

Intrinsically conducting metal–organic frameworks

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The development of metal–organic frameworks (MOFs) as microporous electronic conductors is an exciting research frontier that has the potential to revolutionize a wide range of technologically and industrially relevant fields, from catalysis to solid-state sensing and energy-storage devices, among others. After nearly two decades of intense research on MOFs, examples of intrinsically conducting MOFs remain relatively scarce; however, enormous strides have recently been made. This article briefly reviews the current status of the field, with a focus on experimental milestones that have shed light on crucial structure–property relationships that underpin future progress. Central to our discussion are a series of design considerations, including redox-matching, donor–acceptor interactions, mixed valency, and π -interactions. Transformational opportunities exist at both fundamental and applied levels, from improved measurement techniques and theoretical understanding of conduction mechanisms to device engineering. Taken together, these developments will herald a new era in advanced functional materials.

Introduction

Metal–organic frameworks (MOFs) are crystalline, porous coordination solids formed by the self-assembly of metal ions and organic ligands.^{1,2} During the past two decades, MOFs have emerged as a highly versatile platform for wide-ranging potential applications from gas storage to separations, heterogeneous catalysis, and biomedicine, among others.^{3,4} One property that has generated recent attention is electrical conductivity, which, if realized, could provide vast potential technological impacts across the areas of chemiresistive sensing, thermoelectric, and clean-energy technologies (e.g., fuel cells, electrocatalysts, energy storage). While the inherent porosities of MOFs are conducive to applications in gas storage, separations, and catalysis, as well as ionic conductors, this inherent porosity often impedes long-range charge transport. Moreover, many robust MOFs are constructed from redox-inactive metal centers (e.g., Zn^{II}), and carboxylate-based ligands, which do not mediate overlap of the frontier orbitals required to bring about charge delocalization. As a result, MOFs are typically electrical insulators.

Despite the inherent research challenges, the past five years have yielded the first examples of MOFs that exhibit semiconducting and conducting capabilities.^{5–10} In this article, we discuss the exciting research frontier of conducting MOFs, with an emphasis on experimental reports of systems that

display intrinsic conductivity, wherein conductivity is an inherent property, rather than being induced by augmentations such as the exchange of guest molecules⁹ or ionic conduction through the framework pores. We also provide a brief historical perspective of the field, given that conductivity in the broader context of coordination polymers has been of interest for more than two decades.⁶

General design considerations

A prerequisite for conductivity in MOFs is delocalization of charge, either through a highly delocalized connector or by virtue of the close proximity of the components in space. While an understanding of the mechanisms of charge transport in MOFs is in its infancy, it is generally believed that charge hopping between components predominates for semiconducting MOFs, including mixed-valence frameworks such as Prussian blue,^{11,12} and can explain electron transfer in MOF films during electrochemical experiments.¹³ The variable-range hopping model, postulated by Mott¹⁴ and originally developed for highly disordered systems with localized charge carriers, describes low-temperature conductivity (σ) in semiconductor solids with localized charge-carrier states, where conduction in three-dimensional systems follows a temperature (T) dependence of $\log \sigma \sim T^{-1/4}$. This model has had mixed success in the interpretation of MOF

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conductivity data.¹⁵ As electronic delocalization increases, the distinction between redox components diminishes because the thermal barrier to electron transfer between them ceases to exist. In the high delocalization limit, the material approaches a metallic state with essentially “free” charge carriers and the conductivity is perhaps best described by employing band theory.

In light of these general mechanisms, a number of synthesis approaches for the development of MOFs have been identified that promote long-range charge-transport pathways via either charge hopping or band transport.⁷ Many of these exploit donor–acceptor or π -interactions (which can be through-bond or through-space interactions). Through-bond mechanisms take advantage of covalent bonding between appropriately matched metals and ligands; through-space mechanisms rely on noncovalent interactions. While not covered in this article, it is also important to note that post-synthesis modulation (such as via redox-state changes¹⁰ or intercalation of guest molecules⁹) has also been shown to modulate the conductivities of some MOFs.

