

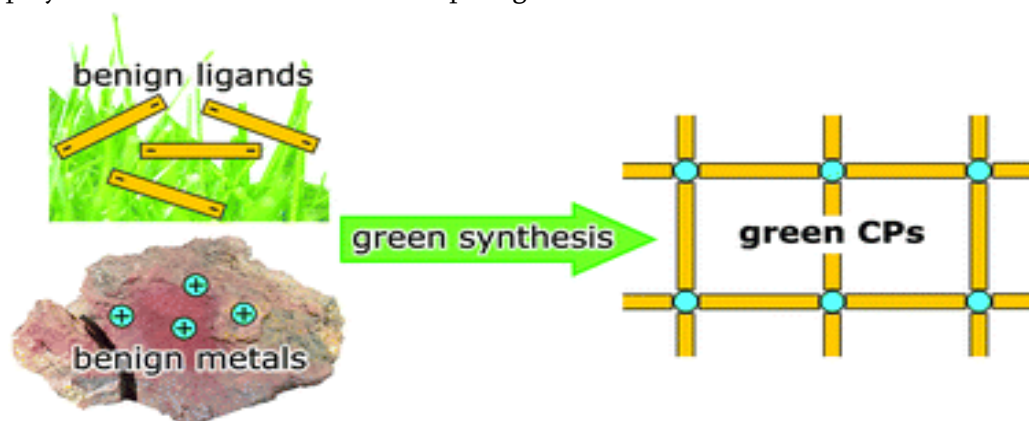
Advances in the Green Chemistry of Coordination Polymer Materials

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ABSTRACT

Coordination polymers, including metal–organic frameworks, are a diverse class of materials with myriad properties and potential applications. However, a number of drawbacks have hindered the scaling up of such materials towards commercial applications. These include health and safety risks, environmental hazards, poor cost efficiency and sustainability shortfalls. In contrast to the systematic progress of organic green chemistry, which has contributed to improvements in the sustainability of chemical processing, the development of green chemistry in the context of coordination polymers has been fragmented and sporadic. This review describes advances in the use of green components: benign sustainable ligands and non-hazardous earth abundant metals. Additionally, solvent considerations, synthesis strategies for improved sustainability and the performance of coordination polymers relative to alternative competing materials are discussed.



I. INTRODUCTION

Coordination polymers (CPs) are metal–ligand coordination compounds that form one-dimensional (1D) extended chains, two-dimensional (2D) sheets or three-dimensional (3D) frameworks. There are two recognised sub-classes: “coordination networks”, which are 2D, 3D or crosslinked 1D CPs, and “metal–organic frameworks” (MOFs) (also referred to as “porous coordination polymers”), which are coordination networks that contain potential voids.¹ Metallopolymers are a distinct class of organic

polymers incorporating metal ions into the backbone or side chains.² “Inorganic–organic hybrid materials” is a related term, which may be appropriate when referring to CPs that resemble extended inorganic compounds;³ however, in accordance with the approach of Biradha et al.,⁴ we have disregarded this term to avoid unnecessary confusion and use a simplified taxonomy as illustrated in

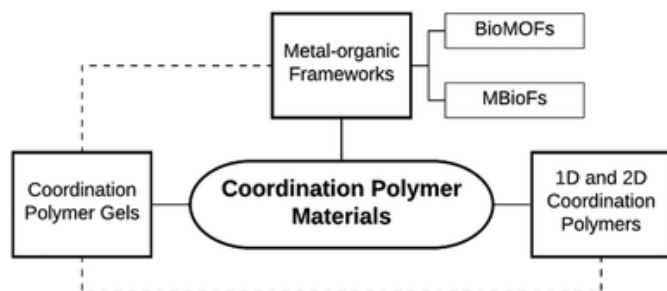


Fig. 1 Relevant classes of CP materials.

Metal biomolecule frameworks (MBioFs) has been proposed as a sub-class of MOFs, where the MOF incorporates “at least one biomolecule” as organic linker and where “biomolecule” refers to naturally-occurring molecules found in living organisms, such as amino acids, nucleobases or sugars.⁵ To be clear, under strict application of this definition, a MBioF may incorporate any metal, including hazardous metal ions, and additional ligands that are not biomolecules. A similar term, BioMOFs, is defined as “metal–organic frameworks for biological and medical applications”.^{6,7} Here the focus is on biocompatibility such that these can be used for applications involving living organisms, including humans. Concern for biological safety does not explicitly include all aspects relating to the principles of green chemistry, such as the minimisation of waste or the elimination of hazardous solvents used during synthesis. Nevertheless, CPs that qualify as BioMOFs tend to comprise environmentally benign components, such as MIL-88A, which is constructed from Fe(III) and fumaric acid.⁸ The prefix “MIL” is used for a variety of porous 3D CPs discovered by researchers at Materials Institute Lavoisier.⁹ “Bio-based MOFs” is an emerging category that has not yet been explicitly defined.

Within the field of CP materials, MOFs have received the bulk of research attention in recent years. Fig. 2a shows the number of publications in a given year containing the term “coordination polymer” and those containing “metal–organic framework” in the title, abstract or keywords. The term “metal–organic framework” surpassed “coordination polymer” in 2014 and is now clearly dominant.

