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Efficient and tunable one-dimensional charge transport in layered lanthanide metal-organic frameworks

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ABSTRACT

The emergence of electrically conductive metal-organic frameworks (MOFs) has led to applications in chemical sensing and electrical energy storage, among others. The most conductive MOFs are made from organic ligands and square-planar transition metal ions connected into two-dimensional (2D) sheets that stack similarly to graphene sheets in graphite. Their electrical properties are thought to depend critically on the covalency of the metal-ligand bond, and less importance is given to charge transport normal to the sheets. Here, we report exquisite control over the sheet stacking in a series of materials made from 2D layers of organic ligands connected in the third dimension by infinite lanthanide-oxygen chains. Contrary to transition metal MOFs, here, efficient charge transport occurs primarily normal to the 2D sheets. These results demonstrate that increasing the covalency of the metal-ligand bond is not the only viable route to high conductivity in 2D-related MOFs, and that interactions of organic ligands alone can produce efficient charge transport pathways.

MAIN TEXT

Electrically conductive metal-organic frameworks (MOFs) have recently attracted attention as potential materials for supercapacitors,^{1,2} batteries,³ thermoelectric devices,⁴ chemiresistive sensors,^{5,6} and electrocatalysts.⁷⁻¹⁰ Significant effort is devoted towards the development of MOFs with increasingly higher conductivities.^{11,12} Current record values of 2500 S/cm at room temperature for non-porous coordination polymers¹³ and 40 S/cm for porous MOFs,¹⁴ with many others approaching them,¹⁵⁻¹⁷ were reported in hexagonal layered frameworks based on hexa-substituted triphenylenes and benzenes connected by first-row divalent transition metal ions such as Ni²⁺ and Cu²⁺. The high conductivity values of these materials are often attributed to the strong in-plane conjugation between the ligands' π -systems and the d orbitals of the metals.¹⁸⁻²¹ Because of this assumption, to our knowledge there are no studies of charge transport normal to the metal-organic sheets. Despite attempts to make 2D MOFs with varying degrees of covalency in the metal-ligand bonding,²² which could answer fundamental questions related to charge transport in these materials, details on their structures or electronic properties do not exist.

One class of metal ions that is well suited for systematic investigations of structure-function relationships is the lanthanides. In their trivalent states, lanthanide ions (Ln³⁺) have empty $5d$ -shells, with all valence electrons lying in heavily shielded, deep $4f$ orbitals. Because the $4f$ orbitals do not participate significantly in bonding, Ln³⁺ ions typically form considerably more ionic compounds than the transition metals.²³ This is attractive for MOF synthesis, where more labile, reversible bonds form more crystalline materials, which is crucial for attaining systematic control over the electronic structure of the materials. One added benefit of using Ln³⁺ to target conductive MOFs is their nearly identical chemical behaviour stemming from their ionicity, and their otherwise very different ionic radius, which decreases by more than 15% from La³⁺ to Lu³⁺.²⁴ These properties make them ideal for studying structure-function correlations where covalency is essentially decoupled from structural considerations.

Here, we report a family of MOFs made from Ln³⁺ and 2,3,6,7,10,11-hexahydroxytriphenylene (H₆HHTP). Although the more ionic bonding between Ln³⁺ and the catecholate ligands may be expected to diminish the efficiency of charge transport within the 2D plane, the materials exhibit conductivity values reaching 0.05 S/cm

in two-probe polycrystalline pellet measurements, on par with the most conductive MOFs reported to date.^{11,12,25} The high crystallinity of the materials allows systematic control of structural parameters and reveals a direct correlation between the stacking distance, the conductivity, and the optical band gap of MOFs made from four different lanthanides spanning the entire *4f* series.