Experimental milestones in intrinsically conducting MOFs

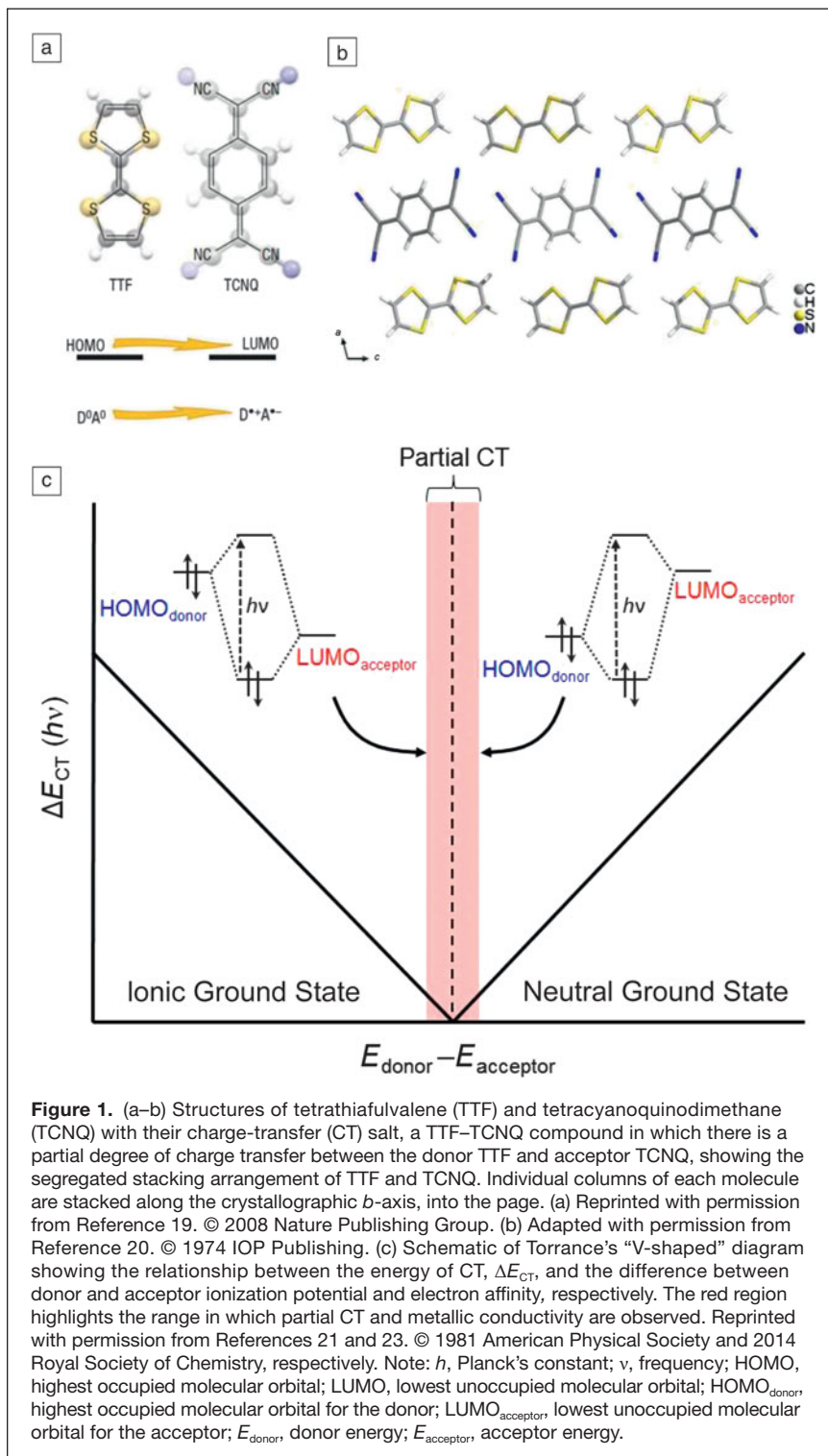
In this section, we review key developments in the field within the context of different strategies that have been employed to achieve long-range conductivity in MOFs.

