

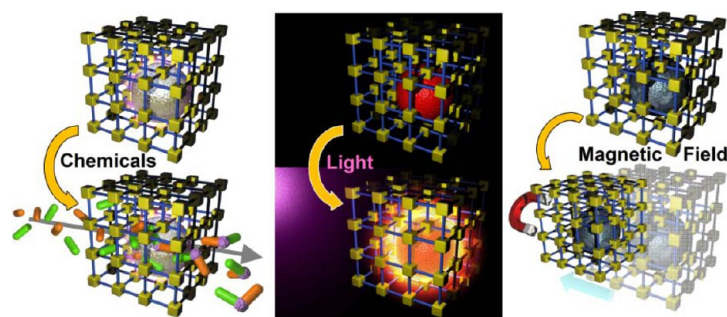
Using Functional Nano- and Microparticles for the Preparation of Metal–Organic Framework Composites with Novel Properties

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CONSPECTUS



A critical materials challenge over the next quarter century is the sustainable use and management of the world's natural resources, particularly the scarcest of them. Chemistry's ability to get more from less is epitomized by porous coordination polymers, also known as metal–organic frameworks (MOFs), which use a minimum amount of material to build maximum surface areas with fine control over pore size. Their large specific surface area and tunable porosity make MOFs useful for applications including small-molecule sensing, separation, catalysis, and storage and release of molecules of interest. Proof-of-concept projects have demonstrated their potential for environmental applications such as carbon separation and capture, water purification, carcinogen sequestration, byproduct separation, and resource recovery. To translate these from the laboratory into devices for actual use, however, will require synthesis of MOFs with new functionality and structure.

This Account summarizes recent progress in the use of nano- and microparticles to control the function, location, and 3D structure of MOFs during MOF self-assembly, creating novel, hybrid, multifunctional, ultraporos materials as a first step towards creating MOF-based devices. The use of preformed ceramic, metallic, semiconductive, or polymeric particles allows the particle preparation process to be completely independent of the MOF synthesis, incorporating nucleating, luminescent, magnetic, catalytic, or templating particles into the MOF structure. We discuss success in combining functional nanoparticles and porous crystals for applications including molecular sieve detectors, repositionable and highly sensitive sensors, pollutant-sequestering materials, microfluidic microcarriers, drug-delivery materials, separators, and size-selective catalysts. In sections within the Account, we describe how functional particles can be used for (1) heterogeneous nucleation (seeding) of MOFs, (2) preparation of framework composites with novel properties, (3) MOF positioning on a substrate (patterning), and (4) synthesis of MOFs with novel architectures.

Introduction

Self-assembly offers a straightforward approach to build highly architected ordered porous materials without the need for external manipulation. Metal–organic frameworks

(MOFs), also called coordination polymers (CPs),¹ represent an important class of ultraporos crystalline materials originated through the self-assembly of polydentate bridging ligands (usually carboxylate, sulfonate, or phosphonate)

coordinated by inorganic centers (metal ions or metal-ion clusters) resulting in the formation of well-defined low density networks.² The vast combination of ligands, presenting different molecular functionalities and architectures, with inorganic nodes offers a versatile methodology for the preparation of porous networks with unique chemical and physical properties.^{3–5} Despite the versatility of the technique, the need to obey the chemistry coordination rules superimposes limitations on the successful combination of both ligands and inorganic centers. These rules could be considered a barrier if particular properties are required to achieve specific functionalities. However, once the building blocks (ligands and inorganic nodes) for the framework construction are selected, additional strategies involving exogenous species (species that are not involved in the framework formation) can be used to impart new functionalities to the porous crystals that cannot be easily obtained from the MOF alone.

Three different strategies can be identified to permanently modify the original functional MOF properties (Figure 1a). The first method involves the use of dopants that modify the inorganic nodes' functional properties without changing the coordination properties (Figure 1b). A meaningful example is provided where lanthanide metal ions are used as dopants;^{6,7} the resulting MOFs show light emitting properties, and they can be efficiently employed for device fabrication based on stimuli-responsive luminescent properties.⁶ The second strategy is based on ligands with functional groups that can be used for subsequent chemical grafting (Figure 1c). An example is the use of amino functionalized ligands that can covalently bond a luminescent dye (e.g., fluorescein isothiocyanate).⁸ This functionalization has been successfully used for sensing applications.⁹ A third approach is to entrap functional molecules, nano- or micro-species, within the framework hence forming the so-called framework composites (FCs, Figure 1d).^{10,11} Alternatively, functional particles can be grown within preformed MOFs in a *two-step approach* (Figure 1e); different examples of MOFs infiltrated with nanoparticle precursors were proposed by Fisher's group who pioneered this important research field.¹² An alternative route is based on preformed particles that can be added into the MOF precursor solution exploiting the self-assembly process originating the porous framework using a *one-pot approach* (Figure 1f).¹¹

In this Account, we focus on the latter approach (Figure 1f), which takes advantage of functional nano- and microparticles to impart either new functional properties or novel architectures into MOFs. The use of preformed ceramic,

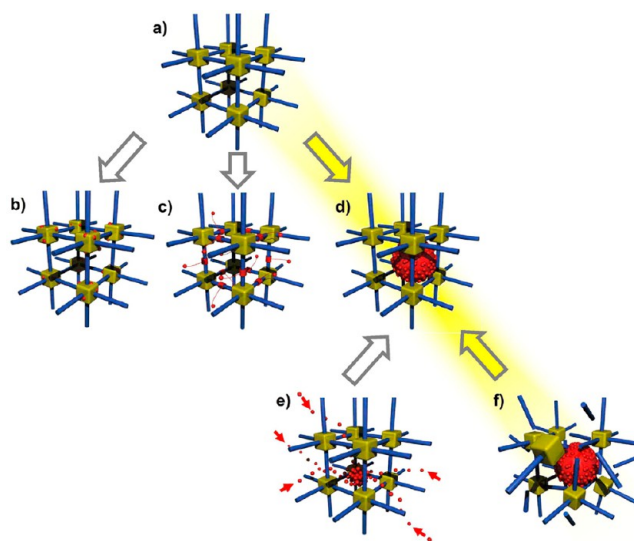


FIGURE 1. Various strategies to functionalize MOFs (a): incorporation of dopants in the coordination centers (b), chemical grafting on the functional MOF ligands (c), and entrapment of functional particles or molecules within the framework (d). Strategies to embed particles within the framework (e, f) using postprocessing functionalization (e, impregnation or infiltration) or embedding the particles during the self-assembly process (one-pot approach, f).

metallic, semiconductive, or polymeric particles allows the particle preparation process to be completely independent of the MOF synthesis, hence allowing the exploitation of nucleating, luminescent, magnetic, catalytic, or templating particles for the MOF technology. The success of combining functional nanoparticles and porous crystals was proven with a variety of applications such as molecular sieve detectors,¹¹ repositionable and highly sensitive sensors,^{13,14} pollutant sequestrators,¹⁵ microcarriers in microfluidics,¹⁶ drug delivery materials,^{17,18} separators,^{19,20} and size selective catalysts.²¹ This Account is organized into four sections describing how functional particles can be used for (1) heterogeneous nucleation (*seeding*) of MOFs, (2) preparation of FCs with novel properties, (3) MOF positioning on a substrate (*patterning*), and (4) synthesis of MOFs with novel architectures.

