Isoreticular Linker Substitution in Conductive Metal–Organic Frameworks with Through-Space Transport Pathways

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Abstract
The extension of reticular chemistry concepts to electrically conductive three-dimensional metal-organic frameworks (MOFs) has been challenging, particularly for cases in which strong interactions between electroactive linkers create the charge transport pathways. Here, we report the successful replacement of tetrathiafulvalene (TTF) with a nickel glyoximate core in a family of isostructural conductive MOFs with Mn2+, Zn2+, and Cd2+. Different coordination environments of the framework metals lead to variations in the linker stacking geometries and optical properties. Single crystal conductivity data are consistent with charge transport along the linker stacking direction, with conductivity values only slightly lower than those reported for the analogous TTF materials. These results serve as a case study demonstrating how reticular chemistry design principles can be extended to conductive frameworks with significant intermolecular contacts.
Electrically conductive metal–organic frameworks (MOFs) are a promising class of porous conductors.[1,2] They are appealing for applications benefitting from facile charge transport and high surface area, including chemiresistive sensing,[3–6] electrochemical energy storage,[7–11] and electrocatalysis.[12–14] Many conductive MOFs have incorporated building blocks from molecular organic conductors into frameworks.[15–21] Although a diverse library of ligands exists, techniques to regulate the spatial arrangement of electroactive units are less developed.[22–24] Since electronic coupling among linkers often facilitates charge transport, synthetic control over stacking interactions would enable conductive MOFs with tailored structures and transport properties.

Many studies of linker stacking interactions in conductive MOFs have focused on the tetrathiafulvalene tetrabenzoate (TTFTB) linker.[16,22,23,25–27] These materials exhibit a variety of stacking arrangements involving the tetrathiafulvalene (TTF) cores, with close and continuous stacking correlating with the highest conductivities (up to $10^{-4}$ S cm$^{-1}$).[22,23,27] Importantly, a comparative analysis of MOFs with tetratopic carboxylate linkers indicated that TTFTB frameworks tend to exhibit unique topologies due to this linker’s propensity for $\pi-\pi$ interactions and structural flexibility.[23] These characteristics are responsible for the interesting electronic properties, but also hinder translation of design strategies from TTFTB-based MOFs to other linkers. Extending the scope of reticular chemistry – i.e. the controlled assembly of frameworks based on conserved secondary building units (SBUs)[28] – to include structures with pronounced intermolecular interactions is hence an unmet need.[29]

Complexes of nickel(II) with glyoximate ligands have been known for more than a century,[30] and have been employed for analytical determination of nickel content.[31] Like TTF derivatives,[32] they stack extensively in the solid state[33] and form conductive charge transfer salts.[34] Therefore, we hypothesized that a tetratopic linker with a nickel glyoximate core would behave similarly to TTFTB. Here, we present a new metallolinker, nickel(II) bis(dibenzoateglyoximate) (Ni(dbg)$_2$), and show that it forms frameworks with Mn$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ exhibiting the same topology as the corresponding TTFTB MOFs. These structures contain helical linker stacks with Ni···Ni distances as close as 3.70 Å, resulting in electrical conductivities up to $10^{-6}$ S cm$^{-1}$. These results demonstrate a novel instance of isoreticular substitution of linkers in MOFs with through-space transport pathways.

The H$_4$Ni(dbg)$_2$ linker was synthesized via metalation of the glyoxime dibenzoic acid (dbg) ligand (Scheme 1), which was obtained via benzoin condensation of methyl 4-formylbenzoate and
subsequent oxidation and treatment with hydroxylamine (a cobaloxime MOF linker was recently obtained via a similar route\(^{[35]}\)). Combining \(\text{H}_4\text{Ni(dbg)}_2\) with \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\), \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\), and \(\text{Cd(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) under solvothermal reaction conditions mimicking those used for the \(\text{M}_2(\text{TTFTB})\) MOFs\(^{[16,22]}\) led to the isolation of \(\text{Mn}_2[\text{Ni(dbg)}_2] (\text{Mn})\), \(\text{Zn}_2[\text{Ni(dbg)}_2] (\text{Zn})\), and \(\text{Cd}_2[\text{Ni(dbg)}_2] (\text{Cd})\).

