

# Electrical conductivity in a porous, cubic rare-earth catecholate

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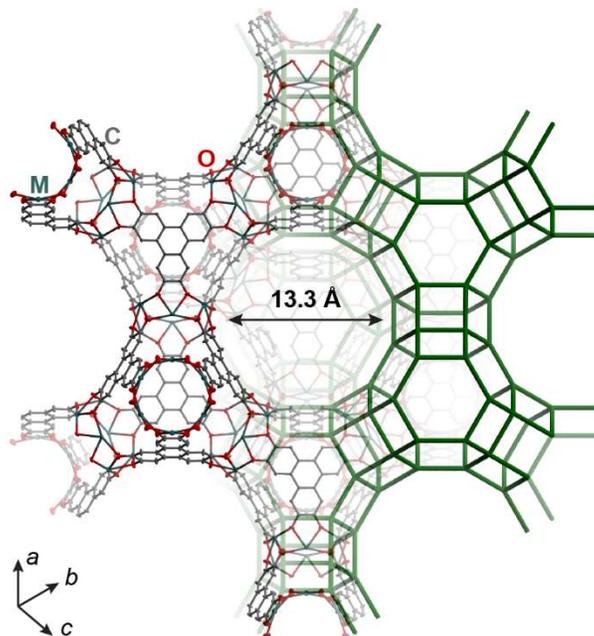
## **ABSTRACT:**

Electrically conductive metal-organic frameworks (MOFs) provide a rare example of porous materials that can efficiently transport electrical current, a combination favorable for a variety of technological applications. The vast majority of such MOFs are highly anisotropic in both their structures and properties: only two electrically conductive MOFs reported to date exhibit cubic structures that enable isotropic charge transport. Here, we report a new family of intrinsically porous frameworks made from rare earths and hexahydroxytriphenylene that are cubic, porous, and intrinsically conductive with conductivities reaching  $10^{-5}$  S/cm and surface areas of up to 780 m<sup>2</sup>/g. By expanding the list of MOFs with isotropic charge transport, these results will help improve our understanding of design strategies for porous electronic materials.

Recent advances in electrically conductive metal-organic frameworks (MOFs) significantly expanded the range of applications for this broad class of hybrid organic-inorganic materials, achieving important milestones in charge storage materials,<sup>1,2</sup> electrochemical catalysts,<sup>3,4</sup> and chemiresistive sensors.<sup>5</sup> Much work focuses on expanding the library of electrically conductive porous MOFs, yet the vast majority of such materials exhibit charge transport that occurs preferentially along a low-dimensional pathway, such as a 1D metal-ligand chain,<sup>6,7</sup> a  $\pi$ - $\pi$  stacked column,<sup>8</sup> or a  $\pi$ -conjugated sheet.<sup>9</sup> Although anisotropic transport may be desired in certain instances, as evidenced by the rapidly developing fields of low-dimensional materials such as graphene<sup>10</sup> and silicon nanowires,<sup>11</sup> it is of significant fundamental interest to develop conductive MOFs with isotropic charge transport.<sup>12</sup> Remarkably, to date only two<sup>13,14</sup> MOFs with cubic symmetry have been reported to show intrinsic (non-guest-based) electrical conductivity.

Highest conductivities to date are observed in MOFs based on ligands with catechol- and semiquinone-derived functional groups, such as hexaaminotriphenylene,<sup>9,15</sup> and hexahydroxytriphenylene (HHTP).<sup>3,16</sup> A number of factors makes these ligands especially viable for making electrically conductive frameworks, including the strong  $\pi$ -d conjugation between the metal and the ligand, the ligands' propensity for  $\pi$ - $\pi$  stacking and, crucially, their redox activity: oxidation of the catechol moieties forms semiquinoid radicals which serve as the charge carriers in the materials.<sup>17</sup> It is therefore unsurprising that of the two conductive MOFs with cubic symmetry, one is based on a ligand belonging to this class, dihydroxybenzoquinone (DHBQ). The cubic framework  $[\text{Fe}_2(\text{DHBQ})_3][\text{Bu}_4\text{N}]$  shows an impressive conductivity of 0.16 S/cm.<sup>14</sup> This value is controllable through post-synthetic redox chemistry, where the radical semiquinoid linkers can be reduced to their closed shell catechol form to lower the free carrier concentration. This framework, however, is non-porous due to the bulky charge-compensating tetrabutylammonium cations blocking the small pores. Nevertheless, inspired partly by these results, we turned to the larger, chemically related HHTP ligand to target a potentially porous, isotropically conductive MOF.