Nano- and Microparticles for Seeding

In addition to the research efforts creating novel MOF configurations and perfecting MOF synthesis, there is a growing interest in synthesis methods that can enhance MOF applicability on a larger scale. These techniques aim to create the basis for MOF mass production and the development of MOF-based devices. Research goals in such areas include precise control over MOF nucleation and growth, as well as the development of procedures to induce MOF formation on specific substrates.^{11,22} Seed-mediated MOF

synthesis potentially satisfies both of these purposes.²³ Traditional seeding approaches involve the homogeneous nucleation of MOF crystals by means of presynthesized nanocrystals of the same target MOF. The technique proved successful in the preparation of continuous MOF membranes and films on flat substrates. Horcajada et al.²⁴ used a seed mediated technique to form optical-quality and flexible thin films of MIL-89 on silicon substrates that swell when adsorbing certain molecules, such as water; the resulting films showed humidity-dependent volume, thickness, and refractive index. More recently, Hu et al.²⁵ and Nan et al.²⁶ developed protocols for the formation of continuous MIL-53 and MIL-96 membranes on porous inorganic supports (Al_2O_3). This was achieved by functionalizing the substrates with nanoseeds of the corresponding MOF. The membranes showed differential permeability toward certain gases, as well as high selectivity for dehydration of the azeotrope of ethyl acetate (EAC) aqueous solution by pervaporation.

Since the seeds themselves are nanocrystals of the target MOF, the homogeneous nucleation approach is inherently constrained to the characteristics and potential limits of the synthesis of the corresponding MOF. In fact, the low yield of the seed synthesis might restrict the large-scale applicability of this technique. Alternatively, an approach based on the use of readily available heterogeneous nano- and microspecies capable of seeding MOFs offers additional degrees of freedom.

Indeed it has been shown that using heterospecies to promote MOF formation can alter the observed kinetics of MOF crystallization.^{11,22} As a consequence, heterogeneous seeds can be described as crystallization “facilitators”,²⁷ in the sense that they not only can trigger MOF formation but also can promote faster MOF growth. Either dispersed in solution or coupled to a substrate, these species are capable of crystallizing MOFs in the presence of conventional MOF precursors by altering the usual kinetics of MOF formation.

In 2011, Buso et al.²² demonstrated that the presence of SiO_2 nanoparticles can efficiently promote $\text{Zn}_4\text{O}(\text{bpdc})_3$ (MOF-5) nucleation when the nanoparticles are modified with amino and carboxyl groups. The concept combines functional groups previously used by Fischer's group^{30,31} to control the MOF growth on functionalized flat surfaces with the higher surface areas provided by the nanoparticle system. The nanoparticles can be synthesized on the order of grams using a conventional sol–gel route,³² and their chemical composition can be readily customized. The authors reported a 10-fold increase of the MOF-5 formation, with MOF microcrystals of homogeneous size forming within a few

hours. The nucleation driven kinetics allowed for the preparation of small MOF crystals with narrow size distribution, without the use of growth limiting surface agents. Advantageously, the particles can be deposited on substrates that do not need to be prefunctionalized, thus promoting localized MOF-5 formation.²² Subsequently, Xie et al.²⁸ adopted a similar protocol using amino-modified Al_2O_3 particles (0.5 μm diameter) to grow ZIF-8 membranes on alumina substrates. The authors created continuous membranes by controlling the density of seed particles on the substrate, showing remarkable H_2 permeance and H_2/N_2 selectivity of 15.4. In 2012, Lee et al. used commercial carboxyl-terminated silica particles for the preparation of core–shell Gd and Er based MOFs,³³ while Liu et al.²⁹ used micro-sized zeolite crystals, which were broken into nanosized rods during the hydrothermal process, as seeds for the formation of several MOFs, MIL-100 (Cr), MIL-104 (Co), and MIL-53 (Fe).

In 2011, Falcaro et al.¹¹ demonstrated that heterogeneous seeds can also be formed within the MOF-5 precursor solution itself and subsequently trigger the fast MOF formation; the formation rate is three times faster than that usually observed for MOF-5 when synthesized by the conventional DEF-based solvothermal route.³⁴ The addition of a phosphate-rich block copolymer surfactant (Pluronic F-127) into the conventional MOF precursor solution stimulates the formation of zinc phosphate microparticles (named desert rose microparticles, DRMs) within the first minute of synthesis.³⁵ DRMs can advantageously be separated from the reaction batch and used as external seeds to promote MOF-5 formation on a variety of substrates, irrespective of the substrate chemical nature or geometric configuration. An example reports the growth of MOF-5 on a seeded alumina substrate where MOF is only grown on the seeded area (Figure 2i,j).¹¹

Nano- and Microparticles for New Functionalities

The incorporation of nano- and microparticles provides additional functionalities such as magnetic, luminescent,³⁶ and catalytic^{37,38} properties to the inherent MOF properties. Initial research in combining functional guest species into the MOF framework mainly focused on incorporating particles³⁹ or molecules (e.g., polyoxometalates,⁴⁰ porphyrins,³⁶ and drugs⁴¹) into the framework after crystallization of the MOF structure (*postfunctionalization*). Interest in *one-pot* methods for the introduction of stimuli-responsive guests has recently increased. The advantage of preparing framework composites

