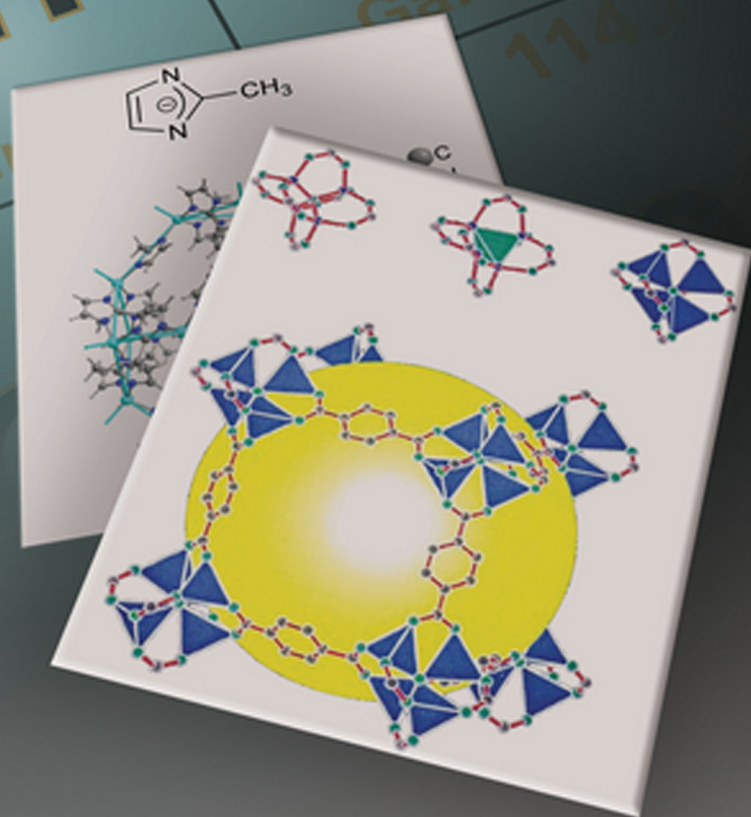Editors

Leonard R. MacGillivray • Charles M. Lukehart

Metal-Organic Framework Materials
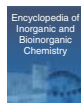
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METAL-ORGANIC FRAMEWORK MATERIALS

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Encyclopedia of Inorganic and Bioinorganic Chemistry

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Series Preface

The success of the *Encyclopedia of Inorganic Chemistry* (EIC), pioneered by Bruce King, the founding Editor in Chief, led to the 2012 integration of articles from the *Handbook of Metalloproteins* to create the newly launched *Encyclopedia of Inorganic and Bioinorganic Chemistry* (EIBC). This has been accompanied by a significant expansion of our Editorial Advisory Board with international representation in all areas of inorganic chemistry. It was under Bruce's successor, Bob Crabtree, that it was recognized that not everyone would necessarily need access to the full extent of EIBC. All EIBC articles are online and are searchable, but we still recognized value in more concise thematic volumes targeted to a specific area of interest. This idea encouraged us to produce a series of EIC (now EIBC) Books, focusing on topics of current interest. These will continue to appear on an approximately annual basis and will feature the leading scholars in their fields, often being guest coedited by one of these leaders. Like the Encyclopedia, we hope that EIBC Books continue to provide both the starting research student and the confirmed research worker a critical distillation of the leading concepts and provide a structured entry into the fields covered.

The EIBC Books are referred to as *spin-on* books, recognizing that all the articles in these thematic volumes are destined to become part of the online content of EIBC, usually forming a new category of articles in the EIBC topical structure. We find that this provides multiple routes to find the latest summaries of current research.

I fully recognize that this latest transformation of EIBC is built on the efforts of my predecessors, Bruce King and Bob Crabtree, my fellow editors, as well as the Wiley personnel, and, most particularly, the numerous authors of EIBC articles. It is the dedication and commitment of all these people that are responsible for the creation and production of this series and the "parent" EIBC.

Robert A. Scott
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October 2014

Volume Preface

The field of metal-organic frameworks (MOFs) has experienced explosive growth in the past decade. The process of mixing readily available metal precursors with organic linkers has captured the imagination of chemists and materials scientists worldwide to an extent that discussions on uses of MOFs for energy storage, catalysis, and separations, as well as integrations into technologies such as fuel cells and electronics, have become commonplace. At the core of the explosion are uses of fundamental principles that define our understanding of inorganic chemistry and, more specifically, coordination chemistry. A main thesis that drives the design and formation of a MOF is that the linking of components will be sustained by coordination bonds and that the linkages will be propagated in space to reflect coordination geometries and requirements of metals. A critical backdrop is the field of solid-state chemistry that provides primary assessments and insights into the structure and properties of MOFs where concepts of crystal engineering help to drive new directions in design, synthesis, and improvement. Organic synthesis plays a vital role in not only the formation of molecules that link metals but also equipping a MOF with function that can be tailored. Moreover, it has been synergism between these highly fundamental disciplines that, collectively, have enabled the field of MOFs to grow and flourish to the exciting and highly interdisciplinary status that the field enjoys today.

Metal-Organic Framework Materials covers topics describing recent advances made by top researchers in MOFs including nanoparticles and nanoscale frameworks, mesoporous frameworks, photoreactive frameworks, polyrotaxane frameworks, and even edible frameworks, as well as functionalized frameworks based on porphyrins, fluorine, and aluminum. In addition, the volume features aspects on mechanochemical synthesis and post-synthetic modification, which provide discussions on new vistas on the "before" and "after" of framework design and construction.

