The Organic Secondary Building Unit: Strong Intermolecular π-Interactions Define Topology in MIT-25, a Mesoporous MOF with Proton-Replete Channels

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Supporting Information Placeholder

ABSTRACT: The structure-directing role of the inorganic secondary building unit (SBU) is key for determining the topology of metal-organic frameworks (MOFs). Here, 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. We demonstrate the importance of the organic SBU in the formation of Mg2H6(H3O)(TTFTB)3, a mesoporous MOF with the new ssp topology. A delocalized electronic hole is critical in the stabilization of the TTF triad organic SBUs and exemplifies a design principle for future MOF synthesis.

The topology of a metal-organic framework (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. It has allowed the synthesis of thousands of new materials with increasingly complex topologies even though the experimental conditions that lead to the self-assembly of a given inorganic SBU are largely empirical. The premise of reticular chemistry is that most common SBUs are thermodynamic sinks whose formation and structure are rarely disturbed by non-covalent interactions. However, 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. This results in surprising and often new topologies.

We have set out to learn whether we can predict when thermodynamic products are likely to deviate from those predicted by reticular chemistry and what are the causes that lead to these exceptions. We further ventured to test whether the non-covalent interactions that prevent the formation of empirically expected SBUs may be used to direct topology themselves. This would provide access to new materials and contribute to a deeper understanding of the physical principles governing MOF synthesis.

Here, we report the synthesis and characterization of a new three-dimensionally connected MOF, Mg2H6(H3O)(TTFTB)3 (TTFTB = tetrathiafulvalene-tetrabenzoate), denoted as MIT-25, whose topology is defined by strong intermolecular π- and hydrogen bonding interactions. MIT-25 exhibits permanent 26.4 × 30.5 Å mesopores running parallel to smaller pores occluded by hydronium ions. Controlling topology by employing π-stacked organic supramolecular building blocks (i.e. organic secondary building units) serves as a powerful paradigm for the design of novel hybrid frameworks.

In some cases, π interactions provide a stabilization energy of at least –13.0 kcal/mol, far greater than hydrogen bonding in water (1-6 kcal/mol depending on the conditions), and competitive with even some metal-ligand bonds frequently found in MOFs. It is therefore conceivable that using ligands with a high propensity for strong π interactions will be competitive with the self-assembly of canonical inorganic SBUs, leading instead to the formation of unusual topologies centered around the organic SBUs. Hints of strong π interactions influencing topology in MOFs came from previous work with H4TTFTB, 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 (i.e. weaker) metal-carboxylate bonds, such as Mg2+, would promote the isolation of topologies where organic SBUs play prominent roles.

Reaction of H4TTFTB with Mg(NO3)2·6H2O in a mixture of N,N-dimethylformamide (DMF), water, and ethanol yielded red needles of [Mg2H6(H3O)(TTFTB)3] 1.5(DMF)·(H2O), which crystallizes in space group R3 (Figure 1a). Three TTFTB ligands form a tightly packed organic SBU with TTF–TTF distances of 3.73 Å. These triad organic SBUs do not form infinitely continuous π-stacks, but exhibit close inter-triad S–S contacts of 3.56 Å (Figure 1b and c). The twelve carboxylates in each triad are connected to four Mg2+ ions, and each octahedral Mg2+ ion is connected facially to two independent triads. Although individual Mg2+ ions are separated by at least 10.23 Å, thereby forming monometallic inorganic SBUs, the coordination environment around each Mg2+ ion is further supported by three μ2-protons that are shared between neighboring carboxylates bound to the same Mg2+ ion (Figure 1c).
Figure 1. (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. (c) The structure exhibits a mononuclear octahedral Mg\(^{2+}\) inorganic SBU supported by three additional protons that bridge pairs of carboxylate groups. (d) Ligand and metal nodes are represented by grey and blue shapes, respectively. (e) Four neighboring Mg\(^{2+}\) sites are linked by a TTFTB triad. (f) A representation of a single ssp net within MIT-25, exhibiting a ‘three-tier’ hexagonal pore structure. (g) The small pore is helical, and the ssp net allows interpenetration of two densely woven frameworks, forming the terminal TTF stacks in the c-direction.
The crystallographic positions of these shared protons could not be determined from X-ray diffraction analysis alone. Their position bridging between two oxygen atoms was assigned from density functional theory (DFT) calculations (Figure 1c). This unusual inorganic SBU was further explored by construction of a cluster model, [Mg(OAc)₆]⁻ shown in Figure S1, which upon geometric relaxation converged to a tri-pyridine-H⁺ conformation analogous to that observed in MIT-25. Importantly, omission of the pyridine protons in this acetate-based model system resulted in the destruction of the octahedral coordination environment around Mg²⁺, inferring that the protons serve both charge-balancing and structural roles.