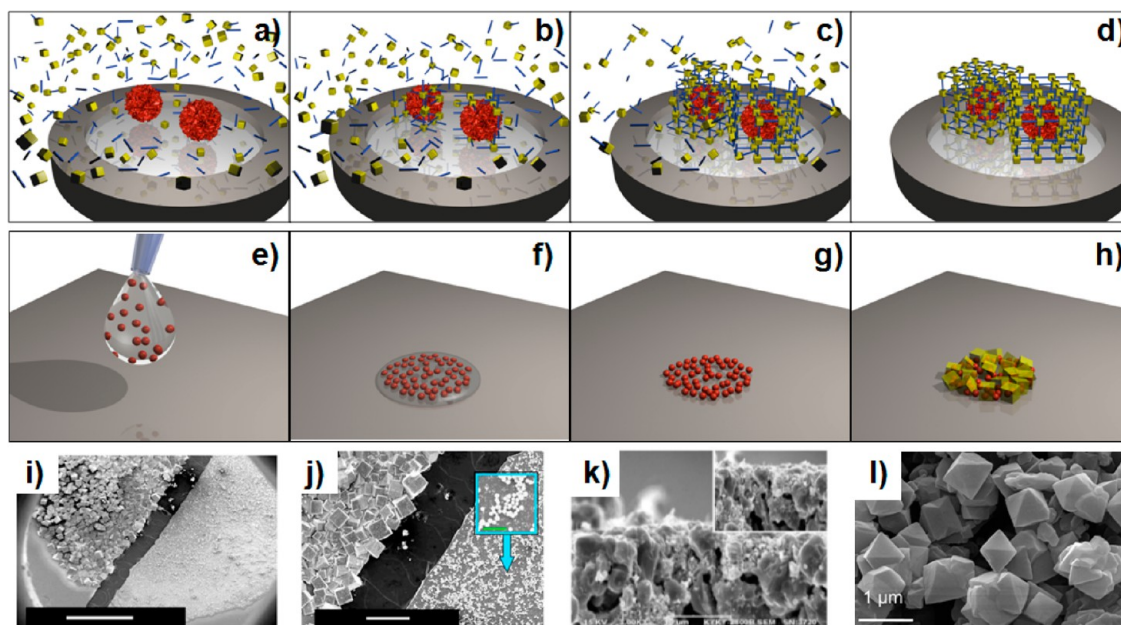


FIGURE 2. Schematic of the seeding approach where the MOFs grow around the nano- or microparticles (a–d). Using this approach, Falcaro and Buso controlled the MOF growth in desired locations (e–h).^{11,22} Examples of MOF growth using the seeding technique on α -hopeite (i, j; MOF-5),¹¹ alumina (k; ZIF-8),²⁸ and zeolites (l; MIL-101)²⁹ particles. The inset in panel j shows the α -hopeite microparticles, while that in panel k details the ZIF-8 growth on NH₂-functionalized Al₂O₃ particles.

(FCs) via a *one-pot* process is that the MOF assembles around the functional particles, permanently encapsulating them within the porous host to be used for sensing, repositioning, or catalysis. The first crystalline MOF composite materials prepared via a one-step process were reported by Park's group where they added multiwalled carbon nanotubes (MWCNTs) into a DMF precursor solution of MOF-5 (Figure 3a,b).⁴² The obtained composite materials had higher surface areas, a 50% increase in hydrogen storage capability, and improved stability in ambient conditions compared with the pristine MOF-5.^{42,43}

The first study proposing a versatile protocol to carry a variety of extrinsic functionalities within MOF crystals was proposed by Falcaro et al.; the authors synthesized highly porous inorganic microparticles in solutions containing functional metallic, semiconducting, and polymeric nanoparticles.¹¹ Taking advantage of the exceptional nucleating properties of the microparticles, the positioning of an extrinsic functionality (e.g., metallic, semiconducting, and polymeric nanoparticles) within the center of MOF-5 cubic crystals was achieved. For the first time, the positioning of a particle clearly presenting semiconductive properties (quantum dots (QDs) with bright luminescence) localized in the MOF-5 core was successfully demonstrated. By adjusting the surface chemistry of the functional nanoparticles, Buso et al. demonstrated a one-pot synthesis method for the

preparation of a luminescent sensor based on QDs.⁴⁴ Alternatively, by directly adjusting the surface chemistry of the functional nanoparticles, Buso et al. demonstrated a one-pot synthesis method for the preparation of a luminescent sensor based on semiconductive particles (i.e., QDs). In both cases, the MOF-5 framework surrounding the QDs forms a molecular gate, only permitting small thiols through the uniform crystalline porous structure. Large molecules were prevented from entering the FC and were therefore unable to quench the QD luminescence. Another application with particles presenting an optical response was elegantly proposed by Sada's group;¹⁴ the authors formed a surface-enhanced Raman scattering (SERS)-active FC by growing MOF-5 on functionalized high-aspect-ratio gold nanorods (AuNRs). Sada et al. showed how the AuNRs within the MOFs maintain the surface plasmon effect and SERS activity and demonstrated how the functional properties of the framework composite could be used for in situ monitoring of molecular diffusion.¹⁴

Industrially promising FCs were obtained by incorporating magnetic nanoparticles and nanofibers into the MOF structures in order to allow control over the position of the particles.⁴⁵ Sweigart's group pioneered the field of combining Fe₂O₃ nanoparticles with coordination polymers,⁴⁶ with the [(η^4 -quinone)Mn(CO)₃][−] anion (QMTC), the synthesis of Fe₃O₄ decorated by [_n{Cd(QMTC)₂(dmsO)₂}]_n and

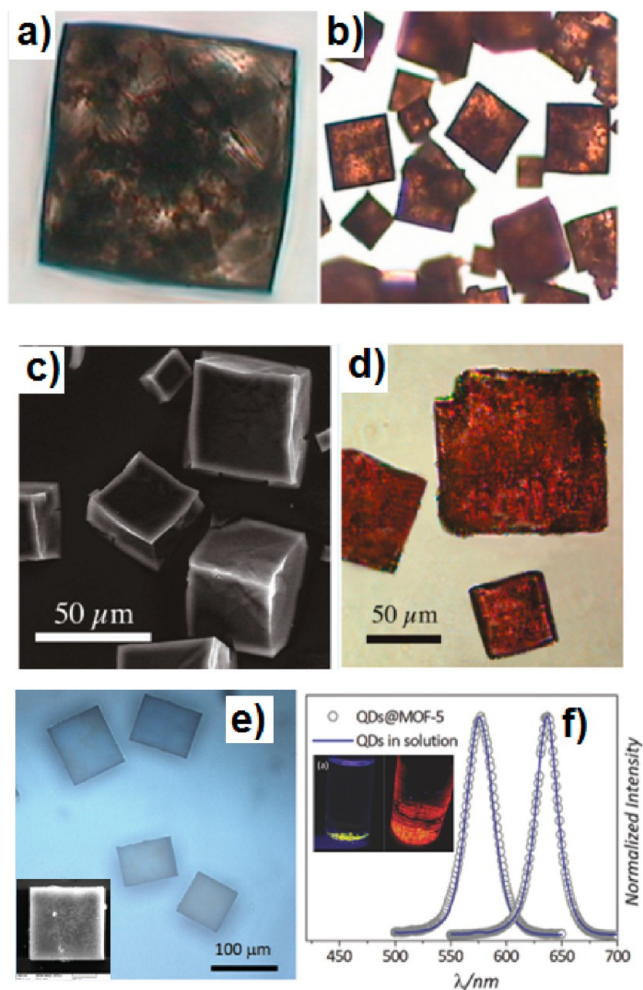


FIGURE 3. MOF-5 embedding functional nanomaterials such as multi-walled carbon nanotubes (a, b),⁴² gold nanorods (c, d)¹⁴ and quantum dots (e, f).³⁵