Metal-Organic Framework Materials also gives up-to-date descriptions of the many properties and applications evolving from MOFs. Magnetic properties are highlighted as related to formates and single-molecule magnets while host–guest properties are discussed in terms of uptake and sequestering of gases, hydrocarbons, alcohols, and metals, as well as uses of open metal sites and photoreactive components in host design. Applications of MOFs to semiconductors, materials for patterning, integrations in mixed-matrix membranes, uses in electrochemical materials, and uses in analytical chemistry are also presented. Investigations that stem from solid-state chemistry based on characterizing MOFs using solid-state NMR analyses as well as studying single-crystal reactions of MOFs and understanding interpenetration and entanglement help us further understand the fundamentals of the field.

While the rapid and accelerating development of MOFs will prohibit a comprehensive treatment of the status of the field, we believe that *Metal-Organic Framework Materials* provides readers a timely update on established and fresh areas for investigation. The reader will develop firsthand accounts of opportunities related to fundamentals and applications of MOFs, as well as an emerging role of MOFs in defining a new materials space that stems from the general and main topic of inorganic chemistry.

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October 2014

Periodic Table of the Elements

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

Period / Atomic number / Atomic weight

Period 1

| 1 H 1.0079 | | | | | | | | | | | | | | | | | 2 He 4.0026 |

Period 2

| 3 Li 6.941 | 4 Be 9.0122 | | | | | | | | | Zintl border | | 5 B 10.811 | 6 C 12.0107 | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984 | 10 Ne 20.179 |

Period 3

| 11 Na 22.9898 | 12 Mg 24.305 | | | | | | | | | | | 13 Al 26.9815 | 14 Si 28.0855 | 15 P 30.9738 | 16 S 32.066 | 17 Cl 35.453 | 18 Ar 39.948 |

Period 4

| 19 K 39.0983 | 20 Ca 40.078 | 21 Sc 44.9559 | 22 Ti 47.867 | 23 V 50.9415 | 24 Cr 51.996 | 25 Mn 54.9380 | 26 Fe 55.845 | 27 Co 58.933 | 28 Ni 58.693 | 29 Cu 63.546 | 30 Zn 65.409 | 31 Ga 69.723 | 32 Ge 72.64 | 33 As 74.9216 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.798 |

Period 5

| 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y 88.9059 | 40 Zr 91.224 | 41 Nb 92.9064 | 42 Mo 95.94 | 43 Tc 98.9062 | 44 Ru 101.07 | 45 Rh 102.9055 | 46 Pd 106.42 | 47 Ag 107.8682 | 48 Cd 112.41 | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.760 | 52 Te 127.60 | 53 I 126.9045 | 54 Xe 131.29 |

Period 6

| 55 Cs 132.9054 | 56 Ba 137.327 | 57-71 lanthanoids | 72 Hf 178.49 | 73 Ta 180.9479 | 74 W 183.84 | 75 Re 186.207 | 76 Os 190.2 | 77 Ir 192.22 | 78 Pt 195.08 | 79 Au 196.9665 | 80 Hg 200.59 | 81 Tl 204.3833 | 82 Pb 207.2 | 83 Bi 208.9804 | 84 Po (209) | 85 At (210) | 86 Rn (222) |

Period 7

| 87 Fr (223) | 88 Ra (226.0254) | 89-103 actinoids | 104 Rf (261.1088) | 105 Db (262.1141) | 106 Sg (266.1219) | 107 Bh (264.12) | 108 Hs (277) | 109 Mt (268.1388) | 110 Ds (271) | 111 Rg (272) | 112 Cn copernicium | | 114 Fl flerovium | | 116 Lv livermorium | | |

Lanthanoids

| 57 La lanthanum 138.9 | 58 Ce 140.12 | 59 Pr 140.9077 | 60 Nd 144.24 | 61 Pm (147) | 62 Sm 150.36 | 63 Eu 151.96 | 64 Gd 157.25 | 65 Tb 158.9254 | 66 Dy 162.50 | 67 Ho 164.9304 | 68 Er 167.26 | 69 Tm 168.9342 | 70 Yb 173.04 | 71 Lu 174.967 |

Actinoids

| 89 Ac actinium | 90 Th 232.0381 | 91 Pa 231.0359 | 92 U 238.0289 | 93 Np 237.0482 | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (260) | 102 No (259) | 103 Lr (262) |

Based on information from IUPAC, the International Union of Pure and Applied Chemistry (version dated 1st May 2013).
For updates to this table, see http://www.iupac.org/reports/periodic_table.

PART 1
Design and Synthesis

Porous Coordination Polymer Nanoparticles and Macrostructures

Julien Reboul and Susumu Kitagawa

Kyoto University, Kyoto, Japan

1 INTRODUCTION

The concept of "chemistry of organized matter" aims to extend the traditional length scales of synthetic chemistry through the assembly of nanostructured phases and the establishment of long-range organization.[1] Materials created by this approach possess properties that are either amplified versions of the properties of the smallest building blocks or emerged properties, not necessarily related to the building blocks.[1,2] Synthesized from the regular assembly of coordination complexes, porous coordination polymers (PCPs) are striking examples of such organized materials. Since the beginning of the development of PCPs in the early 1990s, PCPs were intensively studied due to scientific interest in the creation of nanometer-sized spaces and their enormous potential in applications such as gas storage, separation, photonics, and heterogeneous catalysis. Compared to other conventional porous solids such as zeolites and carbons, PCPs are of particular interest because they are synthesized under mild conditions and can be easily designed based on the appropriate choice or modification of the organic ligands and metal centers.

Beside the conventional research that aims at tuning PCP crystal characteristics at the molecular scale, recent research efforts focused on the extension of the level of design and organization of PCP crystals from the molecular to the nano- and macroscale.

