

High Electrical Conductivity in Ni₃(2,3,6,7,10,11-hexaminotriphenylene)₂, a Semiconducting Metal–Organic Graphene Analogue

Dennis Sheberla,[†] Lei Sun,[†] Martin A. Blood-Forsythe,[‡] Süleyman Er,[‡] Casey R. Wade,[†] Carl K. Brozek,[†] Alán Aspuru-Guzik,[‡] and Mircea Dincă^{*,†}

[†]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[‡]Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

S Supporting Information

ABSTRACT: Reaction of 2,3,6,7,10,11-hexaminotriphenylene with Ni²⁺ in aqueous NH₃ solution under aerobic conditions produces Ni₃(HITP)₂ (HITP = 2,3,6,7,10,11-hexaminotriphenylene), a new two-dimensional metal–organic framework (MOF). The new material can be isolated as a highly conductive black powder or dark blue-violet films. Two-probe and van der Pauw electrical measurements reveal bulk (pellet) and surface (film) conductivity values of 2 and 40 S·cm⁻¹, respectively, both records for MOFs and among the best for any coordination polymer.

Two-dimensional (2D) electronic materials are of considerable interest due to their potential applications in future electronics.^{1–3} The most prominent example is graphene, an atomically thin organic 2D material with in-plane π -conjugation.⁴ Although graphene exhibits exceptional charge mobility and mechanical stability, its use in semiconductor-based devices is limited by its zero bandgap.^{5–7} Dimensional reduction⁸ and chemical functionalization⁹ can increase the bandgap, rendering graphene semiconducting, but these methods drastically reduce its charge mobility and can introduce numerous defects. This has led to a sustained effort toward identifying 2D materials with intrinsic non-zero bandgaps that could replace conventional semiconductors. Two broad classes of materials have dominated these efforts: layered metal chalcogenides (e.g., MoS₂, WSe₂) and 2D covalent–organic frameworks (COFs). The former can be deposited as large-area single sheets in a “top-down” approach.^{10,11} They have been shown to perform well in device testing^{12–14} but do not easily lend themselves to chemical functionalization and tunability. In contrast, COFs are prepared by “bottom-up” solution-based synthetic methods and are attractive because they are subject to rational modification.^{15,16} Nevertheless, the electronic properties of COFs are largely inferior to those of metal chalcogenides because the functional groups used to connect their building blocks typically do not allow in-plane conjugation.^{17,18}

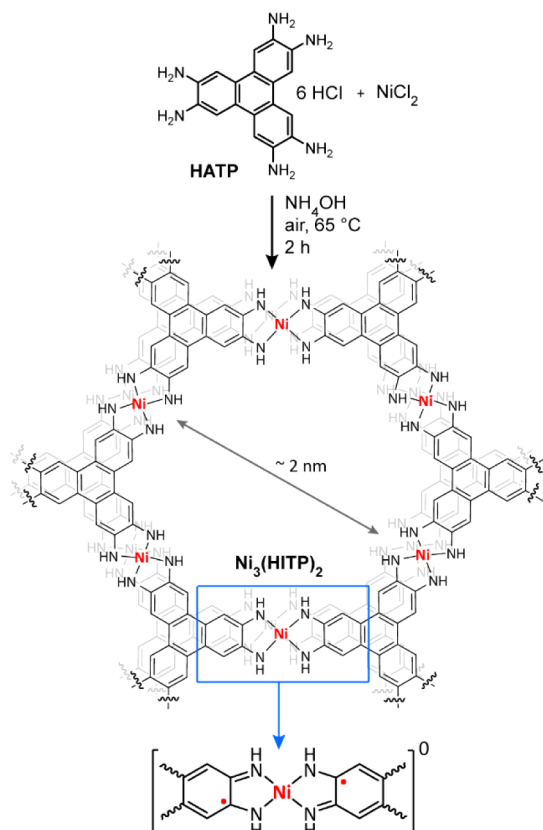
Bridging the divide between 2D inorganic and organic materials is a recent class of “bottom-up” compounds assembled from multitopic dithiolene and *o*-semiquinone aromatic organic moieties bridged by square-planar metal

ions. These 2D metal–organic networks exhibit non-zero bandgaps and good electrical conductivity, enabled by full charge delocalization in the 2D plane.^{19–21} They can therefore be described as semiconducting metal–organic graphene analogues (*s*-MOGs). Certain members of this class have also recently been predicted to behave as topological insulators,^{22,23} a realm currently dominated by purely inorganic compounds.²⁴ Clearly, the synthesis and characterization of new *s*-MOGs could give rise to important new electronic materials with exotic electronic states and potential applications in the semiconductor device industry.

