



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

Citation

Published version

<https://doi.org/10.1021/ja502765n>

Link

<http://nrs.harvard.edu/urn-3:HUL.InstRepos:23597721>

Terms of use

This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Open Access Policy Articles (OAP), as set forth at

<https://harvardwiki.atlassian.net/wiki/external/NGY5NDE4ZjgzNTc5NDQzMGIzZWZhMGFIOWI2M2EwYTg>

Accessibility

<https://accessibility.huit.harvard.edu/digital-accessibility-policy>

Share Your Story

The Harvard community has made this article openly available.

Please share how this access benefits you. [Submit a story](#)

High Electrical Conductivity in $\text{Ni}_3(2,3,6,7,10,11\text{-hexaiminotriphenylene})_2$, a Semiconducting Metal-Organic Graphene Analogue

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

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

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

Supporting Information Placeholder

ABSTRACT: Reaction of 2,3,6,7,10,11-hexaaminotriphenylene with Ni^{2+} in aqueous NH_3 solution under aerobic conditions produces $\text{Ni}_3(\text{HITP})_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene), 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 S cm^{-1} 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 towards identifying 2D materials with intrinsic non-zero bandgaps that could replace conventional semiconductors. Two broad classes of materials have dominated these efforts: the layered metal chalcogenides (e.g. MoS_2 , WSe_2) 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 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 multi-topic 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 $\text{Ni}(\text{dithiolene})_2$ complexes,^{25,26} we identified $\text{Ni}(\text{isq})_2$ (isq = *o*-diiminobenzosemiquinonate) as an attractive target for the construction of a fully charge-delocalized s-MOG. Indeed, although first isolated in 1927²⁷ from *o*-phenylenediamine and NiCl_2 in ammoniacal water, $\text{Ni}(\text{isq})_2$ 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 $\text{Ni}(\text{isq})_2$ itself exhibits high mobility in organic field effect transistors (OFET)³² and increased conductivity upon doping with I_2 .³³ Here, we show that two-dimensional extension of $\text{Ni}(\text{isq})_2$ through the reaction of 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride (HATP 6HCl) with ammoniacal NiCl_2 produces a new crystalline s-MOG with very high electrical conductivity, which is linearly proportional to temperature. Remarkably, the conductivity of the new material vastly exceeds those 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 $\text{Ni}(\text{isq})_2$, HATP 6HCl was treated with an aqueous solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under air, followed by the addition of aqueous

Nc1nc(N)c2c(N)c(N)nc2c1 + 6 HCl + NiCl₂

Reaction conditions: NH₄OH, air, 65 °C, 2 h

Product: Ni₃(HITP)₂

Distance between clusters: ~ 2 nm

Final product structure: [Ni₃(HITP)₂]₀

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

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 3.3 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 shown in Figure 2 was obtained by interpolating DFT total energies using 2D Lagrange polynomials. This potential energy surface 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 (~1.8 Å) along the *a* or *b* vectors, gave the lowest energy on the potential energy surface. These calculations do not rule out closely related slipped-parallel structures containing a mixture of displacements to these minima in the potential energy surface, which is consistent with the poorer long-range order along the *c* direction. Altogether, the PXRD, EXAFS, and DFT data evidence a hexagonal Ni₃(HITP)₂ structure with slipped-parallel stacking and unit cell parameters *a* = *b* = 21.75 Å, and *c* = 6.66 Å.

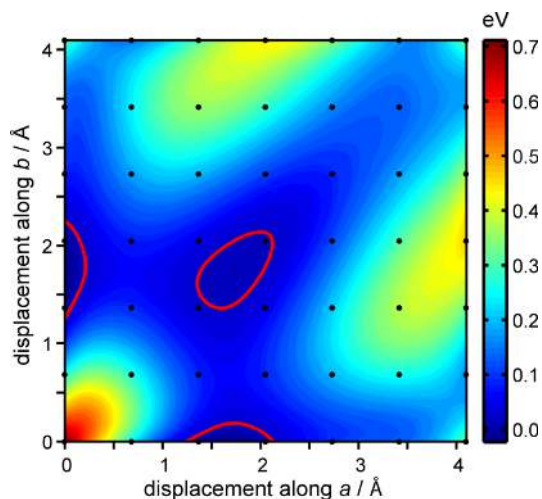


Figure 2. A contour map of the potential energy surface generated by different translations between A and B layers. Black dots correspond to locations of single-point calculations performed using the PBE-D2 functional. Red lines indicate the borders of the ‘thermally accessible region’ (within $k_B T \approx 0.026$ eV of the minima). 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.