Indeed, a special attention is currently given to the size- and shape-dependent properties of PCP crystals. Similarly to the case of zeolite nanocrystals, downsizing PCP crystals is expected to influence the sorption kinetics. The size decrease of porous materials also results in the decrease of the diffusion length within the bulk material toward the active sites, which is of high importance in catalysis and separation, especially in liquid-phase applications.[3] In addition to size-dependent properties related to their porosity, modulation of the size and shape of PCP crystals is expected to influence inherent properties of PCPs, such as their structural flexibility,[4] proton conduction[5] and charge transfer (ligand-to-metal or metal-to-ligand) abilities,[6] or luminosity (resulting from conjugated ligands).[7] Also, the preparation of stable and uniformly distributed suspensions of nanocrystals is a requisite for expanding the range of PCP applications. For instance, nanocrystalline and nontoxic PCPs are envisioned as drug delivery systems[8] and contrast agents.[9]

Regarding the construction of higher scale PCP-based materials, PCP crystals with well-defined shapes are of great interest as building units. A challenge today is to develop efficient strategies that allow the integration of PCPs into readily applicable devices that fully exploit the attributes of these materials. Thin films and patterned surfaces made of oriented and well-intergrown PCP crystals were shown to be promising for molecular separation[10,11] or sensing.[12–14] Three-dimensional PCP-based architectures possessing a multimodal porosity are useful to improve the molecular diffusion when used as separation systems and catalysts.[15,16]

Owing to the highly reactive surfaces of PCPs (composed of partially coordinated organic ligands or uncoordinated metal centers), the possible modulation of the coordination equilibrium, and the large number of PCP framework available (implying a large range of possible synthesis conditions), many of the chemical and microfabrication methods established for the manipulation of both purely organic and inorganic compounds were applied for the synthesis of PCPs. As it will be illustrated later in this chapter, utilization of microwave treatment, microemulsion methods, or capping agents was successful for the control of the size and shape of PCP crystals. PCP crystal assemblies were obtained by employing Langmuir–Blodgett (LB) technology, hard or soft-templating approaches, and pseudomorphic replacement approaches.

This chapter attempts to give an overview of the most promising strategies applied so far for the synthesis of PCP nanocrystals and PCP-based macrostructures and composites. The second section of this chapter focuses on the control of the size and shape of PCP crystals. The third section describes the strategies employed for the synthesis of PCP-based polycrystalline macrostructures and composites.

2   MANIPULATION OF THE SIZE AND SHAPE OF PCP CRYSTALS

2.1   Microwave and Ultrasonication-assisted Synthesis

PCPs are generally synthesized in water or organic solvents at temperatures ranging from room temperature to approximately 250 °C (see *Nanoscale Metal-Organic Frameworks*). Ovens or oil baths for which heat is transferred through conduction and convection are commonly used. Recently, microwave has been employed in order to reduce the energy consumption and the reaction time while increasing the yields.[17] Beside the advantage related to its energy efficiency, microwave heating was shown to have a significant impact on the size and morphology of the PCP crystals synthesized by this means.

In the microwave frequency range, polar molecules in the reaction mixture try to orientate with the electric field. When dipolar molecules try to reorientate with respect to an alternating electric field, they lose energy in the form of heat by molecular friction. Microwave heating therefore provides a rapid and uniform heating of solvents, reagents, intermediates, and products.[18] Application of this fast and homogeneous heating to the synthesis of PCPs provides uniform nucleation and growth conditions, leading to more uniform PCP crystals with smaller size than in the case of conventional heating processes.[19–21]

Examples of microwave synthesis resulting in the formation of PCP crystals with a narrow size distribution and comprised within the submicrometer regime

are still scarce. Masel *et al.* produced nanocrystals of the cubic zinc carboxylate reticular $[Zn_4O(bdc)_3]$ (MOF-5 or IRMOF-1, where bdc = 1,4-benzenedicarboxylate), $[Zn_4O(Br\text{-}bdc)_3]$ (IRMOF2, where Br-bdc = 2-bromo-benzenedicarboxylate), and $[Zn_4O(NH_2\text{-}bdc)_3]$ (IRMOF3, where NH_2-bdc = 2-amino-benzenedicarboxylate) at 150 W, in a few seconds and under relatively diluted concentrations.[22] Chang *et al.* reported the microwave synthesis of nanocrystals of the cubic chromium terephthalate $[Cr_3F(H_2O)_2O(bdc)_3 \cdot nH_2O]$ (MIL-101) with a size range from 40 to 90 nm.[23] The authors clearly demonstrate the impact of irradiation time over the dimension of the crystals and the homogeneity of the sample. Small sizes were observed for materials prepared using short crystallization times (Figure 1). Nevertheless, physicochemical and textural properties of the crystals were similar to those of materials synthesized using the conventional hydrothermal method.