Promoting conduction pathways via redox matching: Exploiting mixed-valency and donor–acceptor interactions

The integration of donor and acceptor components into MOFs to promote charge-transfer (CT) interactions has shown promise for the design and construction of conductive systems.^{5,10,16} Here, appropriate matching of the electronic energy levels of the components can be exploited to bring about CT, which occurs when electron donor (D) and acceptor (A) moieties are arranged in close proximity, interacting either through-bond or through-space (i.e., D to A [$D^0A^0 \leftrightarrow D^{\delta+}A^{\delta-}$, where $0 < \delta < 1$]).¹⁷ The degree of CT (ρ) is largely dictated by the overlap in frontier orbitals and by the ionization potential and electron affinity of D and A, respectively.

The donor–acceptor strategy has also drawn inspiration from the historically rich field of chemistry known as “organic metals.” This area flourished following the 1973 discovery of the archetypal CT material tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), which

was found to exhibit metallic conductivity comparable to that of copper ($1.47 \times 10^4 \text{ S}\cdot\text{cm}^{-1}$ versus $6 \times 10^5 \text{ S}\cdot\text{cm}^{-1}$ in copper) (Figure 1a–b).^{18,19} Of particular interest was the anisotropy of conductivity with respect to the direction of D and A stacking in a TTF-TCNQ crystal.²⁰ Systematic investigations of purely organic CT complexes experimentally demonstrated the

