

Triptycene derivative based Metal-Organic Frameworks: Unusual Topologies and Electronic Properties

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[Abstract]

Research of two-dimensional (2D) semiconductive metal-organic frameworks (MOFs) has been an attractive topic for coordination chemists and material scientists, as these materials intrinsically and perfectly combine two important features: porosity and conductivity together within a sole material. Hence, various applications, such as electrocatalysis, FET devices, chemiresistive sensors and supercapacitors have been pursued for these materials. However, with a rigid planar structure, triphenylene derivative ligands tend to create two-dimensional layered graphene analogue structures with strong π - π interactions and leave little space for chemists to introduce any manipulation. To create some MOFs with potential electric and magnetic properties, herein we introduce a new series of ligands: triptycene derivatives and MOFs based on these ligands. Similar to the triphenylene ligands, triptycene derivatives get spontaneously oxidized and form a triradical linkage in the scaffolds, in contrast, absence of strong intermolecular π - π interactions has resulted 3-D MOF structures with rare topologies and unprecedented connectivity.

[Introduction]

The study of topological insulators has become an extremely hot topic of condensed matter physics, as these materials have unusual band structures like Dirac cones, and exotic electronic properties. To date, most topological materials are solid-state semiconductors, like Bi_2Te_3 , and their band structure is determined by the topology of crystal structures. Very few works have been concerning the construction of interesting topologies with molecule-based materials. On the other hand, in the field of metal-organic frameworks (MOFs), people have established a mature crystal engineering method to build porous coordination networks with desired topologies, but no effort has even been performed to examine the physical properties that arises from these topologies. This research intends to combine the crystal engineering strategies with the study of topological materials, to develop a synthetic strategy of functional MOFs with special topologies, such as Kagome and gyroid, and to understand the relationship between the topologies of MOFs and their electronic and magnetic properties.

In practice, this research focuses on the preparation of triptycene derivative based metal-organic frameworks (MOFs). The triptycene molecule has a rigid structure and a 3-fold axis of rotation, therefore, combining with transition metals with different coordination environment preferences, such as square planar, tetrahedral and octahedral, coordination networks with various topologies, including Kagomé lattices and gyroid structures. Triptycene derivatives have a same feature: when forming a coordination polymer, the ligand will get partially oxidized and form an organic radical with multiple spins. With the special topology of these networks, interesting physical properties, such as high conductivity, molecular magnetism, exotic band structures and Dirac cones, spin frustration and spin liquids may be observed.

[Methods]

Preparation and characterization of the MOFs: To date, two ligands, hexahydroxy triptycene (TripOH-H) and hexahydroxy 13,14-dimethyltriptycene (TripOH-Me) were prepared according to the literature methods. (Fig. 1) Metal-organic frameworks with transition metals were prepared via hydrothermal methods and slow diffusion methods. In these reactions, metal acetate complexes were used to deprotonate the triptycene ligands and the ligands got spontaneously oxidized by air during the hydrothermal reactions and diffusion. Crystals or crystalline powders were collected and subjected to single crystal XRD, PXRD, SEM and TEM measurements to determine their structures and morphologies.

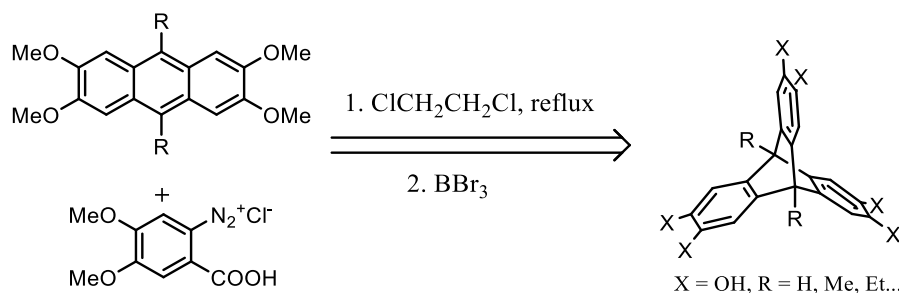


Fig. 1. Preparation of hexahydroxy triptycene derivative ligands.

[Results and Discussion]

Unlike the reported 2D semiconductive MOFs, by varying the metal cations and axial R-groups of the ligand, structures with different topologies could be obtained. In the case of Ni-TripOH-H, SEM image suggested a prism crystal with tetragonal unit cells. For Ni-TripOH-Me, two phases could be found by manipulating the solvent and reaction time. The single crystal of phase B was obtained, and the structure was determined. (Fig. 2) The structure consists the triradical form of TripOH-Me bridging octahedral coordinated Ni(II) with two water molecules filling the coordination sphere. Two type of 1-D rectangular channels are found, one with a dimension of 1.8nm × 1.2nm, and the other with a dimension of 0.7 × 0.6nm. It is noteworthy that the 3-D structure is composed by interweaved ladders, which are not covalently bonded but connected with radical interactions. Therefore, chains of

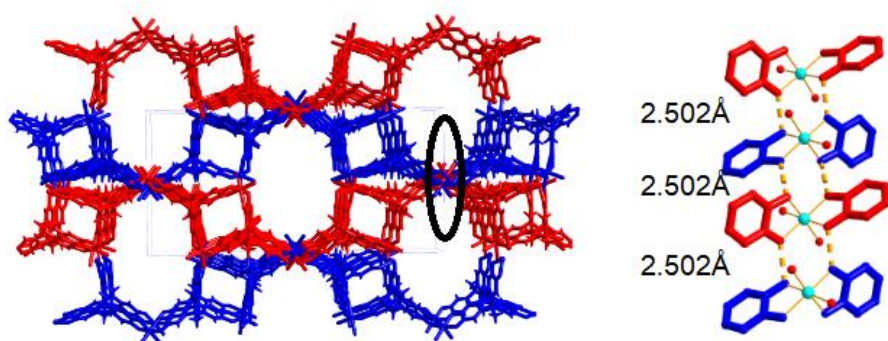


Fig. 2. Structure of Ni-TripOH-Me MOF and an illustration of radical chains in the structure.

continuously interacting radicals are formed in the structure, which provides potential electron conducting pathways.

[References]

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