Inspired by the success of dithiolene-based *s*-MOGs, whose metal linkages mimic classic Class III-delocalized homoleptic Ni(dithiolene)₂ complexes,^{25,26} we identified Ni(isq)₂ (isq = *o*-diiminobenzosemiquinonate) as an attractive target for the construction of a fully charge-delocalized *s*-MOG. Although first isolated in 1927²⁷ from *o*-phenylenediamine and NiCl₂ in ammoniacal water, Ni(isq)₂ evaded structural and electronic characterization for quite a long time^{28,29} but is now known to be fully π -conjugated, with its ground state having partial singlet biradical character.^{30,31} Crystalline Ni(isq)₂ itself exhibits high mobility in organic field effect transistors³² and increased conductivity upon doping with I₂.³³ Here, we show that two-dimensional extension of Ni(isq)₂ through the reaction of 2,3,6,7,10,11-hexaminotriphenylene hexahydrochloride (HATP-6HCl) with ammoniacal NiCl₂ produces a new crystalline *s*-MOG with very high electrical conductivity that is linearly proportional to temperature. Remarkably, the conductivity of the new material vastly exceeds that of previous *s*-MOGs and other conductive MOFs and is higher than even some of the best organic conductors.

Under conditions mimicking the synthesis of Ni(isq)₂, HATP-6HCl was treated with an aqueous solution of NiCl₂·6H₂O under air, followed by the addition of aqueous NH₃ under constant stirring. The reaction mixture was heated to 65 °C and stirred under air for an additional 2 h. This yielded the new material Ni₃(HITP)₂ (HITP = 2,3,6,7,10,11-hexaminotriphenylenesemiquinonate) as a bulk black powder and a very dark blue-violet film (see Scheme 1). Upon extensive washing with water in an ultrasonic bath, the charge neutrality of Ni₃(HITP)₂, and implicitly the formation of monoanionic *o*-

Received: March 18, 2014

Scheme 1. Synthesis of $\text{Ni}_3(\text{HITP})_2$ ^a

^aOnly the closed-shell resonance structure is shown, although diradical Ni-bisdiimine linkages, shown on the bottom and found in $\text{Ni}(\text{isq})_2$, are likely here too.

diiminobenzosemiquinonate moieties (Scheme 1, bottom), was confirmed by elemental analysis and X-ray photoelectron spectroscopy (XPS). As shown in Figures S1 and S2, XPS spectra of both powder and films (vide infra) of $\text{Ni}_3(\text{HITP})_2$ show the presence of only Ni, N, C, and O resonance peaks from the material itself and water guest molecules. Cl peaks, expected for any trapped or charge-balancing anionic chlorides that would compensate a possible cationic structure, are absent. Similarly, high-resolution analysis of the Ni(2p) and N(1s) regions of the XPS spectra show a single type of Ni and N atoms, respectively, suggesting that no extraneous Ni^{2+} or NH_4^+ ions are present. These ions are the only possible cationic species that could balance an anionic material, and they indicate that $\text{Ni}_3(\text{HITP})_2$ is indeed neutral, as expected from its similarity with $\text{Ni}(\text{isq})_2$.

Powder X-ray diffraction (PXRD) analysis of $\text{Ni}_3(\text{HITP})_2$ revealed a crystalline structure with prominent peaks at $2\theta = 4.7^\circ$, 9.5° , 12.6° , and 16.5° , indicative of long-range order within the ab plane (see Figure 1). An additional, weaker and broader peak at $2\theta = 27.3^\circ$, corresponding to the [001] reflections, is indicative of poorer long-range order along the c direction, as expected for covalently linked layered materials. We simulated several possible stacking arrangements for the 2D sheets of $\text{Ni}_3(\text{HITP})_2$, including staggered (AA^{-1}), eclipsed (AA), and slipped-parallel (AB) orientations. As shown in Figure 1, the experimental pattern rules out the AA^{-1} stacking but agrees very well with both the AA and AB sequences. Although the AA and AB sequences are impossible to differentiate on the basis of PXRD alone, Ni K-edge extended

