DOE Award #: **DE-SC0006937, Massachusetts Institute of Technology**
Project Title: **Electronic and Ionic Conductors from Ordered Microporous Materials**
PI: **Mircea Dincă**
Report Date: **10/30/2017**
Research period covered by the report**: 5/16/2012 – 10/30/2017**

Introduction and proposed goals. The proposed work aimed to establish metal-organic frameworks (MOFs) as new classes of high-surface area microporous electronic and ionic conductors. MOFs are crystalline materials with pore sizes ranging from 0.2 to ~ 2 nm (or larger for the latter) defined by inorganic or organic building blocks connected by rigid organic linkers. Myriad applications have been found or proposed for these materials, yet those that require electron transport or conductivity in combination with permanent porosity still lag behind because the vast majority of known frameworks are electrical insulators. Prior to our proposal and subsequent work, there were virtually no studies exploring the possibility of electronic delocalization in these materials. Therefore, our primary goal was to understand and control, at a fundamental level, the electron and ion transport properties of this class of materials, with no specific application proposed, although myriad applications could be envisioned for high surface area conductors. Our goals directly addressed one of the DOE-identified Grand Challenges for Basic Energy Sciences: *designing perfect atom- and energy-efficient syntheses of revolutionary new forms of matter with tailored properties*. Indeed, the proposed work is entirely synthetic in nature; owing to the molecular nature of the building blocks in MOFs, there is the possibility of unprecedented control over the structure and properties of solid crystalline matter. The goals also tangentially addressed the Grand Challenge of *controlling materials processes at the level of electrons*: the scope of our program is to create new materials where charges (electrons and/or ions) move according to predefined pathways.

Achievements towards electronically conducting MOF.

A) Through-space charge transport formalism. In the previous reports, we reported that incorporation of tetrathiafulvalene in a porous MOF, Zn_2TTFTB (H_4TTFTB = tetrathiafulvalene-tetrabenzoate), leads to a material with high charge mobility, 0.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$, as determined by flash-photolysis time-resolved microwave conductivity measurements. We also showed the correlation between the single crystal electrical conductivity and the shortest S···S interaction defined by neighboring TTF cores, which inversely correlates with the ionic radius of the metal ions in the isostuctural MOFs $M_2(TTFTB)$ (M = Mn, Co, Zn and Cd). In these frameworks, TTF moieties form one-dimensional infinite helical π-stacks with 6_5 symmetry, which are responsible for charge transport along the crystallographic *c* axis (Figure 1a). The larger cations cause a pinching of the S···S contact, which is responsible for better orbital overlap between p_z orbitals on neighboring S and C atoms. Density functional theory calculations show that these orbitals are critically involved in the valence band of these materials, such that modulation of the S···S distance has an important effect on band dispersion and, implicitly, on the electrical conductivity.

Because of the anisotropic structure, the electrical conductivity in $M_2(TTFTB)$ along the *c* axis ($\sigma_{\parallel c}$, the direction of TTF stacks) is expected to be higher than that perpendicular to the *c* axis ($\sigma_{\perp c}$). In the last two years, we studied the anisotropy of electrical conduction in $Cd_2(TTFTB)$.