Considering each TTFTB ligand as two three-connected nodes (Figure 1d), and each MgH₃(O₂C–)₆ unit as a six-connected node (Figure 1c), MIT-25 self-assembly into the new spc topology (a 3,3,6-connected net, Figure 1f). The spc topology is most closely related to the nbo net (a comparison is presented in Figure S2). In MIT-25, two spc nets are interpenetrated (Figure 1g) and define two parallel channels parallel to the c axis with geometric pore apertures of 26.4 × 30.5 Å and 5.0 × 5.6 Å (Figures 1a and S3).

MIT-25 is permanently mesoporous. Thermogravimetric analysis of as-synthesized material upon washing with DMF and ethanol, followed by soaking in tetrahydrofuran (THF) revealed a plateau between approximately 100 and 200 °C (Figure S4). Heating a sample of MIT-25 under vacuum at 200 °C followed by an N₂ adsorption isotherm at 77 K revealed Type IV isotherm with a maximal N₂ uptake of ~330 cm³/g. Barrett-Joyner-Halenda (BJH) pore size analysis using Krusk-Jaroniec-Sayari correction for hexagonal pores and Brunauer-Emmett-Teller (BET) fits to this isotherm revealed a pore size of 27.2 Å, in line with crystallographic analysis, and an apparent surface area of 830 m²/g (Figures S5 and S6). The molar surface area, 1756 m²/mol, is also in line with other mesoporous MOFs with similar pore sizes.

Formulating the inorganic SBUs as [MgH₃(O₂C–)₆]⁻ and considering that there are two inorganic SBUs and one organic SBU (i.e. the three-ligand triad) in each formula unit, MIT-25 would carry a doubly negative charge: [Mg₂H₆(H₃O)(TTFTB)₃]²⁻. We employed electron paramagnetic resonance (EPR) to elucidate the nature of the charge compensating species. Indeed, MIT-25 is paramagnetic; the nature of its radicals were further investigated by EPR experiments. Continuous-wave EPR spectra show “powder” rhombic resonance patterns with principal g values of 2.014, 2.010, 2.0061, 2.002 at the turning points. These are consistent with sulfur based radicals (Figure S8). This was confirmed by collecting spectra at two different frequencies (9 and 34 GHz), which showed that the positions of the resonances were caused by g anisotropy rather than hyperfine coupling. All spectra show more than one set of overlapping resonances, indicating either the presence of more than one radical or the same radical in different chemical environments. We then employed DFT calculations to further substantiate the existence of a single radical per triad. Our model systems, detailed below, revealed that the (TTFTB)₃ triad could accommodate a single hole, evenly delocalized across the three TTF cores. Examination of the spin density further suggested that the observed EPR splitting was unlikely arising from hyperfine coupling. Considering these evidences, each organic SBU is best formulated as (TTFTB)⁺⁺.

From elemental analysis, we assign the remaining positive charge to be a hydronium ion, H₃O⁺. An analysis of the electron density and electrostatic potential of hydronium-free MIT-25, shown in Figure 2, revealed regions of high potential only in the small pore, suggesting that they likely accommodate the H₃O⁺ ions. Indeed, although the small pore is narrow, it is sufficiently large to accommodate H₃O⁺ and water. Thus, the balanced overall formula for MIT-25 is best represented as Mg₂H₆(H₃O)(TTFTB)₃, where the (TTFTB)₃ triad carries a −11 charge and the hydronium is likely found in the small pore.