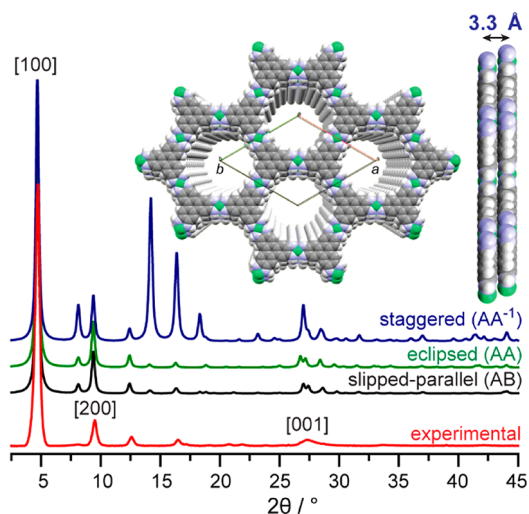


Figure 1. Experimental and simulated PXRD patterns of $\text{Ni}_3(\text{HITP})_2$. The inset shows the slipped-parallel structure with neighboring sheets displaced by $1/16$ fractional coordinates in the a and b directions.

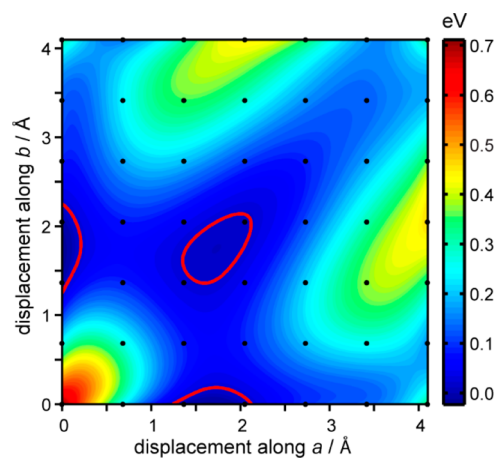


Figure 2. Contour map of the potential energy surface generated by different translations between the A and B layers. Black dots correspond to the locations of single-point calculations performed using the PBE-D2 functional. Red lines indicate the borders of the “thermally accessible region” (within $k_B T \approx 0.026$ eV of the minimum). The surface was produced by interpolation with 2D Lagrange polynomials on a grid of Chebyshev points. The energy per unit cell has been normalized to zero at the minimum.

X-ray absorption fine structure (EXAFS) analysis of a sample of $\text{Ni}_3(\text{HITP})_2$ revealed a spectrum that better agrees with a simulated spectrum of AB than of AA. As shown in Figure S3, a strong Ni··Ni scattering path at $R = 3.0$ Å (actual Ni··Ni distance = 3.33 Å), expected for AA, is absent in the experimental data.

Additional support for a slipped-parallel AB stacking model came from DFT calculations (see SI for full details). A model structure was developed by optimizing a hydrogen-terminated fragment at the B3LYP-D3BJ/6-31G* level and constraining it to $P6/mmm$ symmetry. A unit cell for the structure was then made by fixing an interlayer separation of 3.33 Å. Periodic single-point energy calculations using the GGA-PBE exchange-correlation functional with D2 dispersion correction were carried out for structures with 82 different ab -plane displacements. The potential energy surface (PES) shown in Figure 2 was obtained by interpolating DFT total energies using 2D

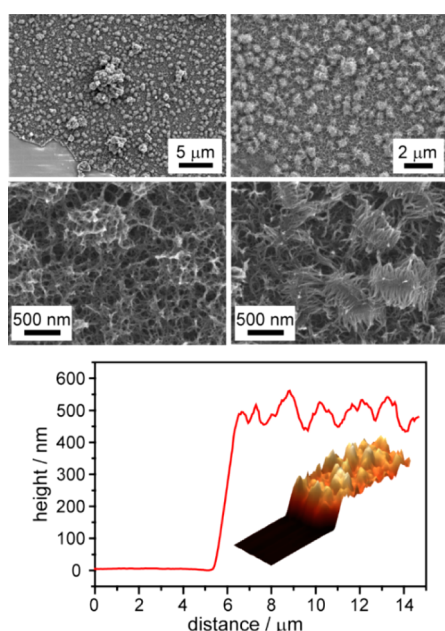


Figure 3. Top: SEM micrographs for films of $\text{Ni}_3(\text{HITP})_2$ at various magnifications. Bottom: AFM thickness profile and corresponding 3D AFM image of a representative $\text{Ni}_3(\text{HITP})_2$ film.

