

Single-Ion Li^+ , Na^+ , and Mg^{2+} Solid Electrolytes Supported by a Mesoporous Anionic Cu-azolate MOF

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Supporting Information Placeholder

ABSTRACT: A novel Cu(II)-azolate metal-organic framework (MOF) with tubular pores undergoes a reversible single crystal to single crystal transition between neutral and anionic phases upon reaction with stoichiometric amounts of halide or pseudohalide salts. The stoichiometric transformation between the two phases allows loading of record amounts of charge-balancing Li^+ , Na^+ , and Mg^{2+} ions for MOFs. Whereas the halide/pseudohalide anions are bound to the metal centers and thus stationary, the cations move freely within the one-dimensional pores, giving rise to single-ion solid electrolytes. The respective Li^+ , Na^+ , and Mg^{2+} -loaded materials exhibit high ionic conductivity values of 4.4×10^{-5} S/cm, 1.8×10^{-5} S/cm, 8.8×10^{-7} S/cm. These are the highest values yet observed for MOF solid electrolytes affording single-ion conduction.

Safety concerns, lack of mechanical robustness, and processing difficulties are some of the drivers of current research into solid ion conductors as electrolytes for energy storage devices.^{1,2} An attractive approach to developing new solid electrolytes is the concept of “single-ion” conduction.³ In liquid electrolytes, both anions and cations are mobile, although only the latter require mobility for a functioning battery. The anions need not be mobile, yet their mobility leads to polarization effects, which decrease the operating voltage of the cell. Accumulation of anions at the anode also eventually leads to decomposition of the liquid electrolyte, one of the primary culprits for declining battery performance over time. In single-ion solid conductors, the anions are fixed to the underlying matrix. This prevents anion movement and accumulation and eliminates the polarization effects present in liquid electrolytes.^{3,4} Although most recent research has focused on the development of single-ion conductors for Li-ion batteries, Na- and Mg-ion batteries are expected to benefit from the development of single-ion Na^+ and Mg^{2+} conductors as well. Here, we show that a new Cu-azolate MOF that allows stoichiometric binding of anions functions as a good conductor for Li^+ , Na^+ , and Mg^{2+} ions. The respective ionic conductivities are the highest for this class materials in the absence of additional anion mobility.

MOFs are excellent platforms for exploring single-ion conductors. They are electrical insulators, are compatible with a wide range of mobile cations, are tunable, and present regular pore networks, which allow, in principle, for swift ion movement. The potential impact of these materials as solid electrolytes has been confirmed by numerous examples of high proton conductivity values reported lately.⁵ Reports of Li^+ , Na^+ , or Mg^{2+} ion conductors are considerably more rare.⁶⁻⁹ This highlights the difficulty of

developing systematic approaches to introduce significant content of free Li^+ , Na^+ , or Mg^{2+} ions in the pores of MOFs.

Several strategies have been effective in this sense. For instance, open metal sites in MOFs may be used to immobilize anions, leaving free, charge-balancing cations in the pores.⁷ This strategy was successful in the preparation of the first Li^+ and Mg^{2+} MOF-based solid electrolytes from $\text{Mg}_2(2,5\text{-dihydroxyterephthalate})$ (Mg-MOF-74). However, because MOFs with open metal sites are often neutral compounds, there is limited driving force for binding anions, and the maximal loading for Li^+ and Mg^{2+} ions using this strategy has been 1.26 wt% and 2.51 wt%, respectively, not counting cation content pertaining to free electrolyte. An alternative strategy is the post-synthetic functionalization of inorganic secondary building units (SBUs), such as dehydrating and grafting of LiO^tBu in $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{terephthalate})_6$ (UiO-66).⁸ A third approach is the aliovalent substitution of trivalent ions in a MOF SBU by a combination of divalent and monovalent ions, the former replacing the trivalent ion structurally, with the latter remaining mobile.⁹ For instance, replacing Sc^{3+} in $\text{ScNa}(\text{pyrimidine-4,6-dicarboxylate})_2(\text{H}_2\text{O})_2$ (EHU-1) by combinations of Cd^{2+} and Li^+ or Mn^{2+} and Na^+ affords materials with mobile Li^+ and Na^+ ions, respectively. Neither of the last two strategies are quantitative, however. Indeed, grafting and substitution are both substoichiometric, and have led to maximal mobile Li^+ loadings of 1.06 wt% and 0.08 wt%, respectively, and mobile Na^+ loadings of 0.26 wt%. The strategy described herein allows for Li^+ , Na^+ , and Mg^{2+} loadings that exceed previous reports, pointing to a potential blueprint for optimizing ion carrier density in solid electrolytes.