Single-crystal X-ray diffraction (SCXRD) showed all three phases are isostructural to one another and to the \(\text{M}_2(\text{TTFTB})\) MOFs, with \(\text{Mn}\) and \(\text{Cd}\) crystallizing in space groups \(P6_5/P6_1\), and \(\text{Zn}\) in space groups \(P6_22/P6_122\). (The measured crystals of \(\text{Mn}\) and \(\text{Cd}\) exhibited inversion twinning, suggesting that the products are not enantiopure.) In each phase, the linkers form helical stacks along the \(c\) axis (Figure 1). The framework metal atoms are coordinated by linker carboxylates and solvent atoms to form one-dimensional (1D) inorganic SBUs. Rhombic 1D pores also extend along the \(c\) direction. Nitrogen adsorption isotherms of activated \(\text{Mn}\), \(\text{Zn}\), and \(\text{Cd}\)

![Scheme 1. Synthesis of \(\text{H}_4\text{Ni(dbg)}_2\).](image)

![Figure 1. Portions of the crystal structure of \(\text{Zn}\), viewed (a) along the \(c\) axis, showing rhombic pores, and (b) perpendicular to the \(c\) axis, showing helical stacking of nickel glyoximate cores. Hydrogen atoms are omitted for clarity.](image)
revealed them to be permanently porous, with Brunauer–Emmett–Teller (BET) surface areas of 543.2(3), 539.8(4), and 486.7(5) m$^2$ g$^{-1}$, respectively (Figure S19), similar to the M$_2$(TTFTB) materials.$^{[16,22]}$

Searches of the Cambridge Structural Database$^{[36]}$ for entries in space groups $P_6_1$, $P_6_5$, $P_6_{12}2$, and $P_6_{52}2$ showed that these M$_2$[Ni(dbg)$_2$] phases (and the isostructural M$_2$(TTFTB) MOFs) are topologically unique among polymeric extended structures. The lack of other MOFs with this topology is consistent with evidence that the geometry and $\pi$–$\pi$ stacking of TTFTB are uncommon among tetratopic linkers.$^{[23,26,29]}$ Closely matched geometries and stacking propensities appear to enable the isoreticular substitution of Ni(dbg)$_2$ for TTFTB.

**Table 1.** Crystallographic linker stacking distances in M$_2$[Ni(dbg)$_2$] MOFs.

| MOF | Interplanar (Å) | Ni--Ni (Å) | Slip (Å) |
|-----|-----------------|-------------|----------|
| Mn  | 3.6663          | 3.8131(9)   | 1.0480(2) |
| Zn  | 3.5767          | 3.7027(6)   | 0.9582(2) |
| Cd  | 3.5887          | 3.7704(11)  | 1.1566(3) |

The pronounced stacking of nickel glyoximate complexes often lead to anisotropic optical and electronic properties.$^{[37,38]}$ Hence, we sought to further quantify the stacking geometries in these MOFs (Figure 2). Each nickel glyoximate core is nearly planar, with < 0.1 Å deviation of all atoms from the least-squares plane (Tables S4–S6). The separation between adjacent least-squares planes is slightly longer for Mn than Zn and Cd (Table 1). Because the Ni(dbg)$_2$ ligands are not exactly centered on the six-fold screw axes, the Ni--Ni distances are longer than the interplanar
spacings. These contact distances are similar to the S···S distances observed in the M$_2$(TTFTTB) analogs (3.65–3.77 Å), and ~0.1–0.6 Å longer than Ni···Ni distances in other nickel glyoximate complexes.[37] The slip distances between adjacent cores (defined as the magnitude of the projection of the Ni···Ni vector onto the least-squares plane) are shortest for Zn and longest for Cd.

Distinctions in the linker stacking geometries can be explained by the different coordination environments of the metal centers in the inorganic secondary building units (SBUs). In each phase, two crystallographically independent framework M$^{2+}$ centers coordinated by linker carboxylates and solvent oxygen atoms form continuous 1D SBUs encircling the three-fold screw axis (Figure 3). The five-coordinate Mn$^{2+}$ centers in Mn form corner-sharing polyhedra that pack relatively inefficiently, resulting in the longest interplanar spacing. In Zn, the alternating tetrahedra and pseudo-octahedra do not share any oxygen atoms. The small ionic radius of Zn$^{2+}$ coupled with a relatively straight SBU results in the shortest interplanar, Ni···Ni, and slip distances.[39] Finally, the Cd$^{2+}$ centers in Cd form edge-sharing polyhedra that effectively compress the pitch of the linker stacking helix while increasing its diameter compared to Mn and Cd. As a result, the interplanar spacing of Cd is similar to Zn, while the slip distance is the largest among the three phases.

