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

Grigorii Skorupskii,† Benjamin A. Trump,‡ Thomas W. Kasel§, Craig M. Brown,‡,ǂ Christopher H. Hendon,§
Mircea Dincă*,†

†Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge,
Massachusetts 02139, United States
‡Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899,
United States
ǂDepartment of Chemical and Biomolecular Engineering, University of Delaware, Newark, Delaware 19716,
United States
§Materials Science Institute, Department of Chemistry and Biochemistry, University of Oregon, Eugene, Oregon
97403, United States

*Email: mdinca@mit.edu
ABSTRACT

The emergence of electrically conductive metal-organic frameworks (MOFs) has been one of the most exciting, if somewhat paradoxical, developments in porous materials, and has already led to applications as varied as chemical sensing and electrical energy storage. The most conductive MOFs are those made from organic ligands and square-planar transition metal ions connected into two-dimensional (2D) sheets that stack in a similar manner to the graphene sheets in graphite. Their electrical properties are thought to depend critically on the covalency of the metal-ligand bond. Much less importance is given to charge transport normal to the 2D sheets, not least because there is little synthetic opportunity to control their stacking sequence or distance. Here, we report exquisite control over the stacking sequence and distance in a series of materials made from 2D sheets of organic ligands connected in the third dimension by infinite lanthanide-oxygen chains. Contrary to transition metal MOFs, efficient charge transport leading to conductivity values of up to 0.5 S/cm in the lanthanide materials occurs primarily normal to the 2D sheets. We further show that the smaller lanthanides Yb$^{3+}$ and Ho$^{3+}$ enforce a shorter stacking distance of only 3.002(6) Å and afford consistently higher conductivity than the larger lanthanides Nd$^{3+}$ and La$^{3+}$, which distend the sheets up to 3.068(2) Å. This first systematic study of structure-function relationships in layered conductive MOFs is enabled by the high degree of crystallinity afforded by the relatively ionic lanthanide-ligand bonds. These results demonstrate that increasing the covalency of the metal-ligand bond is not the only viable path to achieve record conductivity in 2D MOFs, and that the interactions of the organic ligands alone can produce efficient charge transport pathways.
Electrically conductive metal-organic frameworks (MOFs) have recently attracted attention as potential materials for supercapacitors,\textsuperscript{1,2} batteries,\textsuperscript{3} thermoelectric devices,\textsuperscript{4} chemiresistive sensors,\textsuperscript{5,6} and electrocatalysts.\textsuperscript{7–10} Significant effort is devoted towards the development of MOFs with increasingly higher conductivities.\textsuperscript{11,12} Current record values of 2500 S/cm at room temperature for non-porous coordination polymers\textsuperscript{13} and 40 S/cm for porous MOFs,\textsuperscript{14} with many others approaching them,\textsuperscript{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 Ni$^{2+}$ and Cu$^{2+}$. The high conductivity values of these materials are often attributed to the strong in-plane conjugation between the ligands’ $\pi$-systems and the $d$ orbitals of the metals.\textsuperscript{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,\textsuperscript{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 (Ln$^{3+}$) have empty 5$d$-shells, with all valence electrons lying in heavily shielded, deep 4$f$ orbitals. Because the 4$f$ orbitals do not participate significantly in bonding, Ln$^{3+}$ ions typically form considerably more ionic compounds than the transition metals.\textsuperscript{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 Ln$^{3+}$ 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 La$^{3+}$ to Lu$^{3+}$.\textsuperscript{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 Ln$^{3+}$ and 2,3,6,7,10,11-hexahydroxytriphenylene (H$_6$HHTP). Although the more ionic bonding between Ln$^{3+}$ and the catecholate ligands may be expected to diminish the efficiency of charge transport within the 2D plane, the materials exhibit conductivity values reaching 0.5 S/cm in two-probe polycrystalline pellet measurements, on par with the most conductive MOFs reported to date.\textsuperscript{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

