

“Metal-Organic Frameworks: A New Class of Crystalline Porous Materials”

By **B. Seyyedi (University of Maragheh, Iran)**, edited by **S. Bordiga (University of Torino, Italy)**, Lambert Academic Publishing, an imprint of VDM Publishing, Saarbrücken, Germany, 2014, ISBN: 978-3-659-52782-1, £39.00, €55.90

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“Metal-Organic Frameworks: A New Class of Crystalline Porous Materials” published by Lambert Academic Publishing, 2014, is a book written by Dr Behnam Seyyedi on the emerging porous materials of metal-organic frameworks (MOFs). The term MOF was coined by Omar Yaghi in 1995 (1). MOFs consist of both organic and inorganic building entities, where the organic ligands, i.e. spacers, are coordinated to the metal ion clusters, i.e. nodes, to create extended frameworks. In some cases, the frameworks are rigid enough to form internal voids after solvent removal, forming structures with high porosity and surface areas (up to $\sim 7000 \text{ m}^2 \text{ g}^{-1}$). MOFs have shown potential applications in a wide range of fields, such as gas separation and storage, catalysis, sensing and drug delivery.

Focus on Spectral Features

The reviewed book focuses on spectral features (particularly ultraviolet-visible (UV-vis)) of metal phosphonate and carboxylate MOFs, rather than presenting a general picture of MOFs synthesis,

structures and applications. UV-vis is a powerful tool for studying the phosphorescence properties of MOFs, but it is not a common characterisation method since it cannot provide definitive structural information.

The book is organised into six chapters. The first two chapters provide a background introduction to the field of MOFs, while the later four chapters cover spectroscopic studies of four types of MOFs. Lastly, the conclusions summarise the use of spectroscopic techniques to study MOF structure evolution during activation and gas sorption.

Chapter 1 provides a brief overview of the history and development of MOFs. This covers aspects such as the inception of MOF reticular chemistry inspired by the classic sol-gel processes, the similarity between MOFs and the inorganic microporous materials of zeolites and zeotypes, and the recent applications of the modular building strategy to covalent-organic frameworks. A few potential applications of MOFs such as catalysis, gas purification and storage are also discussed.

Chapter 2 offers an introduction to the common analytical methods used for MOF characterisation, like X-ray diffraction (XRD), electron microscopy, atomic force microscopy, UV-vis and infra-red (IR) spectroscopy, and gas sorption measurements. The fundamental principles behind these techniques are provided to facilitate better understanding and choice of applications for the reader. Specifically, IR and Raman spectroscopy provides complementary information about the functional groups and local

chemical environments of solid materials. These modern characterisation techniques established the foundation to discover and study new MOF materials.

Chapter 3 discusses the UV-vis and IR spectra of metal phosphonate MOFs. These MOFs consist of two-dimensional infinite metal-oxygen layers pillared by organophosphorus ligands. The metal phosphonate MOFs exhibit varying dehydration behaviours depending on the metal coordination centre: for example, cobalt phosphonates exhibit good thermal stability during solvent removal but this is not the case for manganese or iron phosphonates. By using UV-vis spectroscopy, it is shown that the Co coordination environment changes from octahedral to a combination of square-pyramidal and tetrahedral during dehydration. Meanwhile, IR characterisation illustrates the framework closure and loss of water molecules upon solvent removal, whereas Raman spectroscopy shows only slight perturbations in the vibrational mode.

Chapter 4 covers the metal carboxylate MOFs and their spectroscopic features. Metal carboxylate MOFs incorporate linear carboxylic acids as the ligands, especially the terephthalate analogues, which have the capacity to form extended large functional pore networks. MIL-53 (MIL: Materials of Institute Lavoisier) and MIL-68 are two prominent examples from this MOF family. Their topologies are made up of infinite chains of oxo-metal clusters linked through the terephthalate ligands. The free ligands and solvent molecules trapped inside these MOFs are difficult to remove to obtain an open structure, even upon prolonged thermal treatment in high vacuum. Ageing is another issue that may cause problems in reproducing results. Nevertheless, the presence of uncoordinated amine functionality in NH₂-MIL-53 helps to increase the absorption energy and capacity of certain gas molecules, like carbon dioxide. Fourier transform (FT)-IR spectroscopy can be used to show the localised sorption sites and the interaction modes of CO₂ with the framework.

Chapter 5 focuses on the cubic octanuclear nickel(II) cluster MOFs. The author took two bis-pyrazolyl coordinated MOFs as examples, which normally contain structural water molecules that cannot be removed without compromising the structural integrity. They have not shown significant sorption reactivity towards probe molecules like carbon monoxide or CO₂,

as shown by FT-IR and UV-vis spectroscopies, but they may have promising magnetic properties.

