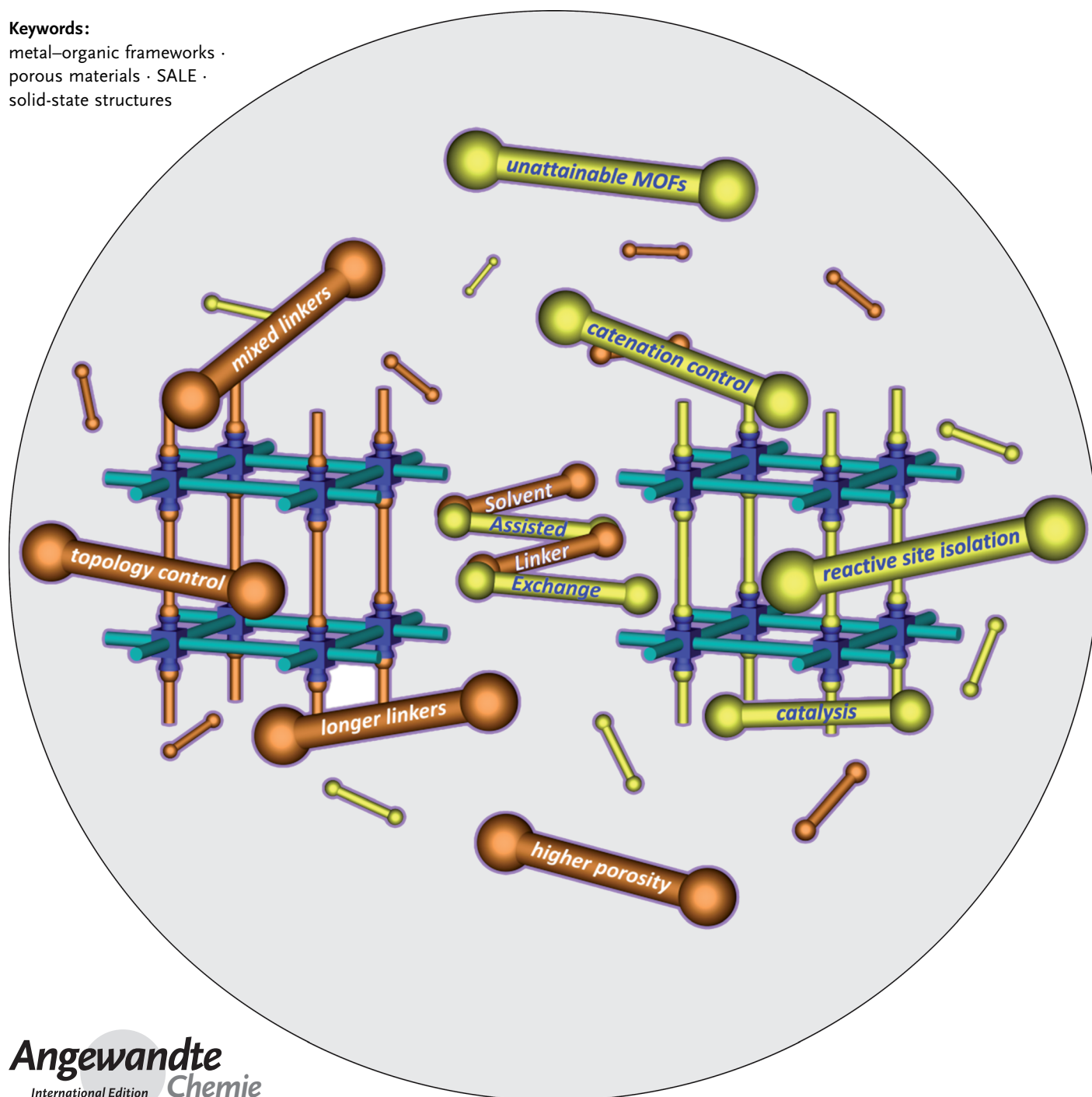


Solvent-Assisted Linker Exchange: An Alternative to the De Novo Synthesis of Unattainable Metal–Organic Frameworks

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Metal-organic frameworks (MOFs) have gained considerable attention as hybrid materials—in part because of a multitude of potential useful applications, ranging from gas separation to catalysis and light harvesting. Unfortunately, *de novo* synthesis of MOFs with desirable function–property combinations is not always reliable and may suffer from vagaries such as formation of undesirable topologies, low solubility of precursors, and loss of functionality of the sensitive network components. The recently discovered synthetic approach coined solvent-assisted linker exchange (SALE) constitutes a simple to implement strategy for circumventing these setbacks; its use has already led to the generation of a variety of MOF materials previously unobtainable by direct synthesis methods. This Review provides a perspective of the achievements in MOF research that have been made possible with SALE and examines the studies that have facilitated the understanding and broadened the scope of use of this invaluable synthetic tool.

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1. Introduction

Metal–organic frameworks (MOFs) are hybrid materials comprised of multitopic organic struts linking metal-based nodes.^[1–3] MOFs feature highly ordered crystalline structures, which when combined with a virtually boundless number of organic linkers give rise to an extremely diverse (both chemically and structurally) class of solid-state compounds. Their crystalline nature enables unambiguous structural determination and in the most favorable cases facilitates predictive discovery of materials.^[4–6] Furthermore, many MOFs are characterized by permanent porosity, which has rendered them valuable candidates for many potential applications, such as gas storage^[4,7,8] and separation,^[9] catalysis,^[10] light harvesting,^[11–15] carbon capture and sequestration,^[16] chemical sensing,^[17] and removal of toxic gas.^[18]

Nevertheless, the implementation of MOF design often encounters multiple challenges when *de novo* syntheses are attempted. The assembly of the framework components into a product possessing a desired topology (which often entails thermodynamically unfavorable characteristics such as low density and high porosity) is not guaranteed.^[19] In addition, the incorporation of linkers that possess desired functional groups is not always trivial, as these groups often lose their functionality by coordinating to the metal centers. Other factors, such as low solubility of the framework components, formation of amorphous by-products and undesirable (e.g., catenated) phases, further complicate the synthesis of novel MOFs. Finally, the *de novo* synthesis of mixed-linker MOFs is not trivial, as linkers exhibiting different binding constants often compete for the metal nodes. Some of these synthetic challenges have been alleviated by high-throughput techniques^[20,21] and post-synthesis modification of existing linkers or nodes;^[22–27] yet more general synthetic strategies are still needed.