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 ~ 500 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 ($\lambda_{\text{max}} = 1,400$ 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 polymers,³⁴ but are absent in molecular complexes such as $\text{Ni}(\text{isq})_2$, which does 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. A thermogravimetric analysis (TGA) of bulk, freshly cleaned $\text{Ni}_3(\text{HITP})_2$, shown in Figure S5, suggested that heating at 150 °C would eliminate all water, and samples used for electrical measurements were dried accordingly.

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 S 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 ($\sigma_{\text{pellet}} = 10 \text{ S cm}^{-1}$).³⁶ Furthermore, the bulk conductivity of $\text{Ni}_3(\text{HITP})_2$ is one order of magnitude higher than that of the best *s*-MOG (Ni-hexathiobenzene, $\sigma = 0.15 \text{ S cm}^{-1}$), and at least 2 orders of

magnitude better than the most conducting MOFs to date.^{37–39}

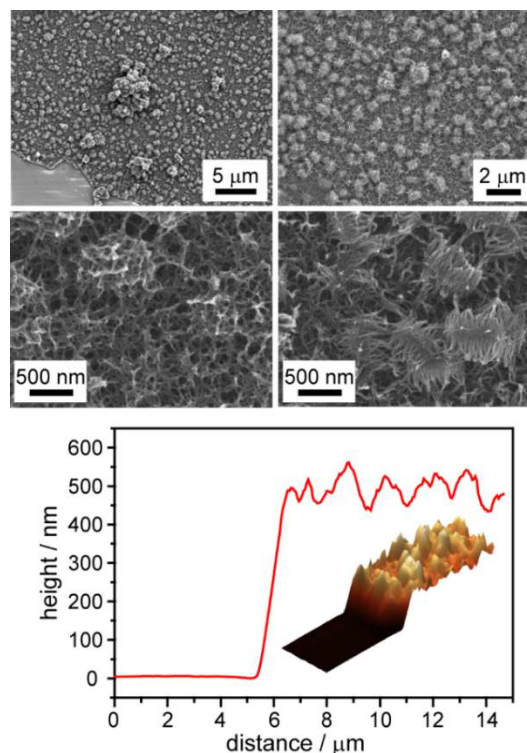


Figure 3. Top: SEMs for films of $\text{Ni}_3(\text{HITP})_2$ at various magnifications. Bottom: AFM thickness profile and corresponding 3D AFM image of a representative $\text{Ni}_3(\text{HITP})_2$ film.

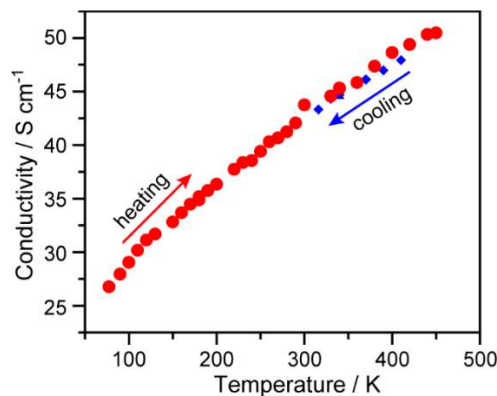


Figure 4. Variable temperature van der Pauw conductivity measurement on a ~ 500 nm thick film on quartz.