Lagrange polynomials. This PES suggested that the fully eclipsed AA structure is energetically unfavorable and that the AB sequence is the most stable. In particular, an AB model wherein the 2D unit cell of one layer is slipped relative to a neighboring layer by slightly more than 1/16th of a cell edge ($\sim 1.8 \text{ \AA}$) along the a or b vectors gave the lowest energy on the PES. These calculations do not rule out closely related slipped-parallel structures containing a mixture of displacements to these minima in the PES, which is consistent with the poorer long-range order along the c direction. Altogether, the PXRD, EXAFS, and DFT data evidence a hexagonal $\text{Ni}_3(\text{HITP})_2$ structure with slipped-parallel stacking and unit cell parameters $a = b = 21.75 \text{ \AA}$ and $c = 6.66 \text{ \AA}$.

With a good structural model in hand, we turned our attention to studying the electronic properties of both bulk and thin films of $\text{Ni}_3(\text{HITP})_2$. To allow for optical measurements, we chose quartz as a substrate for our films. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) of representative films of $\sim 500 \text{ nm}$ thickness, shown in Figure 3, evidence macroporous surface features and excellent film coverage on the quartz substrate. Importantly, the electronic absorption features of such films extend well into the near-infrared (NIR) range ($\lambda_{\text{max}} = 1400 \text{ nm}$), as shown in the UV–vis–NIR spectrum in Figure S4. Such low-energy electronic excitations are common in highly conjugated organics and conducting polymers³⁴ but are absent in molecular complexes such as $\text{Ni}(\text{isq})_2$, which do not absorb at wavelengths above 900 nm.^{29,33}

Encouraged by the possibility of extended 2D conjugation, we measured the electrical properties of $\text{Ni}_3(\text{HITP})_2$. To avoid swelling and other solvent effects, we set out to dry our samples for these measurements. Thermogravimetric analysis (TGA) of bulk, freshly cleaned $\text{Ni}_3(\text{HITP})_2$, shown in Figure S5, suggested that heating at $150 \text{ }^\circ\text{C}$ would eliminate all water, and samples used for electrical measurements were dried accordingly.

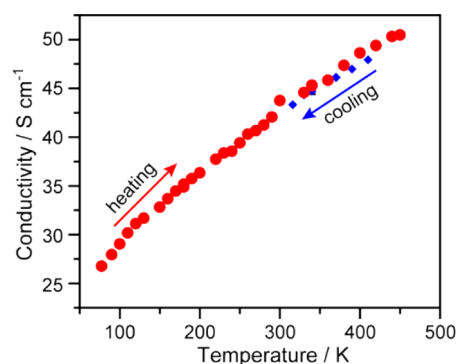


Figure 4. Variable-temperature van der Pauw conductivity measurement on a $\sim 500 \text{ nm}$ thick film on quartz.

The first indication of excellent electrical properties in $\text{Ni}_3(\text{HITP})_2$ came from a two-probe measurement of bulk powder compressed as a pellet between two stainless steel rods.³⁵ Despite the small particle size, the numerous inter-grain boundaries, and the electrode contact resistances, the pellet conductivity of $\text{Ni}_3(\text{HITP})_2$ was $2 \text{ S}\cdot\text{cm}^{-1}$. This is on the same order of magnitude as the two-probe pellet conductivity of some of the best organic conductors,³⁵ including the iconic TTF-TCNQ ($\sigma_{\text{pellet}} = 10 \text{ S}\cdot\text{cm}^{-1}$).³⁶ Furthermore, the bulk conductivity of $\text{Ni}_3(\text{HITP})_2$ is 1 order of magnitude higher than that of the best s -MOG (Ni-hexathiobenzene, $\sigma = 0.15 \text{ S}\cdot\text{cm}^{-1}$), and at least 2 orders of magnitude better than those of the most conducting MOFs to date.^{37–39}

Even more remarkable results were obtained for thin films, configurations that are likely more relevant for future devices. Thus, films of $\text{Ni}_3(\text{HITP})_2$ deposited on quartz substrates consistently gave conductivity values of $40 \text{ S}\cdot\text{cm}^{-1}$ at room temperature, as measured by the van der Pauw method.⁴⁰ The conductivity showed a linear increase with temperature from 77 to 450 K, as shown in Figure 4, a behavior that was reversible upon cooling. Although we have been unable to find a model that unequivocally explains this behavior over the entire temperature range, organic-based semiconductors are notorious for having complicated, mixed charge transport mechanisms;^{41–43} further theoretical and experimental studies will probe the mechanism that is operative here. Most notably, among all coordination polymers,⁴⁴ the film conductivity of $\text{Ni}_3(\text{HITP})_2$ is exceeded only by that of $\text{Cu}(4\text{-hydroxythiophenolate})$ ($\sigma = 120 \text{ S}\cdot\text{cm}^{-1}$).⁴⁵