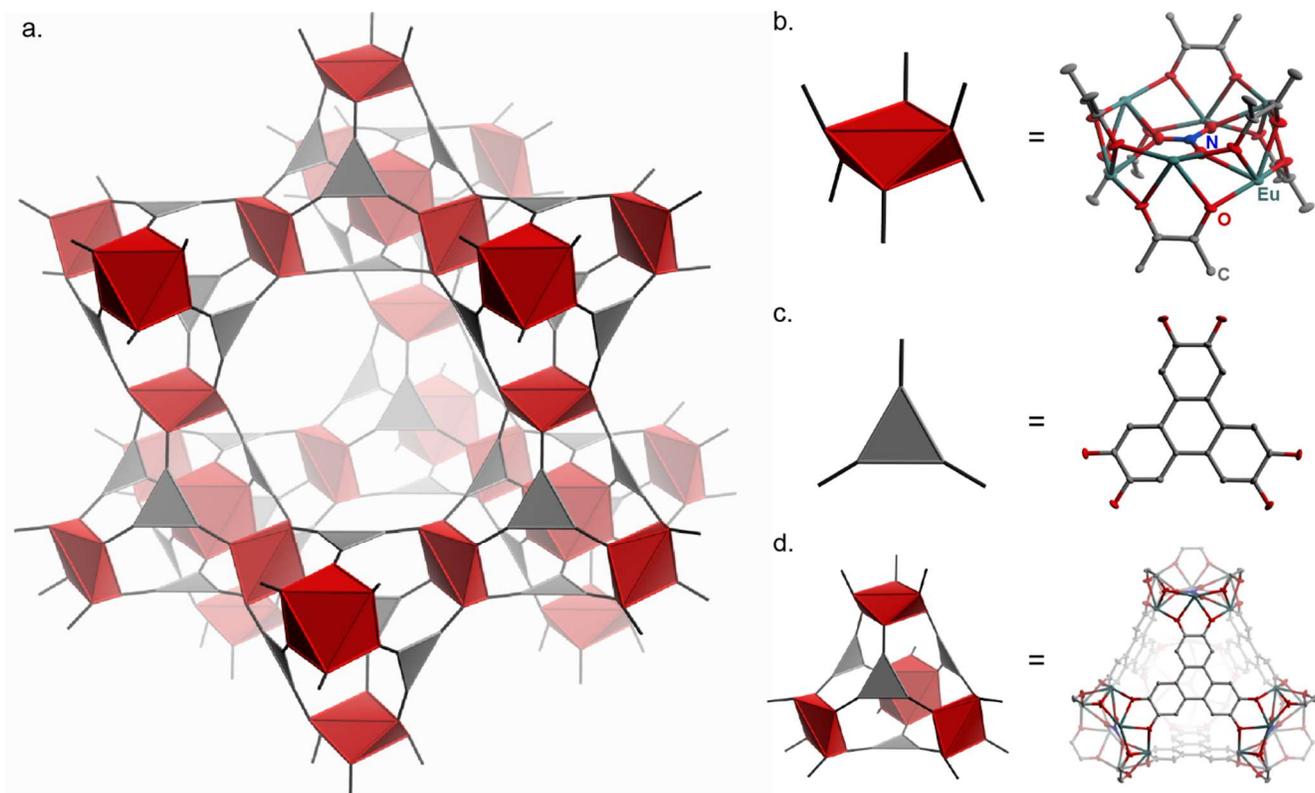
Reaction of concentrated solutions ( $>0.5$  M) of hydrated rare earth nitrates  $\text{M}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Y}, \text{Eu}, \text{La}$ ) with HHTP in a mixture of water and *N,N*-dimethylimidazolidinone (DMI) at temperatures above 150 °C yields large octahedral yellow crystals of  $[\text{M}_6(\mu_6\text{-NO}_3)(\text{HOTP})_2]^{5+}$  (**M<sub>6</sub>HOTP<sub>2</sub>**,  $\text{M} = \text{Y}, \text{Eu}$ ; HOTP = 2,3,6,7,10,11-hexaoxytriphenylene). The framework's charge is balanced by five monoanions (hydroxides or nitrates) per formula unit, resulting in an overall charge state of 6<sup>-</sup> for the HOTP linker, i.e., fully reduced. This assignment is corroborated by the color of the crystals: yellow-brown color matches the color of HHTP solutions, while minor oxidation of HHTP leads to formation of intensely colored blue or purple species. X-ray diffraction analysis of single crystals revealed that all three compounds crystallize in the cubic space group  $Fd\bar{3}m$  (see Figure 1 and Tables S1-2 for structural parameters). The secondary building units (SBUs) consist of hexanuclear  $\mu_6$ -nitrate catecholate clusters (Fig. 2b), wherein the metal ions alternate above and below the plane of the central nitrate ion in a chair-like conformation. Six HHTP ligands surround each SBU and connect neighboring SBUs into tetrahedral cages (Fig. 2c). The cages themselves are connected at the vertices to provide a net with 6- and 3-connected nodes and overall *spn* topology (Fig. 2a). The same topology has been observed before in several MOFs, most notably in MOF-808,<sup>18</sup> and is homologous to the faujasite zeolite structure type (Fig. 1).