Solvothermal reaction between bis(1H-1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo-[1,4]dioxin (H_2BTDD) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in an acidic mixture of *N,N*-dimethylformamide (DMF) and isopropyl alcohol at 65 °C yields emerald-green rod-shaped crystals of $((\text{CH}_3)_2\text{NH}_2)[\text{Cu}_2\text{Cl}_3\text{BTDD}](\text{DMF})_4(\text{H}_2\text{O})_{4.5}$ (**MIT-20**). X-ray diffraction analysis of a single crystal of MIT-20 revealed a structure consisting of infinite linearly-bridged Cu SBUs with a single crystallographically unique Cu atom. Each Cu^{2+} ion displays a square pyramidal geometry and is coordinated by three independent triazolate ligands, disposed equatorially, and two chlorides, one terminal equatorial, the other bridging to a neighboring Cu atom (Figure 1). Alternate pairs of Cu atoms are connected either by two BTDD²⁻ ligands, or by two BTDD²⁻ ligands and a $\mu_2\text{-Cl}$. The infinite Cu SBUs are connected by BTDD²⁻ linkers and line one-dimensional hexagonal channels with a crystallographic diameter of ~22 Å. The structure of **MIT-20** is similar to BTDD-based MOFs reported with Mn, Co, and Ni, and is topologically identical to the MOF-74 series, but differs from these in one criti-

cal aspect: whereas the latter are neutral, **MIT-20** is formally anionic, with the charge balance provided by dimethylammonium (DMA) cations residing in the pores. Although X-ray analysis revealed significant positional disorder of the DMA cations, ^1H NMR spectroscopy of an acid-digested sample of **MIT-20** confirmed their identity and a ratio of nearly 1:1 of DMA:BTDD, in line with our proposed formula (Figure S1).

The free DMA suggested that **MIT-20** could function as a host for various cationic species, including Li^+ , Na^+ , or Mg^{2+} , and thus provide a platform for developing solid electrolytes in the presence of appropriate solvents. To test this hypothesis, we attempted to remove guest DMF and water molecules from the as-synthesized material. Thus, we subjected **MIT-20** to a Soxhlet extraction with hot methanol. During this treatment, the initially emerald green crystals gradually turned greenish-yellow (Figure S2), but retained their single-crystal nature. To our surprise, X-ray analysis of one of these resulting crystals revealed that methanol treatment removes one full equivalent of DMACl from **MIT-20** to provide an overall neutral framework where all remaining halides are bridging. Cu atoms in this neutral phase are octahedral, with a methanol molecule completing the coordination sphere along with three *mer*-oriented triazolates and two *trans*-oriented μ_2 -chlorides (Figure S3). Heating a single crystal of the greenish-yellow neutral phase to $100\text{ }^\circ\text{C}$ led to a color change to dark red (Figure S2). Single crystal X-ray diffraction analysis revealed that this colour is associated with the loss of the methanol molecule and formation of $\text{Cu}_2\text{Cl}_2\text{BTDD}$ (**MIT-20d**). **MIT-20d** exhibits square pyramidal Cu centers with *mer*-oriented triazolate linkers and *trans*- μ_2 -chlorides and is identical to those of $\text{M}_2\text{Cl}_2\text{BTDD}$ ($\text{M} = \text{Mn, Co, Ni}$) (Figure 1).¹⁰