We conjecture that the radical TTF-based organic SBU is critical in forming the spc net with Mg²⁺, but is it unique in doing so? To investigate whether other four-connected ligands might give rise to the same net when combined with Mg²⁺ ions, we substituted the TTF core with pyrene, another well-known electron-rich aromatic moiety with a propensity to create interacting aromatic π-systems, and investigated the reactivity of 1,3,6,8-tetakis(p-benzoic acid)pyrene (H₂TBAPy) with various Mg²⁺ precursors. Despite systematically changing reaction conditions including temperature, solvent system, and reagent concentration, we were not able to isolate the spc net with H₂TBAPy. Instead, it exclusively formed [Mg₂(H₃O)(TBAPy)](μ₂-OH)₂(H₂O)₂; (DMF)₆H₂O(dioxane)₀.₅ (MIT-26). Crystallizing in space group P1, MIT-26 is a two-dimensional MOF wherein neighboring pyrene moieties exhibit short contacts of 3.59 Å, but fail to reproduce the triad organic SBUs that are critical for the formation of the spc net (Figure S9). Thus, despite having similar molecular dimensions and rectangular geometry, H₂TTFTB and H₂TBAPy form vastly different topologies, highlighting the unique role of TTF cores and the organic SBUs in defining overall MOF structure.

Insight into the particular role of TTF, especially as contrasted with pyrene, comes from in-depth computational analysis of the electronic structure of the two ligands, as well as their supramolecular synthons. The calculated electronic structure of H₂TTFTB is similar to that found for TTF itself, with the electrostatic potential map revealing an electron-rich core centered on the sulfur atoms (Figure S10a). H₂TBAPy exhibits a comparable electronic structure, with electron density localized on the pyrene core (Figure S10c). Stacking of two neutral H₂TTFTB or H₂TBAPy is energetically favored, with formation energies of −1.62 and −1.84
kcal/dimer, respectively (Table 1). Calculations suggest that both dimers are further stabilized by the presence of a fully delocalized hole, with the formation energies for the oxidized dimers reaching −5.52 and −4.53 kcal/dimer, respectively (Figure 3a,c). Although oxidation by one electron leads to relative stabilization in both cases, only TTF has a readily accessible oxidation potential (E = 0.34 V vs. Ag/AgCl in MeCN), whereas TBAPy remains neutral under similar experimental conditions (E = 1.16 V vs. SCE in MeCN). Thus, we would not expect H₄TBAPy to oxidize in air to form the hypothetical dimer presented in Figure 3c.

The addition of a second neutral H₄TTTB ligand to a (H₄TTTB)⁺⁺ dimer provides significant further stabilization to the (H₂TTTB)⁺⁺ trimer (−13.73 kcal/trimer), with the hole now fully delocalized over all three TTF cores (Figure 3b). Delocalization of the hole over all three TTF cores in the (TTFTB)⁺⁺ SBU in MIT-25 is supported experimentally by X-ray crystallographic analysis, from examination of the C–S and central C=C bond lengths, which vary by only 0.0015 Å and 0.007 Å, respectively (Table S2). This indicates that all three TTF units in a single triad carry equivalent (partial) oxidation states.¹⁷

Table 1. Formation energies for neutral and oxidized dimeric or trimeric H₄TTTB and H₄TBAPy species, as calculated from DFT.

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<th>Species</th>
<th>Formation energy (kcal/mol)</th>
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<tr>
<td>(H₂TTTB)₂</td>
<td>−1.62</td>
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<tr>
<td>(H₄TTTB)⁺⁺</td>
<td>−5.52</td>
</tr>
<tr>
<td>(H₂TTTB)⁺⁺</td>
<td>−13.73</td>
</tr>
<tr>
<td>(H₄TBAPy)₂</td>
<td>−1.84</td>
</tr>
<tr>
<td>(H₄TBAPy)⁺⁺</td>
<td>−4.53</td>
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Although the formation of π-interacting motifs provides overall stabilization, as seen with MIT-26 and numerous other examples, these studies emphasize the importance of accessing oxidized species as well as delocalizing the holes to stabilize organic SBUs. These principles are illustrated in MIT-25, whose unique mesoporous structure and new topology only arise because of the organic SBU. The formation of π-stabilized organic SBUs by the deliberate introduction of holes may serve as a general strategy for the formation of materials with new topologies.

ASSOCIATED CONTENT

Supporting Information
Detailed experimental procedures and computational details; single crystal and powder X-ray diffraction data, N₂ adsorption isotherms, TGA and EPR. 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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