A solvothermal reaction of $\text{H}_6\text{HHTP}$ with hydrated $\text{Ln(NO}_3\text{)_3}$ ($\text{Ln} = \text{La, Nd, Ho, Yb}$) in a mixture of water and $N,N'$-dimethylimidazolidinone (DMI) produced dark green-blue microcrystalline powders of $\text{Ln}_{1+x}\text{HHTP(H}_2\text{O)}_n$ ($x = 0$ to $0.2$; referred to as $\text{LnHHTP}$). Scanning electron microscopy (SEM) showed that the powders consisted of well-shaped hexagonal needles (Fig. 1e, Supplementary Fig. 1), varying in length between 1 $\mu$m and 200 $\mu$m 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 refinement$^{26}$ of powder X-ray diffraction (PXRD) data, which provided excellent structural models for the Nd$^{3+}$ (Fig. 1) and the Yb$^{3+}$ 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 Yb$^{3+}$ compared to Nd$^{3+}$. 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, Ln$^{3+}$ ions bind the triangular HHTP ligands into honeycomb-like two-dimensional nets featuring solvent-accessible pores with a crystallographic diameter of $\sim 1.94$ nm for NdHHTP. The experimental pore diameters of all four materials (Supplementary Fig. 10), measured by fitting $\text{N}_2$ 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 $\text{N}_2$ adsorption isotherms gave BET$^{28}$ surface areas of 200-510 m$^2$/g, also in good agreement with the values reported for the related two-dimensional $d$-metal-based MOFs (490 m$^2$/g for the Co-based framework Co-CAT-1, and 425 m$^2$/g for the Ni-based framework Ni-CAT-1).$^{17}$
Figure 1. A representation of the crystal structure of \textbf{NdHHTP}: (a) viewed along the $c$ direction; (b) displaying the metal-ligand connectivity of the seven-coordinate Nd atoms; (c) displaying the layer stacking. Hydrogen atoms are omitted for clarity. (d) Rietveld refinement of the average \textbf{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 $\text{GoF} = 3.73$. Triangle sizes are commensurate with error bars from standard deviations. (e) Scanning electron micrograph of a \textbf{NdHHTP} crystal. Scale bar: 1 $\mu$m.

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$_2$O$_3$ (Supplementary Fig. 18).$^{29}$ The lanthanide sites are not fully occupied in either \textbf{NdHHTP} or \textbf{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 in the Supplementary Information.

PXRD patterns for \textbf{LaHHTP} and \textbf{HoHHTP} (Supplementary Fig. 11) are qualitatively identical to those of \textbf{NdHHTP} and \textbf{YbHHTP}, suggesting that all four materials are isostructural. Pawley refinements$^{30}$ 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 S1): 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.

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 Yb3+ and Ho3+. 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), and are semiconducting in the ab plane (Γ-K-M), with otherwise insignificant differences between the Lu and La models. As expected, lanthanide valence orbitals do not participate 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.
**Figure 2.** Electronic band structure and density of states (DOS) of LaHHTP, including spin-orbit coupling effects. The DOS is plotted in logarithmic coordinates to emphasize the non-zero density at the Fermi level. The inset shows the first Brillouin zone.

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 ~0.3 eV for La and Nd, and at ~0.7 eV for Ho and Yb. These absorption features, however, do not conform to a linear region when plotted on a Tauc plot for direct or indirect bandgaps, and can therefore be attributed to absorption by defects. 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, InP, Ge, 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, as well as for some indirect-gap semiconductors, including Si. 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 HHTP, whereas the experimental formula indicates slight variations of this oxidation state towards more reduced ligands, which would shift the Fermi energy higher.
Figure 3. (a) Kubelka-Munk transforms of the diffuse reflectance spectra for LnHHTP (Ln = La, Nd, Ho, Yb). (b) Same data plotted in Tauc coordinates for direct allowed transitions. Pale dashed lines show extrapolation of the linear fit regions; grey line follows $(a h v)^2 = 0$.

Inset: variation of the estimated optical bandgaps of the four materials with the unit cell parameter $c$.

The electrical conductivities of polycrystalline pellets made from LnHHTP materials are on par with the most conductive MOFs to date, ranging from $1 \cdot 10^{-4}$ S/cm for LaHHTP to 0.5 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, 0.5 S/cm, is within the range of the most conductive three-dimensionally connected MOFs to date, which is remarkable given the low degree of covalency provided by Ln–O bonds in LnHHTP materials. 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. Conductivity improvements of more than two orders of magnitude have been reported for single-crystal measurements of MOFs compared to 2-probe pellets.

