Large Single Crystals of Two-Dimensional π-Conjugated Metal–Organic Frameworks via Biphasic Solution-Solid Growth

Dong-Gwang Ha, Mehdi Rezaee, Yimo Han, Saima A. Siddiqui, Robert W. Day, Lilia S. Xie, Brian J. Modtland, David A. Muller, Jing Kong, Philip Kim, Mircea Dincă,* and Marc A. Baldo*

ABSTRACT: Two-dimensional (2D) π-conjugated metal–organic frameworks (πMOFs) are a new class of designer electronic materials that are porous and tunable through the constituent organic molecules and choice of metal ions. Unlike typical MOFs, 2D πMOFs exhibit high conductivity mediated by delocalized π-electrons and have promising applications in a range of electrical devices as well as exotic physical properties. Here, we develop a growth method that generates single-crystal plates with lateral dimensions exceeding 10 μm, orders of magnitude bigger than previous methods. Synthesis of large single crystals eliminates a significant impediment to the fundamental characterization of the materials, allowing determination of the intrinsic conductivity and mobility along the 2D plane of πMOFs. A representative 2D πMOF, Ni-CAT-1, exhibits a conductivity of up to 2 S/cm, and Hall measurement reveals the origin of the high conductivity. Characterization of crystalline 2D πMOFs creates the foundation for developing electronic applications of this promising and highly diverse class of materials.

INTRODUCTION

Metal–organic frameworks (MOFs) are porous materials with a customizable crystalline structure that can be designed from building blocks of organic molecules and metal ions.1–3 They are typically insulators, but two-dimensional (2D) π-conjugated MOFs (πMOFs) can exhibit high electrical conductivity, making them good candidates for a range of electrical devices.4–6 Similar to other 2D electronic materials such as graphene, 2D πMOFs exhibit π-conjugation in the basal plane, with neighboring layers associated more loosely through van der Waals forces along the c axis. Numerous theoretical calculations have suggested that some of these 2D πMOFs should exhibit exotic electronic properties arising from topologically nontrivial band structures.7–9 This potentially new physics has sparked additional interest in this novel class of electronic materials and has inspired the synthesis of various 2D πMOFs.10,11 Nevertheless, a major bottleneck toward exploring such properties has been crystal growth, especially within the basal plane where intrinsic high conductivity is expected. Because of limitations in the available crystal size of 2D πMOFs, conventional electrical characterization including a Hall effect measurement of the basal plane has been technically challenging. The typical basal plane domain size afforded by conventional crystal growth techniques has thus far been limited to less than 200 nm,5,12–17 which is challenging for multiterminal device fabrication especially given the needle-like morphology. As such, one of the key challenges preventing a deeper understanding of the electronic properties of these materials has been the growth of sufficiently large single crystals.

Two methods are commonly used to synthesize 2D πMOFs for electrical characterization: single-phase solution synthesis and liquid–liquid interfacial synthesis. The former typically consists of homogeneous reactions carried out by dissolving and heating the constituent organic ligands and metal salts in a solvent. The primary crystal growth direction is usually the c axis, yielding needle-shaped crystals with very small cross sections in the basal plane.12–15 It has proven exceedingly difficult to increase the basal plane crystal cross-section through single-phase solution growth. We hypothesize that the large reaction volume reduces the collision probability of reactants and crystal nuclei. The reaction is further impeded as the small nuclei precipitate and become covered by other nuclei. Conversely, the challenge for the liquid–liquid interfacial method is that the reaction occurs at the boundary of immiscible solutions. Unlike in the single-phase method, liquid–liquid interfacial reactions are performed at room temperature,17–22 or with marginal heating. Because the reaction temperature is a key parameter governing crystal...
growth kinetics, an insufficient supply of energy to the system often leads to limited crystallinity.\textsuperscript{24,25} Other approaches, including layer-by-layer approaches,\textsuperscript{26} biphase liquid–gas interfacial methods,\textsuperscript{16} and vapor-induced growth\textsuperscript{27} have also been limited thus far to polycrystalline films with crystallites exhibiting small basal plane domains.