**Figure 1.** Crystal structure of  $M_6HOTP_2$  ( $M = Y, Eu$ ), seen along the (111) crystallographic direction, is similar to the well-known faujasite zeolite structure type (green schematic overlay), and consists of diamondoid cages with permanent solvent accessible pores approximately 13.3 Å in diameter; carbon atoms are shown in grey, nitrogen in blue, oxygen in red, metals in teal; thermal ellipsoids shown at 50% probability level. Hydrogen atoms, as well as nitrate and aqua ligands are omitted for clarity.

The SBU shows significant crystallographic disorder, as may be expected given the coordination flexibility of rare earth ions. Metal atoms in  $Eu_6HOTP_2$  and  $Y_6HOTP_2$  have similar eight-coordinate environments (Fig. S5), with each metal connected to one oxygen atom of the central bridging nitrate, four catecholate oxygen atoms of three different HOTP linkers, and a disordered combination of aqua and nitrate ligands oriented towards the pore or the inner cavity of the tetrahedral cage. Notably, although this SBU has not been observed in MOFs previously, it is a close mimic of a molecular hexalanthanide cluster that has been reported previously (Fig. S6).<sup>19</sup> This similarity reinforces the strategy of targeting high-symmetry clusters known in molecular chemistry as potential SBUs for novel MOFs, a strategy commonly employed in reticular chemistry with more traditional functional groups such as carboxylates and azolates.<sup>20</sup>

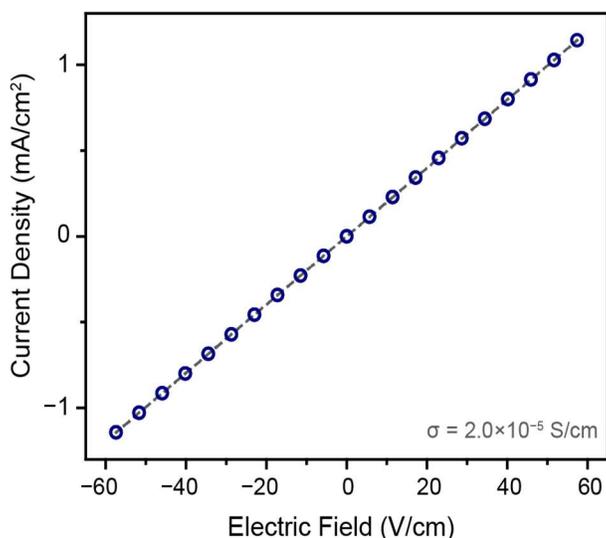
Owing to its propensity to  $\pi$ -stack, HHTP rarely forms three-dimensional structures.<sup>12</sup> Indeed, only one other report details the formation of isotropic, three-dimensional MOFs from HHTP.<sup>17</sup> Instead, this ligand preferably leads to stacked structures<sup>16</sup> reinforced by close contacts between its extended aromatic cores. Notably, although the two-dimensional sheets and/or the close contacts in most HHTP-based materials lead to some of the highest electrical