$\{[Mn(QMTC)_2(dmsO)_2]_n\}$ coordination polymers was shown (Figure 4). Ke et al. prepared magnetic HKUST-1 MOF nanocomposites in a one-pot process with Fe_3O_4 nanoparticles. The composite was loaded with a drug infiltrated in the porous MOF framework, and the magnetic properties were utilized to control the position of the porous composite material for localized drug delivery.^{47,48} Lohe et al. further developed the drug delivery system using superparamagnetic AIOH(ndc) (DUT-4), AIOH(bpdc) (DUT-5), and HKUST-1 composites that heat up when placed in an external alternating magnetic field, hence triggering the release of the drug from the heated framework.⁴⁹

Falcaro et al. demonstrated magnetic FCs for other industrial applications such as repositionable sensing¹³ and as a recoverable vessel to sequester carcinogenic molecules.¹⁵ Cobalt nanoparticles were added to the MOF-5 precursor solution to form the magnetic FC (MFC).⁴⁵ The Co FCs were

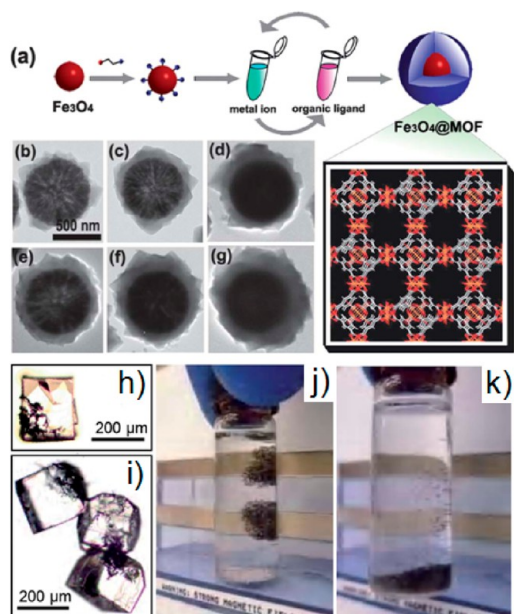


FIGURE 4. Schematic of the step-by-step strategy used for the preparation of MOFs embedding Fe_3O_4 nanoparticles (a) with TEM showing growth of the MOF around the magnetic core (b–g).⁴⁸ Optical image of framework composite crystals based on $NiFe_2O_4$ (h) and $CoFe_2O_4$ (i) fibers and MOF-5; the proximity of a magnet attracts the framework composites (j) that can be released by moving away the magnet (k).¹⁵

collected with small magnets and doped with fluorescein isothiocyanate. The luminescence was gradually quenched upon infiltration into the framework of an amine (1,4-diaminobenzene) hence demonstrating the potential to use these multifunctional FCs for position-controlled sensing applications.¹³ Magnetic field responsive MOF-5 FCs were also obtained using superparamagnetic nanofibers; the nanocomposites were tested for the sequestration of a carcinogenic molecule (1,2-benzanthracene) and subsequently collected and removed from solution utilizing their magnetic properties.¹⁵ Based on the $\pi-\pi$ interactions, the ability to collect polycyclic aromatic hydrocarbons (PAHs) was predicted by Allendorf et al.⁵⁰ Huo et al. have presented a similar concept testing a FC based on MIL-101 and silica-coated Fe_3O_4 microparticles for sequestration of different PAHs.⁵¹

With the presynthesized nanoparticle route to prepare FCs, there has been a flurry of recent activity demonstrating the ability to use these materials in various applications. Hupp's group encapsulated a variety of preformed functional nanoparticles into $Zn[2\text{-methylimidazolate}]_2$ (ZIF-8) frameworks.²¹ They produced materials with catalytic, magnetic, and optical properties by using polyvinylpyrrolidone as a nonionic amphiphilic polymer to control the size and shape of the nanoparticles.²¹ Liu et al.⁵² grew HKUST-1 on

carboxy functionalized silicon nanowires combining semiconductors with MOFs.

Nano- and Microparticles for MOF Positioning

Advancements in technologies to position MOFs in precise locations are crucial for the fabrication of integrated devices that could benefit from the ultraporos framework properties. A recent review by Falcaro et al.⁵³ has detailed the methods available to prepare patterned MOF materials for potential use in miniaturized devices. Of the known approaches for positioning MOFs, the use of nano- and microparticles to pattern MOF materials represents one of the more promising methods. Functional particles offer two different routes for MOF positioning.

The first method takes advantage of heterogeneous nucleation for the permanent localization of MOFs on a substrate. Efficient seed deposition in targeted regions offers the ability to use the particles to locate the MOF nucleation and growth in preferential areas. This approach has been demonstrated by Falcaro et al. using functionalized and porous ceramic particles, respectively.^{11,22} Zinc phosphate based seeds, deposited in micrometer sized wells, provide an efficient route to grow and confine the MOFs in precise locations; seeds nucleate the MOFs, while the wells confine and direct MOF crystal growth (Figure 5).

The second method involves the controlled localization of preformed MOFs incorporating magnetic particles, where an external magnetic field is used to position single MOF particles in precise locations. Falcaro et al.¹⁶ showed how a 50 μm amino-functionalized mixed component MOF cubic particle can be moved and positioned within microfluidic circuits. This method could potentially open up the opportunity to exploit the functional MOF properties “on demand” in confined volumes. Small magnets could be used to position MOFs with embedded ferromagnetic or superparamagnetic particles. The magnetic positioning can be combined with secondary growth to increase the amount of MOF in a confined location.¹³

A significant advantage of these methods is that the MOF synthesis is independent of the surface chemistry of the substrate and the use of magnetic particles offers the ability to use substrates for MOF type devices that cannot withstand the MOF synthetic conditions.

