Deutsche Ausgabe: DOI: 10.1002/ange.201411854
Internationale Ausgabe: DOI: 10.1002/anie.201411854

Cu_3(hexaiminotriphenylene)$_2$: An Electrically Conductive 2D Metal–Organic Framework for Chemiresistive Sensing**

*Michael G. Campbell, Dennis Sheberla, Sophie F. Liu, Timothy M. Swager, and Mircea Dincă**

Abstract: *The utility of metal–organic frameworks (MOFs) as functional materials in electronic devices has been limited to date by a lack of MOFs that display high electrical conductivity. Here, we report the synthesis of a new electrically conductive 2D MOF, $Cu_3(HITP)_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene), which displays a bulk conductivity of 0.2 $S\,cm^{-1}$ (pellet, two-point-probe). Devices synthesized by simple drop casting of $Cu_3(HITP)_2$ dispersions function as reversible chemiresistive sensors, capable of detecting sub-ppm levels of ammonia vapor. Comparison with the isostructural 2D MOF $Ni_3(HITP)_2$ shows that the copper sites are critical for ammonia sensing, indicating that rational design/synthesis can be used to tune the functional properties of conductive MOFs.*

In recent years, there has been increasing interest in using metal–organic frameworks (MOFs) as next-generation functional materials in electronic and optoelectronic devices.[1–3] Owing to their high surface area and robust chemical tunability based on a “bottom-up” synthetic approach, MOFs have been especially targeted for use in sensors.[4] An ongoing challenge, however, has been a lack of efficient signal transduction due in part to the fact that the vast majority of MOFs are insulators. The emergence of MOFs with high intrinsic charge mobility or electrical conductivity provides an opportunity for the development of a new class of MOF-based sensory devices. Herein, we report the synthesis of a new 2D MOF with high electrical conductivity and its application to chemiresistive sensing of ammonia vapor. To our knowledge, this work represents the first successful use of conductive MOFs in chemiresistive sensors.

Among the handful of electrically conductive MOFs reported to date,[5–9] 2D MOFs have shown the highest conductivity values, likely as a result of in-plane charge delocalization and extended π-conjugation in the 2D sheets,[10] mediated by electronic communication through the metal nodes. Part of our team has recently reported the 2D MOF $Ni_3(HITP)_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene), which displays the highest conductivity of any microporous MOF reported to date.[11] These results indicate that 2D MOFs with *o*-phenylenediamine linkages are attractive material candidates along with structurally related 2D MOFs with dithiolene[12–14] or *o*-semiquinone[15] linkages. Therefore, we have targeted a family of MOFs based on the $Ni_3(HITP)_2$ framework, to probe the effect of structural changes on resulting electronic properties. We postulated that through systematic variation of the metal center, the overall electronic structure of the 2D sheets may be tuned, leading to diverse properties and functionality. In this work, we describe that replacement of the Ni sites in $Ni_3(HITP)_2$ with Cu results in an isostructural material that maintains high electrical conductivity. The choice of metal has a dramatic effect on the response of conductivity to analytes such as ammonia vapor, highlighting the potential for rational tuning of conductive MOFs.

The synthesis of $Cu_3(HITP)_2$ was accomplished using similar conditions as for $Ni_3(HITP)_2$. A solution of $CuSO_4$ in dilute aqueous ammonia was combined with 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride (HATP·6HCl) under ambient atmosphere at 23 °C, resulting in rapid precipitation of a black solid. After washing with water and acetone, followed by drying under vacuum, $Cu_3(HITP)_2$ was isolated as a black crystalline solid in 95% yield (Figure 1). Powder X-ray diffraction (PXRD) analysis revealed that $Cu_3(HITP)_2$ is isostructural with $Ni_3(HITP)_2$ and adopts a hexagonal 2D structure with a slipped-parallel stacking of the 2D sheets (Figure 2). The unit cell parameters for the simulated structure are $a = b = 22.3$ Å and $c = 6.6$ Å. The broadness of the peak at $2\theta = 27.8°$, corresponding to the [001] reflections, suggests poorer long-range order along the *c* direction as compared to the *ab* plane, which is typical for layered 2D materials.[16–19] A two-point-probe measurement of a pressed pellet of bulk $Cu_3(HITP)_2$ at room temperature revealed an electrical conductivity of 0.2 $S\,cm^{-1}$. This value is slightly lower than measured for $Ni_3(HITP)_2$ (2 $S\,cm^{-1}$) but is higher than for the majority of conductive MOFs reported to