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 S cm^{-1} at room temperature, as measured by the van der Pauw method.⁴⁰ The conductivity showed linear increase with temperature from 77 K 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 Ni₃(HITP)₂ is exceeded only by Cu(4-hydroxythiophenolate) ($\sigma = 120 \text{ S cm}^{-1}$).⁴⁵

Clearly, the nature of charge transport in Ni₃(HITP)₂ and its undoubtedly 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 details, EXAFS, XPS, TGA, 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

ACKNOWLEDGMENT

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 DE-SC0006937. Physical measurements were supported as part of the Center for Excitronics, 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, 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.

REFERENCES

- (1) Weiss, N. O.; Zhou, H.; Liao, L.; Liu, Y.; Jiang, S.; Huang, Y.; Duan, X. *Adv. Mater.* **2012**, *24*, 5782–5825.
- (2) Xu, M.; Liang, T.; Shi, M.; Chen, H. *Chem. Rev.* **2013**, *113*, 3766–3798.
- (3) Butler, S. Z. et al. *ACS Nano* **2013**, *7*, 2898–2926.
- (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*, 666–669.
- (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*, 197–200.
- (6) Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. *Rev. Mod. Phys.* **2009**, *81*, 109–162.
- (7) Avouris, P. *Nano Lett.* **2010**, *10*, 4285–4294.
- (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*, 6930–6935.
- (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*, 6156–6214.
- (10) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- (11) Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H. *Nat. Chem.* **2013**, *5*, 263–275.
- (12) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- (13) Baugher, B. W. H.; Churchill, H. O. H.; Yang, Y.; Jarillo-Herrero, P. *Nat. Nanotechnol.* **2014**, in press.
- (14) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. *Nat. Nanotechnol.* **2012**, *7*, 699–712.
- (15) Gutzler, R.; Perepichka, D. F. *J. Am. Chem. Soc.* **2013**, *135*, 16585–16594.
- (16) Colson, J. W.; Dichtel, W. R. *Nat Chem* **2013**, *5*, 453–465.
- (17) Bertrand, G. H. V.; Michaelis, V. K.; Ong, T.-C.; Griffin, R. G.; Dincă, M. *Proc. Natl. Acad. Sci.* **2013**, *110*, 4923–4928.
- (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.; Ihoe, 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*, 3511–3513.
- (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*, 2462–2465.
- (21) Cui, J.; Xu, Z. *Chem. Commun.* **2014**, in press.
- (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*, 2842–2845.
- (24) Kong, D.; Cui, Y. *Nat. Chem.* **2011**, *3*, 845–849.
- (25) Sproules, S.; Wieghardt, K. *Coord. Chem. Rev.* **2011**, *255*, 837.
- (26) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **2011**, *50*, 9741–9751.
- (27) Feigl, F.; Fürth, M. *Monatsh. Chem.* **1927**, *48*, 445–450.
- (28) Stiefel, E. I.; Waters, J. H.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3016–3017.
- (29) Herebian, D.; Bothe, E.; Neese, F.; Weyhermüller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **2003**, *125*, 9116–9128.
- (30) Bachler, V.; Olbrich, G.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4179–4193.
- (31) Fukui, H.; Shigeta, Y.; Nakano, M.; Kubo, T.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E. *J. Phys. Chem. A* **2011**, *115*, 1117–1124.
- (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*, 10012–10013.
- (33) Lelj, F.; Morelli, G.; Ricciardi, G.; Brigatti, M. F.; Rosa, A. *Polyhedron* **1989**, *8*, 2603–2610.
- (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*, 3916–3925.
- (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. – A Eur. J.* **2012**, *18*, 10595–10601.

- (38) Kobayashi, Y.; Jacobs, B.; Allendorf, M. D.; Long, J. R. *Chem. Mater.* **2010**, *22*, 4120–4122.
- (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* **2013**.
- (40) Van der Pauw, L. J. *Philips Tech. Rev.* **1958**, *20*, 220–224.
- (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: USA, 1998.
- (42) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926–952.
- (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*, 115–147.
- (45) Low, K.-H.; Roy, V. A. L.; Chui, S. S.-Y.; Chan, S. L.-F.; Che, C.-M. *Chem. Commun.* **2010**, *46*, 7328–7330.

TOC graphic