Thermogravimetric analysis (TGA) of methanol-exchanged **MIT-20** confirmed that methanol loss occurs also in the bulk above $75\text{ }^\circ\text{C}$ (Figure S4). Accordingly, bulk samples of **MIT-20d** were obtained as red microcrystalline powders by heating methanol-exchanged **MIT-20** at $100\text{ }^\circ\text{C}$ under reduced pressure. The structural changes occurring in moving from anionic **MIT-20** to neutral **MIT-20d** in bulk crystalline samples are evident by powder X-ray diffraction (PXRD) analysis: from the single crystal X-ray diffraction analysis, the neutral compound has a larger *a* parameter, $38.819(4)\text{ \AA}$, relative to that of the anionic phase, $37.171(6)\text{ \AA}$ (Table S3), which leads to a shift of the peaks corresponding to the $(2\bar{1}0)$ and (300) reflections to lower values of 2θ (Figure 2). N_2 adsorption analysis for **MIT-20d** at 77 K revealed a type IV isotherm, indicative of mesoporosity, with total uptake of $\sim 750\text{ cm}^3/\text{g}$ (Figure S5). Fits to this isotherm gave a Brunauer-Emmett-Teller (BET) apparent surface area of $2066\text{ m}^2/\text{g}$ and a pore size distribution peaking at $22.5\text{ \AA}$ (Figure S6), in line with the value expected from crystallography (ca. $23\text{ \AA}$) and with the values reported for other $\text{M}_2\text{Cl}_2\text{BTDD}$ materials.¹⁰

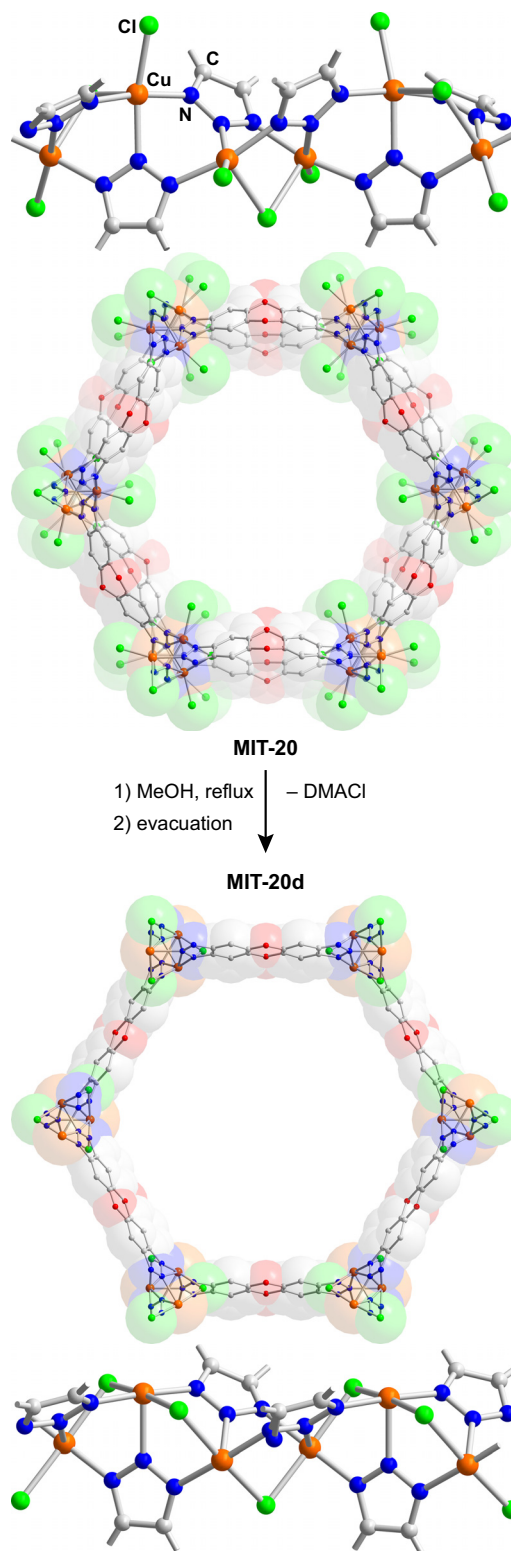


Figure 1. X-ray crystal structures of **MIT-20** and **MIT-20d**, formed from the former by loss of DMACl . The structures of **MIT-20-X** ($\text{X} = \text{LiCl, LiBr, Na, Mg}$), are analogous to **MIT-20**. H atoms are omitted for clarity.