In Chapter 6, CPO-27 is taken as an example to illustrate the use of spectroscopic techniques for MOFs characterisation. CPO-27, also known as MOF-74, is a series of honeycomb-structured MOFs with 1D porous channels (**Figure 1(a)**). The framework is formed by linking the transition metal coordination centres (Zn²⁺, Mg²⁺, Mn²⁺ or Ni²⁺) through 2,5-dihydroxyterephthalate linkers. There are five oxygen atoms contributed by the ligand in each coordination sphere of the metal ion (**Figure 1(b)**), and the sixth site is occupied by water or other solvent molecules after synthesis. The removal of these solvent molecules by activation leads to the formation of open metal sites along the porous channels. These unsaturated metal sites supply preferential absorption sites for gas molecules, like CO₂ and methane, due to increased enthalpies of absorption. *Ab initio* calculations show that there is a slight electrostatic potential variance along the MOF framework, with the oxygens from the carboxylate group being the most negatively charged (**Figure 1(c)**).

The FT-IR spectrum (**Figure 2**) shows a blue shift of CO stretching vibration in CPO-27-Mn compared to

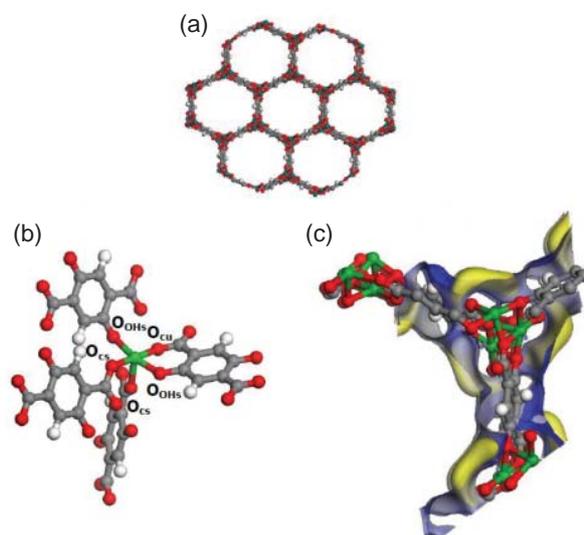


Fig. 1. (a) View of the 1D channel porous structure in CPO-27 along the (100) direction; (b) a first coordination sphere of 2,5-dihydroxyterephthalate ligand surrounding the M²⁺; (c) electrostatic potential maps of the CPO-27 framework skeleton. Colour code: -0.015 a.u. (yellow) to +0.015 a.u. (blue) with a continuous linear gradient (Reproduced by permission of VDM Publishing)

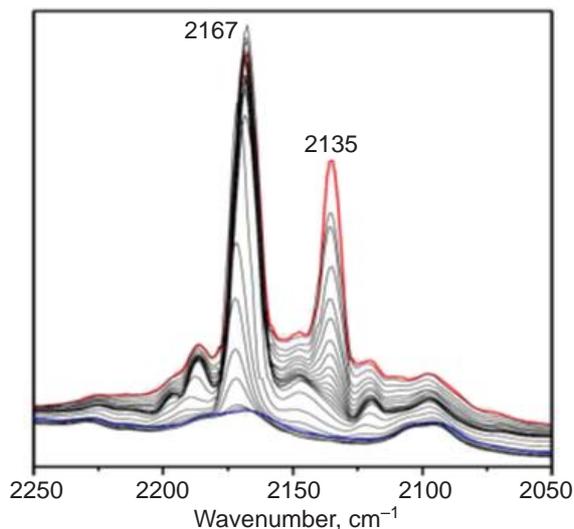


Fig. 2. FT-IR spectra of CO absorptions in CPO-27-Mn at varying temperatures, from liquid nitrogen temperature (red) up to room temperature (blue) (Reproduced by permission of VDM Publishing)

the free gas molecules, implying strong electrostatic bonding with CO. A separate study on CO₂ adsorption shows that magnesium coordinated CPO-27 MOF has a higher sorption capacity than other coordination metals, due to the higher heat of absorption and the lighter weight of metal.

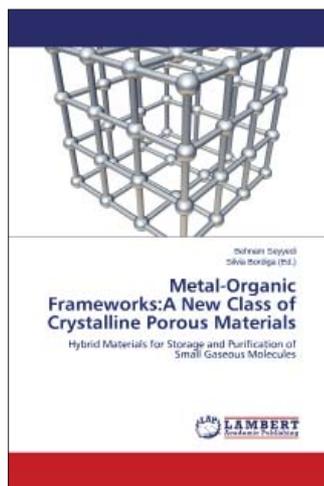
Conclusions

Overall, the reviewed book offers a primer for people interested in the vibrational spectroscopic aspects of carboxylate and phosphonate MOFs. The more advanced reader might like to consider publications

such as “Metal-Organic Frameworks: Applications from Catalysis to Gas Storage” published by Wiley (2), or review articles like ‘Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites’ published in *Chemical Reviews* (3), which cover the topic in much more breadth and depth. Lastly, this book possibly needs more editing work to offer an improved reading experience.

References

1. O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, (6558), 703
2. “Metal-Organic Frameworks: Applications from Catalysis to Gas Storage”, ed. D. Farrusseng, Wiley-VCH Verlag GmbH & Co KGaA, Weinheim, Germany, 2011
3. N. Stock and S. Biswas, *Chem. Rev.*, 2012, **112**, (2), 933



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