Significant effort has been recently devoted to a new approach to MOF synthesis—solvent-assisted linker

exchange (SALE).^[28–44] The great appeal of SALE lies in its versatility and efficiency combined with its facile implementation. SALE involves a heterogeneous reaction of parent MOF crystals with a concentrated solution of linkers. A successful outcome of SALE is a material that features the linkers from the solution incorporated into a framework that possesses the topology of the parent crystal. Fundamentally, SALE removes problems associated with linker solubility by fixing the concentration of one component within the MOF, and typically leads to an almost quantitative synthesis of the daughter material, thus ensuring an efficient use of the often precious linkers.^[40,44] In other words, SALE provides a way to circumvent many challenges associated with MOF synthesis and in many cases has led to the production of desirable MOF materials.

Although SALE has only been utilized in MOFs quite recently, it is worth noting that similar approaches have been utilized in various solid-state systems, such as metal oxides, metal phosphates, silica, and organic polymers.^[45–48] Further-

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more, SALE is also known as “bridging-linker replacement”^[41] or “postsynthetic exchange”.^[37] Nevertheless, in this Review we will refer to the process as “SALE”.

The discovery that MOF crystals can be altered through a heterogeneous reaction pathway by using multitopic linkers has drastically changed our view of MOFs as “inert” systems that are impervious to such invasive chemistry. In fact, some of the most robust MOFs (e.g., UiO-66 and zeolitic imidazolate frameworks, see Section 2.2) have been successfully subjected to SALE, leading to the formation of numerous daughter MOFs that had been challenging to prepare directly. SALE is proving effective at addressing some of the prominent challenges in MOF synthesis, including controlling catenation, accessing polymorphs with comparatively high energy, and producing MOFs with longer linkers, mixed linkers, and/or larger cages. Moreover, SALE has been usefully deployed in various application-driven efforts. Examples include the synthesis of catalytically active materials from catalytically inactive parents^[39] and site-isolation of reagents to obtain control over a challenging chemical transformation.^[44]



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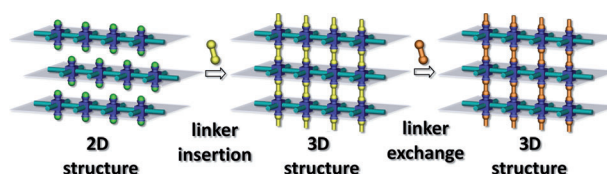
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Herein, we describe the application of SALE to the synthesis of novel MOFs. Our discussion will be limited to examples of heterogeneous crystal-to-crystal reactions performed on 2D or 3D MOFs; the homogeneous insertion and replacement of linkers in soluble molecular systems (metal–organic polyhedra,^[49,50] cobaloximes)^[51] is beyond the scope of this Review. We begin by discussing linker insertion—studies that set the stage for the discovery of SALE within MOFs. Subsequently we will discuss the implementation of SALE involving multitopic linker exchange. Particular emphasis will be placed on the utilization of SALE for the synthesis of MOFs that can perform concrete applications. We will conclude with our thoughts on the most compelling topics for further investigation.

2. Solvent-Assisted Linker Exchange

2.1. Prelude to SALE: Linker Insertion

The first experimental endeavors that set the scene for SALE involved a strategy called “linker insertion”.^[12,52–58] During linker insertion, a multitopic pillar typically links two distinct metal centers in a MOF structure by replacing the monotopic solvent (or other) molecules weakly bound to these metal clusters in a single-crystal-to-single-crystal fashion. In contrast, linker exchange (again a single-crystal-to-single-crystal process) involves replacement of a multitopic linker in a MOF by another multitopic linker and will be discussed in more depth below (Scheme 1).



Scheme 1. Linker insertion and linker exchange.

Most studies on linker insertion examine a very specific category of systems, namely pillared-paddlewheel MOFs. These systems feature 2D sheets comprised of polycarboxylate paddlewheel structural building units connecting binuclear metal clusters, which are in turn pillared by ditopic nitrogen donor linkers. The attractiveness of these mixed-linker MOFs lies in the fact that the strength of the metal–oxygen bonds between the clusters and the carboxylate moieties in the 2D sheets significantly exceeds that of the metal–nitrogen bonds between the clusters and the pillars.^[59] As a result, the removal and insertion of the pillars can be performed relatively easily, providing a change in dimensionality that is accompanied by a lateral plane movement of the 2D sheets. Various linker-insertion processes were studied prior to the discovery of linker exchange.

The conversion of a 2D material to a 3D material can be extremely useful, as it can dramatically increase the porosity and therefore the functional properties of MOFs. As early as 2001, Seki et al. synthesized a series of 2D structures based on

copper(II) and various bicarboxylate linkers.^[52,53] Upon exposing these structures to dabco in *N,N*-dimethylformamide (DMF) or methanol (MeOH) at 40 °C, they witnessed the pillaring of these materials by dabco. Similar results were later observed by Kitaura et al. in the related 2D material Cu(tfbdcc)-(MeOH), which was successfully pillared by dabco in a MeOH solution at 100 °C (Figure 1).^[54] They were

as well as the ditopic nitrogen donor molecules.^[55] They synthesized two pillared structures by first growing crystals of the 2D MOF $\text{Zn}_3(\text{bdc})_3(\text{H}_2\text{O})_2$ and then reacting them with a solution of DMF containing additional H_2bdc at elevated temperatures in the presence of different amines (which served both as bases to deprotonate H_2bdc and as modulators; see Figure 1). Finally, Chen et al. used the MOF $\text{Zn}_2(\text{bdc})_2$ -