In this work, we demonstrate the single-crystal growth of Ni-CAT-1. It is one of the first reported 2D π-MOFs,\textsuperscript{12} and it is based on a stable organic ligand in contrast to air-sensitive ligands adopted in more conductive 2D π-MOFs.\textsuperscript{15,20,23} Hence this material is chosen as the testbed for a new growth technique for 2D π-MOFs that promotes the growth of plate-shaped rather than needle-shaped single crystals.

\section*{RESULTS AND DISCUSSION}

The aim is to increase the rate of metal–ligand bond formation, leading to π–d conjugation, relative to the rate of layers stacking along the $c$ axis. This is achieved by maintaining high concentrations of the reactants and a high temperature. We employ a biphasic solution–solid approach shown in Figure 1, wherein the organic ligand, here hexahydroxytriphenylene (HHTP), is deposited as a thin film on a silicon substrate by vacuum thermal evaporation. A planar molecular structure and strong hydrogen bonding act\textsuperscript{28,29} to align the HHTP molecules in the plane of the silicon substrate, thereby defining the growth direction for the 2D π-MOF crystals. Indeed, an ellipsometric measurement of an HHTP film deposited on silicon demonstrates horizontal alignment. HHTP has higher polarizability along the molecular plane, and the measured ordinary refractive index exceeds the extraordinary index (Figure S1). The order parameter of the film is $-0.22$, which is typical for small molecules that exhibit preferential horizontal alignment after vacuum thermal evaporation.\textsuperscript{28} For reference, the measured order parameter is $-0.5$ if the molecules have perfect horizontal alignment and 0 if they are randomly oriented.\textsuperscript{28} Importantly, because essentially all organic ligands used to synthesize 2D π-MOFs have planar structures, thermal evaporation should afford similarly ordered and oriented films with many such ligands.

Another key aspect of our growth method is to confine the reaction volume to a very thin layer between substrates tightly held together by magnets, one in contact with a substrate for the ligand film, the other in contact with a substrate for a solid film of the metal salt precursor. The entire assembly is
immersed in a solvent and heated to an appropriate temperature (Figure 1C). This configuration provides several key advantages: (1) it allows only a very small thin layer of solvent to be present during the reaction; (2) the limited solvent exposure in the thin layer maintains HHTP largely in the solid phase; and (3) the magnet assembly minimizes crystal growth in the c direction but allows essentially unimpeded growth in the basal plane. For our testbed material Ni-CAT-1, an oriented film of HHTP is placed in contact with a solid film dropcast from a solution of nickel acetate, Ni(OAc)2. The two films, both deposited on silicon covered by a thin layer of SiO2, are squeezed between two commercial neodymium coin magnets and heated in water at 95 °C (Figure 1C). The narrow space (less than 1 μL; see supplementary text) between the films of the two reactants permits small amounts of water between the metal and organic substrates. Because of the poor solubility of HHTP in water (0.2 g/L at 95 °C), the 40 nm film of HHTP remains largely solid, whereas Ni(OAc)2 dissolves. Consequently, MOF nuclei can form on the HHTP film, growing rapidly in the high concentration of aligned HHTP molecules. Since MOF crystals are porous, we speculate that the metal ions can easily penetrate the HHTP layer as the reaction proceeds. We confirm the persistence of a solid film of HHTP in water when confined between two substrates in the absence of nickel acetate (Figure S2): when the HHTP film is not covered with another substrate, it dissolves rapidly in water.