---

[*] Dr. M. G. Campbell, Dr. D. Sheberla, S. F. Liu, Prof. T. M. Swager, Prof. M. Dincă
Department of Chemistry, Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139 (USA)
E-mail: mdinca@mit.edu
Homepage: http://web.mit.edu/dincalab

[**] Synthetic and characterization work (excluding vapor sensing experiments) was supported as part of the Center for Excitonics, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001088 (MIT). M.D. thanks the Camille and Henry Dreyfus Postdoctoral Program in Environmental Chemistry for support of M.G.C. We thank Miller Li for assistance with acquiring SEM images and Lei Sun for helpful discussions. M.D. gratefully acknowledges early career support from the Sloan Foundation, the Research Corporation for Science Advancement (Cottrell Scholar), and 3M. S.F.L. and T.M.S. acknowledge support from a Graduate Research Fellowship under Grant No. 1122374, as well as the Army Research Office through the Institute for Soldier Nanotechnologies (sensing experiments). The SEM and XPS characterization data were obtained at the Harvard Center for Nanoscale Systems, which is supported by NSF Grant ECS-0335765.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411854.

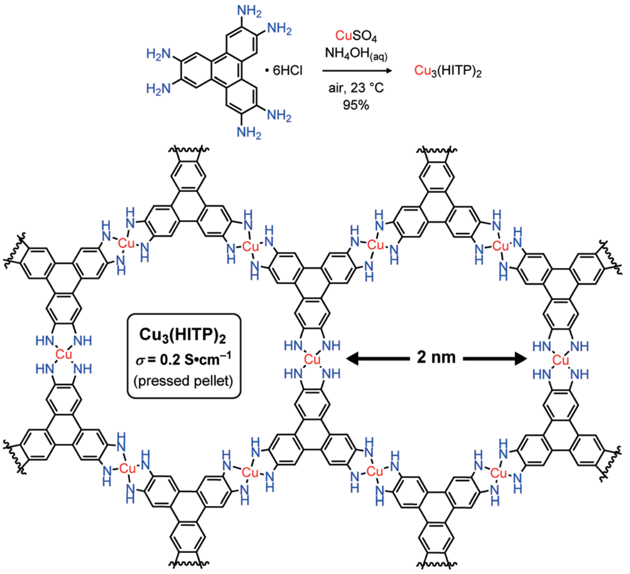

Figure 1. Synthesis and 2D chemical structure of $Cu_3(HITP)_2$.

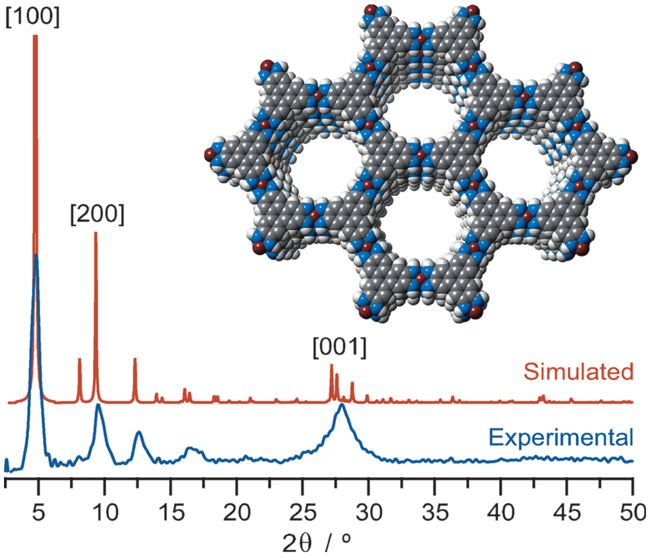

Figure 2. Experimental and simulated PXRD pattern for $Cu_3(HITP)_2$, displaying a slipped-parallel packing structure of the 2D sheets. Inset: structure of $Cu_3(HITP)_2$ viewed down the *c* axis (gray: carbon, white: hydrogen, blue: nitrogen, red: copper).

date,[5,6,9] including 2D MOFs with dithiolene[12–14] or *o*-semiquinone[15] linkages.