(dabco) to demonstrate that the dynamic nature of the metal–nitrogen bond in pillared-paddlewheel systems allows linker insertion to be reversible.^[56] Today, the insertion of linkers into 2D materials to add an extra dimension has been well established as a potent technique that, among other things, can be employed as a stepwise synthetic strategy, for example in the synthesis of robust porphyrinic materials (RPMs).^[60]

The opposite reaction—the replacement of a pillar by a monotopic ligand to convert a 3D MOF into a 2D material—at a first glance seems more challenging, as the pillars should be stabilized within the framework and more tightly bound than solvent molecules. However, when a sufficiently basic ligand is employed, this reaction can be readily achieved. Lee et al. demonstrated this concept in the pillared-paddlewheel structure $\text{Zn}_2(\text{tcpp})(\text{L1})$

(BOP-MOF), in which **L1** is a pyridine-functionalized bipy pillar.^[12] Immersing the crystals of BOP-MOF in neat pyridine, with periodic replacement of the reaction solution, led to a rapid exchange of the **L1** pillars by pyridine and a reduction of the dimensionality of the framework from 3D to 2D.

In a special case, the insertion of a ditopic linker can be performed on a 3D MOF to partition its channels, thus resulting in a 3D daughter material. The NbO-type MOF $\text{Zn}_2(\text{tcpbda})(\text{H}_2\text{O})_2$ (SNU-30) prepared by Park et al. exhibits Zn_2 paddlewheel units in which the axial coordination sites are occupied by solvent molecules and are separated by about 15 Å (Figure 1). The size match between the length of bpta and the distance between the adjacent binuclear Zn clusters in the structure of SNU-30 allowed the insertion of bpta pillars from a DMF solution at 85 °C between these clusters.^[57] Another special case involves the conversion of a 2D-staggered layered material (AB) to a 2D ABAB-type bilayer (Scheme 2). Such reactions were also observed in the

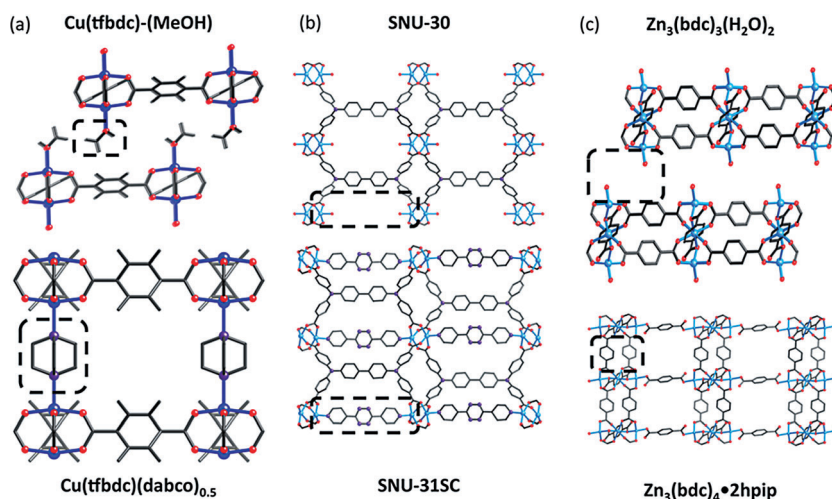


Figure 1. Linker insertion reactions in (a) $\text{Cu}(\text{tfbdcc})(\text{dabco})_{0.5}$, (b) SNU-30, and (c) $\text{Zn}_3(\text{bdc})_3(\text{H}_2\text{O})_2$ (hpic is partially protonated piperazine).

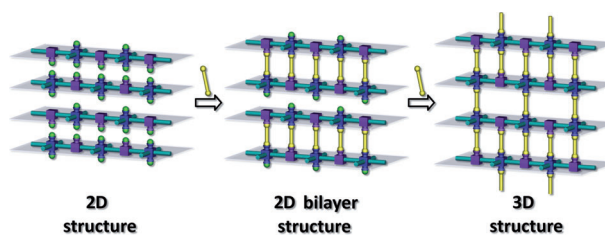
fortunate to collect a single-crystal structure of both the 2D parent and the 3D daughter material, and thus obtain evidence for the lateral plane movement of the 2D layers during the pillar insertion to form an AB structure. Sun et al. demonstrated that bicarboxylate linkers can act as pillars just



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Scheme 2. Linker insertion to transform a 2D AB-type material into a 2D ABAB-type bilayer and a 3D MOF in PPF-type materials.

porphyrin-based MOFs synthesized by Burnett et al. They demonstrated the feasibility of insertion of quite long pillars, such as bipy, bpta, and dpni, to connect the 2D sheets of the MOF $\text{Zn}_2(\text{Zn-tcpp})$ (PPF-1) into bilayer structures $\text{Zn}_2(\text{Zn-tcpp})(\text{bipy})$ (PPF-27), $\text{Zn}_2(\text{Zn-tcpp})(\text{bpta})$ (PPF-21), and $\text{Zn}_2(\text{Zn-tcpp})(\text{dpni})$ (PPF-18).^[58] As in many previous cases, solutions of pillars in DMF and elevated temperatures were used. The reaction could proceed without the lateral translation of the sheets because of the two distinct sites available for the coordination of the pillars (at the binuclear zinc corners and at the metalated center of the porphyrin).

2.2. Employment of SALE: Overcoming De Novo Synthetic Challenges in MOF Chemistry

Now we will proceed to the discussion of what our team has termed SALE—namely the replacement of multitopic linkers throughout MOF crystals by different multitopic linkers. The comparative stability of the coordination bonds in the core of the MOFs should not deter researchers from contemplating SALE—as will be seen, SALE can be applied to some of the most robust MOF systems known. As Cohen and co-workers astutely point out,^[38] even though these materials appear extremely stable to external elements (e.g., water, acid, base, high temperatures), the small energy difference between analogues featuring different linker derivatives results in a dynamic situation and makes their interconversion through SALE possible. In this section, we will provide examples of early exploratory SALE experiments that have helped delineate the scope and the limits of this promising technique, with special emphasis on some of the traditionally viewed “inert” systems, such as imidazolate-based MOFs.