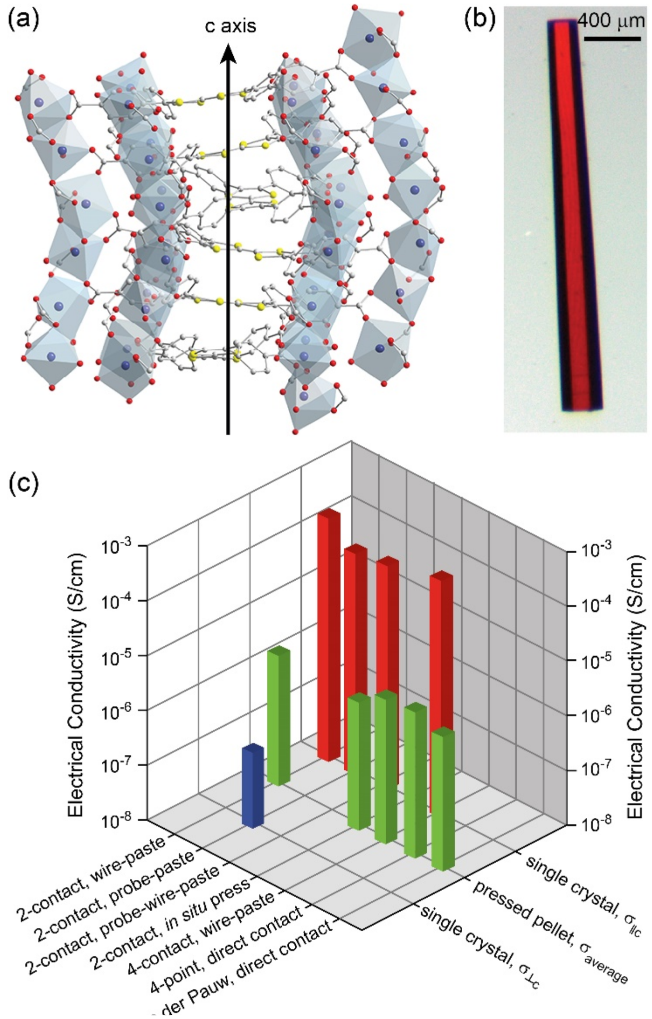


Figure 1. (a) Portions of the crystal structure of Cd_2(TTFTB) viewed along the *c* axis. (b) An optical image of a single crystal of Cd_2(TTFTB) along the *ab* plane. (c) Electrical conductivity data for Cd_2(TTFTB). Blue, yellow, red, and grey spheres represent Cd, S, O, and C atoms, respectively. H atoms and solvent molecules have been omitted for clarity.

We measured the electrical conductivity in pressed pellets of Cd_2(TTFTB) by 2-contact probe, 4-contact probe, 4-point probe, and van der Pauw methods, developed various approaches to fabricate 2-contact-probe single-crystal devices, and measured single-crystal electrical conductivity in the direction either parallel or perpendicular to the crystallographic *c* axis. All electrical measurements were conducted at 297 K, in air with relative humidity of 30%~50%, and in the absence of light. The results are shown in Figure 1c. From this data, it is clear that the two most important factors affecting the conductivity value, when all external variables are controlled for, are the crystallographic direction and the physical form of the sample. Thus, $\sigma_{\parallel c}$ is higher than $\sigma_{\perp c}$ by 2~3 orders of magnitude, clearly attesting the anisotropy of electrical conductivity in this material, and confirming the TTF stacks, which run parallel to the crystallographic *c* axis, as the major charge transport pathway in Cd_2(TTFTB). The anisotropy also suggests that charge hopping between neighboring TTF stacks, which are approximately 19.6 Å apart, is less efficient than within the stacks. Additionally, we find that the electrical conductivity of pressed pellets of Cd_2(TTFTB) lies between $\sigma_{\parallel c}$ and $\sigma_{\perp c}$. This is expected and in line with the single crystal studies because crystallites of Cd_2(TTFTB) in the pressed pellet are randomly oriented, and the electrical conductivity of the pellet is the weighted average of the two directions ($\sigma_{average}$). Indeed, the pressed pellet conductivity lies closer to $\sigma_{\perp c}$, as expected given that $\sigma_{\perp c}$ corresponds to both *a* and *b* crystallographic directions, and is 2~3 orders of magnitude smaller than $\sigma_{\parallel c}$. These results also illustrate how measuring pressed pellets eliminates anisotropy information and in fact tends to underestimate the highest possible conductivity even when grain boundary resistance is minimal. Our results also show that when care is taken to eliminate external variables (e.g. light, atmosphere, temperature), the electrical conductivity values obtained for either single crystals or polycrystalline pellets are consistent across the methods employed, as expected for samples whose conductivity is smaller than the conductivity of the contacts and wires/probes.

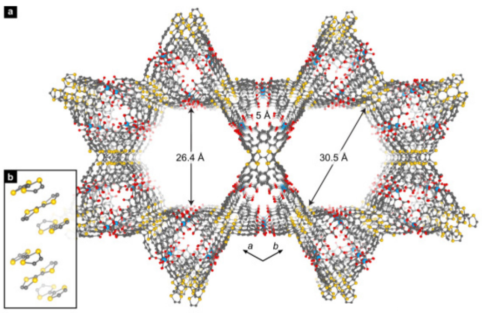


Figure 2. (a) A portion of the X-ray crystal structure of MIT-25 featuring distinct mesopores. (b) The walls are constructed from TTF trimeric stacks aligned along the *c* axis.