RESULTS AND DISCUSSION

Synthesis and structural characterization

A solvothermal reaction of H₆HHTP with hydrated Ln(NO₃)₃ (Ln = La, Nd, Ho, Yb) in a mixture of water and *N,N'*-dimethylimidazolidinone (DMI) produced dark green-blue microcrystalline powders of Ln_{1+x}HHTP(H₂O)_n (*x* = 0 to 0.2; referred to as **LnHHTP**). Scanning electron microscopy (SEM) showed that the powders consisted of well-shaped hexagonal needles (Fig. 1e, Supplementary Fig. 1), varying in length between 1 μm and 200 μm depending on the exact synthetic conditions. Although sufficiently long, these crystals were not sufficiently thick for single-crystal X-ray diffraction studies. Their structures were instead obtained by Rietveld refinement²⁶ of powder X-ray diffraction (PXRD) data, which provided excellent structural models for the Nd³⁺ (Fig. 1) and the Yb³⁺ analogues (Supplementary Fig. 19). The two materials are isostructural, with differences in unit cell parameters and Ln–O bond lengths attributable to the smaller size of Yb³⁺ compared to Nd³⁺. Both structures show two-site disorder, each exhibiting two sets of equally occupied ligand and metal sites. For clarity, Figure 1 presents only one half of the averaged, disordered **NdHHTP** structure. Similar to the reported transition metal analogues, Ln³⁺ ions bind the triangular HHTP ligands into honeycomb-like two-dimensional nets featuring solvent-accessible pores with a crystallographic diameter of ~1.94 nm for **NdHHTP**. The experimental pore diameters of all four materials (Supplementary Fig. 10), measured by fitting N₂ adsorption isotherms at 77 K (Supplementary Figs. 6-9),²⁷ were found to be approximately 1.6 nm, in line with the crystallographic values. The same N₂ adsorption isotherms gave BET²⁸ surface areas of 200-510 m²/g, also in good agreement with the values reported for the related two-dimensional *d*-metal-based MOFs (490 m²/g for the Co-based framework Co-CAT-1, and 425 m²/g for the Ni-based framework Ni-CAT-1).¹⁷

Importantly, whereas transition metals lie in the same plane as the organic ligands and form strictly two-dimensional sheets, here the Ln^{3+} ions lie in-between the planes of the organic ligands, thereby connecting the latter into a three-dimensional network. The lanthanides themselves are bound to six oxygen atoms from neighbouring ligands and one water or hydroxide group. They are bridged into infinite chains that can be represented as edge-sharing capped trigonal prisms, bearing resemblance to the coordination environment and extended structure of rare-earth oxides, including Nd_2O_3 (Supplementary Fig. 18).²⁹ The lanthanide sites are not fully occupied in either **NdHHTP** or **YbHHTP**, with almost a third of the positions empty, as would be expected based on the formula unit. A more detailed structural description, including additional models of the location of empty lanthanide crystallographic sites is provided on p. 7 of the Supplementary Information.

PXRD patterns for **LaHHTP** and **HoHHTP** (Supplementary Fig. 11) are qualitatively identical to those of **NdHHTP** and **YbHHTP**, suggesting that all four materials are isostructural. Pawley refinements³⁰ on multiple batches of the four materials revealed a clear decrease in the unit cell parameters moving across the series from La^{3+} to Yb^{3+} , in line with corresponding decrease in ionic radii (Supplementary Fig. 17). Notably, the size difference between the early and late lanthanides causes further reduction from an already short interlayer stacking distance of 3.068(2) Å for **LaHHTP** to a remarkably short 3.002(6) Å for **YbHHTP**. Such close π -stacking is rarely seen in layered materials (Table S2): in all other triphenylene-based MOFs the average layer spacing is larger than 3.3 Å.^{6,14,17} Even in graphite itself, the layers are separated by 3.36 Å at room temperature,³¹ a distance more than 10% larger than that observed in **YbHHTP**.