The development of de novo synthetic methods is not always straightforward, as such methods are often extremely dependent on the conditions; multiple variables have to be changed even when the synthesis of structurally similar MOFs is contemplated, and the resulting products do not always possess the desired topology. On the other hand, it is much easier to find optimal conditions when undertaking SALE, as the principal variable is the solvent. The single-crystal-to-single-crystal process of SALE ensures retention of the parent topology in the daughter structure.

The first major breakthrough in SALE took place when Burnett et al.

reported transforming a full MOF structure through heterogeneous linker exchange.^[41] They utilized PPF-18, a porphyrin-based 2D bilayer connected by dpni pillars (which could be obtained through a linker insertion experiment); however, in a radically different manner than any previous crystal-to-crystal MOF experiments, they managed to replace all the dpni linkers in PPF-18 by exposing PPF-18 to an *N,N*-diethylformamide/ethanol (DEF/EtOH) solution of bipy at 80 °C, thus creating the MOF PPF-27 that was previously unattainable de novo (Figure 2). They were capable of performing similar dpni to bipy replacement experiments on a 3D MOF $\text{Zn}_2(\text{Zn-tcpp})(\text{dpni})_4$ (PPF-20). The process was established to occur in a single-crystal-to-single-crystal fashion, which was confirmed by performing the SALE reaction on the scale of a single crystal and observing no appreciable morphological differences between the parent and the daughter crystals throughout the course of the reaction. Single crystal and powder X-ray diffraction measurements further corroborated their conclusions. The findings of Burnett et al. had a great impact on MOF synthesis and made many researchers change the way they view MOFs (i.e., as chemically inert, solid structures whose linkers are difficult to replace). Moreover, they established SALE as a promising

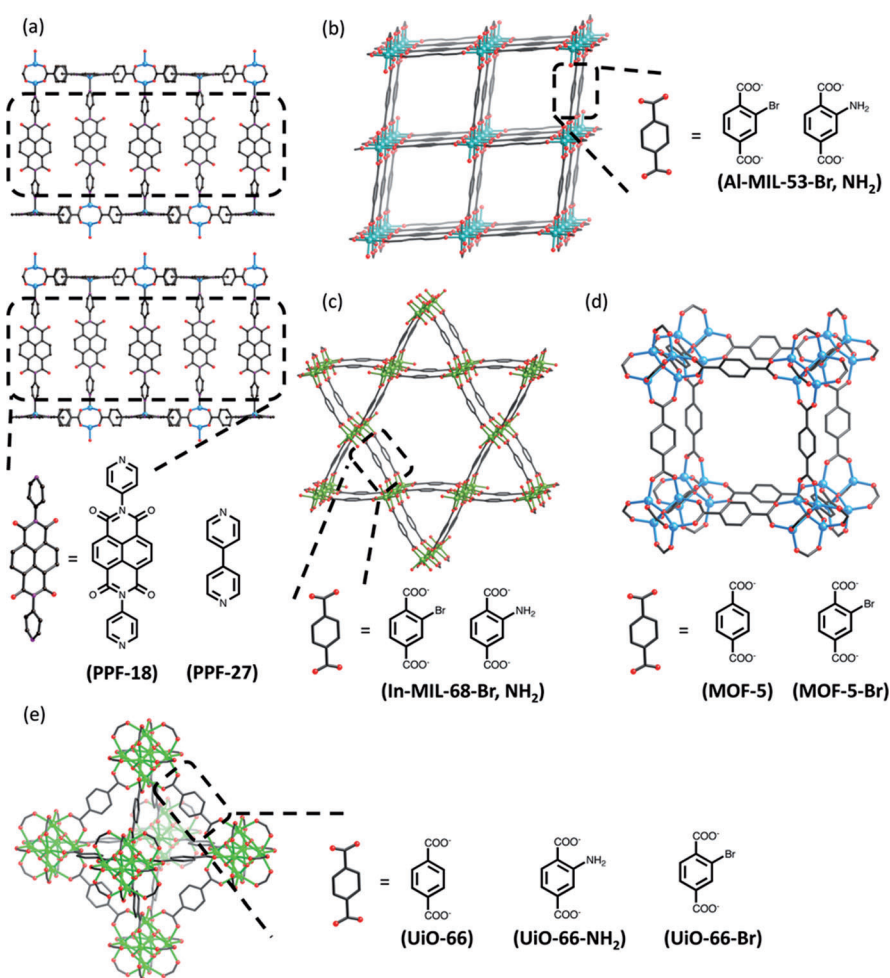


Figure 2. SALE in MOFs containing carboxylate-based linkers (a) PPF-18, (b) Al-MIL-53, (c) In-MIL-68, (d) MOF-5, and (e) UiO-66.

technique that can lead to the synthesis of otherwise difficult to obtain materials. Naturally, additional reports utilizing SALE in various different systems followed.