The elemental composition of $Cu_3(HITP)_2$ was analyzed using X-ray photoelectron spectroscopy (XPS), which revealed a charge-neutral material, as also previously observed for $Ni_3(HITP)_2$ (see Figures S1,S2). Thus, after washing with water, no residual SO_4^{2-} or Cl^- anions were detected by XPS, and high-resolution scans of the N(1s) region showed a single type of N atom, confirming that additional NH_4^+ cations are also absent. We note that although the chemical structure of $Cu_3(HITP)_2$ shown in Figure 1 is drawn in a closed-shell configuration for simplicity, each of the *o*-phenylenediimine linkages is expected to be oxidized to a radical anion form, which results in a charge-neutral complex with the Cu^{2+} centers.[20] Interestingly, a high-resolution XPS spectrum of the Cu(2p) region suggests a mixture of Cu^I and Cu^{II} centers in $Cu_3(HITP)_2$, which contrasts with $Ni_3(HITP)_2$, for which a single type of Ni atom is observed. The lack of charge-balancing counterions indicates that the variation from Cu^{2+} is compensated by the redox-active HITP ligands; hexaaminotriphenylene derivatives are well known to accommodate a wide range of redox states.[21] Although the observed XPS data would also be consistent with the co-deposition of Cu metal during $Cu_3(HITP)_2$ synthesis, and Cu metal formation has been reported as a side reaction in the synthesis of complexes of Cu^{2+} with *o*-phenylenediamine,[22] no Cu metal was observed by PXRD (see Figure S3 for comparison). Furthermore, additional control experiments using Cu^I precursors for $Cu_3(HITP)_2$ synthesis show conclusively that Cu metal is not formed during the synthesis of $Cu_3(HITP)_2$ (Figures S5 and S6; see the Supporting Information (SI) for a detailed discussion). We therefore interpret the XPS data as to indicate an inherent mixed valency of the Cu centers in $Cu_3(HITP)_2$.

Scanning electron microscopy (SEM) was used to probe the morphology of bulk $Cu_3(HITP)_2$, and revealed submicron-sized crystallites that pack together to form a denser polycrystalline material (Figure 3). Films obtained by drop casting a suspension of $Cu_3(HITP)_2$ in acetone onto substrates such as indium-tin-oxide (ITO)-coated glass are mechanically robust and do not separate from the substrate upon vigorous washing in an ultrasonic bath. The ability to process films of conductive MOFs by simple methods such as drop casting is potentially valuable for device manufacturing, as we demonstrate here for the fabrication of chemiresistive sensors with $Cu_3(HITP)_2$.

The use of MOFs as chemical sensors has been a topic of great interest in recent years,[3,4] but the lack of electrical conductivity in most MOFs presents a hurdle to efficient signal transduction. Therefore, the majority of MOF-based chemical sensors have been limited to transduction mechanisms such as luminescence quenching or enhancement,[23–28] or more complicated device architectures such as MOF-coated microcantilevers[29] or quartz crystal microbalan-