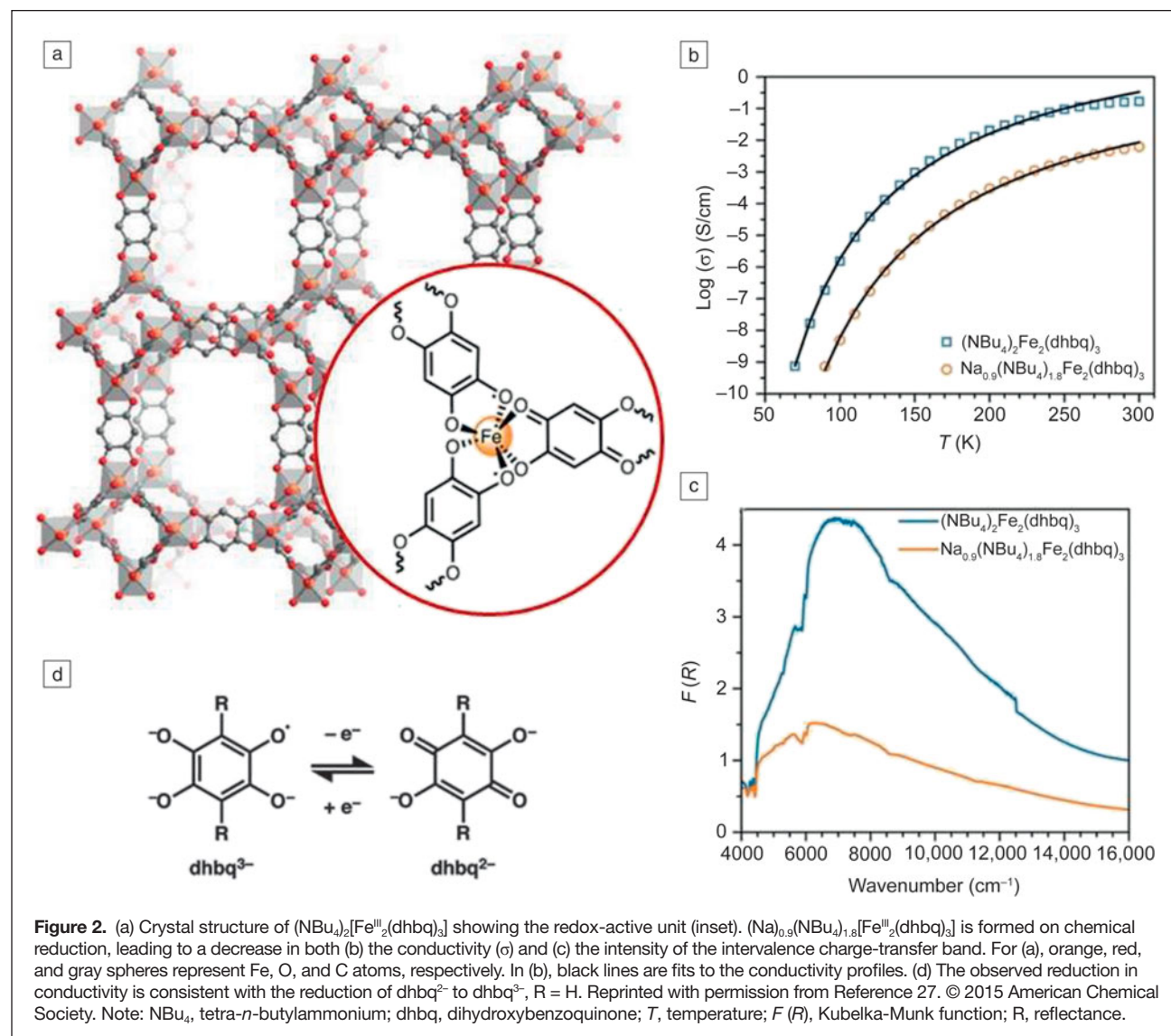


“Torrance V-shaped diagram” (see Figure 1c), which shows the relationship between the redox match of the D and A components (difference in their redox potentials) and the energy of the CT transition.²¹ The extent of the redox match, and therefore the degree of ρ , gives rise to three regimes: an ionic system where $\rho = 1$, a neutral system where $\rho = 0$, and an intermediate region where $0 < \rho < 1$. It is in this intermediary region where transitions can occur between neutral and ionic states upon application of external stimuli such as temperature, pressure, and light.²² Importantly, CT complexes exhibit metallic behavior in the “sweet spot,” where $0.5 < \rho < 0.75$ (the minimum in Figure 1c),²³ which is known to be highly dependent on the stacking arrangement of donor and acceptor units (i.e., mixed-stack materials) (\cdots DADADA \cdots) typically exhibit insulator or semiconducting behavior, whereas segregated stack materials (\cdots DDDDD \cdots and \cdots AAAAA \cdots such as TTF-TCNQ) tend toward metallic conductivity.

While the donor and acceptor can have different identities, they may also be alike in all respects other than their formal

oxidation states. In cases where the D and A units are the same, mixed valency may be found, as exemplified by Prussian blue, with formula $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$, which has been used as a pigment since the early 17th century.²⁴ While not strictly a MOF, this framework comprises the donor and acceptor units Fe^{II} and Fe^{III} , respectively, and exhibits intervalence CT (IVCT) between D and A units (i.e., rapid oscillation of electrons between these units). In this case, IVCT is mediated by CN^- bridges (through-bond) and accounts for the semiconductor-type conductivity ($5.5 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$) in this material.^{25,26} The conductivity can be improved through substitution of $\text{Fe}^{\text{II/III}}$ with second-row transition metals such as $\text{Ru}^{\text{II/III}}$. In the latter case, $\text{K}_{1.2}\text{Ru}^{\text{III}}_{3.6}[\text{Ru}^{\text{II}}(\text{CN})_6]_3 \cdot 16\text{H}_2\text{O}$ exhibited a markedly improved conductivity of $5.69 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$, which was attributed to the more diffuse frontier orbitals of ruthenium.²⁶

More recently, Long and co-workers reported the highest intrinsic conductivity in a three-dimensional MOF to date ($0.16(1) \text{ S}\cdot\text{cm}^{-1}$) (Figure 2).²⁷ $[(\text{NBu}_4)_2\text{Fe}^{\text{III}}_2(\text{dhbq})_3]$