Optical microscope and scanning electron microscope (SEM) images of typical single-crystal plates of Ni-CAT-1 grown by the method described above are shown in Figure 2. The morphology of these crystals strongly contrasts with previously reported Ni-CAT-1 needle-shaped crystals. The lateral dimension of the solution-solid grown crystals is more than 2 orders of magnitude larger than the needle-shaped ones.12,13 After allowing the reaction to proceed for 1 h, part of the HHTP film is converted to MOF crystal plates due to the solution-solid growth as shown in Figure 2A. When we varied the reaction time from 30 min to 12 h, SEM images suggested increased crystallinity with longer reaction time (Figures 2A,B, S3). This indicates the reaction is reversible, allowing multiple nuclei to merge and/or allowing for error correction during crystal growth. To test the effect of horizontal alignment of the HHTP precursor, we repeated the process with a drop-cast polycrystalline film of HHTP with random crystallite orientation. The drop-cast HHTP generates crystals with small grains, and a greater fraction of out-of-plane crystal growth is observed compared with the crystals grown from the evaporated HHTP (Figure S4). Furthermore, using a "good" solvent for HHTP, that is, a solvent that solubilizes HHTP readily such as a water-dimethylformamide (30%) mixture,

Figure 3. Characterization of the 2D πMOF crystals. (A) Low-magnification bright-field TEM image of a Ni-CAT-1 crystal. Because of the large unit cell of the MOF, the lattice is visible at this low magnification, with its expected uniform hexagonal structure. A hexagonal vertex of a single crystal is clearly visible in the bottom right corner. Inset: The corresponding Fourier transform image confirms a lattice spacing of 2.1 nm. (B) High-magnification bright-field TEM image superimposed with a generated crystal structure of Ni-CAT-1. (C) Elemental mapping of the crystals by EDS, showing a uniform distribution of nickel and carbon. The strong oxygen background signal is due to the SiO2 substrate. The elemental analysis is shown in Figure S10. (D) IR spectrum of powder and single crystal Ni-CAT-1, confirming similar vibrational features. The identity of Ni-CAT-1 powder was confirmed by PXRD (Figure S9).
large rod-shape crystals were generated because this solvent mixture dissolved the entire HHTP film, which is no longer oriented (Figure S5). Finally, a systematic increase of the reaction space between the magnets by increasing the diameter of dispersed microspheres from Ø 4 to 49 μm produced crystals with a morphology that varied from plate-like to needle-like (Figure S6). These series of experiments attest to the critical role of a solid, oriented film of HHTP as a precursor. Note that the solution-solid growth method also generates some rod-shape crystals and polycrystals (Figure S7). We speculate that the different morphologies are caused by variation in the local concentration of nickel acetate from the drop-casting and wetting process. Residual HHTP dissolved in water can initiate conventional single-phase solution growth that generates rod-shaped crystals.

Transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FT-IR) confirmed the identity and integrity of the single-crystal plates, as shown in Figure 3. A TEM image of one corner of a crystal plate is shown in Figure 2A. The large crystal has a uniform hexagonal structure. The fast Fourier transform (FFT) of the image confirms single-crystallinity and gives a lattice parameter of 2.1 nm, which is consistent with the powder X-ray diffraction (PXRD) data (Figure S9). The EDS elemental maps demonstrate a uniform distribution of nickel and carbon with a Ni:C ratio of 1:12, in agreement with the stoichiometry of Ni-CAT-1 (Figure S10). FTIR further confirms the identity of the crystals, with the vibrational bands of Ni-CAT-1 single crystals overlapping those observed for powder samples. The latter were independently verified as pure Ni-CAT-1 by PXRD.12 To check the applicability of the solution-solid growth, we changed nickel acetate to cobalt acetate under identical growth conditions, and planar crystals of Co-CAT-1 were produced as shown in Figure S17 and Figure S18.

The large single crystals of Ni-CAT-1 permit measurements of the basal plane’s electrical properties in 2D πMOFs. To minimize damage to the 2D πMOFs during device fabrication, we placed four electrical contacts using a stencil mask technique rather than conventional electron beam lithography. The stencil mask avoids electron beam resist coating, baking, and direct electron-beam exposure. Details of the sample fabrication techniques and conductivities are given in the Supporting Information and Figure S11. Conventional 4-probe pressed pellet samples provided important comparisons with the single crystal devices. We find that the peak basal-plane single-crystal electrical conductivity of the Ni-CAT-1 crystals is 2 S/cm, with an average of 0.8 S/cm and a standard deviation of 0.7 S/cm, whereas the conductivity of a polycrystalline pressed-pellet sample is 3.6 × 10⁻³ S/cm, similar to two previously reported values.11,30 In other words, the conductivity of a polycrystalline pressed pellet of Ni-CAT-1 is
lower by more than 2 orders of magnitude than that of the single crystals as may be expected given the grain boundaries and contributions from the out-of-plane transport. The conductivity along the c axis is estimated at $1 \times 10^{-4}$ S/cm from a two probe device (Figure S12). The presence of traps at grain boundaries is further confirmed by a temperature-dependent conductivity study (Figure 4A). The Arrhenius behavior of the temperature-dependent conductivity yields an activation energy of 0.09 eV for the single crystal, and 0.14 eV for the pressed pellet devices.