Ultrasonication is another alternative strategy to conventional heating processes that competes with microwave irradiation in terms of reduction of the crystallization time and crystal size.[24–26] Sonochemistry relies on the application of high-energy ultrasound to a reaction mixture. The rate acceleration in sonochemical irradiation stems from the formation and collapse of bubbles in solution, termed acoustic cavitation, which produces very high local temperatures (>5000 K) and pressures, resulting in extremely fast heating and cooling rates.[27] Development of sonochemical synthesis for the production of PCPs is still at an early stage. However, some recent reports already demonstrated the power of this means for the production of PCP nanocrystals with uniform sizes and shapes. Qiu *et al.* reported the synthesis of nanocrystals of a fluorescent PCP, $[Zn_3(btc)_2 \cdot 12H_2O]_n$ (with btc = benzene-1,3,5-tricarboxylate), with size ranging from 50 to 100 nm within 10 min. Interestingly, the size and the shape of the crystal were tunable by varying the reaction time.[28] Sonocrystallization of the zeolitic imidazolate frameworks $[Zn(PhIM)_2 \cdot (H_2O)_3]$ (ZIF-7, where PhIM = benzylimidazole), $[Zn(MeIM)_2 \cdot (DMF) \cdot (H_2O)_3]$ (ZIF-8, where MeIM = 2-methylimidazole), $[Zn(PhIM)_2 \cdot (DEF)_{0.9}]$ (ZIF-11), and $[Zn(Pur)_2 \cdot (DMF)_{0.75} \cdot (H_2O)_{1.5}]$ (ZIF-20, where Pur = purine) led to the formation of uniform nanocrystals in shorter time than conventional solvothermal methods (6–9 h) and at lower temperatures (45–60 °C).[29]

2.2   Utilization of Ligand Deprotonating Agents

Addition of a base to deprotonate the organic linker was used as a strategy to regulate the early stage of crystallization. Li *et al.* prepared highly uniform suspensions of ZIF-7 nanocrystal suspensions by dissolving zinc nitrate and benzimidazolate (bim) into a polyethylene imine (PEI)-dimethylformamide (DMF)
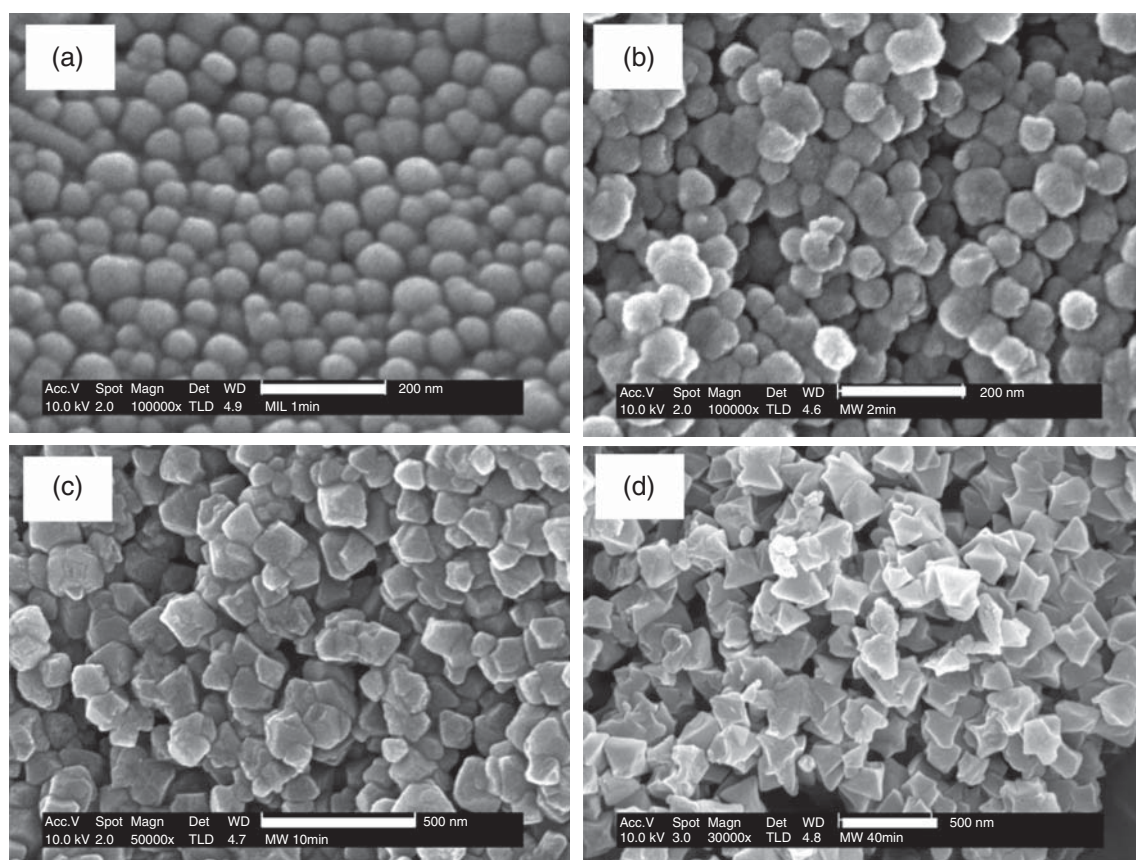
Figure 1   SEM images of MIL-101 prepared using microwave irradiation at 210 °C for various crystallization times: (a) 1, (b) 2, (c) 10, and (d) 40 min. White scale bars indicate (a,b) 200 nm and (c,d) 500 nm. (Adapted from Ref. 23. © WILEY-VCH Verlag GmbH & Co. KGaA, 2007.)

solution at room temperature (Figure 2). The authors could adjust the size of the nanocrystals from 40 to 140 nm by altering the molar ratio of PEI and the reaction duration. PEI has a high density of amino groups, it efficiently deprotonates bim and therefore permits a fast generation of a large number of ZIF-7 nuclei, which is a critical issue for the synthesis of nanoscale crystals.[30]

A similar strategy was followed by Xin *et al.* to produce Zn(ICA) (ZIF-90, where ICA = imidazole-2-carboxyaldehyde) with triethylamine (TEA) as the deprotonating agent at room temperature.[31] TEA was also employed to manipulate the particle size and shape of [Cu$_3$(btc)$_2$][32] and a coordination polymer particle by mixing 4,40-dicarboxy-2,20-bipyridine (H$_2$dcbp) and Cu(OAc)$_2$ in mixed solvents of water at room temperature.[33]