The preferential formation of **MIT-20** under solvothermal conditions suggests that Cu is unique among late first row transition metals in thermodynamically favoring the anionic phase over the neutral one under high chloride concentration. As such, we surmised that treatment of neutral **MIT-20d** with metal halides

would quantitatively yield anionic phases with a large content of free metal cations residing in the pores. Indeed, treatment of **MIT-20d** with one equivalent of LiCl in dry tetrahydrofuran (THF) afforded a green microcrystalline powder exhibiting a PXRD pattern identical to that of **MIT-20** (Fig. 2, green line). Exchange of residual THF with propylene carbonate (PC), a less volatile solvent with a higher dielectric constant that promotes Li ion conductivity yielded $\text{Li}[\text{Cu}_2\text{Cl}_2\text{BTDD}]\cdot 10(\text{PC})$ (**MIT-20-LiCl**) as a free-flowing powder. Inductively-coupled plasma mass-spectrometry (ICP-MS) analysis of an acid-digested sample of **MIT-20-LiCl** confirmed a Li:Cu ratio of 1:2. This ratio did not increase even when **MIT-20d** was treated with excess LiCl, suggesting that the Li content in **MIT-20-LiCl**, 1.38 wt%, is maximized. Importantly, extensive washing and soaking with dry THF at room temperature did not reduce the Li content of **MIT-20-Li**, attesting the strong binding of Cl^- to the Cu^{2+} ions in this material.

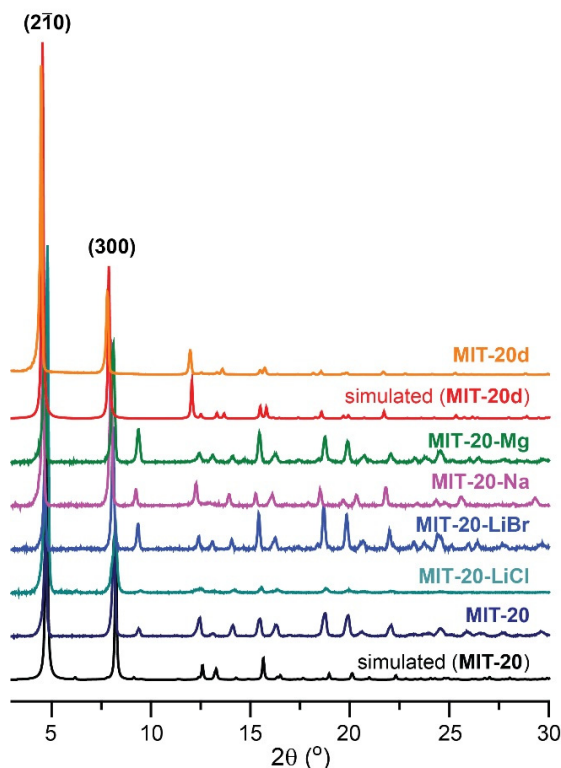


Figure 2. Simulated and experimental PXRD patterns.

The isolation of free cations in the pores of **MIT-20** by reacting neutral **MIT-20d** with metal halides is not limited to Li^+ . Although NaCl and MgCl_2 are nearly insoluble in THF, we were able to access Na^+ and Mg^{2+} -substituted analogs of **MIT-20** by reacting **MIT-20d** with one equivalent of NaSCN or MgBr_2 in THF. Upon exchange of residual THF with PC, this led to quantitative formation of $\text{Na}[\text{Cu}_2\text{Cl}_2(\text{SCN})\text{BTDD}]\cdot 9(\text{PC})$ (**MIT-20-Na**) and $\text{Mg}_{0.5}[\text{Cu}_2\text{Cl}_2\text{BrBTDD}]\cdot 8(\text{PC})$ (**MIT-20-Mg**), respectively, which exhibit record contents of mobile Na^+ and Mg^{2+} ions of 4.23 wt% and 3.76 wt%, respectively. In all cases, structural retention was verified by PXRD analysis (Figure 2) and the precise content of PC, quantified by ^1H NMR of solutions obtained by digesting the respective MOFs with trifluoroacetic acid (Figure S7), were in line with those observed by TGA (Figure S8). Infrared spectroscopy of **MIT-20-Na** showed a C–N stretching mode at 2099 cm^{-1} , indicative of metal-bound SCN^- , and no residual peaks from free SCN^- ($\nu_{\text{CN}} = 2074\text{ cm}^{-1}$) (Figure S9).¹¹ This provides additional evidence that all SCN^- anions in **MIT-20-Na** are immobile.