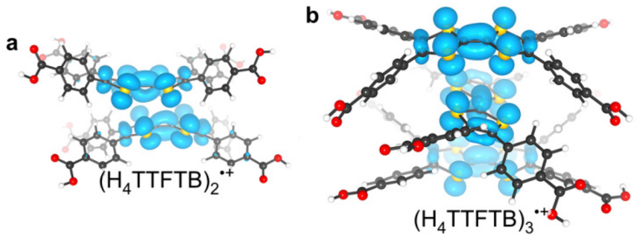
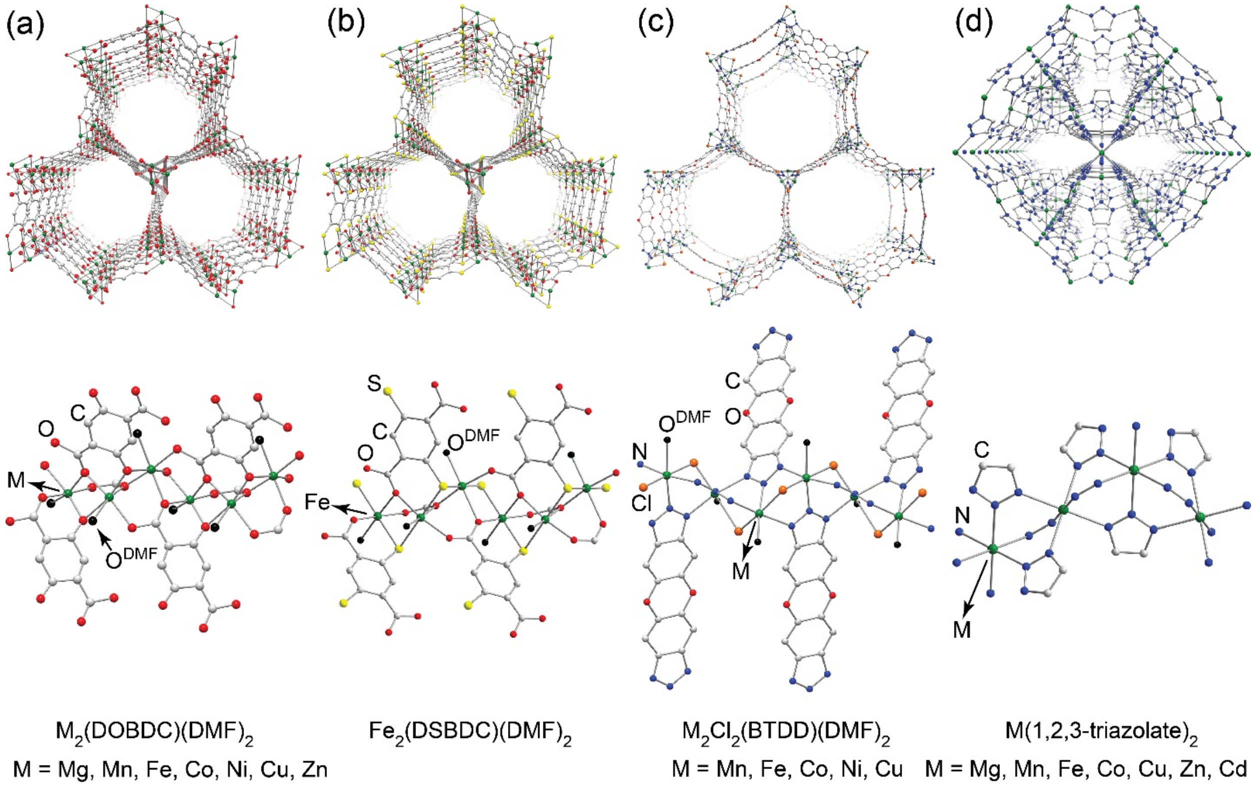


Figure 3. The calculated spin density ($\boldsymbol{\rho}^{\uparrow} - \boldsymbol{\rho}^{\downarrow}$) of (a) $(H_4TTFTB)_2^{\bullet+}$ and (b) $(H_4TTFTB)_3^{\bullet+}$ show full hole delocalization across the TTF core.

Because understanding intermolecular π-stacking interactions is important for designing through-space charge transport materials, we studied the significance of how the organic secondary building unit (SBU), which is energetically competitive with the formation of common inorganic SBUs, can also define MOF topology. Typically, the topology of a MOF is dictated by the geometries of both the inorganic secondary building units (SBUs) and the ligands. Predicting topology by combining SBUs and ligands with predefined geometry is a feature of reticular chemistry. Because reticular chemistry relies on strong, directional bonding between ligands and metals/metal clusters, its predictions break down when non-covalent interactions compete energetically with coordination bonds.

In this study, we show that organic building units relying on strong π interactions that are energetically competitive with the formation of common inorganic SBUs can also play a role in defining topology. Hints of strong π interactions influencing topology in MOFs came from previous work with H_4TTFTB, which formed unusual helical stacks of TTF within frameworks made with transition metals. We reasoned that reacting this ligand with metals exhibiting even more ionic metal-carboxylate bonds, such as Mg^{2+}, would promote the isolation of topologies where organic SBUs play prominent roles. As a result, a new three-dimensionally 3,3,6-connected MOF, $Mg_2H_6(H_3O)(TTFTB)_3$ (TTFTB = tetrathiafulvalene-tetrabenzoate), denoted as **MIT-25**, whose topology is defined by strong intermolecular π and hydrogen bonding interactions, is formed. **MIT-25** exhibits permanent 26.4 × 30.5 Å mesopores running parallel to smaller pores occluded by hydronium ions (Figure 2). Spontaneous