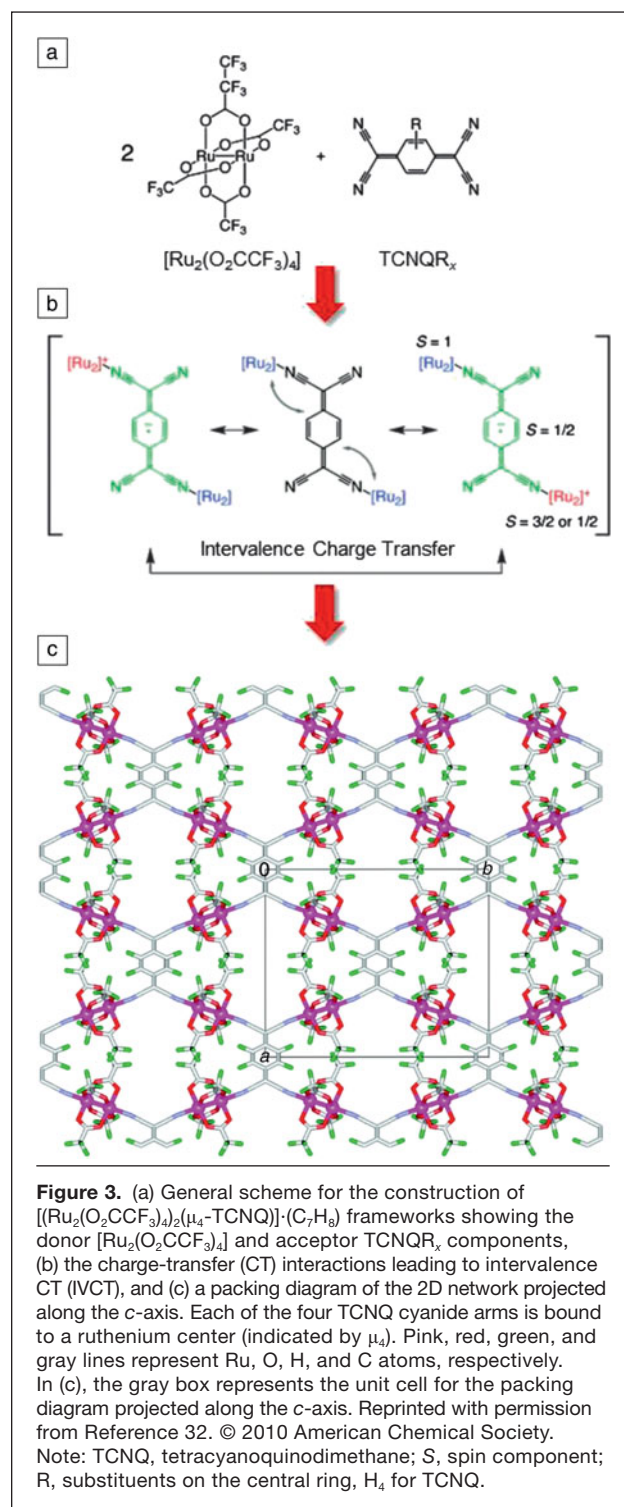


(where NBu_4 = tetra-*n*-butylammonium and dhbq = dihydroxybenzoquinone [Figure 2]) exhibited through-bond mixed valency due to dhbq²⁻³⁻ ligand-based IVCT (Figure 2d). Chemical reduction of the MOF to $\text{Na}_{0.9}([\text{NBu}_4]_{1.8}\text{Fe}_2[\text{dhbq}]_3)$ produced more of the radical dhbq³⁻ species, resulting in a lowering in the intensity of the IVCT band (Figure 2c) as well as a decrease in the material's conductivity ($0.0062(1) \text{ S}\cdot\text{cm}^{-1}$ [Figure 2b]). It is interesting to note the link between the spectroscopic IVCT transitions and the conductivity properties, which are discussed further.^{27,28}

Mixed valency has also been implicated as the origin of conductivity in $\text{Cu}[\text{Cu}(\text{pdt})_2]$ (pdt = 2,3-pyrazinedithiolate) developed by Kitagawa and co-workers, which contains the donor Cu^{I} and acceptor $[\text{Cu}^{\text{III}}(\text{pdt})_2]^-$.²⁹ The reasonably high conductivity of $6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 300 K was attributed to bistability of the mixed-valence $\text{Cu}^{\text{I}}[\text{Cu}^{\text{III}}(\text{pdt})_2]$ and $\text{Cu}^{\text{II}}[\text{Cu}^{\text{II}}(\text{pdt})_2]$ states. The possibility of an IVCT band in the infrared spectrum of $\text{Cu}[\text{Cu}(\text{pdt})_2]$ also suggested the significance of a relationship between low-energy CT interactions and conductivity. A related material, $\text{Cu}[\text{Ni}(\text{pdt})_2]$, was found to have significantly lower conductivity ($1 \times 10^{-8} \text{ S}\cdot\text{cm}^{-1}$), consistent with its larger optical bandgap.³⁰