Figure 4. (a) Two-probe pressed pellet conductivities of LnHHTP (Ln = Yb, Ho, Nd, and La) measured at 29 °C. Squares, downward-facing triangles and upward-facing triangles denote three independent batches. Circles mark average values. (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).

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.

Although thermally-activated transport is a defining characteristic for semiconducting materials, appearing to contradict the calculated band structures, grain boundaries can dominate electrical transport behaviour in polycrystalline pellets. 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. An additional source of thermally-activated conductivity may lie in the defect states that we observe both by X-ray diffraction, in the form of the cationic vacancies, and by diffuse-reflectance spectroscopy, as noted above.

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) Ln(NO$_3$)$_3$·$n$H$_2$O in 3.0 mL deionized water, the solution of 0.063 mmol (1.0 equiv, 20. mg) H$_6$HHTP 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:

LaHHTP (calcd., found for La$_{6.2}$(HHTP)$_6$(H$_2$O)$_{26.1}$(CH$_3$C(O)CH$_3$)$_{4.3}$(DMI)$_{0.5}$): La (24.39, 24.39), C (41.71, 41.71), H (3.38, 3.38), N (0.39, 0.39), Na (0, 0).

NdHHTP (calcd., found for Nd$_{7.2}$(HHTP)$_6$(H$_2$O)$_{19.3}$(DMI)$_{0.4}$): Nd (31.17, 31.15), C (39.47, 39.45), H (2.37, 2.19), N (0.32, 0.35), Na (0, 0.06).

HoHHTP (calcd., found for Ho$_{7.4}$(HHTP)$_6$(DMI)$_{0.6}$(H$_2$O)$_{50.2}$): Ho (29.64, 29.57), C (32.46, 32.37), H (3.52, 2.88), N (0.41, 0.54), Na (0, 0).

YbHHTP (calcd., found for Yb$_{7.1}$(HHTP)$_6$(H$_2$O)$_{12.4}$(CH$_3$C(O)CH$_3$)$_{3.9}$(DMI)$_{0.4}$): Yb (33.79, 33.79), C (40.24, 40.24), H (2.44, 2.44), N (0.30, 0.30), Na (0, 0).
Powder X-ray Diffraction

Laboratory powder X-ray diffraction patterns were collected on a Bruker D8 diffractometer fitted with a Goebel mirror and a Lynxeye Si strip position-sensitive detector, operating in reflection mode with Ni-filtered Cu Kα_{1,2} radiation (Kα_1 = 1.5406 Å, Kα_2 = 1.5444 Å, Kα_2/Kα_1 = 0.5). Samples were prepared by placing a thin layer of the appropriate material on a zero-background silicon crystal plate.

High resolution powder X-ray diffraction data were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory (λ = 0.45212 Å). Activated samples of both NdHHTP and YbHHTP were loaded into quartz capillaries in a N_2 glovebox and data were collected utilizing an amorphous-Si area detector, with the two-dimensional diffraction patterns reduced to one-dimensional data with GSAS-II. Measurements were conducted under vacuum at room temperature. Additional measurements were taken upon heating to 373 K, though no notable differences occurred.

Diffuse reflectance spectroscopy.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Bruker Tensor 37 (MIR source and KBr beam splitter) with a liquid nitrogen-cooled mercury cadmium telluride detector fitted with the DiffusIR accessory (Pike Technologies). Samples were ground in air with dry potassium bromide (99.9%, Pike technologies) to produce 0.5-1% wt. MOF mixtures. The data were averaged over 64 scans between 8000 – 600 cm^{-1} (4 cm^{-1} resolution).

Diffuse reflectance spectra between 350 and 3000 nm were collected on a Cary 5000i spectrophotometer, fitted with the UV-Vis DiffusIR accessory (Pike Technologies), at scan rates of 600 nm/min for the range from 350 to 800 nm, and 200 nm/min from 800 to 3000 nm, under ambient conditions. A KBr baseline was collected prior to the sample measurements. Samples were prepared as described above for the DRIFTS measurements.