$M_2(DOBDC)(DMF)_2$
M = Mg, Mn, Fe, Co, Ni, Cu, Zn

$Fe_2(DSBDC)(DMF)_2$

$M_2Cl_2(BTDD)(DMF)_2$
M = Mn, Fe, Co, Ni, Cu

M(1,2,3-triazolate)$_2$
M = Mg, Mn, Fe, Co, Cu, Zn, Cd

Figure 4. Portions of crystal structures of four families of MOFs emphasizing pores (top) and coordination environment of metal ions (bottom). H atoms and part of DMF molecules have been omitted for clarity.

oxidation of the TTFTB ligand and subsequent formation of the highly stable trimeric TTFTB π-stacked organic SBUs simultaneously gives rise to a novel mononuclear octahedral Mg^{2+} inorganic SBU. This supported by three additional protons that bridge pairs of dangling carboxylates. A delocalized electronic hole is critical in the stabilization of the TTF triad organic SBUs are supported by density functional theory calculations (Figure 3). This study exemplifies a design principle for future through-space charge transport MOF synthesis.

B) Through-bond charge transport formalism. Another strategy to realize porous and electrically conductive MOFs is to enable charge transport through the skeleton of MOFs. In the previous reports, we showed high charge mobility in Mn_2(DSBDC) ($DSBDC^{4-}$ = 2,5-disulfhydrylbenzene-1,4-dicarboxylate) in which charges possibly transport through $(–Mn–S–)_\infty$ chains, compared electrical conductivity in M_2(DEBDC) (M = Mn, Fe; E = O, S; $DOBDC^{4-}$ = 2,5-dihydroxybenezene-1,4-dicarboxylate), and hypothesized that Fe^{2+} improves electrical conductivity in MOFs. In the last two years, to ascertain the influence of the metal cation on electrical conductivity systematically, we targeted MOFs that feature a broad array of chemical connectivity and composition, and studied $M_2(DOBDC)(DMF)_2$ (M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; DMF = *N,N*-dimethylformamide), $M_2(DSBDC)(DMF)_2$ (M = Mn^{2+}, Fe^{2+}), $M_2Cl_2(BTDD)(DMF)_2$ (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}; H_2BTDD = bis(1*H*-1,2,3-triazolo[4,5-b],[4,'5'-i]dibenzo[1,4]dioxin), and $M(1,2,3\text{-triazolate})_2$ (M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}).The first three families of MOFs display honeycomb structures with 1D tubular pores, whereas the $M(1,2,3\text{-triazolate})_2$ materials exhibit cubic structures with three-dimensional pore networks. The metal ions in all these MOFs are formally divalent and octahedrally coordinated (Figure 4).