2.3   Reverse Microemulsion

Reverse micelles or water-in-oil microemulsion systems are thermodynamically stable liquid dispersions containing surfactant aggregates with well-defined structures, typically characterized by a correlation length in the nanometer scale. Small water droplets in the microemulsion can be considered as nanoscopic reactors. They were used for the synthesis of a range of nanomaterials,[34] including organic polymers, semiconductors, and metal oxide and recently for the synthesis of nanoscale PCP crystals. Lin's group was the first to adapt the water-in-oil microemulsion-based methodology to the field of PCP for the production of [Gd(bdc)$_{1.5}$·(H$_2$O)] nanorods by stirring a microemulsion of GdCl$_3$ and bis(methylammonium)benzene-1,4-dicarboxylate in a 2:3 molar ratio in the cationic cetyltrimethylammonium bromide (CTAB)/isooctane/1-hexanol/water system for 2 h (Figure 3).[35,36] As the crystal formation takes place inside the droplet during the reverse microemulsion process, the morphologies and sizes of the colloidal particles are generally affected by the droplet structure and its ability to exchange the micellar-containing content.[37] Accordingly, the type of surfactant and the water-to-surfactant ratio (*w*) are critical parameters. For the same surfactant, Lin *et al.* demonstrated that the morphologies and sizes of the PCP
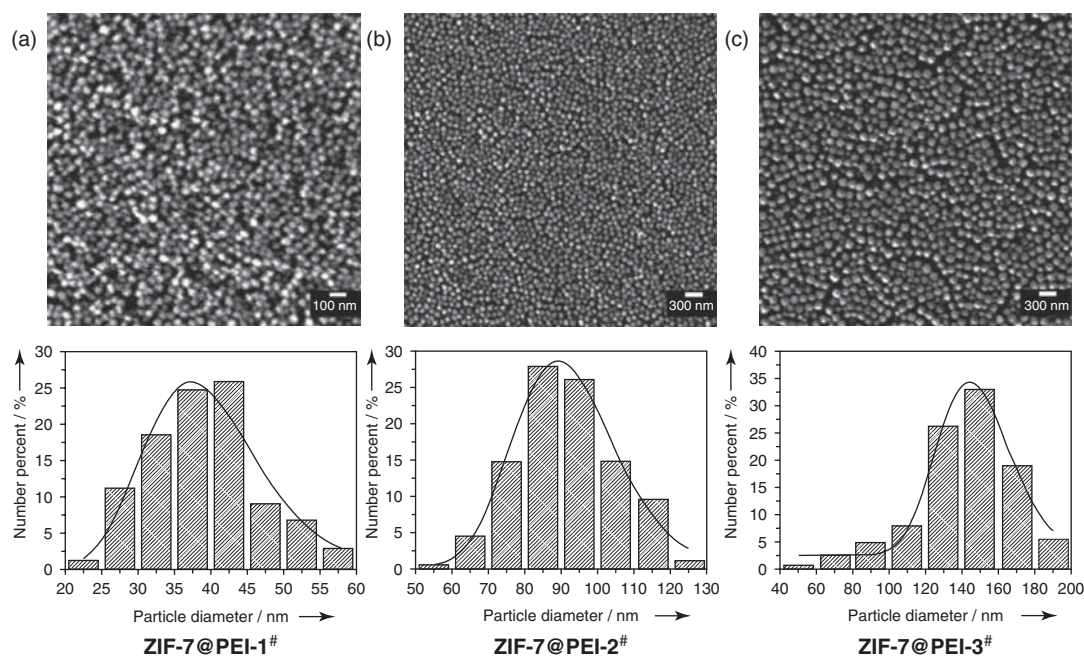
Figure 2 SEM images and size distributions of the ZIF-7 nanoparticles synthesized by adding various amount of a branched PEI (average Mw = 25 000): 0.140, 0.140, and 0.360 g for ZIF-7@PEI-1# (a), ZIF-7@PEI-2# (b), and ZIF-7@PEI-3# (c), respectively. (Adapted with permission from Ref. 30. © WILEY-VCH Verlag GmbH & Co. KGaA, 2010.)

nanorods were influenced by the *w* value of the microemulsion systems. Nanorods of 100–125 nm in length by 40 nm in diameter were obtained with *w* = 5. Significantly longer nanorods (1–2 μm in length and approximately 100 nm in diameter) were obtained with *w* = 10 under otherwise identical conditions. The authors also showed that a decrease in the concentration of reactants or a deviation of the metal-to-ligand molar ratio resulted in a decrease of the particle size.