Clearly, the nature of charge transport in $\text{Ni}_3(\text{HITP})_2$ and its potentially superior single sheet electrical properties warrant further studies, as do its magnetic behavior and its inclusion in electronic devices. The more general picture afforded by these studies, nevertheless, is that metals can mediate very efficient 2D conjugation pathways between electroactive organic molecules, leading to new materials with impressive electrical properties. Although this could perhaps be already gleaned from the vast literature on molecular conductors, the successful application of these concepts to two- and three-dimensionally extended crystalline networks is just emerging and promises to take us on a thrilling intellectual ride.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental and computational details; EXAFS, XPS, TGA, and UV–vis plots; and additional AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

mdinca@mit.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Synthetic work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (U.S. DOE-BES), under award no. DE-SC0006937. Physical measurements were supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. DOE-BES under award no. DE-SC0001088 (MIT). M.D. gratefully acknowledges early career support from the Sloan Foundation, the Research Corporation for Science Advancement (Cottrell Scholar), and 3M. C.K.B. is partially supported by an NSF Graduate Research Fellowship through Grant 1122374. M.B.-F. acknowledges support by the U.S. DOE, Graduate Fellowship Program, administered by ORISE-ORAU under contract no. DE-AC05-06OR23100. S.E. performed work as part of the Fellowships for Young Energy Scientists program of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organization for Scientific Research (NWO). A.A.-G. acknowledges support from the NSF Center for Integrated Quantum Materials (CIQM) through grant NSF-DMR-1231319. Computational research was carried out in part at the Center for Functional Nanomaterials (Brookhaven National Lab), which is supported by the U.S. DOE under contract no. DE-AC02-98CH10886. We also thank Dr. Jeffrey Miller for assistance with the collection of X-ray absorption data at the Advanced Photon Source, beamline 10-BM, which is operated for the U.S. DOE by Argonne National Laboratory and supported under contract no. DE-AC02-06CH11357. Part of the characterization was performed at the Harvard Center for Nanoscale Systems, which is supported by NSF Grant ECS-0335765.