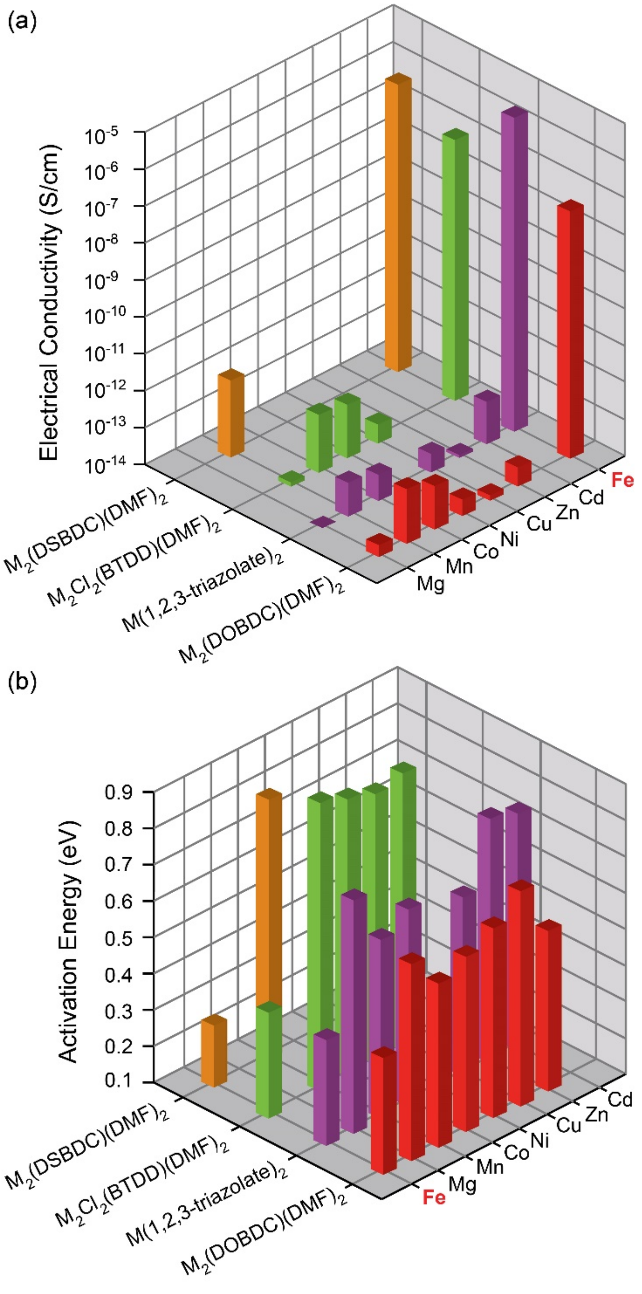


Figure 5. (a) Electrical conductivity and (b) activation energies of $M_2(DOBDC)(DMF)_2$, $M_2(DSBDC)(DMF)_2$, $M_2Cl_2(BTDD)(DMF)_2$, and $M(1,2,3\text{-triazolate})_2$.

We measured electrical conductivity (at 300 K) and activation energies (at 300-350 K) of these four families of MOFs. The Fe-based MOFs exhibit electrical conductivity on the order of $10^{-8} – 10^{-6}$ S/cm, whereas the observed electrical conductivity in all other MOFs is six orders of magnitude lower, on the order of $10^{-14} – 10^{-12}$ S/cm (Figure 5a). Similarly, the Fe analogs exhibit significantly smaller activation energies than the MOFs based on the other metal ions (Figure 5b). To probe the possible existence of Fe^{3+} in the Fe-based frameworks, we characterized them with ^{57}Fe Mössbauer spectroscopy and electron paramagnetic resonance. ^{57}Fe Mössbauer spectroscopy indicated a majority of Fe^{2+}, while the more sensitive technique, electron paramagnetic resonance, revealed existence of Fe^{3+} in Fe(1,2,3-triazolate)$_2$. Although EPR spectra of Fe_2(DOBDC)(DMF)$_2$, Fe_2(DSBDC)(DMF)$_2$, and Fe_2Cl_2(BTDD)(DMF)$_2$ revealed only very broad signals, likely due to significant spin-spin relaxation stemming from closely connected high-spin Fe^{2+} ions, these materials are even more air-sensitive than Fe(1,2,3-triazolate)$_2$. It is therefore reasonable to operate under the assumption that all of our Fe MOFs contain Fe^{3+}.

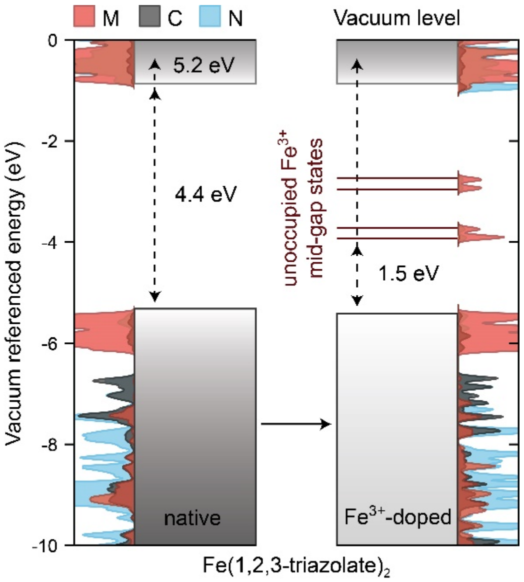


Figure 6. Calculated energy bands and projected density of states of native Fe(1,2,3-triazolate)$_2$ and the hypothetical materials. Valence band minimum energies are shown on the top and the band gaps are shown in the middle of each sub-figure.

To further probe the influence of Fe on the electrical properties of MOFs, we evaluated the electronic structures of the M_2(DOBDC), M_2(DSBDC), and M(1,2,3-triazolate)$_2$ families using density functional theory (DFT) calculations. In the M_2(DOBDC) and M_2(DSBDC) families where Fe^{2+} is in high-spin state (S = 2), Fe_2(DOBDC) and Fe_2(DSBDC) display higher valence band maximum energy and smaller band gap compared with their analogs, respectively, which are consistent with the high electrical conductivity and small activation energies of these two frameworks. However, in the M(1,2,3-triazolate)$_2$ family where Fe^{2+} is in low-spin state (S = 0), Fe_2(1,2,3-triazolate)$_2$ exhibits larger band gap compared with the Mn, Co, and Cu analogs. Taking Fe^{3+} into account, we further calculated a hypothetical material $Fe^{III}_{1/6}Fe^{II}_{5/6}$(1,2,3-triazolate)$_2^{1/6+}$, wherein one sixth of all Fe^{2+} centers are replaced by Fe^{3+}. In this hypothetical material, Fe^{3+} contributes mid-gap states that lower the activation energy and promote the formation of hole carriers (Figure 6). In addition, spin density distribution reveals shows that unpaired electrons are partially delocalized among Fe centers, facilitating inter-iron charge hopping and improving charge mobility. Therefore, we attributed the high electrical conductivity of Fe(1,2,3-triazolate)$_2$ to the presence of mixed-valent $Fe^{3+/2+}$.