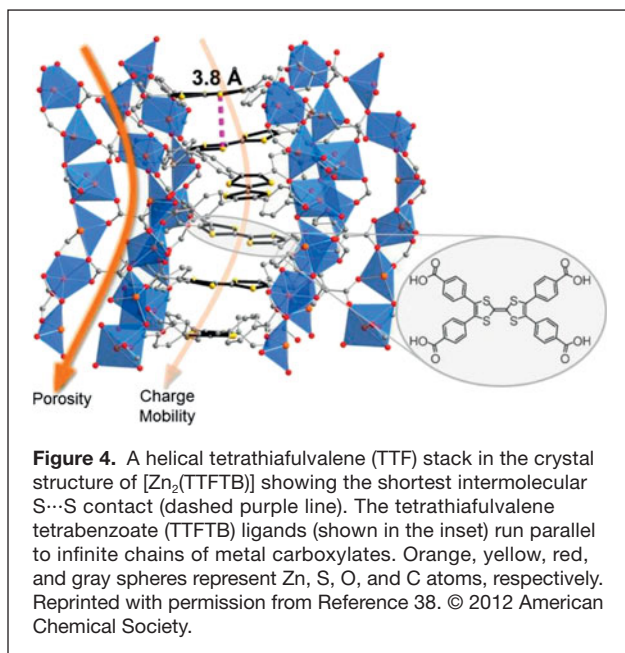
Seminal work by Miyasaka and Dunbar involved two-dimensional (2D) layered materials with the chemical formula $[(\text{M}_2(\text{O}_2\text{CCF}_3)_2(\text{TCNQ}))\cdot\text{C}_7\text{H}_8]$ (where $\text{M} = \text{Ru}, \text{Rh}$, O_2CCF_3 = trifluoroacetate, and C_7H_8 = toluene) which integrated the electron-rich dinuclear complex $[\text{M}_2(\text{O}_2\text{CCF}_3)_4]$ and electron-acceptor TCNQ (Figure 3).^{31,32} Partial CT was observed from the metal node to TCNQ, which was attributed to significant metal–ligand π -backbonding. As a result, the materials are mixed valence. By substituting TCNQ for its more electron-deficient derivative TCNQF₄, one-electron transfer from $[\text{Ru}_2(\text{O}_2\text{CCF}_3)_4]$ to TCNQF₄ was observed.³³ This manifested in strong intralayer magnetic coupling as well as 100× greater conductivity ($4.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$).

Clearly, the strategy of redox matching between donor and acceptor components can be exploited to modulate CT, leading to conducting behavior. Dincă and co-workers developed analogues of the MOF-74 series of frameworks in which the oxygen donor atoms were replaced with sulfur donors, $[\text{M}_2(\text{DSBDC})]$ ($\text{M} = \text{Mn}^{\text{II}}$ and Fe^{II} , DSBDC = 2,5-disulfhydrylbenzene-1,4-dicarboxylate).³⁴ In the Mn^{II} analogue, a relatively high AC charge mobility of $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was derived from time-resolved microwave conductivity measurements, which is comparable to organic semiconductors. Infinite Mn–S chains found within the framework were proposed to serve as conduction pathways. Substitution of the O for S as the donor atom resulted in an order of magnitude increase in conductivity, from 3.0×10^{-13} to $1.2 \times 10^{-12} \text{ S}\cdot\text{cm}^{-1}$ for the Mn^{II} analogue and 4.6×10^{-8} to $5.8 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1}$ for the Fe^{II} analogue.³⁵ Redox matching has also been implicated in an iron 1,2,3-triazolate framework, $[\text{Fe}(\text{C}_2\text{N}_3\text{H}_2)]$ ($\text{C}_2\text{N}_3\text{H}_2 = 1\text{H}-1,2,3\text{-triazole}$), which showed a room-temperature conductivity of $0.77 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$; however, the origins of this behavior were not elucidated.³⁶



Exploiting π -interactions (π - π stacking and π -conjugation)