Ionic conductivity measurements for **MIT-20-X** ($\text{X} = \text{LiCl}, \text{Na}, \text{Mg}$) were performed on powder pellets using alternating current (ac) impedance spectroscopy. Pellets were sandwiched between two stainless steel electrodes under dry N_2 in an air-tight cell. Under these conditions, the Nyquist plots obtained for **MIT-20-X**, shown in Figure 3, exhibit a semi-circle at high frequency and a linear tail at low frequency. The latter is commonly attributed to blocking effects at the electrode and is typical for ionic conductors.^{7–9} These plots revealed similar Li^+ and Na^+ conductivity values of $1.3 \times 10^{-5}\text{ S/cm}$ and $1.8 \times 10^{-5}\text{ S/cm}$ for **MIT-20-LiCl** and **MIT-20-Na**, respectively, at 25°C (Table 1). The value for Li^+ is of the same magnitude as those of $\text{Mg}_2(\text{dobdc})\cdot 0.06\text{LiO}^i\text{Pr}$ ($\sigma = 1.2 \times 10^{-5}\text{ S/cm}$)^{7a} and LiO^iBu -grafted UiO-66 ($\sigma = 1.8 \times 10^{-5}\text{ S/cm}$),⁸ whereas the Na^+ conductivity is highest among single-ion conducting MOFs. The Mg^{2+} ion conductivity in **MIT-20-Mg** was lower, $8.8 \times 10^{-7}\text{ S/cm}$, as expected for the transport of divalent ions carrying a higher charge density through the otherwise conserved electric field environment of **MIT-20**. To exclude the contribution of electronic conduction, we measured current-voltage curves for $\text{Cu}_2\text{Cl}_2\text{BTDD}(\text{DMF})_2$ (Figure S10), which confirmed an electrically insulating behavior, with a conductivity of only 10^{-14} pS/cm in N_2 atmosphere at 25°C (Figure S11).

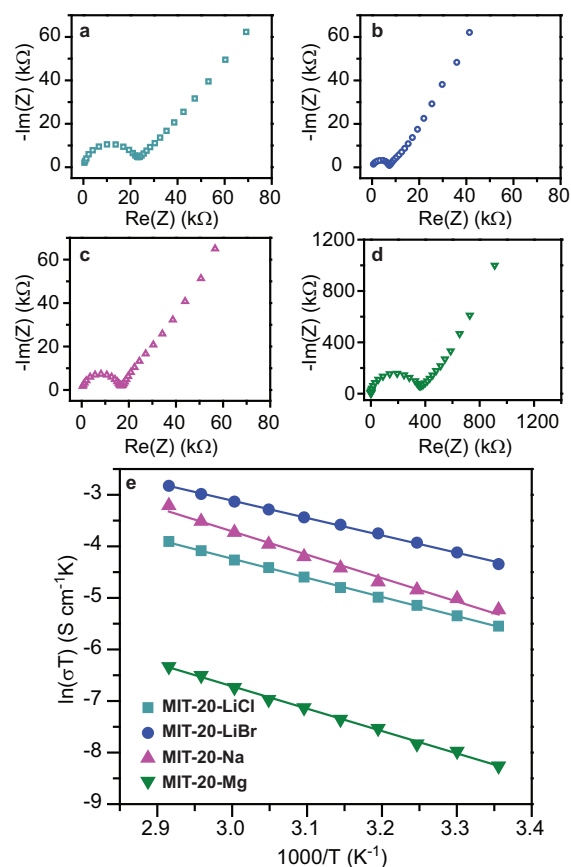


Figure 3. Nyquist plots for (a) **MIT-20-LiCl** (b) **MIT-20-LiBr**, (c) **MIT-20-Na**, and (d) **MIT-20-Mg**. (e) Ionic conductivities as a function of temperature in the range of 25°C to 70°C .