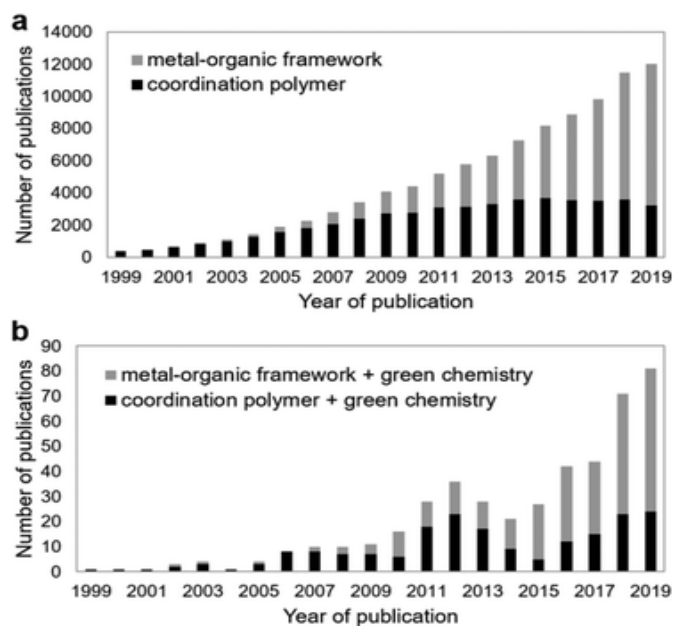


Fig. 2 Number of publications in a given year, for the period 1999–2019, mentioning the terms (a) “metal–organic framework” and “coordination polymer” and (b) “metal–organic framework” + “green chemistry” and “coordination polymer” + “green chemistry” by Web of Science search of topics, which entails a search of titles, abstracts and keywords.

Ligand selection

CPs incorporate a variety of synthetic and naturally-occurring ligands. The earliest high surface area, thermally stable MOFs employed rigid ligands bearing carboxylate, imidazolite or pyridyl moieties, often incorporating aromatic groups or polyaromatic spacers.³³ Such rigid aromatic ligands are usually fossil carbon-based and some may be harmful to humans and the environment, but are useful for preparing rigid 3D networks with permanent porosity and high internal surface areas. Engineering permanent porosity has been a major focus of MOF research; however, research on “soft porous crystals”³⁴ has grown, where ligand flexibility and labile coordination bonds are of interest, and there remains huge potential for materials based on 1D and 2D CPs.

Naturally-occurring and bio-based ligands for CPs have received growing attention as green chemistry approaches have gained traction and as researchers have broken with the received wisdom that only rigid 3D MOFs have potential as new technologies. 'Green ligands' should be obtainable from renewable sources (e.g. biomass), and be environmentally benign and biodegradable, unless recycling of the CP is feasible. Among the most widely exploited are aliphatic diacids, amino acids and nucleobases. Beobide and co-authors have produced a useful review of metal-carboxylato-nucleobase architectures.⁴⁴ Here we focus on selected aliphatic diacids, amino acids and cyclodextrins as examples of important green ligands (Table 1). We highlight a range of existing CPs based on these ligands to illustrate their utility. However, many of these examples incorporate unfavourable metal ions and would not be considered green CPs. A great deal more work is required to match sustainable ligands and metals. Metal ion selection will be discussed separately.

Aliphatic diacids

Key aliphatic diacids employed as green ligands in CP materials are shown in Fig. 3. The unsaturated linear aliphatic dicarboxylic acids are the series with general formula $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$. Those that are readily available as commodity or fine chemicals range from the smallest, oxalic acid, with $n = 0$ to hexadecanedioic acid, with $n = 14$. Most are considered to be of low risk, are biodegradable and some are already available by fermentation from bio-based feedstocks as commodity chemicals.³⁶ Adipic acid and oxalic acid are important CP ligands that are candidates for industrial production by fermentation. Industrial fermentation processes for adipic acid production^{36,37} are advanced as compared with fermentation-based oxalic acid, which is not yet commercially viable.⁴¹ Beyond the $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ series, itaconic acid and 2,5-furandicarboxylic acid are bio-based ligands that are produced at large

scale and have been explored for the construction of CPs. Large quantities of itaconic acid are produced by fermentation.^{36,39} 2,5-Furandicarboxylic acid is obtainable from biomass at scale but not yet by green synthesis.⁴⁰

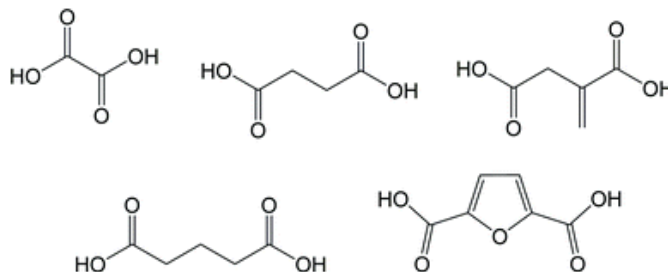


Fig. 3 Important aliphatic diacids employed as green ligands, from left to right: oxalic acid, succinic acid, itaconic acid (2-methylenesuccinic acid), adipic acid and 2,5-furandicarboxylic acid.