Recall from the discussion of pillar insertion that the replacement of a nitrogen donor pillar is inherently more facile than the exchange of a carboxylate-based linker, because of the greater strength of the bonds that are formed between a metal corner and the carboxylate moiety. Performing SALE on a carboxylate-based MOF was therefore viewed as a synthetic challenge. The first report of success came from Kim et al.^[37] They worked on the notoriously robust system $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_6$ (UiO-66),^[61] which features oxophilic Zr_6O_4 structural building units and various bdc derivatives (e.g., Br-bdc in UiO-66-Br and NH_2 -bdc in UiO-66- NH_2 ; see Figure 2).^[37] Interestingly, they achieved linker exchange on UiO-66 derivatives in two ways: 1) in the particle-to-particle fashion, which involved physically mixing UiO-66-Br and UiO-66- NH_2 crystallites in water at ambient temperature (or, alternatively, rigorously separating the two types of crystals, and controlling the heterogeneous linker replacement to be carried out through solvent diffusion),^[38] and 2) in the solution-to-particle fashion, during which UiO-66-Br and UiO-66- NH_2 were independently exposed to solutions containing NH_2 -bdc and Br-bdc respectively. The products of SALE in both cases were mixed-linker particles that contained both Br-bdc and NH_2 -bdc; the presence of both linkers in individual UiO-66 particles was detected by aerosol time-of-flight mass spectrometry (ATOFMS). Particle-to-particle SALE has been implemented in other robust carboxylate-based MOFs, such as $\text{Al}(\text{OH})(\text{bdc})$ (Al-MIL-53)^[62,63] and $\text{In}(\text{OH})(\text{bdc})$ (In-MIL-68),^[38,62,64] whereas solution-to-particle SALE has been successfully performed on $\text{Zn}_4\text{O}(\text{bdc})_3$ (MOF-5; see Figure 2).^[33,65] The optimal conditions for SALE in carboxylate-based MOFs are somewhat system-dependent, but certain trends can be discerned. The temperature at which the reactions are performed can vary from ambient temperature to 85 °C, but it is always lower than the temperature required for the synthesis of the parent material, which helps to preclude the possibility of dissolution and reassembly. The solvents selected are typically polar, coordinating solvents (DMF, DEF, water). Notably, despite the variety of carboxylate-based systems on which SALE has been performed, Cr-based $\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}(\text{bdc})_3$ (MIL-101),^[66] has evaded successful linker replacement. It has been postulated that its Cr^{3+} kinetically inert nodes prohibit the replacement of the bdc linkers coordinated to them.^[38]

Another particularly robust category of MOFs consists of the zeolitic imidazolate frameworks (ZIFs).^[67] The imidazolate derivatives have significantly higher Lewis basicity than the carboxylate derivatives, which often translates into exceptionally strong metal–linker bonds, especially in zinc-based ZIFs. However, even these seemingly “inert” materials are not immune to SALE (Figure 3). Karagiari et al. achieved extensive linker exchange in the eim-based Cd(eim)₂-rho (CdIF-4).^[68] The eim linkers of this ZIF were fully exchanged to mim and nim in DMF, *N,N*-dimethylacetamide (DMA) and *n*-butanol (*n*BuOH) to generate the daughter materials Cd(mim)₂-rho (SALEM-1) and Cd(nim)₂-rho

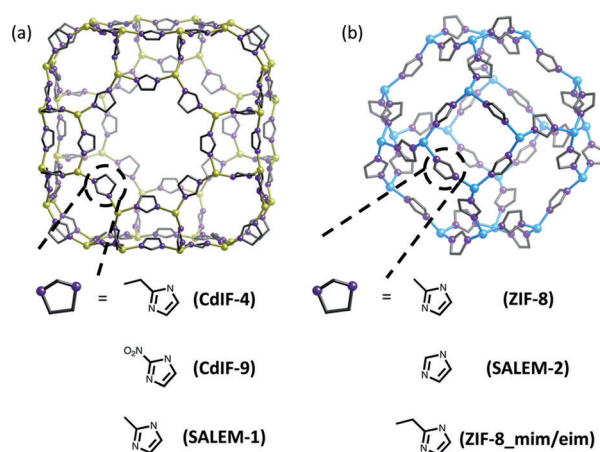


Figure 3. SALE in ZIFs (a) CdIF-4 and (b) ZIF-8.

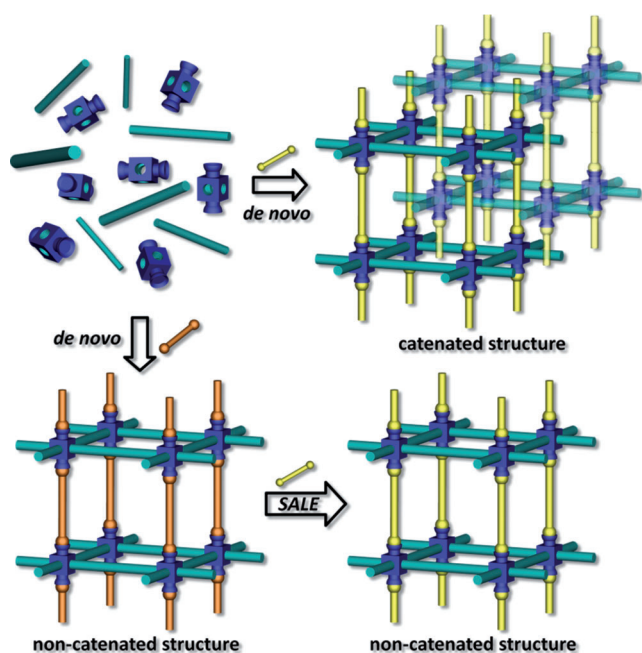
(CdIF-9).^[40] SALE was also performed on the more iconic and robust zinc-based system $\text{Zn}(\text{mim})_2\text{-sod}$ (ZIF-8), leading to a replacement of its mim linkers with unsubstituted im (85 % exchange) in *n*BuOH^[39] and with eim in MeOH (10–20 % exchange).^[34] Similarly, another zinc-based ZIF, $\text{Zn}(\text{dcim})_2\text{-rho}$ (ZIF-71) has undergone successful 35 % replacement of its linkers with 4-bromimidazolate.^[34] Interestingly, unlike in carboxylate-based MOFs, only solution-to-particle SALE (and no particle-to-particle SALE) has been demonstrated in ZIFs to date. Apart from that, the use of polar solvents appears to be a defining factor in the successful linker exchange in both classes of systems. Presumably the limited solubility of the parent linker in the SALE solution after its extrusion from the framework has led to an incomplete (< 100 %) SALE in some of the examined systems.