Electronic band structure calculations

Excited by the possibility of the close π -stacking promoting efficient ligand orbital overlap in the crystallographic c direction, which could promote charge transport normal to the 2D sheets, we investigated the electronic structures of the materials by density functional theory (DFT). To avoid prohibitive computationally intensive spin-polarized calculations, we performed calculations on the closed shell **LaHHTP** structure and a hypothetical **LuHHTP** structure as a model for the smaller lanthanides Yb^{3+} and Ho^{3+} . These calculations suggest that the materials should exhibit metallic behaviour along the c direction (A to Γ vector in the Brillouin zone in Fig. 2), as evidenced by the bands crossing the Fermi level. In contrast, the Fermi level lies inside a band gap

within the *ab* plane (Γ -K-M), suggesting semiconductive behaviour in the plane parallel to the organic layers (Γ -K-M). As expected, lanthanide valence orbitals do not contribute significantly to bands around the Fermi level, suggesting that in-plane electronic communication between ligands is minimal. Indeed, the bands along the Γ -K-M vectors are essentially flat and form ‘in-plane’ band gaps of approximately 0.7-1.2 eV that are strongly dependent on the stacking distance (Supplementary Figs. 21-22). This is in stark contrast with the band structure along the A to Γ vector (‘cross-plane’), where the bands are spread very widely and give rise to low density of states. Furthermore, modelling structures with different metal atoms leads to insignificant changes in shifting from La to Lu. For more information on interpreting band structures, see Refs. 32 and 33.

Optical spectroscopy

Diffuse reflectance spectra for the four materials (Fig. 3a) show clear absorption edges in the 0.7-1 eV range, which we assign as the ‘in-plane’ gap predicted by DFT calculations. The four MOFs also show absorption features below this edge, at \sim 0.3 eV for La and Nd, and at \sim 0.7 eV for Ho and Yb. These absorption features, however, do not conform to a linear region when plotted on a Tauc plot³⁴ for direct or indirect bandgaps, and can therefore be attributed to absorption by defects. Unambiguous identification of these defects is beyond the scope of the current work, but possibilities include: metal vacancies, as supported by PXRD analysis; ligand vacancies, which DFT confirms as possibly giving rise to such absorption features (see p. 10 of the Supplementary Information for more detail); or mixed-valent states within the ligand set. This last possibility is supported by prior work, where absorption features at 2000-3000 nm in a $[\text{Ru}_3\text{HHTP}]^{2+}$ complex were attributed to intra-ligand charge transfer.³⁵ Plotted in Tauc coordinates for direct allowed transitions (Fig. 3b), the spectra reveal a surprising trend of narrowing optical bandgaps in transitioning from the larger lanthanides, 0.85 eV for **LaHHTP**, to the smaller ones, 0.73 eV for **YbHHTP**. This trend is opposite to what is observed in most classical semiconductors, including GaAs,³⁶ InP,³⁷ Ge,³⁸ where pressurization and decreasing unit cell parameters lead to widening bandgaps. The trend in **LnHHTP** materials conforms, however, to what is observed for semiconductors such as PbE (E = S, Se, Te), where band inversion occurs,³⁹ as well as for some indirect-gap semiconductors, including Si.³⁸ The precise assignment of this trend warrants further systematic experiments; we note, however, that the DFT calculations here position the Fermi energy at a ligand oxidation of HHTP³⁻, whereas the

experimental formula indicates slight variations of this oxidation state towards more reduced ligands, which would shift the Fermi energy higher.

Electrical conductivity

The electrical conductivities of polycrystalline pellets made from **LnHHTP** materials are on par with the most conductive porous MOFs to date, ranging from $0.9 \cdot 10^{-4}$ S/cm for **LaHHTP** to 0.05 S/cm for **HoHHTP** at 29 °C (Fig. 4a). Although relatively wide batch-to-batch variation is observed for each material, higher averages and higher champion device conductivities are consistently achieved for the smaller lanthanides (Ho, Yb), which produce the more densely stacked structures. The conductivity of **HoHHTP** pellets, 0.05 S/cm, is within the range of the most conductive three-dimensionally connected MOFs to date,²⁵ which is remarkable given the low degree of covalency provided by Ln–O bonds in **LnHHTP** materials.²³ Importantly, the values for all **LnHHTP** MOFs are likely significantly underestimated due to the potentially anisotropic nature of charge transport, as well as additional contact and grain boundary resistances.¹¹ Although these contributions are difficult to quantify, they are assumed to be reasonably similar for the different materials because all MOFs present similar morphologies and crystallite size (Supplementary Fig. 44). Conductivity improvements of more than two orders of magnitude have been reported for single-crystal measurements of MOFs compared to 2-probe pellets.⁴⁰