Succinic acid

This compound is already commercially produced, via fermentation, at large scale and economically competitive rates.³⁵ Its good water solubility (8.7 g per 100 g water at 298 K (ref. 45)) makes succinate CP synthesis in aqueous medium relatively straightforward and, as a CP ligand, succinate is associated with a large degree of structural diversity and a broad range of different metal centres.

Rare earth (mainly lanthanide) metal succinate CPs are particularly prevalent in literature and are well documented in the recent review by Bernini et al., which includes mixed ligand CPs.⁴⁶ Worth noting are the Ho(III) succinate CPs prepared from succinylsalicylic acid, which was hydrolysed *in situ*⁴⁷ and a broad series of lanthanide succinate CPs, including 2D architectures and 3D architectures with relatively large calculated solvent-accessible volumes, synthesised with 5-sulfosalicylate as templating agent.⁴⁸ The near-infrared luminescence of lanthanide succinate and lanthanide *p*-toluylate-acetate CPs has been explored, with enhancement of luminescence noted for *p*-toluylate-acetate only, confirming that

succinate itself tends not to contribute to electromagnetic properties.⁴⁹

Of course, transition metal succinate CPs are also common. A Cu(II) succinate 1D CP, reported as a 3D framework based on hydrogen bonding, has been subjected to low temperature magnetic studies.⁵⁰ Several Co(II) succinate CPs are known, with thirteen unique Cambridge Structural Database (CSD) entries at the time of writing containing Co(II) as the only metal and succinate as the only organic ligand (CSD reference codes: 221317, 830032, 620466, 138985, 257268, 157785, 161392, 165917, 268305, 830034, 156110, 1050327, 1050331). Analysis of results of high throughput screening experiments showed that varying temperature, pH, concentration and time of hydrothermal reactions could produce seven unique Co(II) succinate CPs, two of which were novel at the time.⁵¹ Reversible dehydration, where crystallinity is preserved, accompanied by colour change has been demonstrated for a Co(II) succinate CP.⁵² A systematic study of mixed metal succinates containing Co(II), Fe(II) and Mn(II) found evidence of partial ordering of the different metal cations across the crystallographic metallic nodes of the framework.⁵³ In a separate mixed metal study, by varying the Co/Ni ratio in the reaction mixture, four different metal succinate CP structures (including mixed metal CPs) were isolated from constant reaction conditions (Fig. 4).⁵⁴ Unusual low temperature magnetic transitions were observed for a Mn(II) CP.⁵⁵ However, while many succinates have been explored for their magnetic properties, mostly modest results are reported. CPs based on Li, succinic acid, methyl succinic acid and malic acid were prepared by a solvent-free method.⁵⁶ A rare example of an Ag(I)-based succinate CP was reported in 1993,⁵⁷ while spontaneous symmetry breaking was achieved to obtain a rare homochiral succinate CP with a uranyl metal centre.

Conclusion

Progress in the development of green CP materials has accelerated in recent years. The emergence of new CPs incorporating bio-based ligands and earth abundant metal ions is very encouraging. Remarkable materials such as CD-MOFs and the BioMIL series demonstrate that entirely benign, sustainable CPs are possible. However, despite environmental, energy and other sustainability applications being the target for many new CP materials, most CP research demonstrates little consideration for the sustainability of the novel materials themselves. There is great scope and a strong societal imperative for more extensive, direct research into CPs based on sustainable components and green synthetic procedures.

Researchers investigating CP materials should be more intentional about their selection of reagents and their approach to synthesis, particularly where large-scale applications of bulk materials are envisioned. While elaborate ligands can be designed to impart specific properties, scalability will prove challenging if these are challenging to synthesise. As we have shown, a number of naturally-occurring and bio-based ligands, some of which are already available as commodity chemicals, hold promise as useful ligands for green CPs. Selecting these increases the chances of good scalability of the final material. Every effort should be made to avoid harsh reaction conditions, involving hazardous organic solvents, which have been common in CP research. Sonochemical and electrochemical synthesis present some specific advantages over conventional solvothermal methods. However; the replacement of hazardous organic solvents with green alternatives or switching to solvent-free or low-solvent synthesis by continuous processing techniques like twin-screw extrusion is arguably a far more promising strategy for efficient scalable green synthesis.

It will not be sufficient to focus solely on improving the sustainability of CP materials. Cost is another important factor. One strategy has been to concentrate on bio-based ligands that are becoming increasingly important as commodity chemicals, such as lactic acid and 2,5-furandicarboxylic acid, because such chemicals are likely to become more affordable as demand increases and production efficiencies improve.

Furthermore, it will be important to demonstrate that sustainable CPs can at least match or, better yet, outperform existing alternative materials. This is a major challenge. Thousands of CPs have been discovered but many have proven to be appealing only as curiosities. While some have broken through to industrial testing, particularly in gas storage, textiles and catalysis,^{238,239} CPs have arguably not yet lived up to their promise as novel materials for the numerous potential applications envisioned.

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