To determine the portion of current carried by lithium ions in **MIT-20-LiCl**, we conducted lithium transference number measurements using a potentiostatic polarization method.¹² The transference number was $t_{\text{Li}^+} = 0.68 (\pm 0.056)$, with certain devices reaching numbers as high as $t_{\text{Li}^+} = 0.86$ (Figure S12). These are significantly higher than the values observed for liquid lithium-ion electrolytes, typically less than 0.4,¹³ and support our assertion

that the current carried by **MIT-20-LiCl** is dominated by Li^+ transport.

One approach to changing the polarity of the pore and potentially increasing the conductivity is the installation of softer, less electronegative anions that interact more weakly with the mobile cations, decreasing the activation energy for transport.⁸ Owing to its unique ability to allow for large cation loading, **MIT-20** is well suited for this purpose. Indeed, reaction of **MIT-20** with LiBr followed by exchange of THF with PC led to the isolation of a material with the formula $\text{Li}_{0.8}[\text{Cu}_2\text{Cl}_2\text{Br}_{0.8}\text{BTDD}]\cdot 10(\text{PC})$ (**MIT-20-LiBr**). Remarkably, even though the molar Li^+ content of this material is 20% lower than that of **MIT-20-LiCl**, its conductivity of 4.4×10^{-5} S/cm, determined by ac impedance spectroscopy, is higher, and exceeds the values reported for other MOF-based single-ion Li-ion conductors (i.e. in the absence of added Li^+ electrolyte).

To ascertain the influence of the pore environment and cation identity on conductivity, we determined the activation energy for ion transport by collecting variable-temperature ac impedance data at 5 °C intervals between 25 °C and 70 °C (Figure S14). In each case, pellets were subjected to a heating-cooling-heating routine (i.e. initial heating to 70 °C, followed by cooling to 25 °C, and re-heating to 70 °C). PXRD analysis after these measurements indicated no significant loss in crystallinity (Figure S15), while infrared spectroscopy showed that all SCN^- remained bound within **MIT-20-Na** (Figure S9). Thus, our materials maintain structural integrity during ion transport measurements. As shown in Figure 3 and Table 1, the activation energy for **MIT-20-LiBr**, 0.29 eV, is indeed lower than that for **MIT-20-LiCl**, 0.32 eV, which suggests that further systematic changes in anion identity may improve the ionic conductivity in **MIT-20-X**, as also shown previously with MOF-74-type materials.^{7b}

Table 1. Ionic conductivity and activation energies for **MIT-20-X** (X = LiCl, LiBr, Na, Mg).

compound	Mobile ion	Guest per mole MOF	σ (S/cm)	E_a (eV)	PC per mole of MOF
MIT-20-LiCl	Li^+	1	1.3×10^{-5}	0.32	10
MIT-20-LiBr	Li^+	0.8	4.4×10^{-5}	0.29	10
MIT-20-Na	Na^+	1	1.8×10^{-5}	0.39	9
MIT-20-Mg	Mg^{2+}	0.5	8.8×10^{-7}	0.37	8

In summary, the reversible phase transitions from an anionic phase to a neutral one supported by a new copper azolate MOF enable the isolation of stoichiometric amounts of mobile Li^+ , Na^+ , and Mg^{2+} ions in one-dimensional mesopores. The respective Li-, Na-, and Mg-loaded materials function as single-ion solid electrolytes, with conductivity values that are among the highest for these types of electrolytes and activation energies that depend on the nature of the immobile anions. The strategy reported here is enabled by the thermodynamic stability of the anionic MOF phase, its formation presenting a strong driving force for the immobilization of large molar amounts of free ions. Identification of other anionic MOFs that become neutral upon loss of stoichiometric salt equivalents may serve as a blueprint for the design of other single-ion electrolytes.

ASSOCIATED CONTENT

Supporting Information

Synthetic details, single crystal and powder X-ray diffraction data, N_2 adsorption isotherms, TGA, NMR and ac impedance spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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