Variable-temperature conductivity measurements revealed thermally-activated transport for the four studied materials (Fig. 4b). Fitting the conductance versus temperature data to the Arrhenius equation $G = G_0 \exp\left(\frac{E_A}{kT}\right)$, where G is the conductance, G_0 is a prefactor, E_A is the activation energy, k the Boltzmann constant, and T the temperature, in the temperature range 225 K to 300 K revealed similar E_A values of approximately 0.25 eV for all four materials (Supplementary Figs. 34-37). These values are in line with those reported for other highly conductive MOFs, including chemically-related 2,5-dihydroxybenzoquinone and chloranilic acid-based materials.^{21,41} Although thermally-activated transport is a defining characteristic for semiconducting materials,³³ appearing to contradict the calculated band structures, grain boundaries can dominate electrical transport behaviour in polycrystalline pellets.¹⁵ We further note that the DFT calculations predict metal-like transport to be anisotropic along the c direction, with semiconducting behaviour in the ab plane. Because the density of states at

the Fermi level is significantly lower than in the region of the ‘in-plane’ bands, transport in these materials may intrinsically display some degree of thermal activation. Defect states that we observe both by X-ray diffraction, in the form of the cationic vacancies, and by diffuse-reflectance spectroscopy, can also change transport behaviour from metallic to semiconducting, as has been shown in literature.⁴² Additionally, our DFT calculations on **LaHHTP** with linker vacancies (Supplementary Figs. 47-48) show localisation of the ligand electronic wavefunction, forming flat bands around the Fermi level. Although the simulated (i.e., ideal) defective material maintains its metallicity through the undisrupted ligand stacks, local transport through the missing linker defects would presumably be thermally activated.

OUTLOOK

With the most intense current interest in two-dimensional materials focused on ‘in-plane’ electronic properties, the ‘out-of-plane’ transport properties have received comparatively less attention. Contrasting with traditional inorganic 2D materials, MOFs lend themselves to facile ligation to produce functional materials with two-dimensional layers connected by strong bonds. We demonstrate that reacting lanthanide cations with ligands traditionally used for synthesizing conducting 2D MOFs leads to layered materials where organic ligands form sheets with insignificant in-plane electronic communication. Electrical transport instead occurs primarily normal to the plane and is highly modulated by the inter-sheet stacking distance, which in turn varies proportionally with the size of the lanthanide cation. These results offer an alternative point of view to the canonical interpretation of transport in conductive 2D MOFs, which has focused almost entirely on ‘in-plane’ arguments. Our findings enlarge the spectrum of possible interactions that can give rise to efficient transport in these porous materials, thereby providing an additional design strategy towards MOFs with record conductivities and charge delocalization in all three dimensions.

METHODS

Synthesis of LnHHTP (Ln = La, Nd, Ho, Yb).

In air, to a 20 mL scintillation vial containing the solution of 0.629 mmol (10.0 equiv) $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ in 3.0 mL deionized water, the solution of 0.063 mmol (1.0 equiv, 20. mg) H_6HHTP in 0.4 mL DMI is added. Then the solution of 0.189 mmol (3.0 equiv, 15 mg) of anhydrous sodium acetate in 0.6 mL deionized water is added to the mixture, inducing the formation of a cloudy grey precipitate. The vial is then capped and left at 80 °C for 16 hours, during which the precipitate slowly turns green, and then dark blue. The precipitate is then collected by centrifugation, and transferred to a N_2 -filled glove box containing, but not saturated with water vapour. The precipitate is then soaked four times for at least 30 minutes in deionized water, followed by four times for at least 30 minutes in acetone, both solvents degassed by freeze-pump-thawing three times. The vial containing the precipitate is then fitted with a vacuum adapter, and the precipitate is dried *in vacuo* on a Schlenk line for 1 hour at 90 °C. For elemental analysis and N_2 adsorption measurements, the samples are then dried overnight under the same conditions. The samples are then transferred into a dry N_2 -filled glove box. No deterioration in the physical properties or the phase purity was observed over the course of at least 4 months. Prolonged exposure to air had no observed impact on the phase purity based on powder X-ray diffraction. Elemental analysis results are shown on p. 5 of the Supplementary Information.