Nano- and Microparticles for New 3D Architectures

Achieving practical use of MOFs in industry requires the shaping of materials at the macroscopic scale. Indeed, as previously discussed, significant effort has focused on

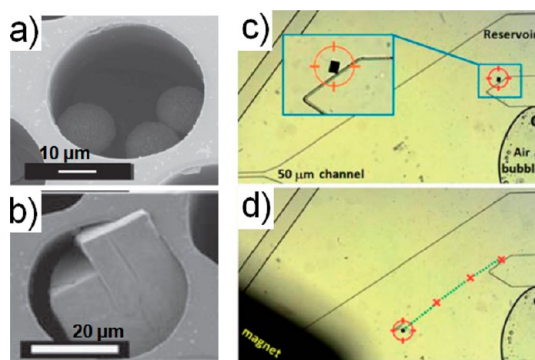


FIGURE 5. SEM picture of a well seeded with zinc phosphate based seeds (a) and the corresponding MOF-5 growing due to the heterogeneous nucleation (b).¹¹ Optical image of a microfluidic circuit with a mixed component metal–organic framework encapsulating cobalt nanoparticles (c); the porous crystal can be positioned using an external magnet (shadow in the corner) (d).¹⁶

fabricating MOF thin films or patterns on substrate supports. The next challenge is to construct three-dimensional (3D) macroscopic architectures comprised of MOF crystals. In particular, architected shapes that feature macropores would give further opportunity to advance the potential applications of MOFs. Such a collaborative alliance between the intrinsic microporosity of MOFs and the structured macroporosity, namely hierarchical porous systems, will induce the benefits for applications in separation, heterogeneous catalysis, ion/electron transport and photonic devices. Emerging research into hierarchical MOF manufacturing has recently been reported with the majority of studies relying on the use of nano- and microparticles as structure-directing and templating agents as shown in Figure 6.

The key concept for the creation of 3D macroscopic architectures is to spatially control the MOF crystallization nucleation and growth processes and thus to spatially regulate the self-assembly process between precursor metal ions and organic ligands in solution. Ameloot et al.⁵⁴ beautifully demonstrated such spatial control of self-assembly by using immiscible solvents containing metal ions and organic ligands. Aqueous microdroplets containing copper acetate were formed in the flow of water-immiscible alcohol containing H_3BTC . In this situation, the copper acetate and the organic ligands were allowed to only react together at the liquid–liquid interfaces, which resulted in the fabrication of hollow sphere architectures of $\text{MOF Cu}_3(\text{BTC})_2$. The resulting internal large void was used to entrap guest species, and the size-selective permeability of MOF capsules was demonstrated, confirming the defect-free formation of the hollow architectures.

The synthesis of MOF-based hollow architectures was also demonstrated using polystyrene microparticles as

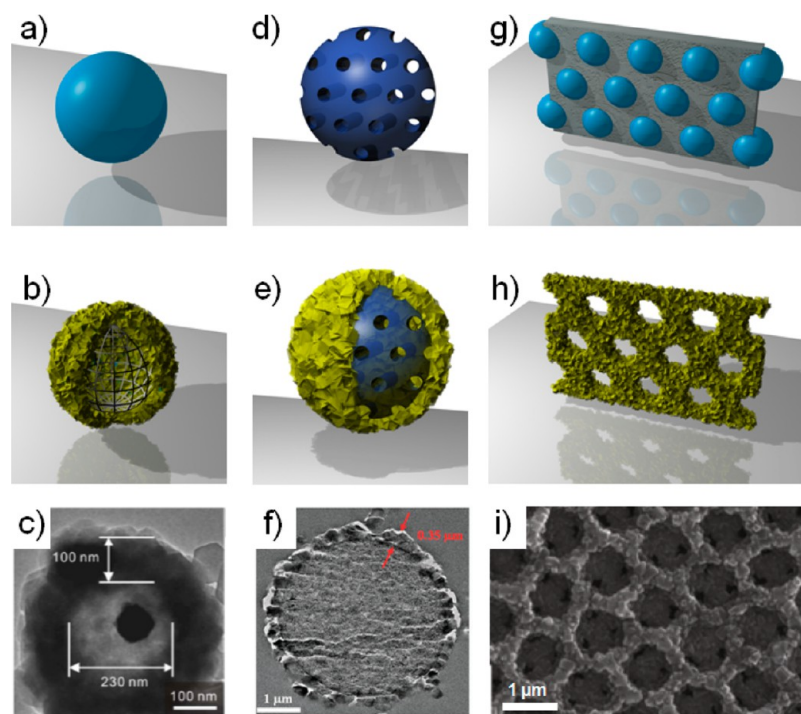


FIGURE 6. Use of carboxylated functionalized polystyrene nanoparticles (a); as the MOFs are formed on the surface, the sacrificial-templating particle is dissolved using a proper solvent (b).⁵⁵ With this method yolk–shell structures can be fabricated as presented in the TEM picture of a Pd nanoparticle contained in a ZIF-8 shell (c).⁵⁶ Mesoporous particle (d) used as scaffold and decorated with ZIF-8 (e) as presented in the SEM cross section (f).⁵⁹ Polymeric particles embedded in an alumina matrix prepared by sol–gel method (g); the subsequent removal of the templates and the pseudomorphic replication allow for the transformation from a ceramic to a MOF (Al(OH)(ndc) (h). The SEM (i) illustrates the perfect order of the achieved MOF inverse opal.¹⁹

templates, followed by chemical etching of the template.⁵⁵ The key for success was to use carboxylate-terminated polystyrene particles for the entrapment of zinc ions on their surfaces, which act as heterogeneous nucleation centers reacting with 2-methylimidazole for the formation of ZIF-8 crystals around the particles. The resulting core–shell particles, were simply etched with DMF, dissolving the core polystyrene, leading to ZIF-8 hollow architectures (Figure 6a,b). This sacrificial template approach was further implemented for the fabrication of interesting yolk–shell architectures.⁵⁵ By this technique, nanocrystals of palladium covered with Cu₂O were used as a template for the growth of ZIF-8 on the clean surface of Cu₂O.⁵⁶ Spontaneous growth and simultaneous etching process of Cu₂O during the formation of ZIF-8 gave yolk–shell architectures of Pd@ZIF-8 (Figure 6c). Interestingly, this unique architecture provided size-selective catalytic performance; the ZIF-8 shell worked as size-selective sieve for gas-phase hydrogenations based on Pd nanocrystals embedded as the yolk.⁵⁶ This approach provides a great example of the importance of architecturing MOFs to achieve improved material properties.

Alternative to the soft-templating approach for architecturing MOFs, particles of hard materials can be used for the fabrication of MOF composites with core–shell architectures. Indeed, crystalline alumina macroparticles^{57,58} or mesoporous silica particles⁵⁹ (Figure 6d–f) were used as hard templates or as supports for the synthesis of ZIF-8 as the shell materials. This composite approach allowed for the manufacture of 3D MOF architectures by simply assembling these particles into colloidal crystal thin films. Wu *et al.*⁶⁰ and Lu *et al.*⁶¹ separately demonstrated this approach toward the fabrication of photonic devices, which sense the presence of chemical vapors by using polystyrene nanoparticles of 330 nm and silica nanoparticles of 390 nm, respectively. The opals were alternately soaked into the solutions of copper acetate and H₃BTC, leading to the deposition of Cu₃(BTC)₂ nanocrystals on the surface of the colloidal crystals.