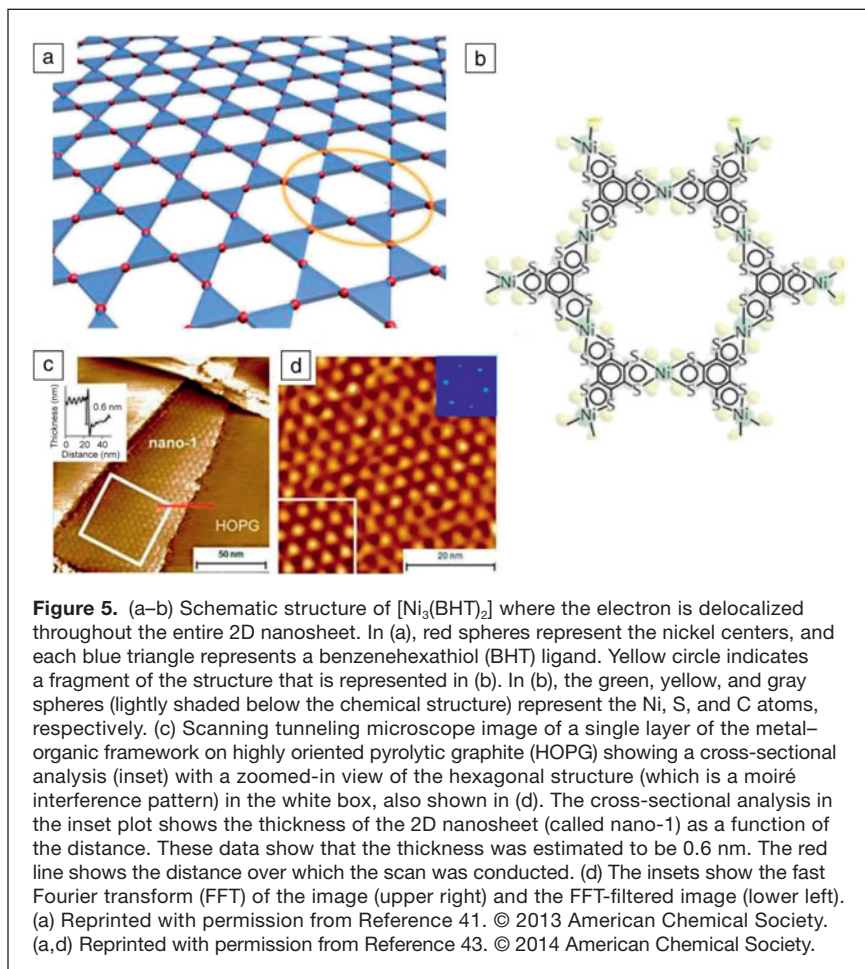
Both through-bond and through-space π -interactions have proven to be particularly effective in promoting conductivity in MOFs.³⁷ Dincă and co-workers employed a ligand, based on the well-known electron donor TTF, which was decorated with benzoate groups for incorporation into the family of



MOFs $[M_2(TTFTB)]$ ($M = Mn^{II}, Co^{II}, Zn^{II}, Cd^{II}$; $TTFTB^{4-}$ = tetrathiafulvalene tetrabenzoate).^{38,39} These MOFs exhibited a similar stacking arrangement between the TTF moieties

as that observed in the aforementioned “organic-metal” TTF-TCNQ ($S \cdots S$ stacking distance $\approx 3.8 \text{ \AA}$ in both) (Figure 1).¹⁹ As shown in **Figure 4**, the MOFs are composed of alternating channels and infinite π - π stacked helical TTF moieties along the c -axis.^{38,39} The conductivity was found to be strongly dependent on the separation between the TTF layers, which was in turn dictated by the size of metal ions, with single-crystal conductivity values ranging from approximately $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ ($M = Zn^{II}$ and Co^{II}) to 10^{-5} and $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ for $M = Mn^{II}$ and Cd^{II} , respectively, in accord with the increase in the cation radii (and the corresponding decrease in the $S \cdots S$ contact distance). The origin of the intrinsic conductivity was attributed to partial oxidation of the TTF moieties to radical cations in the as-synthesized state, which improves the charge-carrier density. The incorporation of stable organic radicals thus represents an important tactic for improving long-range charge mobility.¹⁶