Electrical conductivity measurements

Two-contact probe measurements were carried out at 302 K in a dry nitrogen-filled glove box on pressed pellets using a home-built two-point probe setup described previously.⁴⁰ For each measurement, the powder was loaded in a glass tube, and compressed between two stainless steel rods, which also served as current collectors. The cell was then transferred into a hydraulic press, and the press was tightened fast by hand. No additional pressure was applied. Linear I–V curves were then obtained by sweeping the voltage and measuring the current using a sourcemeter (Keithley 6517b or Keithley 2450) connected to the press with test leads. The voltage limits were chosen depending on the resistance of the pellet measured, but generally were between -0.5 V and +0.5 V. The cell was then allowed to stand pressurised for 10 minutes, then re-tightened, and I-V curves were collected

again. This process was repeated several times until the change in observed resistance was low (Supplementary Fig. 45). Pellet thicknesses were determined after the electrical measurements using a micrometer (Mitutoyo).

Variable temperature conductivity data were collected using a Quantum Design PPMS DynaCool equipped with the Electrical Transport Option.

Computational methods

Beginning with the crystallographic structure of **NdHHTP**, models for **LaHHTP** and **LuHHTP** were built by substituting the metal atoms. The materials were then geometrically equilibrated using the DFT functional PBEsol⁴³ with plane-augmented-wave (PAW) pseudopotentials and an energy cutoff of 500 eV, as implemented in VASP.⁴⁴ Ln-bound O were single protonated to form terminal hydroxide to achieve bulk charge neutrality. Scalar relativistic effects were included in the PAW pseudopotentials. The equilibrium geometry and electronic ground state were computed with ionic and electronic convergence criteria of 0.005 eV/Å and 10⁻⁶ eV respectively, resulting in tightly converged structures.

Due to the large crystal system size of MOFs, a Γ -only k-grid was utilized during optimization. Electronic band structures and DOS plots were calculated using the PBEsol functional⁴³ with added spin-orbit-coupling effects through inclusion of non-collinear electron spins on a higher resolution k-grid of 2 x 2 x 4. The maximum band dispersion was found by sampling the intersheet direction, which had closest contacts of 2.98 Å for the optimized structure. For comparison, the DFT-D3 method of Grimme^{45,46} and the same method above were used to obtain a second equilibrium geometry, electronic band structure, and DOS plot for **LaHHTP**. The results were qualitatively similar – the dispersion correction resulted in an intersheet contraction (2.91 Å), and minor increase in band dispersion. The c-spacing of **LaHHTP** sheets was experimentally determined to be 3.1 Å, thus a third equilibrium geometry, electronic band structure, and DOS plot were calculated for **LaHHTP** with an artificially increased c-spacing matching experimental data. This system showed an expected reduction in band curvature, which typically scales inversely with interatomic distance. Additional band structures and DOS plots of both **LaHHTP** and **LuHHTP** excluding spin-orbit coupling effects and using PW91 functional⁴⁷ were also examined.

We were unable to geometrically equilibrate the spin-polarized Nd, Ho, or Yb materials due to computational limitations.

Further information on the experimental and computational methods, structural details, scanning electron micrographs, thermogravimetric analysis results, nitrogen adsorption isotherms, infrared spectra, Tauc plots, powder X-ray diffraction patterns, current-voltage characteristics, calculated band structures, and variable temperature conductivity plots are provided in the Supplementary Information.

Data availability

Crystallographic information obtained by Rietveld refinement of powder X-ray diffraction data has been deposited in the Cambridge Crystallographic Data Centre under accession codes CCDC 1874834 (**NdHHTP**) and CCDC 1874835 (**YbHHTP**). All other data supporting the findings of this study are available within the Article and its Supplementary Information, or from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

G.S. and M.D. planned and designed the experiments. G.S. executed the syntheses, chemical, spectroscopic, and electrical characterisation. G.S., B.A.T., and C.M.B. collected and analysed the powder X-ray diffraction data. T.W.K. and C.H.H. performed the DFT studies. All authors were involved in the writing of the manuscript and have given consent to this publication.