Three-dimensional MOF architectures without a solid support were fabricated using the above-mentioned sacrificial template approach. Wu *et al.*⁶² synthesized an inverse-opal macroscopic structure based on MOF nanocrystals by dissolving the polystyrene templates from the MOF

composite photonic thin film described above. The resulting highly ordered 3D architectures maintained the sensing ability for chemical vapors as photonic devices. More recently, Reboul et al.¹⁹ proposed a versatile synthetic protocol for 3D MOF architectures using pseudomorphic replication, the morphologic replacement of a shaped sacrificial metal oxide used as both a metal source and as an architecture-directing agent by an analogous MOF architecture (Figure 6g–i). The key element of this method was spatio-temporal synchronization of the metal oxide dissolution and the MOF crystallization, which allowed the preservation of very fine morphological details of parent metal oxide architectures. Three different MOF architectures based on an aluminum framework (Al(OH)(ndc)), 2D honeycomb structures, 3D inverse-opal structures, and 3D randomly structured aerogels, were synthesized using corresponding alumina parent phases. These 3D randomly structured MOF aerogels possessing hierarchical porosities synergistically enhanced the material's selectivity and mass transfer for water/ethanol separation. Since the fabrication of 3D architectures based on metal oxide is widely applied, this emerging method of MOF processing into 3D architectures allows the processing of MOF materials in almost any desired shape.

Concluding Remarks and Prospects

In this Account, we have demonstrated multiple ways to combine functional particles into MOF architectures, which enable control over the synthesis process including growth rate and positioning. The additional advantage of incorporating functional micro- or nanoparticles into the frameworks creates advanced composite materials, which can be used for a host of applications including sensing, separation, catalysis, and storage and release. Several methods of fabrication have also been presented including the seeding approach and the construction of 3D hierarchical MOF structures. These techniques will potentially be used in the future to assemble state-of-the-art engineering devices where the ultimate fabrication method will be fast, cheap, and versatile, offering the combined functionality of the MOF and the functional particles.

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Paolo Falcaro, Ph.D. in Material Engineering, completed his Postdoctoral Fellowship at CSIRO. He currently works as a research scientist at CSIRO (Australia) and an Australian Research Council Discovery Early Career Research Fellow. Paolo Falcaro's research group investigates self-assembled porous materials and patterning techniques to control functional material location.

FOOTNOTES

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The authors declare no competing financial interest.

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REFERENCES

- Kitagawa, S.; Kitaura, R.; Noro, S. Functional Porous Coordination Polymers. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334–2375.
- Della Rocca, J.; Liu, D.; Lin, W. Nanoscale Metal–Organic Frameworks for Biomedical Imaging and Drug Delivery. *Acc. Chem. Res.* **2011**, *44*, 957–968.
- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705–714.
- Deng, H.; Doonan, C. J.; Furukawa, H.; Ferreira, R. B.; Towner, J.; Knobler, C. B.; Wang, B.; Yaghi, O. M. Multiple Functional Groups of Varying Ratios in Metal–Organic Frameworks. *Science* **2010**, *327*, 846–850.
- Zhao, D.; Timmons, D. J.; Yuan, D.; Zhou, H.-C. Tuning the Topology and Functionality of Metal–Organic Frameworks by Ligand Design. *Acc. Chem. Res.* **2011**, *44*, 123–133.
- Chui, Y.; Yue, Y.; Qian, G.; Chen, B. Luminescent Functional Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 1126–1162.
- Falcaro, P.; Furukawa, S. Doping Light Emitters into Metal–Organic Frameworks. *Angew. Chem., Int. Ed.* **2012**, *51*, 8431–8433.