![Figure 3. Different coordination environments in the inorganic secondary building units of (a) Mn, (b) Zn, and (c) Cd, which comprise carboxylate-bridged chains of metal centers.](image-url)
Because stacking often influences the electronic transitions of $d^8$ square planar complexes in the solid state,\cite{40} we examined the diffuse reflectance UV–visible (DRUV–vis) spectra of Mn, Zn, and Cd (Figure 4). Bands in the region 30,000 to 40,000 cm$^{-1}$ are likely transitions with predominantly $\pi \rightarrow \pi^*$ character from the dbg ligand (Figure S20).\cite{38} Bands between 22,000 and 28,000 cm$^{-1}$ are assigned to metal-to-ligand charge transfer (MLCT) transitions from Ni 3d orbitals to states with $\pi^*$ character.\cite{38,41} All of these features are present in the solution-phase absorbance spectrum of $H_4Ni(dbg)_2$, with the bands blue-shifted by 1,000–3,000 cm$^{-1}$ compared to the MOFs.

Bands between 16,000 and 22,000 cm$^{-1}$ are present in all of the solid-state MOF spectra, but absent from the solution-phase linker spectrum. We tentatively assign these features to transitions originating from filled Ni 3d orbitals to the empty Ni 4pz orbitals. Closer Ni--Ni distances result in red-shifted bands in this region for nickel glyoximate complexes.\cite{37,38,42} The presence of these features in the MOF spectra and their absence in the solution-phase spectrum of $H_4Ni(dbg)_2$ are consistent with previous suggestions that the $3d_z^2 \rightarrow 4p_z$ transition is intensified by mixing with interatomic charge transfer interactions in the solid state.\cite{41} The more intense features in Zn and Cd likely correlate with their closer Ni--Ni distances and interplanar spacings compared to Mn.

![Figure 4. Kubelka–Munk-transformed diffuse reflectance UV-visible spectra of Mn, Zn, and Cd, and absorption spectrum of a 0.025 mM solution of $H_4Ni(dbg)_2$ in DMF.](image)

Motivated by the structural analogy to the conductive $M_2$(TTFTB) MOFs and the precedent of stacking-dependent transport properties in nickel glyoximate complexes,\cite{43} we investigated the
electrical conductivities of Mn, Zn, and Cd. Two-contact probe single-crystal devices of Mn and Cd (Figures S21 and S22) revealed champion conductivity values of $2.0 \times 10^{-7}$ S cm$^{-1}$ for Mn and $2.7 \times 10^{-6}$ S cm$^{-1}$ for Cd along the stacking direction (Tables S7 and S8). These values are about 2–3 orders of magnitude lower than the TTFTB analogs\textsuperscript{[22]} but higher than neutral nickel glyoximate complexes with similar interplanar spacings.\textsuperscript{[34]} (Due to crystal size limitations, we were unable to carry out single-crystal measurements on Zn.) Two-contact probe pressed pellets yielded typical values of $< 10^{-10}$ S cm$^{-1}$ for Mn, Zn, and Cd (Tables S9–S11 and Figure S23). The lower pellet conductivities are consistent with the expected anisotropic charge transport pathways. One important distinction from the M$_2$(TTFTB) analogs\textsuperscript{[16,22]} is the lack of linker oxidation or mixed-valency in the as-synthesized M$_2$[Ni(dbg)$_2$] MOFs. Neither DRUV–vis nor electron paramagnetic resonance spectroscopies exhibited signatures of radical species (Figure S24), suggesting that the somewhat inferior charge transport properties of these materials relative to their TTFTB congeners are likely due to their lower carrier concentrations. However, attempts to post-synthetically oxidatively or reductively dope these materials have not resulted in higher conductivities thus far (Table S12).

In summary, whereas TTFTB stood out thus far in forming unique MOF topologies with strong stacking that engendered good charge transport, isoreticular substitution of TTFTB with new nickel glyoximate complexes yielded three new materials with identical topology and similar electrical properties in line with their reduced charge carrier density. This work introduces square planar metal glyoximate complexes as a metallolinker platform for MOFs in which the intermolecular arrangements of linkers delineate their optical and electronic properties. In general, further development of isoreticular strategies for linkers exhibiting strong stacking interactions can inform the targeted design of new conductive MOFs.

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