2.3. Solving Application Challenges with SALE

The next logical step after the exploration of the scope of SALE as a synthetic strategy is its utilization toward the synthesis of new, otherwise inaccessible, materials with useful applications. Given that SALE is an emerging method, the amount of work that has focused on this area is still relatively small. The goal of this section is to highlight some of the most important SALE-generated materials with advantageous functionalities that cannot be introduced *de novo* in the parent systems, such as lack of catenation, larger cages, catalytic behavior and site-isolation of linkers.

2.3.1. Catenation Control

One example of an application-based utilization of SALE involves its employment to control catenation in pillared-paddlewheel compounds in order to achieve an increase in porosity (Scheme 3). Mulfort et al. reported the structure of $\text{Zn}_2(\text{tcpb})(\text{dped})$ (DO-MOF),^[69] an inherently non-catenated framework as a result of the hydrogen-bonding interactions of the dped pillars (Figure 4). On the contrary, isostructural pillared-paddlewheel MOFs that feature bipy or abp pillars formed two-fold catenated structures when grown *de novo*.



Scheme 3. Control over catenation by SALE.

By using DO-MOF as a template and utilizing SALE to replace its dped pillars with bipy and abp, Bury et al. arrived at noncatenated analogues of these materials (SALEM-3 and SALEM-4). The lack of catenation was confirmed by computational modeling, thermogravimetric analysis (TGA), and PXRD measurements.^[35]

2.3.2. Opening Up Cages and Channels

Another, related approach toward MOFs featuring larger cages and higher porosity involves employing SALE to replace existing MOF linkers with longer ones. Li et al. were the first to demonstrate the feasibility of this application of SALE.^[30] Their system of choice was $\text{Zn}_8(\text{ad})_4(\text{ndc})_6(\text{OH})_2$ (bio-MOF-101), a mesoporous MOF of *lcs* topology. In an attempt to diversify this family of mesoporous MOFs of this topology and create materials with larger cages, they used SALE to replace *ndc* with *bpdc*, a linker approximately 2 Å longer than *ndc*, and *abdc* (approximately 4 Å longer than *ndc*). The reactions respectively yielded a previously synthesized MOF, $\text{Zn}_8(\text{ad})_4(\text{bpdc})_6(\text{OH})_2$ (bio-MOF-100),^[70] and a novel MOF, $\text{Zn}_8(\text{ad})_4(\text{abdc})_6(\text{OH})_2$ (bio-MOF-102), which both featured larger pore volumes than bio-MOF-101 (4.30 cm³ g⁻¹ and 4.36 cm³ g⁻¹ vs. 2.83 cm³ g⁻¹). Finally, the *abdc* linkers in bio-MOF-102 were replaced with *tpdc* linkers (~2 Å longer than *abdc*) to generate the last member of the family, $\text{Zn}_8(\text{ad})_4(\text{tpdc})_6(\text{OH})_2$ (bio-MOF-103). Notably bio-MOF-102 and bio-MOF-103 could not be previously obtained *de novo*. Similarly, Karagiari et al. synthesized pillared-paddlewheel MOFs with progressively longer linkers by replacing the *dped* pillars in $\text{Zn}_2(\text{Br-tcpb})(\text{dped})$ (SALEM-5) with 2,3,5,6-tetramethyl-1,4-bis(4-pyridyl)benzene (2 Å longer than *dped*), 2,6-bis(4-pyridyl)naphthalene (5 Å longer than *dped*), and 4-bis(4'-pyridylethynyl)durene (7 Å longer than *dped*; almost double its size).^[43] The presence of larger cages in the resulting materials SALEM-6, SALEM-7, and SALEM-8 was demonstrated by analyzing their PXRD patterns. Additionally, TGA revealed that these materials possess a greater solvent-accessible space than their parent SALEM-5.

2.3.3. Catalysis

SALE has been successfully used as a method to produce new catalytically active MOFs. In a study mentioned earlier, 85 % of the *mim* linkers of ZIF-8 were exchanged with unsubstituted imidazolate, resulting in the first documented synthesis of the thermodynamically unfavorable $\text{Zn}(\text{im})_2$ material SALEM-2 possessing *sod* topology.^[39] The *im* linkers endowed SALEM-2 with larger apertures than the parent ZIF-8, as TGA experiments demonstrated uptake of cyclohexane and toluene by this material (to which ZIF-8 was impervious). Moreover, it was found that treatment of SALEM-2 with