- 8 Ma, M.; Gross, A.; Zacher, D.; Pinto, A.; Noei, H.; Wang, Y.; Fischer, R. A.; Metzler-Nolte, N. Use of Confocal Fluorescence Microscopy to Compare Different Methods of Modifying Metal–Organic Framework (MOF) Crystals with Dyes. *CrystEngComm* **2011**, *13*, 2828–2832.
- 9 Zhang, L.; Jian, Y.; Wang, J.; He, C.; Li, X.; Liu, T.; Duan, C. Post-Modification of a MOF Through a Fluorescent-Labeling Technology for the Selective Sensing and Adsorption of Ag⁺ in Aqueous Solution. *Dalton Trans.* **2012**, *41*, 10153–10155.
- 10 Müller, M.; Devaux, A.; Yang, C.-H.; De Cola, L.; Fischer, R. A. Highly Emissive Metal–Organic Framework Composites by Host–Guest Chemistry. *Photochem. Photobiol. Sci.* **2010**, *9*, 846–853.
- 11 Falcaro, P.; Hill, A. J.; Naim, K. M.; Jasieniak, J.; Mardel, J. I.; Bastow, T. J.; Mayo, S. C.; Gimona, M.; Gomez, D.; Whitfield, H. J.; Riccò, R.; Patelli, A.; Marmiroli, B.; Amenitsch, H.; Colson, T.; Villanova, L.; Buso, D. A New Method to Position and Functionalize Metal–Organic Framework Crystals. *Nat. Commun.* **2011**, *2*, A237–A244.
- 12 Meilikhov, M.; Yusenko, K.; Esken, D.; Turner, S.; Van Tendeloo, G.; Fischer, R. A. Metals@MOFs – Loading MOFs with Metal Nanoparticles for Hybrid Functions. *Eur. J. Inorg. Chem.* **2010**, 3701–3714.
- 13 Falcaro, P.; Normandin, F.; Takahashi, M.; Scopece, P.; Amenitsch, H.; Costacurta, S.; Doherty, C. M.; Laird, J. S.; Lay, M. D. H.; Lisi, F.; Hill, A. J.; Buso, D. Dynamic Control of MOF-5 Crystal Positioning Using a Magnetic Field. *Adv. Mater.* **2011**, *23*, 3901–3906.
- 14 Sugikawa, K.; Furukawa, Y.; Sada, K. SERS-Active Metal/Organic Frameworks Embedding Gold Nanorods. *Chem. Mater.* **2011**, *23*, 3132–3134.
- 15 Doherty, C. M.; Knystautas, E.; Buso, D.; Villanova, L.; Konstas, K.; Hill, A. J.; Takahashi, M.; Falcaro, P. Magnetic Framework Composites for Polycyclic Aromatic Hydrocarbon Sequestration. *J. Mater. Chem.* **2012**, *22*, 11470–11474.
- 16 Falcaro, P.; Lapiere, F.; Marmiroli, B.; Styles, M.; Zhu, Y.; Takahashi, M.; Hill, A. J.; Doherty, C. M. Positioning an Individual Metal–Organic Framework Particle using a Magnetic Field. *J. Mater. Chem. C* **2013**, *1*, 42–45.
- 17 Lohe, M. R.; Gedrich, K.; Freudenberg, T.; Kockrick, E.; Dellmann, T.; Kaskel, S. Heating and Separation using Nanomagnet-Functionalized Metal–Organic Frameworks. *Chem. Commun.* **2011**, *47*, 3075–3077.
- 18 Ke, F.; Yuan, Y.-P.; Qiu, L.-G.; Shen, Y.-H.; Xie, A.-J.; Zhu, J.-F.; Tian, X.-Y.; Zhang, L.-D. Facile Fabrication of Magnetic Metal–Organic Framework Nanocomposites for Potential Targeted Drug Delivery. *J. Mater. Chem.* **2011**, *21*, 3843–3848.
- 19 Reboul, J.; Furukawa, S.; Horike, N.; Tsotsalas, M.; Hirai, K.; Uehara, H.; Kondo, M.; Louvain, N.; Sakata, O.; Kitagawa, S. Mesoscopic Architectures of Porous Coordination Polymers Fabricated by Pseudomorphic Replication. *Nat. Mater.* **2012**, *11*, 717–723.
- 20 Silvestre, M. E.; Franzreb, M.; Weidler, P. G.; Shekhan, O.; Wöll, C. Magnetic Cores with Porous Coatings: Growth of Metal–Organic Frameworks on Particles Using Liquid Phase Epitaxy. *Adv. Funct. Mater.* **2013**, *23*, 1210–1213.
- 21 Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C. J.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Huo, F. Imparting Functionality to a Metal–Organic Framework Material by Controlled Nanoparticle Encapsulation. *Nat. Chem.* **2012**, *4*, 310–316.
- 22 Buso, D.; Naim, K. M.; Gimona, M.; Hill, A. J.; Falcaro, P. Fast Synthesis of MOF-5 Microcrystals Using Sol-Gel SiO₂ Nanoparticles. *Chem. Mater.* **2011**, *23*, 929–934.
- 23 Bétard, A.; Fischer, A.; Metal/Organic, R. A. Framework Thin Films: From Fundamentals to Applications. *Chem. Rev.* **2012**, *112*, 1055–1083.
- 24 Horcajada, P.; Serre, C.; Grosso, D.; Boissière, C.; Perruchas, S.; Sanchez, C.; Férey, G. Colloidal Route for Preparing Optical Thin Films of Nanoporous Metal–Organic Frameworks. *Adv. Mater.* **2009**, *21*, 1931–1935.
- 25 Hu, Y.; Dong, X.; Nan, J.; Jin, W.; Ren, X.; Xu, N.; Lee, Y. M. Metal–Organic Framework Membranes Fabricated via Reactive Seeding. *Chem. Commun.* **2011**, *47*, 737–739.
- 26 Nan, J.; Dong, X.; Wang, W.; Jin, W. Formation Mechanism of Metal–Organic Framework Membranes Derived from Reactive Seeding Approach. *Microporous Mesoporous Mater.* **2012**, *155*, 90–98.
- 27 Buso, D.; Falcaro, P. Crystallization facilitator useful for promoting and synthesizing crystal growth of a metal-organic framework, comprises a metal or its ionic form, or a compound including a metal, comprising actinides, and/or lanthanides. International Patent WO2011133999-A1, 2011.
- 28 Xie, Z.; Yang, J.; Wang, J.; Bai, J.; Yin, H.; Yuan, B.; Lu, J.; Zhang, Y.; Zhou, L.; Duan, C. Deposition of Chemically Modified α -Al₂O₃ Particles for High Performance ZIF-8 Membrane on a Macroporous Tube. *Chem. Commun.* **2012**, *48*, 5977–5979.
- 29 Liu, S.; Zhang, Y.; Meng, Y.; Gao, F.; Jiao, S.; Ke, Y. Fast Syntheses of MOFs Using Nanosized Zeolite Crystal Seeds In Situ Generated from Microsized Zeolites. *Cryst. Growth Des.* **2013**, *13*, 2697–2702.
- 30 Shekhan, O.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Wöll, C. Step Route for the Synthesis of Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2007**, *129*, 15118–15119.
- 31 Shekhan, O.; Wang, H.; Zacher, D.; Fischer, R. A.; Wöll, C. Growth Mechanism of Metal–Organic Frameworks: Insights into the Nucleation by Employing a Step-by-Step Route. *Angew. Chem., Int. Ed.* **2009**, *48*, 5038–5041.
- 32 Brinker, J. C. *The Physics and Chemistry of Sol-Gel Processing*, Academic Press Inc.: San Diego, CA, 1990.
- 33 Lee, H. J.; Park, J.-U.; Choi, S.; Son, J.; Oh, M. Synthesis and Photoluminescence Properties of Eu³⁺-Doped Silica@Coordination Polymer Core–Shell Structures and Their Calcinated Silica@Gd²⁰³:Eu and Hollow Gd²⁰³:Eu Microsphere Products. *Small* **2013**, *9*, 561–569.
- 34 Stock, N.; Biswas, S. Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composite. *Chem. Rev.* **2012**, *112*, 933–969.
- 35 Buso, D.; Hill, A. J.; Colson, T.; Whitfield, H. J.; Patelli, A.; Scopece, P.; Doherty, C. M.; Falcaro, P. Complete Characterization of α -Höppite Microparticles: An Ideal Nucleation Seed for Metal Organic Frameworks. *Cryst. Growth Des.* **2011**, *11*, 5268–5274.
- 36 Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Luminescent Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
- 37 Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. B. T.; Hupp, J. T. Metal–Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- 38 Dhakshinamoorthy, A.; Garcia, H. Catalysis by Metal Nanoparticles Embedded on Metal–Organic Frameworks. *Chem. Soc. Rev.* **2012**, *41*, 5262–5284.
- 39 Schröder, F.; Fischer, R. A. Doping of Metal–Organic Frameworks with Functional Guest Molecules and Nanoparticles. *Top. Curr. Chem.* **2010**, *293*, 77–113.
- 40 Juan-Alcañiz, J.; Gascon, J.; Kapteijn, F. Metal–Organic Frameworks as Scaffolds for the Encapsulation of Active Species: State of the Art and Future Perspectives. *J. Mater. Chem.* **2012**, *22*, 10102–10118.
- 41 Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J.-S.; Hwang, Y. K.; Marsaud, V.; Bories, P. N.; Cynober, L.; Gil, S.; Férey, G.; Couvreur, P.; Gref, R. Porous Metal–Organic Framework Nanoscale Carriers as a Potential Platform for Drug Delivery and Imaging. *Nat. Mater.* **2010**, *9*, 172–178.
- 42 Yang, S. J.; Choi, J. Y.; Chae, H. K.; Cho, J. H.; Nahm, K. S.; Park, C. R. Preparation and Enhanced Hydrostability and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite. *Chem. Mater.* **2009**, *21*, 1893–1897.
- 43 Yang, S. J.; Cho, J. H.; Nahm, K. S.; Park, C. R. Enhanced Hydrogen Storage Capacity of Pt-loaded CNT@MOF-5 Hybrid Composites. *Int. J. Hydrogen Energy* **2010**, *35*, 13062–13067.
- 44 Buso, D.; Jasieniak, J.; Lay, M. D. H.; Schiavuta, P.; Scopece, P.; Laird, J.; Amenitsch, H.; Hill, A. J.; Falcaro, P. Highly Luminescent Metal–Organic Frameworks Through Quantum Dot Doping. *Small* **2012**, *1*, 80–88.
- 45 Riccò, R.; Malfatti, L.; Takahashi, M.; Hill, A.; Falcaro, P. Applications of Magnetic Metal Organic Framework Composites. *J. Mater. Chem. A* **2013**, *1*, 13033–13045.
- 46 Kim, S. B.; Cai, C.; Sun, S.; Sweigart, D. A. Incorporation of Fe₃O₄ Nanoparticles into Organometallic Coordination Polymers by Nanoparticle Surface Modification. *Angew. Chem., Int. Ed.* **2009**, *48*, 2907–2910.
- 47 Ke, F.; Yuan, Y.-P.; Qiu, L.-G.; Shen, Y.-H.; Xie, A.-J.; Zhu, J.-F.; Tian, X.-Y.; Zhang, L.-D. Facile Fabrication of Magnetic Metal–Organic Framework Nanocomposites for Potential Targeted Drug Delivery. *J. Mater. Chem.* **2011**, *21*, 3843–3848.
- 48 Ke, F.; Qiu, L.-G.; Yuan, Y.-P.; Jiang, X.; Zhu, J.-F. Fe₃O₄@MOF Core–Shell Magnetic Microspheres with a Designable Metal–Organic Framework Shell. *J. Mater. Chem.* **2012**, *22*, 9497–9500.
- 49 Lohe, M. R.; Gedrich, K.; Freudenberg, T.; Kockrick, E.; Dellmann, T.; Kaskel, S. Heating and Separation using Nanomagnet-Functionalized Metal–Organic Frameworks. *Chem. Commun.* **2011**, *47*, 3075–3077.
- 50 Greathouse, J. A.; Ockwig, N. W.; Criscenti, L. J.; Guiling, T. R.; Pohl, P.; Allendorf, M. D. Computational Screening of Metal–Organic Frameworks for Large-Molecule Chemical Sensing. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12621–12629.
- 51 Huo, S.-H.; Yan, X.-P. Facile Magnetization of Metal–Organic Framework MIL-101 for Magnetic Solid-Phase Extraction of Polycyclic Aromatic Hydrocarbons in Environmental Water Samples. *Analyst* **2012**, *137*, 3445–3451.
- 52 Nian Liu, N.; Yao, Y.; Cha, J. J.; McDowell, M. T.; Han, Y.; Cui, Y. Functionalization of Silicon Nanowire Surfaces with Metal–Organic Frameworks. *Nano Res.* **2012**, *5*, 109–116.
- 53 Falcaro, P.; Buso, D.; Hill, A. J.; Doherty, C. M. Patterning Techniques for Metal Organic Frameworks. *Adv. Mater.* **2012**, *24*, 3153–3168.
- 54 Ameloot, R.; Vermoortele, F.; Vanhove, W.; Roefsaers, M. B. J.; Sels, B. F.; De Vos, D. E. Interfacial Synthesis of Hollow Metal–Organic Framework Capsules Demonstrating Selective Permeability. *Nat. Chem.* **2011**, *3*, 382–387.
- 55 Lee, H. J.; Cho, W.; Oh, M. Advanced Fabrication of Metal–Organic Frameworks: Template-Directed Formation of Polystyrene@ZIF-8 Core–Shell and Hollow ZIF-8 Microspheres. *Chem. Commun.* **2012**, *48*, 221–223.