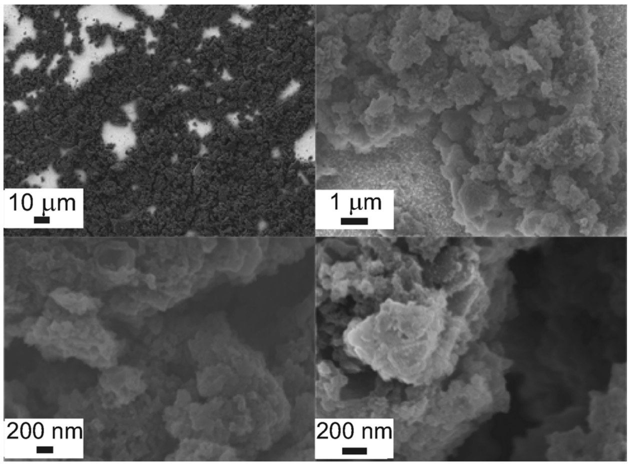

Figure 3. SEM images at various magnifications for $Cu_3(HITP)_2$, drop-cast onto an ITO glass slide from a suspension in acetone.

ces.[30–32] To our knowledge, only one example of chemical sensing based on the innate electrical response of MOFs has been reported to date, using impedance spectroscopy.[33] We demonstrate here that a simple device, fabricated by drop casting an acetone suspension of Cu$_3$(HITP)$_2$ onto interdigitated gold electrodes, can be used for the reversible chemiresistive sensing of ammonia vapor.

The Cu$_3$(HITP)$_2$ device was encased in a Teflon gas flow chamber, with its electrodes connected to a potentiostat (Figure 4a). During a measurement, a constant potential of 100 mV was applied, and the current was monitored while a continuous gas stream was passed over the device at a constant flow rate, which could be switched between N$_2$ and an ammonia/N$_2$ mixture. A stable baseline current was established under N$_2$ flow, and a sharp increase in current was observed within seconds upon exposure to dilute ammonia vapor (Figure 4b). The starting current level was recovered when the ammonia flow was replaced with pure N$_2$. The reversible change in current was reproducible over more than 10 cycles. Ammonia concentrations of ≤ 0.5 ppm were detected even after exposure to higher concentrations (0.5 ppm was the lowest experimentally accessible concentration of ammonia for our apparatus). Because the ability to sense ammonia under ambient conditions, rather than an inert N$_2$ atmosphere, is important for potential applications, we have also demonstrated that the Cu$_3$(HITP)$_2$ devices perform comparably when the N$_2$ carrier gas is replaced with an air stream containing atmospheric oxygen and natural humidity (9% relative humidity was measured for our in-house air stream). Increasing the relative humidity to significantly higher levels had only a small detrimental effect on the sensing performance with Cu$_3$(HITP)$_2$ devices, which were still able to reliably detect ammonia concentrations of ≤ 5 ppm under air with 60% relative humidity (see Figure S11).