Reverse emulsion in which water is replaced by a nonaqueous polar solvent such as ethylene glycol, acetonitrile, or DMF was obtained using the surfactant dioctyl sulfosuccinate sodium salt (also named Aerosol-OT, AOT).[38] Regarding PCP nanocrystal synthesis, utilization of such microemulsions was found to be of interest when PCP precursors are insoluble in water. Kitagawa *et al.* synthesized nanocrystals of a flexible PCP [Zn(ip)(bpy)] (CID-1, where ip = isophthalate and bpy = 4,4′-bipyridyl) in the nonaqueous system AOT/*n*-heptane/*N,N*-DMF.[39] Both the metal precursor ($Zn(NO_3)_2 \cdot 6H_2O$) and the ligands (H_2ip and bpy) being insoluble in water, a precursor solution was first prepared with DMF as solvent. A volume of AOT/*n*-heptane solution was then injected into the precursor solution and the microemulsion hence formed was sonicated for 10 min. Figure 4 illustrates the PCP nanocrystal formation and growth mechanism proposed by the authors. Briefly, the formation of the microemulsion under sonication is at the origin of the rapid apparition of a multitude of PCP
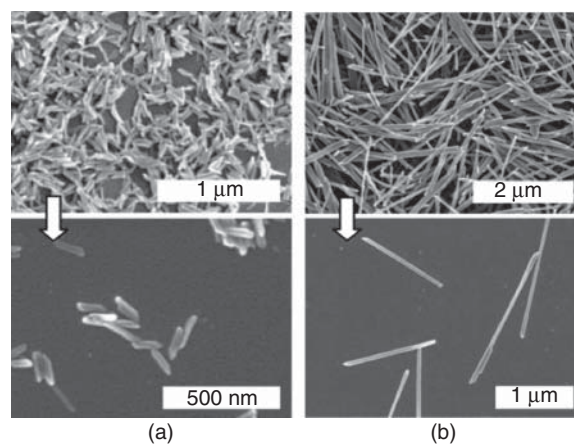
Figure 3 SEM images of $[Gd(bdc)_{1.5} \cdot (H_2O)_2]$ (1) nanorods synthesized with *w* = 5 (a) and *w* = 10 (b). (Adapted with permission from Ref. 35. Copyright (2006) American Chemical Society.)

nuclei within the DMF droplets. Merging of droplets during the process leads to the growth of the particles. As the particle size extends, their aggregation occurs, leading to the surface coordination of AOT. This surface coordination of AOT limits diffusion of metal ions and ligands to the crystal surface, which finally limits the particle growth and the reaction yield.

Figure 4 Model for PCP nanoparticle formation and growth through a nonaqueous reverse microemulsion process. (Reprinted by permission from Macmillan Publishers Ltd: Nature Chemistry, (Ref. 39), copyright (2010). http://www.nature.com/nchem/index.html.)
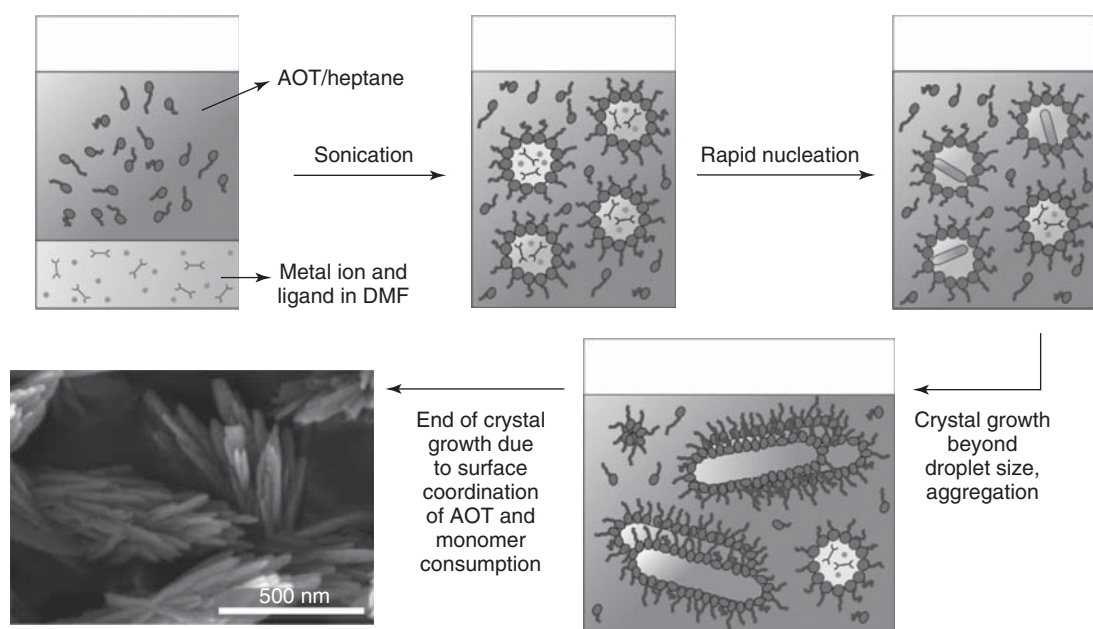
2.4 Utilization of Organic Additives

Modulation of the surface energy of crystals by the addition of various organic or inorganic additives is a well-known strategy for tuning their equilibrium morphology and size in a predictable way.[40]

The high interface energy of PCP crystals originates from the presence of partially uncoordinated organic linkers and unsaturated metal cations on their external surfaces. Ionic, dipolar, highly polarizable, or hydrophobic forces may thus exist on the crystal faces depending on the chemical nature of the organic ligands and of the pH of the medium. Consequently, saturation of the surface-dangling functions can be achieved with a wide variety of additives (via ionic or coordinative bonding, dipole–dipole, hydrogen bonding, van der Waals interactions, etc.). So far, control of the shape and size of PCP crystals was achieved using various polymers,[41] ionic surfactants,[42–45] and mixtures of polymers and surfactants.[46]

Coordination modulation approach consists in the utilization of monofunctional capping agents bearing the same functionality than the multifunctional ligands involved in the construction of the PCP frameworks. This strategy relies on the regulation of the coordination equilibrium at the crystal surface through the competition between the monofunctional and the multifunctional ligands for the complexation of the metal centers.[47]

Hermes *et al*. utilized *p*-perfluoromethylbenzene-carboxylate (pfmbc) as a modulator to block the growth of MOF-5.[48] A growth habit where a fast nucleation step precedes a slower step of particle growth was first verified by means of a time-resolved static light scattering (TLS) investigation without addition of the modulator. The addition of an excess of pfmbc to the reaction mixture after initiating the PCP growth stabilized the crystal extension around 100 nm, leading to the formation of highly stable colloidal suspensions at 25 °C. This result was in contrast to the uncapped case, for which the sedimentation occurs after a while. As observed by TLS, crystals grow in the shape of perfect cubes from the very beginning reflecting the 3D cubic framework of MOF-5. In the case of such isotropic crystal, where all the outer faces are similar, modulators most likely cover the entire crystal surface and induce the reduction of the overall crystal growth rate. In this system, the modulator quenches the crystal growth and prevents the aggregation of the nanocrystals.