- 56 Kuo, C.-H.; Tang, Y.; Chou, L.-Y.; Sneed, B. T.; Brodsky, C. N.; Zhao, Z.; Tsung, C.-K. Yolk–Shell Nanocrystal@ZIF-8 Nanostructures for Gas-Phase Heterogeneous Catalysis with Selectivity Control. *J. Am. Chem. Soc.* **2012**, *134*, 14345–14348.
- 57 Aguado, S.; Canivet, J.; Farrusseng, D. Facile Shaping of an Imidazolate-Based MOF on Ceramic Beads for Adsorption and Catalytic Applications. *Chem. Commun.* **2010**, *46*, 7999–8001.
- 58 Aguado, S.; Canivet, J.; Farrusseng, D. Engineering Structured MOF at Nano and Macroscales for Catalysis and Separation. *J. Mater. Chem.* **2011**, *21*, 7582–7588.
- 59 Sorribas, S.; Zornoza, B.; Téllez, C.; Coronas, J. Ordered Mesoporous Silica–(ZIF-8) Core–Shell Spheres. *Chem. Commun.* **2012**, *48*, 9388–9390.
- 60 Wu, Y.-N.; Li, F.; Xu, Y.; Zhu, W.; Tao, C.-A.; Cui, J.; Li, G. Facile Fabrication of Photonic MOF Films Through Stepwise Deposition on a Colloid Crystal Substrate. *Chem. Commun.* **2011**, *47*, 10094–10096.
- 61 Lu, G.; Farha, O. K.; Kreno, L. E.; Schoenecker, P. M.; Walton, K. S.; Van Duyne, R. P.; Hupp, J. T. Fabrication of Metal–Organic Framework-Containing Silica-Colloidal Crystals for Vapor Sensing. *Adv. Mater.* **2011**, *23*, 4449–4452.
- 62 Wu, Y.-N.; Li, F.; Zhu, W.; Cui, J.; Tao, C.-A.; Lin, C.; Hannam, P. M.; Li, G. Metal–Organic Frameworks with a Three-Dimensional Ordered Macroporous Structure: Dynamic Photonic Materials. *Angew. Chem., Int. Ed.* **2011**, *50*, 12518–12522.