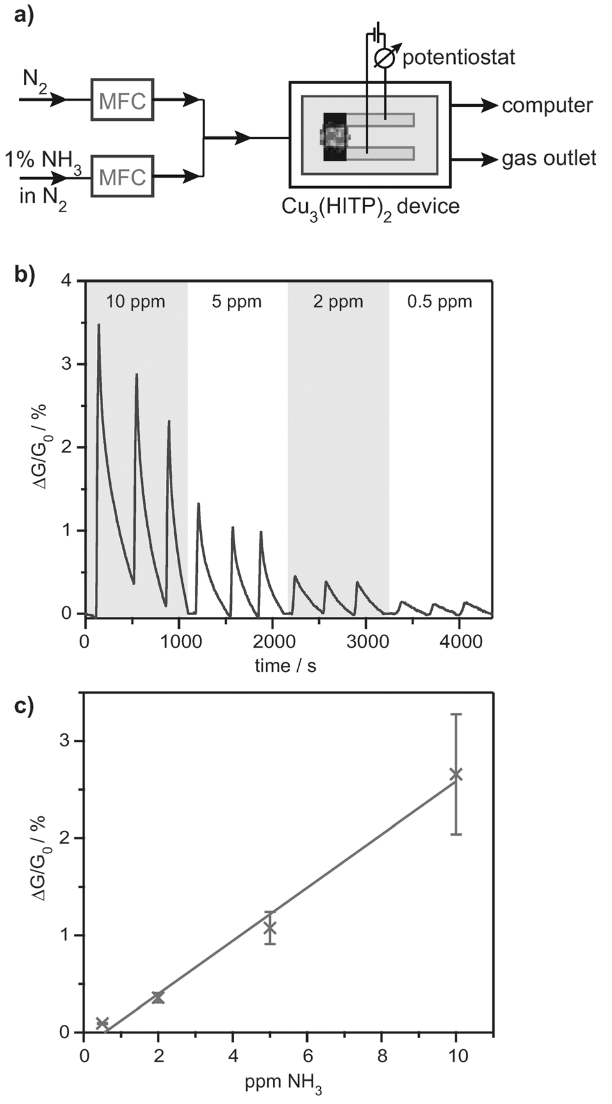

Figure 4. a) Schematic of experimental apparatus; MFC = mass flow controller. b) Relative responses of a Cu$_3$(HITP)$_2$ device to 0.5, 2, 5, and 10 ppm ammonia diluted with nitrogen gas. c) Device response as a function of ammonia concentration (R^2 value for linear fit: 0.99).

The sensitivity observed for our material toward ammonia vapor is competitive with values reported for chemiresistive sensors based on pristine carbon nanotubes (CNTs)[34] and conductive polymers such as PEDOT,[35,36] as well as recently reported chemical sensors based on transistors fabricated from monolayer 2D crystals of MoS$_2$ grown by chemical vapor deposition (CVD).[37] Furthermore, detection of sub-ppm levels of ammonia is sufficient for air quality monitoring according to EPA guidelines,[38] as well as for typical agriculture and livestock applications.[39,40] Within the measured range of ammonia concentrations, the change in relative response was linear, indicating that devices fabricated from Cu$_3$(HITP)$_2$ could be used for quantitative sensing (Figure 4c). The "turn-on" response to ammonia vapor observed for Cu$_3$(HITP)$_2$ devices is also of interest: in many reported chemiresistive sensors, such as those based on CNTs and conductive polymers, ammonia exposure results in decreased conductance due to hole quenching.[36,41,42] Sensors based on metal chalcogenides, on the other hand, typically exhibit a turn-on response similar to Cu$_3$(HITP)$_2$.[37,43] Our data therefore indicate that Cu$_3$(HITP)$_2$ is likely not a hole conductor, and may find complementary uses to existing CNT and polymer sensor materials.

In contrast to the results obtained for Cu$_3$(HITP)$_2$, devices fabricated from Ni$_3$(HITP)$_2$ did not display any observable response to ammonia vapor exposure under identical experimental conditions. These results indicate that rational synthetic variation of conductive MOFs can have a direct impact on functionality such as chemiresistive sensing. Although further work will be needed to elucidate the difference in behavior between the Cu- and Ni-based materials, recent theoretical studies have described how the identity of the metal center is expected to impact the electronic properties of M$_3$(HITP)$_2$ materials (M = transition metal). For example, replacement of Ni with metals of higher d-electron count, such as Cu, is predicted to significantly increase the energy of the Fermi level as compared to Ni$_3$(HITP)$_2$.[44] Such changes in electronic structure are likely related to observed differences in chemiresistive response, and point to a potential strategy for tuning the selectivity of the material toward different types of analytes.

In conclusion, we have reported the synthesis of Cu$_3$(HITP)$_2$, a new 2D MOF with high electrical conductivity.

Our results demonstrate that targeting 2D frameworks based on *o*-phenylenediamine linkages is a general strategy for the synthesis of conductive MOFs. We also establish for the first time that such materials can be used for the fabrication of simple chemiresistive sensor devices, and that the response of isostructural MOFs to an analyte can be tuned by choice of metal node. These results suggest a promising approach toward the targeted synthesis of new sensing materials based on rational synthetic variation of conductive MOFs. The relationship between a framework's chemical structure, electronic structure, and selective chemiresistive response is a topic of ongoing investigation in our team.