For the Tauc plots and the determination of the optical bandgaps, the UV-vis-NIR spectra were stitched manually with the DRIFTS spectra obtained for the same samples. The UV-vis-NIR spectra were scaled and offset to achieve near-perfect overlap with the DRIFTS spectra from 0.5 eV to 0.75 eV.
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.\textsuperscript{37} Linear I–V curves were 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 within -0.5 V to +0.5 V. Pellet thicknesses were measured after the measurement using a micrometer (Mitutoyo).

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

Further information on the experimental and computational methods, structural details, scanning electron micrograms, 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. Crystallographic information has been deposited in the Cambridge Crystallographic Data Centre under accession codes CCDC 1874834 (NdHHTP) and CCDC 1874835 (YbHHTP).
ACKNOWLEDGEMENTS

This work was supported by the Army Research Office (grant number W911NF-17-1-0174). Computational work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the NSF (ACI-1053575). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. This work was performed in part at the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Coordinated Infrastructure Network, which is supported by the National Science Foundation under NSF award no. 1541959. CNS is part of Harvard University. We thank the staff of 17-BM for help with synchrotron X-ray data collection; Dr. Robert W. Day and Dr. Lei Sun for assistance with scanning electron microscopy; Dr. Ivo Stassen, Dr. Maxx Q. Arguilla, and Lilia S. Xie for helpful discussions.

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.

CORRESPONDING AUTHOR

Correspondence to Mircea Dincă.
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. Cu$_3$(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 Ni$_3$(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 Ni$_3$(hexaiminotriphenylene)$_2$. ACS Catal. 7, 7726–7731 (2017).

9. Miner, E. M., Wang, L. & Dincă, M. Modular O$_2$ 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.*
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$_2$O$_3$ (Ln = La–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. Tauc, J. Optical properties and electronic structure of amorphous Ge and Si. *Mater. Res. Bull.* **3**, 37–46 (1968).

33. 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).
34. Müller, H., Trommer, R., Cardona, M. & Vogl, P. Pressure dependence of the direct absorption edge of InP. *Phys. Rev. B* **21**, 4879–4883 (1980).

35. Balslev, I. Influence of Uniaxial Stress on the Indirect Absorption Edge in Silicon and Germanium. *Phys. Rev.* **143**, 636–647 (1966).

36. Nabi, Z., Abbar, B., Méçabi, S., Khalfi, A. & Amrane, N. Pressure dependence of band gaps in PbS, PbSe and PbTe. *Comput. Mater. Sci.* **18**, 127–131 (2000).

37. Sun, L., Park, S. S., Sheberla, D. & Dincă, M. Measuring and Reporting Electrical Conductivity in Metal–Organic Frameworks: Cd$_2$(TTFTB) as a Case Study. *J. Am. Chem. Soc.* **138**, 14772–14782 (2016).

38. 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).

39. Kittel, C. *Introduction to solid state physics*. (Wiley, 2004).

40. Toby, B. H. & Von Dreele, R. B. GSAS-II: The genesis of a modern open-source all purpose crystallography software package. *J. Appl. Crystallogr.* **46**, 544–549 (2013).
Figure 1. A representation of the crystal structure of NdHHTP: (a) viewed along the c direction; (b) displaying the metal-ligand connectivity of the seven-coordinate Nd atoms; (c) displaying the layer stacking. Hydrogen atoms are omitted for clarity. (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 $\text{GoF} = 3.73$. 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, including spin-orbit coupling effects. The DOS is plotted in logarithmic coordinates to emphasize the non-zero density at the Fermi level. The inset shows the first Brillouin zone.
Figure 3. (a) Kubelka-Munk transforms of the diffuse reflectance spectra for LnHHTP (Ln = La, Nd, Ho, Yb). (b) Same data plotted in Tauc coordinates for direct allowed transitions. Pale dashed lines show extrapolation of the linear fit regions; grey line follows $(\alpha h\nu)^2 = 0$. Inset: variation of the estimated optical bandgaps of the four materials with the unit cell parameter $c$. 
Figure 4. (a) Two-probe pressed pellet conductivities of LnHHTP (Ln = Yb, Ho, Nd, and La) measured at 29 °C. Squares, downward-facing triangles and upward-facing triangles denote three independent batches. Circles mark average values. (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).
Graphical abstract.