Planar MOFs with extended 2D π -conjugation and graphene-like structures are currently among the most conductive frameworks known. These materials exhibit stacked honeycomb lattices that often incorporate benzene or triphenylene-based ligands with square planar metal centers (**Figure 5**). An interesting property is the relative disposition of the sheets, which can be eclipsed, stepped-parallel,



or staggered, giving rise to one-dimensional pores of differing dimensions. One reason for the high conductivities of these materials is believed to be the presence of increased charge density: to achieve charge balance and a neutral framework with the M^{II} centers, each of the ligands is expected to be oxidized.⁷

A number of relatively highly conductive 2D MOFs have been developed. These include the family of metal catecholate frameworks of Ni^{II} and Co^{II} constructed from hexahydroxytriphenylene (H_6HHTP), which consist of 2D sheets layered between discrete HHTP complexes.⁴⁰ More recently, the groups of Nishihara and Dincă have reported the 2D MOFs $[Ni_3(BHT)_2]$ (BHT = benzenehexathiol)⁴¹ and $[Ni_3(HITP)_2]$ (HITP = hexaiminotriphenylene), respectively.⁴² These materials exhibited strong π -conjugation within their structures, with conductivities of 0.15 and $2 \text{ S}\cdot\text{cm}^{-1}$, respectively.

The materials $[Ni_3(BHT)_2]$ and $[Ni_3(HITP)_2]$ also serve to illustrate the importance of fabrication methods and growth conditions for conductive MOFs. For example, a bulk powder of $[Ni_3(BHT)_2]$ consisted of staggered honeycomb layers, but single nanosheets produced at the liquid–liquid interface revealed a conductivity of $160 \text{ S}\cdot\text{cm}^{-1}$.⁴³ An analogous Cu^{II} structure produced as a thin film revealed

a conductivity of $1580 \text{ S}\cdot\text{cm}^{-1}$ —a record value at room temperature.⁴⁴

A number of related 2D MOFs have subsequently been reported,⁴⁵ and their range of applications have been expanded to include electrocatalysis^{46–49} and chemiresistive sensing.^{50,51} Extensive computational modeling is also underway to understand the influence of structural features such as the stacking geometries.⁵²

Conclusions and outlook

The remarkable structural characteristics of MOFs, coupled with their permanent porosities and the exquisite levels of control that can now be achieved in their synthesis, provides an extraordinary foundation for the discovery of conducting microporous solids. During the past five years, important advances have been made in this area. Building upon the foundations laid in coordination polymers,⁶ a number of clear design parameters have now been outlined that provide a future roadmap for the field.

Elucidating these structure–function relationships in conductive MOFs, however, is still in its infancy. In tandem with experimental work, theoretical calculations are now emerging that tackle the significant challenge of understanding charge transport in large, periodic, multidimensional systems. The long-range connectivity and, unavoidably, the non-uniform or defective nature of MOFs pose challenges for reconciling computational calculations with experimental observations.⁵³

A critical issue mentioned in this article and discussed in detail elsewhere,^{6,7} is the enormous variability in measurement methods used to assess conductive MOFs. The most commonly used method is the four-point probe technique on pressed pellets;⁶ however, there are issues with grain-boundary effects, to which single crystals represent a superior option, enabling measurements of the conduction anisotropy. To circumvent the existence of a contact–sample interface, which can introduce significant variation into the measurements, the development of nondestructive contactless techniques has received considerable attention. One such technique, microwave conductivity, has been widely used to determine the intrinsic conductivity of semiconducting and superconducting materials and has recently been applied to MOFs.^{34,38}

Despite the range of different conductivity techniques available, no direct comparison between them has been made to date, which is essential for the standardization of results. It is also interesting to note the connection drawn between spectroscopic measurements of the CT bands and conducting properties. This spectroscopic approach has received limited attention;^{11,27,28} however, it may become an important complement to conventional conductivity measurements. While the as-synthesized state of a MOF may not be conducting, others may be, and solid-state spectroelectrochemical methods have emerged as useful tools for exploring redox-accessible states.^{10,54,55}

As a relatively new field of research, MOFs have demonstrated myriad unique and desirable properties that are not found in discrete or polymeric systems. Though faced with a number of key challenges, the development of conductive MOFs is envisioned to produce an emergent class of tunable solid-state conductors with substantial untapped potential for areas of technological and industrial interest.

Acknowledgment

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