Experimental Section

Synthesis of $Cu_3(HITP)_2$: Under air, a solution of $HATP\cdot 6\,HCl$ (10 mg, 1.9×10^{-2} mmol, 1.0 equiv) in distilled water (3 mL) was added all at once to a standing solution of $CuSO_4\cdot 5\,H_2O$ (7.0 mg, 2.8×10^{-2} mmol, 1.5 equiv) in distilled water (2 mL) and concentrated aqueous ammonia (14 M; 100 μL) at 23 °C. Immediate precipitation of dark solids was observed, and the reaction mixture was allowed to stand for 3 h. The mixture was then centrifuged and the supernatant decanted. The solids were vigorously stirred with distilled water (15 mL) at 23 °C for three days, and the water exchanged twice daily. Finally, the solids were stirred with acetone (15 mL) at 23 °C for one day, isolated by centrifugation, and then dried under vacuum ($\leq$ 20 mTorr) at 23 °C, affording $Cu_3(HITP)_2$ as a black solid (7.2 mg, 95 % yield). Anal calcd for $Cu_3(C_{18}H_{12}N_6)_2$: C, 53.03; H, 2.97; N, 20.62. Found: C, 52.95; H, 2.91; N, 20.44.

Keywords: ammonia · conductivity · copper · metal–organic frameworks · sensors

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4349–4352
Angew. Chem. **2015**, *127*, 4423–4426