Tsuruoka *et al*. extended the use of modulators to control the size and morphology of a crystal system based on an anisotropic framework.[47] The three-dimensional porous coordination framework $[Cu_2(ndc)_2(dabco)]$ (where ndc = 1,4-naphthalenedicarboxylate and dabco = 1,4-diazabicyclo[2.2.2]octane) has a tetragonal crystal system, in which the dicarboxylate layer ligands (ndc) link to the dicopper clusters to form two-dimensional square lattices, which are connected by amine pillar ligands (dabco) at the lattice points. The selective modulation of one of the coordination modes (ndc–copper) with acetic acid as the modulator resulted in the formation of nanocrystals with a square-rod morphology. The electron diffraction pattern of individual nanorods revealed a correlation between

the anisotropic crystal morphology and the tetragonal framework system; the major axis of the nanorod was coincident with the [001] direction of the framework. Therefore, the coordination mode of dabco–copper in the [001] direction is the more preferable interaction for crystal growth than the coordination mode of ndc–copper in the [100] direction. The ndc–copper interaction, which forms the two-dimensional layer, was impeded by the presence of acetic acid as the modulator because both ndc and acetate have the same carboxylate functionality. Therefore, the selective coordination modulation method enhanced the relative crystal growth in the [001] direction. Interestingly, transmission electron microscopy (TEM) time course analysis of this anisotropic crystal growth revealed an aggregation-mediated crystal growth mechanism where the modulator adsorbs onto specific faces of nanocrystals, thus coding for a subsequent aggregation process. Such oriented attachments are known to occur for the kinetically controlled regime in the presence of stabilizing additives.[49] Figure 5 illustrates the mechanism proposed by the authors for the formation of the $[Cu_2(ndc)_2(dabco)]$ nanorods. The growth process of nanocubes is a consequence of nanoparticle aggregation-mediated crystal growth. The selective coordination modulation on the (100) surfaces of the nanocubes induces the oriented attachment leading to growth of nanorods in the [001] direction.

Do *et al.* demonstrated the synthesis of $[Cu_2(ndc)_2(dabco)]$ with cubic and sheet-like morphologies by simultaneously modulating both copper–ndc and copper–dabco coordination modes.[50] In addition to the monocarboxylic acid that competes with ndc for the coordination of copper, the authors cunningly added amines containing a nitrogen atom with a lone pair capable of impeding the coordination between copper and dabco. As a result, both [100] and [001] directions of the crystal growth could be regulated to form nanocubes using both modulators, nanosheets using only the amine (pyridine), and nanorods using only the acetic acid.

A crucial consequence of the competitive interaction between the coordination mode used to construct the framework and the modulator–metal center is the reduction of the nucleation rate. This feature makes possible the formation of highly crystalline nanocrystals even under kinetically controlled regime where the fast nucleation would lead to poorly crystalline crystals in the absence of a modulator.

On the basis of these considerations, Diring *et al.* developed a strategy for the multiscale synthesis of PCP combining the coordination modulation method with the microwave-assisted synthesis, two apparently antagonistic conditions.[51] On one hand, microwave-assisted heating considerably accelerates nucleation and crystal growth processes, providing phase-pure materials with a homogeneous size distribution. On the other hand, a high concentration of monocarboxylic acid additive effectively slows down the reaction rate of carboxylate-based PCPs through the stabilization of the monomer precursors, thus allowing the formation of highly crystalline materials. The size of the cubic framework $[Cu_3(btc)_2]$ could be successfully tuned from 20-nm globular particles up to 2-μm cubic crystals through the modulation effect the *n*-dodecanoic acid as additive.

As summarized in Figure 6, increasing the concentration of monocarboxylic acid modulator unambiguously leads to the increased mean size of the resulting crystals (variation of *r* in Figure 6; *c* is the global concentration of reactants).

This tendency, which has already been observed with polymer additives,[52] is in opposition with conventional methods for tuning the crystal size, where higher concentrations of additives usually yield smaller crystals because of the efficient suppression of the framework extension. In this case, the monocarboxylic acid is expected to
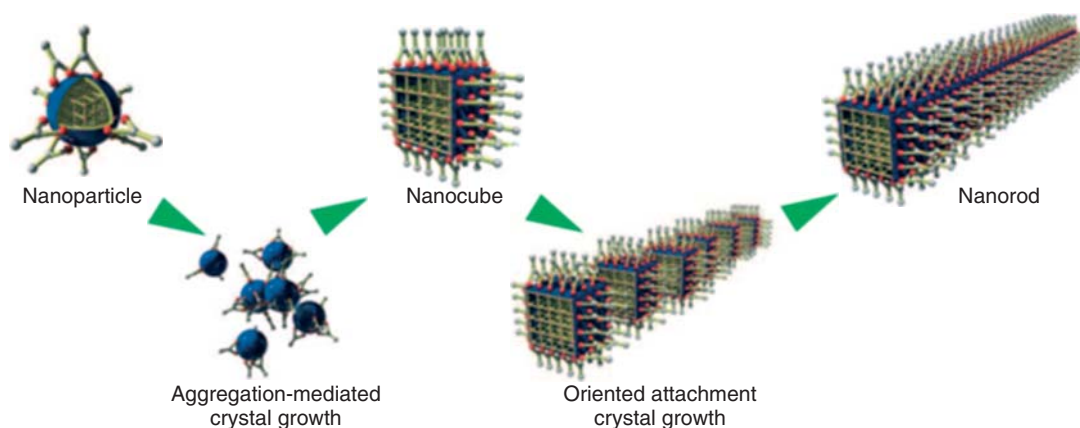