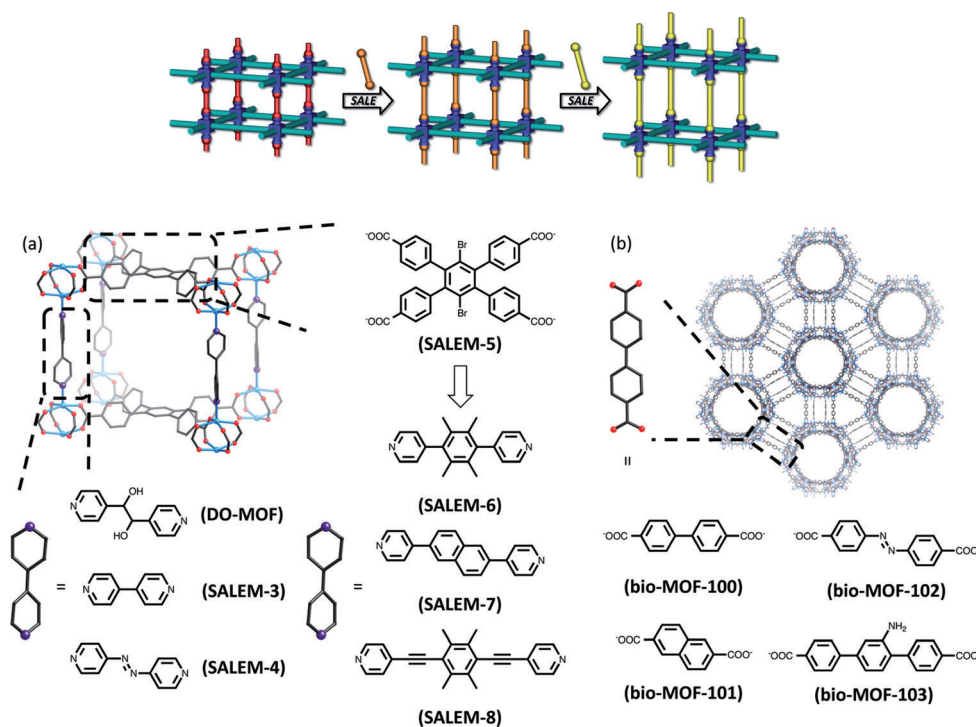


Figure 4. Top: Schematic representation of the incorporation of longer linkers into a MOF through SALE. Bottom: SALE in (a) DO-MOF and SALEM-5, and (b) bio-MOF-101.

n-butyllithium enabled its use as a Brønsted base catalyst in the conjugate addition of alcohol to an α,β -unsaturated ketone.^[71] Catalysis was presumed to take place on the surface of the MOF, given the large kinetic diameter of the substrate molecules. Nevertheless, the catalytic behavior was attributed to the formation of an NHC-like species upon the deprotonation of the imidazolate at the C2 position. This activated SALEM-2 species was a few orders of magnitude more catalytically active than the classical molecular NHC catalyst 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). Notably, the parent material ZIF-8, whose mim linkers were unavailable for deprotonation at C2, was not catalytically active after similar treatment with *n*-butyllithium.

In a second catalytic study, SALE was used by Takaishi et al. for the incorporation of a catalytically active pillar into an RPM.^[29] RPMs, which were developed by Farha et al., are pillared-paddlewheel MOFs constructed from tcpp and dipy.^[60] Each porphyrin moiety can be metalated with a different metal. The incorporation of a metal-free porphyrin pillar, however, proved challenging *de novo*, as the conditions employed for the solvothermal synthesis of an RPM were essentially promoting the metalation of the porphyrin with the zinc source required for the formation of the RPM corners. Moreover, the introduction of the metals Co^{2+} , Al^{3+} and Sn^{4+} could not be achieved because of problems with solubility and formation of amorphous phases instead of the desirable product. Exchange of M-dipy (where $\text{M} = \text{Al}^{3+}$, Sn^{4+} , or 2H^+) into the RPM $\text{Zn}_2(\text{Zn-tcpp})(\text{Zn-dipy})$ through SALE was used to resolve this challenge. Moreover, post-synthesis metalation of the SALE product $\text{Zn}_2(\text{tcpp})(\text{Zn-dipy})$ allowed the incorporation of Co^{2+} . The resulting SALE materials featuring different metals were subsequently tested as potential catalysts for the ring-opening of styrene epoxide, and the product $\text{Zn}_2(\text{Zn-tcpp})(\text{Al-dipy})$, was found to be catalytically active. Because of the presence of two distinct metal centers (with different catalytic functionalities) in their two porphyrin linkers, RPMs can be potentially employed as tandem catalysts; the use of SALE expands the number of metals that can be inserted into these structures and thus opens new perspectives for this function.

2.3.4. MOFs as Protecting and Site-Isolating Agents

SALE has further been recognized as a powerful auxiliary technique in obtaining synthetically challenging MOFs with the goal of their subsequent employment as molecular flasks and protecting agents (Scheme 4). Vermeulen et al. aimed to demonstrate the feasibility of performing olefin metathesis on

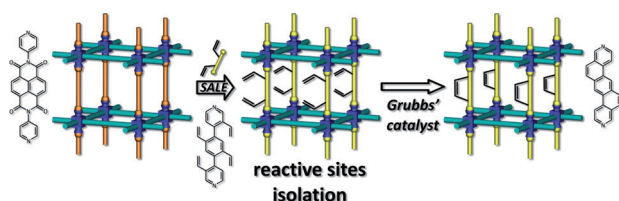
dpbv in order to convert it to a polycyclic aromatic hydrocarbon (PAH).^[44] However, when performed in solution, this reaction faces multiple challenges. First, the presence of pyridyl groups can poison the Grubbs–Hoveyda catalyst that is needed for the metathesis reaction; second, it is difficult to control intermolecular olefin metathesis, which results in the formation of an insoluble polymer. These issues can be circumvented by incorporating dpbv molecules into a MOF—an approach that leads both to the protection of the pyridyl moieties by the metal corners and the site-isolation of the dpbv molecules to prevent unproductive intermolecular chemistry. However, *de novo* synthesis of a pillared-paddle-wheel MOF featuring dpbv pillars has not been successful, presumably as a result of the polymerization of the pillar under the synthetic conditions. Resorting to SALE of dpbv into a previously reported framework $\text{Zn}_2(\text{Br-tcbp})(\text{dpni})$, whose dpni pillars are relatively easy to replace, was an efficient solution to this challenge. Grubbs catalysis performed on the resulting material, $\text{Zn}_2(\text{Br-tcbp})(\text{dpbv})$ (SALEM-14), resulted in an almost quantitative transformation of the dpbv pillars into the desired PAH, as was confirmed by ^1H NMR spectroscopy and single-crystal X-ray diffraction. Besides serving as the first example of the utilization of Grubbs catalysis toward post-synthesis modification of MOFs, this method provides a route for generating MOFs with PAH linkers (which are challenging to insert *de novo* because of their low solubility).

3. Conclusion and Outlook

SALE is quickly becoming a useful technique in MOF chemistry. Surprisingly, SALE can be applied to some of the most stable MOFs known and multiple examples now exist demonstrating that it can be used to overcome problems associated with conventional (*de novo*) synthesis methods. In the most intriguing instances, control can be gained over pore volume, functionality, and aperture size.