COMPETING INTERESTS

The authors declare no competing interests.

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REFERENCES

1. Sheberla, D. *et al.* Conductive MOF electrodes for stable supercapacitors with high areal capacitance. *Nat. Mater.* **16**, 220–224 (2016).
2. Feng, D. *et al.* Robust and conductive two-dimensional metal–organic frameworks with exceptionally high volumetric and areal capacitance. *Nat. Energy* **3**, 30–36 (2018).
3. Wada, K., Sakaushi, K., Sasaki, S. & Nishihara, H. Multielectron-transfer-based rechargeable energy storage of two-dimensional coordination frameworks with non-innocent ligands. *Angew. Chemie Int. Ed.* **57**, 8886–8890 (2018).
4. Erickson, K. J. *et al.* Thin film thermoelectric metal-organic framework with high Seebeck coefficient and low thermal conductivity. *Adv. Mater.* **27**, 3453–3459 (2015).
5. Smith, M. K. & Mirica, K. A. Self-organized frameworks on textiles (SOFT): conductive fabrics for simultaneous sensing, capture, and filtration of gases. *J. Am. Chem. Soc.* **139**, 16759–16767 (2017).
6. Campbell, M. G., Sheberla, D., Liu, S. F., Swager, T. M. & Dincă, M. Cu₃(hexaiminotriphenylene)₂: an electrically conductive 2D metal-organic framework for chemiresistive sensing. *Angew. Chemie Int. Ed.* **54**, 4349–4352 (2015).
7. Miner, E. M. *et al.* Electrochemical oxygen reduction catalysed by Ni₃(hexaiminotriphenylene)₂. *Nat. Commun.* **7**, 10942 (2016).
8. Miner, E. M. *et al.* Mechanistic evidence for ligand-centered electrocatalytic oxygen reduction with the conductive MOF Ni₃(hexaiminotriphenylene)₂. *ACS Catal.* **7**, 7726–7731 (2017).
9. Miner, E. M., Wang, L. & Dincă, M. Modular O₂ electroreduction activity in triphenylene-based metal–organic frameworks. *Chem. Sci.* **9**, 6286–6291 (2018).
10. Clough, A. J., Yoo, J. W., Mecklenburg, M. H. & Marinescu, S. C. Two-dimensional metal–organic surfaces for efficient hydrogen evolution from water. *J. Am. Chem. Soc.* **137**, 118–121 (2015).

11. Sun, L., Campbell, M. G. & Dincă, M. Electrically conductive porous metal-organic frameworks. *Angew. Chemie Int. Ed.* **55**, 3566–3579 (2016).
12. Stassen, I. *et al.* An updated roadmap for the integration of metal–organic frameworks with electronic devices and chemical sensors. *Chem. Soc. Rev.* **46**, 3185–3241 (2017).
13. Huang, X. *et al.* Superconductivity in a Copper(II)-based coordination polymer with perfect kagome structure. *Angew. Chemie Int. Ed.* **57**, 146–150 (2018).
14. Sheberla, D. *et al.* High electrical conductivity in Ni₃(2,3,6,7,10,11-hexaiminotriphenylene)₂, a semiconducting metal-organic graphene analogue. *J. Am. Chem. Soc.* **136**, 8859–8862 (2014).
15. Dou, J.-H. *et al.* Signature of metallic behavior in the metal–organic frameworks M₃(hexaiminobenzene)₂ (M = Ni, Cu). *J. Am. Chem. Soc.* **139**, 13608–13611 (2017).
16. Kambe, T. *et al.* Redox control and high conductivity of nickel bis(dithiolene) complex π -nanosheet: a potential organic two-dimensional topological insulator. *J. Am. Chem. Soc.* **136**, 14357–14360 (2014).
17. Hmadeh, M. *et al.* New porous crystals of extended metal-catecholates. *Chem. Mater.* **24**, 3511–3513 (2012).
18. Ko, M., Mendecki, L. & Mirica, K. A. Conductive two-dimensional metal–organic frameworks as multifunctional materials. *Chem. Commun.* **54**, 7873–7891 (2018).
19. Smith, M. K., Jensen, K. E., Pivak, P. A. & Mirica, K. A. Direct self-assembly of conductive nanorods of metal–organic frameworks into chemiresistive devices on shrinkable polymer films. *Chem. Mater.* **28**, 5264–5268 (2016).
20. Clough, A. J. *et al.* Metallic conductivity in a two-dimensional cobalt dithiolene metal–organic framework. *J. Am. Chem. Soc.* **139**, 10863–10867 (2017).
21. Ziebel, M. E., Darago, L. E. & Long, J. R. Control of electronic structure and conductivity in two-dimensional metal–semiquinoid frameworks of titanium, vanadium, and chromium. *J. Am. Chem. Soc.* **140**, 3040–3051 (2018).