The unique role of Fe^{2+} in promoting high electrical conductivity across four different families of MOFs roots in its intrinsic properties. Among Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}, Fe^{2+} exhibits the smallest ionization energy and the smallest Coulombic attraction between its nucleus and its valence electrons, and the standard reduction potential (298 K) of the aqueous $Fe^{3+/2+}$ couple, 0.771 V, is smaller than those of the aqueous $Mn^{3+/2+}$, $Co^{3+/2+}$, and $Cu^{3+/2+}$ couples. Together, these suggest that among the metal ions studied here, the valence electrons of high-spin Fe^{2+} have the highest energy, easing the formation of mixe-valent $Fe^{3+/2+}$ in Fe-based frameworks. Based on this

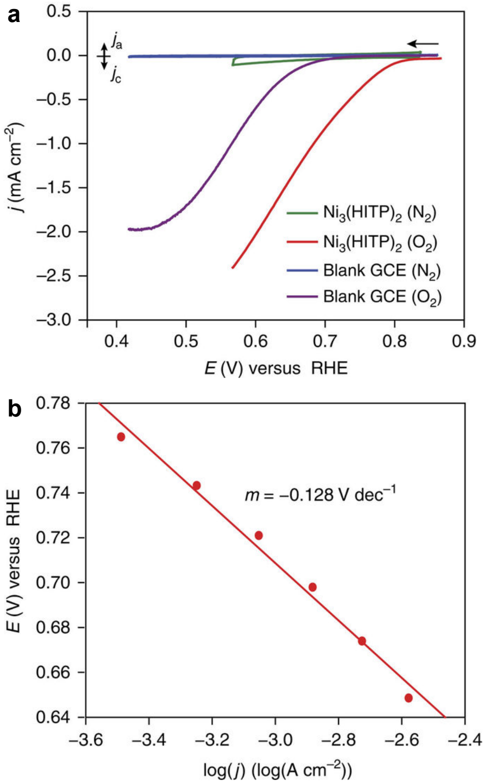


Figure 7. (a) Polarization curves of Ni_3(HITP)$_2$. Scan rate=5 mV s^{-1}, rotation rate = 2,000 r.p.m., counter electrode = Pt mesh, reference electrode = Hg/HgO (1.00 M KOH), working electrode = glassy carbon electrode (GCE). (b) Activation-controlled Tafel plot for Ni_3(HITP)$_2$-electrocatalyzed ORR, derived from the Koutecky–Levich plots.

argument, we hypothesized that Cr^{2+} is also a good candidate for constructing electrically conductive MOFs.

In conclusion, our studies in the past five years on through-bond charge transport in MOFs revealed general design strategies of electrical conductive MOFs. First, redox-active metal ions, such as Fe^{2+}, contribute charge carriers and tend to form mixed valency thus promote electrical conductivity. Second, redox-matching between metal ions and organic ligands is critical because it facilities charge transport. We anticipate that these two design strategies will promote future development of MOFs with high charge mobility and/or electrical conductivity.

C) Applications of electrically conductive MOFs. Developing the heterogeneous oxygen reduction reaction (ORR) electrocatalysts for full cell remains difficult since achieving desired architectural and electronic properties. Several variables must be optimized simultaneously, requiring synthetic tunability which is rare for the solid state materials. The ORR electrocatalysts required high active site density, reproducible synthesis and catalytic activity, stability in the electrolyte and in oxygen and peroxide, and low overpotential relative to the thermodynamic $4e^-$ oxygen-to-water reduction potential of 1.23 V (versus the reversible hydrogen electrode, RHE). One class of materials that could answer these challenges is MOFs. These materials are compelling choices for electrocatalytic applications because their high surface area maximizes active site density, and their tunable chemical structure affords tailor-made microenvironments for controllable reaction conditions within the pores.

We studied electocatalytic activity (Figure 7) with $Ni_3(HITP)_2$ (HITP = 2, 3, 6, 7, 10, 11-hexaiminotriphenylene), which is conductive two-dimensionally layered (σ = 40 S/cm) and structurally reminiscent of the long-studied M-N_x ORR electrocatalysts. Under O_2 atmosphere, the material reduces oxygen with an onset potential ($j = -50\ \mu A\ cm^{-2}$) of 0.82 V in a 0.10 M aqueous solution of KOH (pH = 13.0). The measured ORR onset potential is competitive with the most active nPGM ORR electrocatalysts reported thus far and sits at an overpotential of 0.18 V relative to Pt (E_{onset} = 1.00 V). To the best of our knowledge, the foregoing results demonstrate for the first time electrocatalytic ORR activity in a well-defined, intrinsically conductive MOF. This study highlights conductive MOFs as a powerful platform for the development of tunable, designable electrocatalysts.