[1] D. M. D'Alessandro, J. R. R. Kanga, J. S. Caddy, *Aust. J. Chem.* **2011**, *64*, 718–722.
[2] M. D. Allendorf, A. Schwartzberg, V. Stavila, A. A. Talin, *Chem. Eur. J.* **2011**, *17*, 11372–11388.
[3] V. Stavila, A. A. Talin, M. D. Allendorf, *Chem. Soc. Rev.* **2014**, *43*, 5994–6010.
[4] L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105–1125.
[5] Y. Kobayashi, B. Jacobs, M. D. Allendorf, J. R. Long, *Chem. Mater.* **2010**, *22*, 4120–4122.
[6] F. Gándara, F. J. Uribe-Romo, D. K. Britt, H. Furukawa, L. Lei, R. Cheng, X. Duan, M. O'Keeffe, O. M. Yaghi, *Chem. Eur. J.* **2012**, *18*, 10595–10601.
[7] T. C. Narayan, T. Miyakai, S. Seki, M. Dincă, *J. Am. Chem. Soc.* **2012**, *134*, 12932–12935.
[8] L. Sun, T. Miyakai, S. Seki, M. Dincă, *J. Am. Chem. Soc.* **2013**, *135*, 8185–8188.
[9] A. A. Talin, A. Centrone, A. C. Ford, M. E. Foster, V. Stavila, P. Haney, R. A. Kinney, V. Szalai, F. El Gabaly, H. P. Yoon, et al., *Science* **2014**, *343*, 66–69.
[10] R. Gutzler, D. F. Perepichka, *J. Am. Chem. Soc.* **2013**, *135*, 16585–16594.
[11] D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik, M. Dincă, *J. Am. Chem. Soc.* **2014**, *136*, 8859–8862.
[12] T. Kambe, R. Sakamoto, K. Hoshiko, K. Takada, M. Miyachi, J.-H. Ryu, S. Sasaki, J. Kim, K. Nakazato, M. Takata, et al., *J. Am. Chem. Soc.* **2013**, *135*, 2462–2465.
[13] J. Cui, Z. Xu, *Chem. Commun.* **2014**, *50*, 3986–3988.
[14] T. Kambe, R. Sakamoto, T. Kusamoto, T. Pal, N. Fukui, K. Hoshiko, T. Shimojima, Z. Wang, T. Hirahara, K. Ishizaka, et al., *J. Am. Chem. Soc.* **2014**, *136*, 14357–14360.
[15] M. Hmadeh, Z. Lu, Z. Liu, F. Gándara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, et al., *Chem. Mater.* **2012**, *24*, 3511–3513.
[16] E. L. Spitler, W. R. Dichtel, *Nat. Chem.* **2010**, *2*, 672–677.
[17] M. Dogru, A. Sonnauer, A. Gavryushin, P. Knochel, T. Bein, *Chem. Commun.* **2011**, *47*, 1707.
[18] J. Guo, Y. Xu, S. Jin, L. Chen, T. Kaji, Y. Honsho, M. A. Addicoat, J. Kim, A. Saeki, H. Ihee, et al., *Nat. Commun.* **2013**, *4*, 1–8.
[19] J. W. Colson, W. R. Dichtel, *Nat. Chem.* **2013**, *5*, 453–465.
[20] P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 2213–2223.
[21] R. Breslow, B. Jaun, R. Q. Kluttz, C.-Z. Xia, *Tetrahedron* **1982**, *38*, 863–867.
[22] G. Ricciardi, A. Rosa, G. Morelli, F. Lelj, *Polyhedron* **1991**, *10*, 955–961.
[23] N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo, M. Dincă, *J. Am. Chem. Soc.* **2013**, *135*, 13326–13329.
[24] B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693–1696.
[25] B. Chen, L. Wang, F. Zapata, G. Qian, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2008**, *130*, 6718–6719.
[26] M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, *Chem. Soc. Rev.* **2009**, *38*, 1330.
[27] Z. Xie, L. Ma, K. E. deKrafft, A. Jin, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 922–923.
[28] D. Banerjee, Z. Hu, J. Li, *Dalton Trans.* **2014**, *43*, 10668.
[29] M. D. Allendorf, R. J. T. Houk, L. Andruszkiewicz, A. A. Talin, J. Pikarsky, A. Choudhury, K. A. Gall, P. J. Hesketh, *J. Am. Chem. Soc.* **2008**, *130*, 14404–14405.
[30] E. Biemmi, A. Darga, N. Stock, T. Bein, *Microporous Mesoporous Mater.* **2008**, *114*, 380–386.
[31] R. Ameloot, L. Stappers, J. Fransaer, L. Alaerts, B. F. Sels, D. E. De Vos, *Chem. Mater.* **2009**, *21*, 2580–2582.
[32] O. Zybaylo, O. Shekhah, H. Wang, M. Tafipolsky, R. Schmid, D. Johannsmann, C. Wöll, *Phys. Chem. Chem. Phys.* **2010**, *12*, 8092.
[33] S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kiener, R. Moos, *Sensors* **2009**, *9*, 1574–1589.
[34] K. A. Mirica, J. G. Weis, J. M. Schnorr, B. Esser, T. M. Swager, *Angew. Chem. Int. Ed.* **2012**, *51*, 10740–10745; *Angew. Chem.* **2012**, *124*, 10898–10903.
[35] E. Park, O. S. Kwon, S. J. Park, J. S. Lee, S. You, J. Jang, *J. Mater. Chem.* **2012**, *22*, 1521.
[36] C. M. Hangarter, N. Chartuprayoon, S. C. Hernández, Y. Choa, N. V. Myung, *Nano Today* **2013**, *8*, 39–55.
[37] B. Liu, L. Chen, G. Liu, A. N. Abbas, M. Fathi, C. Zhou, *ACS Nano* **2014**, *8*, 5304–5314.
[38] http://www.epa.gov/oppt/aegl/pubs/results88.htm.
[39] S. Yahav, *Anim. Res.* **2004**, *53*, 289–293.
[40] S. W. Gay, K. F. Knowlton, *Va Coop Ext Publ* **2005**, 442–110.
[41] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622–625.
[42] Y. Wang, J. T. W. Yeow, *J. Sens.* **2009**, *2009*, 1–24.
[43] F. Shao, M. W. G. Hoffmann, J. D. Prades, J. R. Morante, N. López, F. Hernández-Ramírez, *J. Phys. Chem. C* **2013**, *117*, 3520–3526.
[44] B. Zhao, J. Zhang, W. Feng, Y. Yao, Z. Yang, *Phys. Rev. B* **2014**, *90*, 201403.

Received: December 9, 2014
Published online: February 9, 2015