22. Yaghi, O. M., Gandara-Barragan, F., Lu, Z. & Wan, S. Preparation of metal-catecholate frameworks. US 8,742,152 B2 (2014).
23. Cotton, S. A. *Lanthanide and actinide chemistry*. (John Wiley & Sons, Ltd, Chichester, UK, 2006).
24. Shannon, R. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* **32**, 751–767 (1976).
25. Xie, L. S. *et al.* Tunable mixed-valence doping toward record electrical conductivity in a three-dimensional metal–organic framework. *J. Am. Chem. Soc.* **140**, 7411–7414 (2018).
26. Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2**, 65–71 (1969).
27. Barrett, E. P., Joyner, L. G. & Halenda, P. P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **73**, 373–380 (1951).
28. Brunauer, S., Emmett, P. H. & Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**, 309–319 (1938).
29. Wu, B., Zinkevich, M., Aldinger, F., Wen, D. & Chen, L. Ab initio study on structure and phase transition of A- and B-type rare-earth sesquioxides Ln_2O_3 ($\text{Ln} = \text{La}–\text{Lu}$, Y, and Sc) based on density function theory. *J. Solid State Chem.* **180**, 3280–3287 (2007).
30. Pawley, G. S. Unit-cell refinement from powder diffraction scans. *J. Appl. Cryst* **14**, 357–361 (1981).
31. Trucano, P. & Chen, R. Structure of graphite by neutron diffraction. *Nature* **258**, 136–137 (1975).
32. Hoffmann, R. How chemistry and physics meet in the solid state. *Angew. Chemie Int. Ed.* **26**, 846–878 (1987).
33. Kittel, C. *Introduction to solid state physics*. (Wiley, 2004).
34. Tauc, J. Optical properties and electronic structure of amorphous Ge and Si. *Mater. Res. Bull.* **3**, 37–46 (1968).

35. Grange, C. S., Meijer, A. J. H. M. & Ward, M. D. Trinuclear ruthenium dioxolene complexes based on the bridging ligand hexahydroxytriphenylene: electrochemistry, spectroscopy, and near-infrared electrochromic behaviour associated with a reversible seven-membered redox chain. *Dalt. Trans.* **39**, 200–211 (2010).
36. Welber, B., Cardona, M., Kim, C. K. & Rodriguez, S. Dependence of the direct energy gap of GaAs on hydrostatic pressure. *Phys. Rev. B* **12**, 5729–5738 (1975).
37. Müller, H., Trommer, R., Cardona, M. & Vogl, P. Pressure dependence of the direct absorption edge of InP. *Phys. Rev. B* **21**, 4879–4883 (1980).
38. Balslev, I. Influence of uniaxial stress on the indirect absorption edge in silicon and germanium. *Phys. Rev.* **143**, 636–647 (1966).
39. Nabi, Z., Abbar, B., Méçabih, S., Khalfi, A. & Amrane, N. Pressure dependence of band gaps in PbS, PbSe and PbTe. *Comput. Mater. Sci.* **18**, 127–131 (2000).
40. Sun, L., Park, S. S., Sheberla, D. & Dincă, M. Measuring and reporting electrical conductivity in metal–organic frameworks: Cd₂(TTFTB) as a case study. *J. Am. Chem. Soc.* **138**, 14772–14782 (2016).
41. DeGayner, J. A., Jeon, I.-R., Sun, L., Dincă, M. & Harris, T. D. 2D conductive iron-quinoid magnets ordering up to $T_c = 105$ K via heterogenous redox chemistry. *J. Am. Chem. Soc.* **139**, 4175–4184 (2017).
42. Foster, M. E., Sohlberg, K., Allendorf, M. D. & Talin, A. A. Unraveling the semiconducting/metallic discrepancy in Ni₃(HITP)₂. *J. Phys. Chem. Lett.* **9**, 481–486 (2018).
43. Perdew, J. P. *et al.* Restoring the density-gradient expansion for exchange in solids and surfaces. *Phys. Rev. Lett.* **100**, 136406 (2008).
44. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
45. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104