Publications during this period, including full acknowledgment sections: 29

1. Grand Challenges and Future Opportunities for Metal–Organic Frameworks (outlook)
Christopher H. Hendon, Adam J. Rieth, Maciej D. Korzyński, and Mircea Dincă
ACS Cent. Sci. **2017**, *3*, 554–563
DOI: 10.1021/acscentsci.7b00197
Publication Date (Web): **June 6, 2017**

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2. Is iron unique in promoting electrical conductivity in MOFs?
Lei Sun, Christopher H. Hendon, Sarah S. Park, Yuri Tulchinsky, Ruomeng Wan, Fang Wang, Aron Walsh, and Mircea Dincă
Chem. Sci. 2017, *8*, 4450-4457
DOI: 10.1039/C7SC00647K
Publication Date (Web): **April 20, 2017**

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3. The Organic Secondary Building Unit: Strong Intermolecular π Interactions Define Topology in MIT-25, a Mesoporous MOF with Proton-Replete Channels
Sarah S. Park, Christopher H. Hendon, Alistair J. Fielding, Aron Walsh, Michael O'Keeffe, and Mircea Dincă
J. Am. Chem. Soc. **2017**, *139*, 3619–3622
DOI: 10.1021/jacs.6b13176
Publication Date (Web): **February 27, 2017**

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4. Pt Electrodes Enable the Formation of μ4-O Centers in MOF-5 from Multiple Oxygen Sources

Minyuan M. Li and Mircea Dincă

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DOI: 10.1021/acsami.6b16821

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5. Metal–organic frameworks for electronics and photonics (review)

Mircea Dincă and François Léonard

MRS Bull. **2016**, *41*, 854-857

DOI: 10.1557/mrs.2016.240

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6. Measuring and Reporting Electrical Conductivity in Metal–Organic Frameworks: Cd_2(TTFTB) as a Case Study

Lei Sun, Sarah S. Park, Dennis Sheberla, and Mircea Dincă

J. Am. Chem. Soc. **2016**, *138*, 14772–14782
DOI: 10.1021/jacs.6b09345
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7. <u>Photon energy storage materials with high energy densities based on diacetylene–azobenzene derivatives</u>

Ggoch Ddeul Han, Sarah S. Park, Yun Liu, David Zhitomirsky, Eugene Cho, Mircea Dincă, and Jeffrey C. Grossman

J. Mater. Chem. A **2016**, *4*, 16157-16165
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Publication Date (Web): **September 13, 2016**

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8. <u>Frontier Orbital Engineering of Metal–Organic Frameworks with Extended Inorganic Connectivity: Porous Alkaline-Earth Oxides</u>

Christopher H. Hendon, Aron Walsh, and Mircea Dincă

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9. Solid-State Redox Switching of Magnetic Exchange and Electronic Conductivity in a Benzoquinoid-Bridged Mn^{II} Chain Compound

Ie-Rang Jeon, Lei Sun, Bogdan Negru, Richard P. Van Duyne, Mircea Dincă, and T. David Harris
J. Am. Chem. Soc. **2016**, *138*, 6583–6590
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10. Electrochemical oxygen reduction catalysed by Ni_3(hexaiminotriphenylene)$_2$

Elise M. Miner, Tomohiro Fukushima, Dennis Sheberla, Lei Sun, Yogesh Surendranath, and Mircea Dincă
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11. **On the electrochemical deposition of metal– organic frameworks**
Nicolò Campagnol, Tom R. C. Van Assche, Minyuan Li, Linda Stappers, Mircea Dincă, Joeri F. M. Denayer, Koen Binnemans, Dirk E. De Vos, and Jan Fransaer
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12. **Electrically Conductive Porous Metal–Organic Frameworks** **(review)**
Lei Sun, Michael G. Campbell, and Mircea Dincă
Angew Chem. Int. Ed. **2016**, *55*, 3566-3579
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13. **Synthesis and Electrical Properties of Covalent Organic Frameworks with Heavy Chalcogens**
Selma Duhović and Mircea Dincă
Chem. Mater. **2015**, *27*, 5487-5490
DOI: 10.1021/acs.chemmater.5b02358
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14. Million-Fold Electrical Conductivity Enhancement in Fe_2(DEBDC) versus Mn_2(DEBDC) (E = S, O)