**Figure 2. Portions of the crystal structure of  $M_6HOTP_2$ :** **a.** the framework is built from 6-connected SBU nodes and 3-connected linker nodes, resulting in the overall *spn* topology; **b.** the SBU consists of six metal atoms bonded by one bridging nitrate ion in the center, and connected along the sides with catecholate groups from six linkers; **c.** the trigonal  $HOTP^{6-}$  connects the SBUs into tetrahedral cages (**d**). The cavities formed inside the cages appear to be inaccessible to solvent or other guest molecules. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, europium in teal; thermal ellipsoids shown at 50% probability level. Hydrogen atoms are omitted for clarity.

conductivities among porous MOFs,<sup>21</sup> the electrical transport in these materials is anisotropic. In fact, almost all conductive MOFs reported thus far have lower symmetry than cubic and therefore exhibit anisotropic transport.<sup>12</sup>

To probe whether  $M_6HOTP_2$  represents a rare example of a cubic, electrically conductive MOF, we tested the electrical conductivity of activated crystalline powders with a two-probe apparatus that has been described previously.<sup>22</sup> Activation of the crystals involved heating under dynamic vacuum at 95 °C for 18 hours. We note that thermogravimetric analysis of as-synthesized samples exchanged sequentially with water, methanol, and acetonitrile showed a first significant mass loss at approximately 90 °C (Figure S1). A representative sample of  $Y_6HOTP_2$ , activated as described above, also showed permanent porosity, as indicated by a type I  $N_2$  adsorption isotherm, which can be fit to the Brunauer-Emmett-Teller (BET) model<sup>23</sup> to give an apparent surface area of 780 m<sup>2</sup>/g. This value is in line with the reported surface area of the topologically equivalent MOF-808 (1140 m<sup>2</sup>/g),<sup>18</sup> which has near-identical unit cell parameters to those of  $Y_6HOTP_2$ .



**Figure 3. Current-voltage characteristic of  $Y_2HOTP_6$** , obtained on pressed pellets in a two-probe configuration, showing perfect linear behavior in accordance with Ohm's law. Linear fit of the data (dashed line) reveals the conductivity of this representative device to be  $2.0 \times 10^{-5}$  S/cm.

Relevantly, although as-synthesized crystals of  $M_6HOTP_2$  are yellow, they slowly darken over time even under rigorous air-free conditions, likely indicating at least partial oxidation of catechol moieties in  $HOTP^{6-}$  ligands to semiquinones. Heating or exposure to air significantly speeds up the color change, while prolonged exposure to air leads to eventual loss of crystallinity, up to complete amorphization. Most importantly, the color changes attributed to partial oxidation of  $HOTP^{6-}$  are also likely to create charge carriers and improve conductivity. Indeed, both  $Y_2HOTP_6$  and  $Eu_2HOTP_6$  show electrical conductivities on the order of  $10^{-6}$ - $10^{-5}$  S/cm (Fig. 3) upon activation, across several independently synthesized batches. Although not as high as the bulk conductivities of HHTP-derived MOFs that exhibit close HOTP stacking ( $10^{-4}$ - $10^{-2}$  S/cm),<sup>3,16</sup> these values are remarkable<sup>12</sup> for three-dimensional, isotropic porous MOFs, where charges are expected to transport with equal efficiency along the three cartesian coordinates.

It is rare for intrinsic porosity and electrical conductivity to coexist within one material. It is even rarer for such compounds to be structurally isotropic. In this work, we presented a new family of MOFs which combine significant porosity with electrical conductivity in a cubic framework. The relatively high conductivity shown by these materials demonstrates that targeting low-dimensional pathways is not mandatory for achieving efficient charge transport. We hope these results will inspire more detailed studies into the dimensionality of charge transport in this exciting class of materials, and bring forward a better understanding of how porosity interacts with conductivity.

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