Nanoparticle   Nanocube   Nanorod

Aggregation-mediated crystal growth   Oriented attachment crystal growth

Figure 5 Proposed growth mechanism for $[Cu_2(ndc)_2(dabco)]$ nanorods. (Adapted with permission from Ref. 48. Copyright (2007) American Chemical Society.)
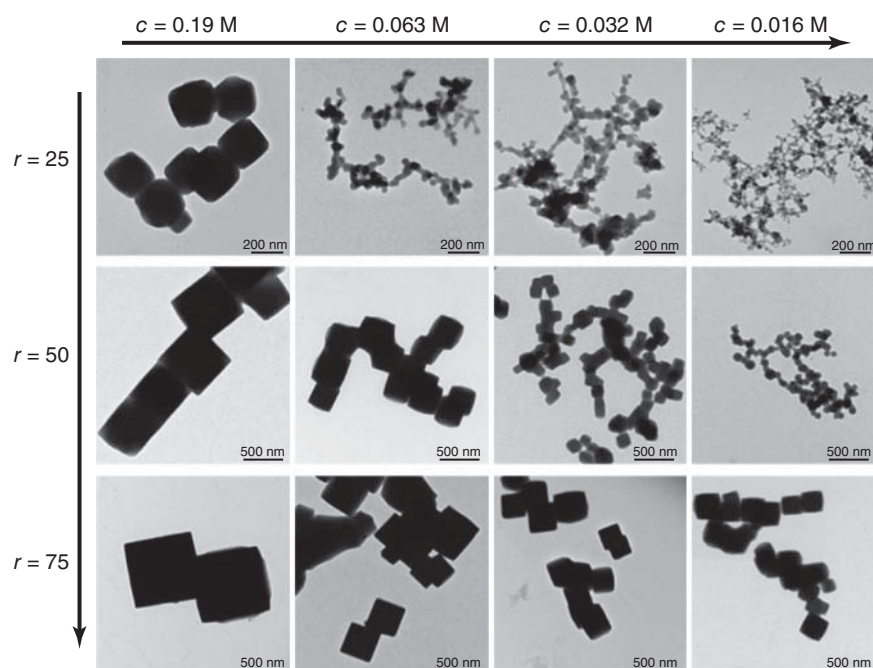
Figure 6 TEM images of samples obtained with various concentrations of dodecanoic acid and benzene-1,3,5-tricarboxylic acid. All samples were prepared under microwave irradiation (140 °C, 10 min). (Adapted with permission from Ref. 51. Copyright (2010) American Chemical Society.)

efficiently influence the nucleation process by creating a competitive situation for the complexation of copper(II) cations, thus decreasing the oversaturation of the precursor materials. Consequently, although the microwave-assisted heating is known to drastically increase the rates of the nucleation and crystal growth processes, high concentrations of additive, however, provide a slow nucleation (fewer nuclei) of the $[Cu_3(btc)_2]$ framework. A smaller number of crystals are indeed growing in line with the persistent nucleation during the heating process, leading to larger crystals with greater size polydispersity. With lower concentrations of the modulator, the nucleation occurs faster. A large number of nuclei are formed and they rapidly grow at the same time, while the available reagents are quickly depleted, affording smaller crystals with homogeneous size distribution. The correlation between the sorption properties and crystallinity of the nanoparticles indicated that the crystallinity of the obtained nanocrystals was comparable to that of bulk crystals obtained from optimized solvothermal methods. It is worth noting that although the excessive stabilization of the PCP precursor (at high modulator concentration) is inadequate for the formation of nanocrystals, it can be of interest for the synthesis of phase-pure sample containing PCP single crystals large enough for single-crystal experiment.[53]

Another example of the beneficial effect of the association of coordination modulation method with the microwave process was reported by Sakata *et al*. who controlled the crystal size and morphology of the zinc framework $[Zn_2(ndc)_2(dabco)]$.[54] Nanosized rod-shaped crystals were successfully synthesized under microwave condition with lauric acid as the modulator. Powder X-ray diffraction measurements and thermogravimetric analysis indicated that the nanocrystals maintain high crystallinity even after miniaturization into nanoscale. Interestingly, the conventional heating procedure using an oil bath with modulators did not give any nanosized crystals but rather resulted in the formation of micrometer-sized crystals. This is because the nucleation process was not accelerated enough to give the nanocrystals. Microwave heating was, therefore, essential to give rapid nucleation of the crystals. On the other hand, the microwave treatment without modulators gave no precipitation. This result indicates that nucleation of this framework system was too fast and that all starting materials were consumed to produce excessively small nuclei that remain in suspension. Here again, the complementary effect of the microwave treatment and coordination modulation method is critical for obtaining both nanosized and highly crystalline PCP crystals. By guaranteeing the production of a high amount of nuclei, microwave process makes the modulation strategy generalizable for the production of PCP nanocrystals with crystal systems for which the low nucleation rate would not permit the success of the coordination modulation under conventional heating.