Lei Sun, Christopher H. Hendon, Mikael A. Minier, Aron Walsh, and Mircea Dincă
J. Am. Chem. Soc. **2015**, *137*, 6164-6167
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15. On the Mechanism of MOF-5 Formation Under Cathodic Bias

Minyuan Li and Mircea Dincă
Chem. Mater. **2015**, *27*, 3203-3206
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16. When the Solvent Locks the Cage: Theoretical Insight into the Transmetalation of MOF-5 Lattices and Its Kinetic Limitations

Luca Bellarosa, Carl K. Brozek, Max García-Melchor, Mircea Dincă, and Núria López
Chem. Mater. **2015**, *27*, 3422-3429
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17. Cation-Dependent Intrinsic Electrical Conductivity in Isostructural Tetrathiafulvalene-Based Microscopic Metal-Organic Frameworks

Sarah S. Park, Eric R. Hontz, Lei Sun, Christopher H. Hendon, Aron Walsh, Troy Van Voorhis, and Mircea Dincă
J. Am. Chem. Soc. **2015**, *137*, 1774-1777
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18. High Electrical Conductivity in Ni$_3$(2,3,6,7,10,11-hexaiminotriphenylene)$_2$, a Semiconducting Metal-Organic Graphene Analogue

Dennis Sheberla, Lei Sun, Martin A. Blood-Forsythe, Süleyman Er, Casey R. Wade, Carl K. Brozek, Alán Aspuru-Guzik, and Mircea Dincă
J. Am. Chem. Soc. **2014**, *136*, 8859-8862
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19. Cation exchange at the secondary building units of metal–organic frameworks (review)
C. K. Brozek and M. Dincă
Chemical Society Reviews **2014**, *43*, 5456-5467
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20. Solvent-Dependent Cation Exchange in Metal–Organic Frameworks
Carl K. Brozek, Luca Bellarosa, Tomohiro Soejima, Talia V. Clark, Nuria López, and Mircea Dincă
Chem. Eur. J. **2014**, *20*, 6871-6874
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21. Ligand Redox Non-innocence in the Stoichiometric Oxidation of Mn_2(2,5-dioxidoterephthalate) (Mn-MOF-74)
Anthony F. Cozzolino, Carl K. Brozek, Ryan D. Palmer, Junko Yano, Minyuan Li, and Mircea Dincă
J. Am. Chem. Soc. **2014**, *136*, 3334–3337
DOI: 10.1021/ja411808r
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22. Selective formation of biphasic thin films of metal – organic frameworks by potential-controlled cathodic electrodeposition
Minyuan Li and Mircea Dincă
Chem. Sci. **2014**, *5*, 107-111
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23. **Ti^{3+}-, $V^{2+/3+}$-, $Cr^{2+/3+}$-, Mn^{2+}-, and Fe^{2+}-Substituted MOF-5 and Redox Reactivity in Cr- and Fe-MOF-5**
Carl K. Brozek and Mircea Dincă
J. Am. Chem. Soc. **2013**, *135*, 12886–12891
DOI: 10.1021/ja4064475
Publication Date (Web): **July 31, 2013**

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24. **Facile Deposition of Multicolored Electrochromic Metal–Organic Framework Thin Films**
Casey R. Wade, Minyuan Li, and Mircea Dincă
Angew. Chem., Int. Ed. **2013**, *52*, 13377-13381
DOI: 10.1002/anie.201306162
Publication date (Web): **October 16, 2013**

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25. **Quantification of Site-Specific Cation Exchange in Metal–Organic Frameworks Using Multi-Wavelength Anomalous X-ray Dispersion**
Carl K. Brozek, Anthony F. Cozzolino, Simon J. Teat, Yu-Sheng Chen, and Mircea Dincă
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26. Mn_2(2,5-disulfhydrylbenzene-1,4-dicarboxylate): A Microporous Metal–Organic Framework with Infinite $(-Mn-S-)_\infty$ Chains and High Intrinsic Charge Mobility
Lei Sun, Tomoyo Miyakai, Shu Seki, and Mircea Dincă
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27. Thiophene-Based Covalent Organic Frameworks
Guillaume H. V. Bertrand, Vladimir K. Michaelis, Ta-Chung Ong, Robert G. Griffin, and Mircea Dincă
Proc. Nat. Acad. Sci. USA **2013**, *110*, 4923-4928
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28. High Charge Mobility in a Tetrathiafulvalene-Based Microporous Metal-Organic Framework
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DOI: 10.1021/ja3059827
Publication Date (Web): **July 24, 2012**

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29. Lattice-imposed geometry in metal–organic frameworks: lacunary Zn_4O clusters in MOF-5 serve as tripodal chelating ligands for Ni^{2+}

Carl K. Brozek and Mircea Dincă
Chem. Sci. 2012, 3, 2110-2113
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