(2010).

46. Grimme, S., Ehrlich, S. & Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **32**, 1456–1465 (2011).
47. Perdew, J. P. & Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **45**, 13244–13249 (1992).

FIGURE CAPTIONS

Figure 1. Structure of **NdHHTP**. a-c, A representation of the crystal structure of **NdHHTP**, viewed along the *c* direction, and displaying the crystallographic pore diameter (a); displaying the metal-ligand connectivity of the seven-coordinate Nd atoms (b); displaying the layer stacking (c). Hydrogen atoms are omitted for clarity. The structure is similar to related transition metal-based materials, however the Nd atoms connect the ligand layers into a three-dimensional framework, and force the organic layers significantly closer together. d, Rietveld refinement of the average **NdHHTP** structure to synchrotron PXRD data. Experimental data is shown as black triangles, model fit in teal, difference curve in grey. The tick marks denote the calculated peak positions. Fit statistics were $R_p = 5.80\%$, $R_{wp} = 7.74\%$, and $GoF = 3.73$. Triangle sizes are commensurate with error bars from standard deviations. e, Scanning electron micrograph of a **NdHHTP** crystal. Scale bar: 1 μm .

Figure 2. Electronic band structure and density of states (DOS) of **LaHHTP**. Calculations include spin-orbit coupling effects. Significant band curvature in the Γ to A direction indicates strong interaction between the layers. Additionally, the Fermi level crosses the bands in this direction, suggesting metallicity. The DOS is plotted in logarithmic coordinates to emphasize the non-zero density at the Fermi level, and shows the much lower contribution of La to the frontier bands. The inset shows the first Brillouin zone – the primitive cell of the reciprocal lattice – to help guide the reader through the wave vector positions within the band diagram.

Figure 3. Diffuse reflectance spectra for **LnHHTP** ($\text{Ln} = \text{La}, \text{Nd}, \text{Ho}, \text{Yb}$). a, Kubelka-Munk transforms of the spectra, showing significant absorption extending into the infrared region. b, Same data plotted in Tauc coordinates for direct allowed transitions. Pale dashed lines show extrapolation of the linear fit regions. The optical band gaps of the materials can be obtained as the abscissa intercepts of the dashed lines. A grey line that follows $(ah\nu)^2 = 0$ is added to aid the reader. Inset: variation of the estimated optical bandgaps of the four materials with the unit cell parameter *c*.

Figure 4. Electrical conductivity of **LnHHTP** ($\text{Ln} = \text{Yb}, \text{Ho}, \text{Nd}, \text{and La}$). a, Two-probe pressed pellet conductivities measured at 29 °C. Squares, downward-facing triangles and upward-facing triangles denote three independent batches of each material. Each point marks an individual pellet measurement. Circles mark average values. **HoHHTP** and **YbHHTP**, where the organic interlayer distance is shorter, consistently show higher conductivities than **LaHHTP** and **NdHHTP**, where the stacking distances are larger. b, Temperature dependence of the normalized conductance G/G_{300} of **LnHHTP** in Arrhenius coordinates, where G_{300} is the conductance at 300 K (Supplementary Figs. 34-37). The four materials show similar temperature-activated conductivity behaviour.