutral frameworks as the net positive charge on the metal ions is satisfied by the negative charge of anionic ligands or the coordinated anions of the metal salt used in synthesis. Although being non-trivial, the synthesis of ionic MOFs (iMOFs) affords several distinct advantages over the routine neutral frameworks by virtue of the isolated charged species in confined nanospaces. The development and potential applications of such cationic or anionic frameworks has been discussed thoroughly in this review. The design principles governing the formation of such charge-polarized MOFs have been outlined through representative examples. The state-of-the-art ion exchange performances of competing materials have been compared and a future perspective of such ionic-MOFs is proposed.

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1. Introduction

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) have emerged as one of the most important class of materials simply because of their plethoric applications in the fields of gas storage [1–4], separation [5–8], catalysis [9–11], drug delivery [12–14], sensing [15–19], conduction [20,21], ion-exchange [22–26] and photonics [27,28]. Build from an organic linker and metal node or clusters, MOFs give rise to a wide variety of architectures which range from one-dimensional coordination polymers (CPs) to three dimensional (3D) PCPs [29]. The large repertoire of organic struts available in nature allows for tailor-made syntheses of MOFs which could be used for targeted applications making them one of the most sought materials for chemists and material chemists. The pore structure and shape can be tuned in view of a specific property allowing fabrication of rationally designed MOFs [30,31] and thus making these materials as an exclusive class of materials which has opened a new domain in the field of research since its discovery in the late 90s [32].

Most of the MOFs reported till date are electrically neutral because the positive charge of the metal ion are satisfied by the negatively charged organic ligands mostly carboxylate based linkers [33,34]. However in some cases MOFs contain some residual charge as non-framework ions either positive or negative making them ionic [35,36]. Such ionic MOFs (iMOFs), are attracting significant attention because the ions inside the channels of the frameworks can be utilized for specific interactions with various incoming guest molecules lading to improved host–guest interactions [37]. These types of ionic MOFs are classified in two types: (i) Anionic frameworks in which the framework is anionic thereby resulting in the existence of a counter cation to balance the overall charge of the framework and (ii) cationic frameworks where the cationic nature of the backbone results in the necessity of anions (either free or weakly coordinated to the metal centre) to neutralize the charge in order to maintain the electrical neutrality. The ions inside such polarized MOFs are often exchanged with other exogenous ions making them a promising candidate to be used in ion exchange resins [38,39]. Moreover presence of charged species inside the framework results in specific interactions and these can be effectively used for diverse applications.

In this review we have focused in the commonly used strategies for the design and syntheses of these sub class of MOFs, i.e. iMOFs. This report gives detailed information of the various ionic MOFs built from both positively charged, neutral and negatively charged organic building blocks. We have also discussed the various applications of these ionic MOFs and given an outlook of these MOFs for fabrication and improvement needed for these MOFs to be used extensively in chemical industries.

2. Ionic MOFs: classifications and brief overview

Ionic MOFs result when the net charge of the framework is mismatched and therefore the need of extra framework ions either positive or negative are present to maintain the overall electrical neutrality. The ionic MOFs are mainly divided into two major subclasses (a) anionic MOFs: one in which the framework is anionic and extra framework cations balance the overall charge or (b) cationic MOFs in which the framework is cationic and subsequently requires some negatively charged species to maintain the neutrality. The role of metal ions/clusters and the choice of ligands are very important to develop ionicity in a MOF which will be discussed in the following part of the review. Also, because of charge-induced dipoles created in such a polarized MOF, specific applications which are characteristic of such an ionic framework result, which may be otherwise difficult to obtain in a neutral MOF.

3. Anionic frameworks

3.1. *Design principles of anionic frameworks*

The routes to build up an anionic framework is challenging as it is often accidental. The conventional strategies which lead to the formation of charged frameworks by rational designing of either positively charged organic linker molecules or charged inorganic clusters are gruesome as they mostly lead to the formation of either cationic frameworks or are difficult to control because of the complexity in their synthetic procedures [40]. In this section we will discuss some of the commonly used strategies to develop anionic MOFs by pre and post-synthetic approaches (Scheme 1).

It is well known that solvents like DMF and DEF can undergo hydrolysis and subsequent decarbonylation in presence of water to form $NH_2Me_2^+$ or $NH_2Et_2^+$ cations (Scheme 2) which resulted in the formation of anionic frameworks.

These extra framework cations often play a templating effects during MOF syntheses [41,42]. Millange and his group used the templating effect of DMA cations to synthesize an anionic framework which contain a regular charge order Fe^{III}/Fe^{II} or Fe^{III} $0.5Fe^{II}$ $0.5(OH,F)(O_2C{-}C_6H_4{-}CO_2){\cdot}0.5DMA$ [43]. Using negatively charged secondary building units (SBUs) in the construction of anionic MOFs represent one of the prime strategies to design anionic frameworks via pre synthetic approach. Various mono, di, tri and polynuclear SBUs have been developed till date which resulted in the formation of anionic MOFs [44–46]. “Zeolite-like metal-organic frameworks” (ZMOFs) [47] are one of the fascinating examples of anionic frameworks based on such anionic mononuclear SBU, i.e. $[In(CO_2)_2N_4]^-$. Using the anionic SBUs Eddaoudi and co-workers have synthesized

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