Since SALE research is comparatively new, much work remains to be done on elucidating the driving force(s) governing these transformations. If these were well understood, conditions for successful SALE could be readily established, as could the scope of the strategy. Thus far SALE has been attempted on only a small number of MOFs representing very few of the numerous topologies presented in the field. The limits and the scope of this reaction remain to be comprehensively explored. More work needs to be done in order to establish which structural aspects (if any) of MOFs determine the successful outcome of SALE—the linker, the metal node, or the overall topology. Furthermore, it is worth noting that only SALE of ditopic linkers has been attempted; to probe the limits of SALE, we are in need of experiments that could determine the feasibility of SALE of linkers with higher connectivity.

The importance of studying the factors governing the course of SALE cannot be emphasized enough. Such research must be supported and encouraged, as without it we are limited to randomly applying SALE toward generating a multitude of new compounds without having a deeper



Scheme 4. Site-isolation through SALE, followed by post-synthesis Grubbs catalysis.

understanding of this promising synthetic tool. Despite the incipient nature of the field, several studies have already been devoted to leveraging our understanding of various components of the SALE process, such as the influence of the solvent,^[38] the pK_a of the incoming and outgoing linkers,^[40,43] the thermodynamic variables governing the process (enthalpy, entropy and Gibbs free energy),^[31,33] and the kinetic aspects of SALE (lability/inertness of the metal nodes, the role of the crystal size in linker diffusion).^[29,38] However, these studies are typically limited to a single system and do not allow the postulation of general rules that govern the progress of SALE. For example, even though it is evident that the nature of solvent influences the success of SALE, thus far only one study has performed a detailed investigation on the effect of the solvent on SALE, and the exact role of the solvent in the course of SALE reactions is not known.^[38] Furthermore, while it appears that in many instances SALE occurs in a single-crystal-to-single-crystal fashion, clearly additional studies will be needed to fully understand the boundary between single-crystal-to-single-crystal and dissolution-reassembly processes. Computational modeling of SALE, which has so far been overlooked, may greatly expedite the progress of the mechanistic studies and should be recruited as an invaluable tool.

Additionally, the role of the porosity of the parent MOF in facilitating SALE needs to be thoroughly investigated. So far, experimental evidence suggests that MOFs subjected to SALE need to possess apertures large enough for the daughter linkers to be able to penetrate into the core of the framework. This picture, however, is different when one speaks of performing SALE solely on the surfaces of the MOF crystals. Such processes have been studied by Kitagawa, Yanai and co-workers.^[32,36,42] Although characterization of the MOF surfaces at the liquid–solid interface is notoriously difficult, and it is hard to distinguish whether the core–shell structures are products of SALE or surface ligation, Kitagawa's pioneering work has provided an understanding of coordination chemistry in MOFs. Investigation of surface linker exchange phenomena employing linkers whose steric hindrance prevents diffusion into the interior of MOFs may provide us with core–shell structures that possess unprecedented combinations of functionalities.

Finally, specific attention needs to be given to realizing the intrinsic potential of SALE to generate novel, otherwise difficult to synthesize MOFs whose functionality can be harnessed toward many useful purposes. We anticipate that MOFs synthesized through SALE will be employed in applications beyond those described above. We believe that it will become increasingly attractive to take advantage of the facile generation of mixed-linker MOFs through SALE to create new materials with multiple functionalities (e.g., MOFs possessing hydrophobic and hydrophilic regions). Moreover, MOFs with linkers that exhibit difficulties toward incorporation, such as flexible linkers or linkers possessing free functional groups, can be developed through SALE. We suspect that the scope of SALE is only starting to be realized and that the future holds many exciting new MOFs, which in turn will find utility in a number of relevant applications!

4. Abbreviations

abdc	azobenzene-4,4'-dicarboxylate
abp	4,4'-azobis(pyridine)
ad	adeninate
ATOFMS	aerosol time-of-flight mass spectrometry
bdc	1,4-benzenedicarboxylate
bipy	4,4'-bipyridine
bodipy	boron dipyrromethene
Br-tcpb	1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene
bpdc	4,4'-biphenyldicarboxylate
bpta	3,6-di(4-pyridyl)-1,2,4,5-tetrazine
CdIF	cadmium imidazolate framework
dabco	1,4-diazabicyclo[2.2.2]octane
dcim	4,5-dichloroimidazolate
DEF	<i>N,N</i> -diethylformamide
dipy	5,15-dipyridyl-10,20-bis-(pentafluorophenyl)-porphyrin
DMA	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
dpbv	4,4'-(2,5-divinyl-1,4-phenylene)bis(3-vinylpyridine)
dped	<i>meso</i> -1,2-di(4-pyridyl)-1,2-ethanediol
dpni	<i>N,N'</i> -di-4-pyridyl-naphthalenetetracarboxydimide
eim	2-ethylimidazolate
EtOH	ethanol
im	imidazolate
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
MeOH	methanol
MIL	Materials Institute Lavoisier
mim	2-methylimidazolate
MOF	metal–organic framework
<i>n</i> BuOH	<i>n</i> -butanol
ndc	2,6-naphthalenedicarboxylate
NHC	N-heterocyclic carbene
nim	2-nitroimidazolate
PAH	polycyclic aromatic hydrocarbon
pip	piperazine
PPF	porphyrin paddlewheel framework
RPM	robust porphyrinic material
SALE	solvent-assisted linker exchange
SALEM	solvent-assisted linker exchanged material
SNU	Seoul National University
tcpb	2,3,5,6-tetrakis(4-carboxyphenyl)benzene
tcpbda	<i>N,N,N',N'</i> -tetrakis(4-carboxyphenyl)bi-phenyl-4,4'-diamine
tcpp	tetrakis(4-carboxyphenyl)porphyrin
tfbdc	tetrafluoroterephthalate
tpdc	2'-amino-1,1':4,1''-terphenyl-4,4'-dicarboxylate
UiO	Universitetet i Oslo
ZIF	zeolitic imidazolate framework

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