REFERENCES

- (1) Weiss, N. O.; Zhou, H.; Liao, L.; Liu, Y.; Jiang, S.; Huang, Y.; Duan, X. *Adv. Mater.* **2012**, *24*, 5782.
- (2) Xu, M.; Liang, T.; Shi, M.; Chen, H. *Chem. Rev.* **2013**, *113*, 3766.
- (3) Butler, S. Z.; et al. *ACS Nano* **2013**, *7*, 2898.
- (4) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
- (5) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* **2005**, *438*, 197.
- (6) Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. *Rev. Mod. Phys.* **2009**, *81*, 109.
- (7) Avouris, P. *Nano Lett.* **2010**, *10*, 4285.
- (8) Ruffieux, P.; Cai, J.; Plumb, N. C.; Patthey, L.; Prezzi, D.; Ferretti, A.; Molinari, E.; Feng, X.; Müllen, K.; Pignedoli, C. A.; Fasel, R. *ACS Nano* **2012**, *6*, 6930.
- (9) Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. *Chem. Rev.* **2012**, *112*, 6156.
- (10) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. *Phys. Rev. Lett.* **2010**, *105*, No. 136805.
- (11) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. *Nat. Chem.* **2013**, *5*, 263.
- (12) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. *Nat. Nanotechnol.* **2011**, *6*, 147.
- (13) Baugher, B. W. H.; Churchill, H. O. H.; Yang, Y.; Jarillo-Herrero, P. *Nat. Nanotechnol.* **2014**, *9*, 262.
- (14) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. *Nat. Nanotechnol.* **2012**, *7*, 699.
- (15) Gutzler, R.; Perepichka, D. F. *J. Am. Chem. Soc.* **2013**, *135*, 16585.
- (16) Colson, J. W.; Dichtel, W. R. *Nat. Chem.* **2013**, *5*, 453.
- (17) Bertrand, G. H. V.; Michaelis, V. K.; Ong, T.-C.; Griffin, R. G.; Dincă, M. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 4923.
- (18) An example of a COF exhibiting full in-plane conjugation has been reported recently: Guo, J.; Xu, Y.; Jin, S.; Chen, L.; Kaji, T.; Honsho, Y.; Addicoat, M. a.; Kim, J.; Saeki, A.; Ihee, H.; Seki, S.; Irle, S.; Hiramoto, M.; Gao, J.; Jiang, D. *Nat. Commun.* **2013**, *4*, 2736.
- (19) Hmadeh, M.; Lu, Z.; Liu, Z.; Gándara, F.; Furukawa, H.; Wan, S.; Augustyn, V.; Chang, R.; Liao, L.; Zhou, F.; Perre, E.; Ozolins, V.; Suenaga, K.; Duan, X.; Dunn, B.; Yamamoto, Y.; Terasaki, O.; Yaghi, O. M. *Chem. Mater.* **2012**, *24*, 3511.
- (20) Kambe, T.; Sakamoto, R.; Hoshiko, K.; Takada, K.; Miyachi, M.; Ryu, J.-H.; Sasaki, S.; Kim, J.; Nakazato, K.; Takata, M.; Nishihara, H. *J. Am. Chem. Soc.* **2013**, *135*, 2462.
- (21) Cui, J.; Xu, Z. *Chem. Commun.* **2014**, *50*, 3986.
- (22) Wang, Z. F.; Liu, Z.; Liu, F. *Nat. Commun.* **2013**, *4*, 1471.
- (23) Wang, Z. F.; Su, N.; Liu, F. *Nano Lett.* **2013**, *13*, 2842.
- (24) Kong, D.; Cui, Y. *Nat. Chem.* **2011**, *3*, 845.
- (25) Sproules, S.; Wieghardt, K. *Coord. Chem. Rev.* **2011**, *255*, 837.
- (26) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **2011**, *50*, 9741.
- (27) Feigl, F.; Fürth, M. *Monatsh. Chem.* **1927**, *48*, 445.
- (28) Stiefel, E. L.; Waters, J. H.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3016.
- (29) Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116.
- (30) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179.
- (31) Fukui, H.; Shigeta, Y.; Nakano, M.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. *J. Phys. Chem. A* **2011**, *115*, 1117.
- (32) Noro, S.; Chang, H.-C.; Takenobu, T.; Murayama, Y.; Kanbara, T.; Aoyama, T.; Sassa, T.; Wada, T.; Tanaka, D.; Kitagawa, S.; Iwasa, Y.; Akutagawa, T.; Nakamura, T. *J. Am. Chem. Soc.* **2005**, *127*, 10012.
- (33) Leij, F.; Morelli, G.; Ricciardi, G.; Brigatti, M. F.; Rosa, A. *Polyhedron* **1989**, *8*, 2603.
- (34) Skotheim, T. A.; Reynolds, J. R., Eds. *Handbook of conducting polymers*, 3rd ed.; CRC Press: Boca Raton, FL, 2007.
- (35) Wudl, F.; Bryce, M. R. *J. Chem. Educ.* **1990**, *67*, 717.
- (36) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
- (37) Gándara, F.; Uribe-Romo, F. J.; Britt, D. K.; Furukawa, H.; Lei, L.; Cheng, R.; Duan, X.; O'Keeffe, M.; Yaghi, O. M. *Chem.—Eur. J.* **2012**, *18*, 10595.
- (38) Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. *Chem. Mater.* **2010**, *22*, 4120.
- (39) Talin, A. A.; Centrone, A.; Ford, A. C.; Foster, M. E.; Stavila, V.; Haney, P.; Kinney, R. A.; Szalai, V.; El Gabaly, F.; Yoon, H. P.; Léonard, F.; Allendorf, M. D. *Science* **2014**, *343*, 66.
- (40) Van der Pauw, L. J. *Philips Technol. Rev.* **1958**, *20*, 220.
- (41) Menon, R.; Yoon, C. O.; Moses, D.; Heeger, A. J. In *Handbook of conducting polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.
- (42) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926.
- (43) Baranovski, S., Ed. *Charge Transport in Disordered Solids with Applications in Electronics*; Wiley: New York, 2006.
- (44) Givaja, G.; Amo-Ochoa, P.; Gomez-Garcia, C. J.; Zamora, F. *Chem. Soc. Rev.* **2012**, *41*, 115.
- (45) Low, K.-H.; Roy, V. A. L.; Chui, S. S.-Y.; Chan, S. L.-F.; Che, C.-M. *Chem. Commun.* **2010**, *46*, 7328.