A Hall measurement on a single crystal device of Ni-CAT-1 provides unique insight into the nature of in-plane electrical transport in 2D πMOFs. The Hall coefficient obtained from fitting the data in Figure 4G, $(−0.46 \pm 0.14) \text{ cm}^2/\text{C}$, is relatively small, suggesting that the origin of the high conductivity in this particular material is a high carrier concentration rather than fast carrier transport. The thermally activated conductivity indicates Ni-CAT-1 is a semiconductor. It may intrinsically possess high densities of electrons and holes at room temperature given its small bandgap of 0.2 eV (Figure S13). However, assuming n-type behavior, consistent with the sign of the Hall coefficient, gives an electron density of $(−1.4 \pm 0.42) \times 10^{19} \text{ cm}^{-3}$, which corresponds to 1% of the HTTP-site density, and a corresponding electron mobility of $(0.16 \pm 0.049) \text{ cm}^2/\text{V} \cdot \text{sec}$; see supplementary Table 1 for representative comparisons with other electronic materials. Whereas the single crystals of Ni-CAT-1 generate a distinct Hall effect, we were unable to measure the Hall effect in pressed pellet samples due to suppression of the charge carrier mobility by grain boundaries. Recalling that the pressed pellet samples also exhibited nearly 3 orders of magnitude decrease in conductivity, these measurements provide an important direct assessment of charge carrier densities in 2D πMOFs and confirm that the single crystal samples exhibit significantly superior electronic properties overall.

Biplanar solution-solid growth of large planar single crystals of Ni-CAT-1 allow characterization of its intrinsic electronic properties along the 2D plane. Based on these promising results, we further anticipate that application of this growth technique will enhance the performance of other, highly conductive 2D πMOFs. Future study of single-crystal 2D πMOFs should clarify fundamental structure–property relationships and allow measurement of intrinsic electronic and topologically protected properties.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c01488.

Materials and Methods, Supplementary Text, Figures S1 to S20, Tables S1 and S2 (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Mircea Dinca – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-1262-1264; Email: mddinca@mit.edu

Marc A. Baldo – Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0003-2201-5257; Email: baldo@mit.edu

**AUTHORS**

Dong-Gwang Ha – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Mehdi Rezaee – School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States

Yimo Han – Department of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, United States; orcid.org/0000-0003-0563-4611

Saima A. Siddiqui – Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Robert W. Day – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Lila S. Xie – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Brian J. Modtland – Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

David A. Muller – Department of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853, United States; Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853, United States

Jing Kong – Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0003-0551-1208

Philip Kim – School of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acscentsci.0c01488

**Author Contributions**


**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

D.-G.H., S.S., B.M., and M.A.B. were supported by the US Department of Energy, Office of Basic Energy Sciences (Award No. DE-FG02-07ER46474). Work in the Dinca lab was supported by the Army Research Office (Grant No. W911NF-17-1-0174). P.K. and M.R. acknowledge support from ONR MURI (N00014-16-1-2921). Y.H. and D.A.M. were supported by NSF Grant (DMR-1719875). D.-G.H. acknowledges supplementary support from the Kwanjeong Educational Foundation Fellowship. We thank K.-H. Kim and C.F.
Perkinson for help with the ellipsometry and polarizing microscopy measurements.

**REFERENCES**


(16) Dinca, M.* Polymers (IUPAC Recommendations 2013)*.


