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Communication

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Redox Control and High Conductivity of Nickel Bis(dithiolene) Complex π-Nanosheet: A Potential Organic Two-Dimensional Topological Insulator

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Supporting Information

ABSTRACT: A bulk material comprising stacked nanosheets of nickel bis(dithiolene) complexes is investigated. The average oxidation number is −3/4 for each complex unit in the as-prepared sample; oxidation or reduction respectively can change this to 0 or −1. Refined electrical conductivity measurement, involving a single microflake sample being subjected to the van der Pauw method under scanning electron microscopy control, reveals a conductivity of 1.6×10^2 S cm^{-1}, which is remarkably high for a coordination polymeric material. Conductivity is also noted to modulate with the change of oxidation state. Theoretical calculation and photoelectron emission spectroscopy reveal the stacked nanosheets to have a metallic nature. This work provides a foothold for the development of the first organic-based two-dimensional topological insulator, which will require the precise control of the oxidation state in the single-layer nickel bisdithiolene complex nanosheet (cf. Liu, F. et al. *Nano Lett.* **2013**, *13*, 2842).

Increasing attention has been paid to nanosheets (two-dimensional crystalline materials), such as graphene[1−5] and MoS_2.[6−9] These nanosheets are promising for use in innovative electronic[10,11] and optonic[12−14] devices. A nickel bis(dithiolene) complex nanosheet created by the authors is part of a new class of two-dimensional material (Figure 1a).[15,16] It is distinctive for its bottom-up synthesis from molecular and ionic components (benzenehexathiol and nickel(II) ions) that results in a single-layer nanosheet. It also features a hexagonal kagomé lattice comprising phenylene linkers and nickel bis(dithiolene) complex units in a π-conjugated electronic structure. It is thus the first conductive bottom-up nanosheet.

The topological insulator (TI) is a new state of matter.[17−20] Its bulk part is an insulator, but its edges (i.e., surfaces or sides) feature a metallic phase. The metallic edge is spin-polarized and, thereby, conveys a spin current. These features make TIs promising materials for electronics and spintronics. TIs

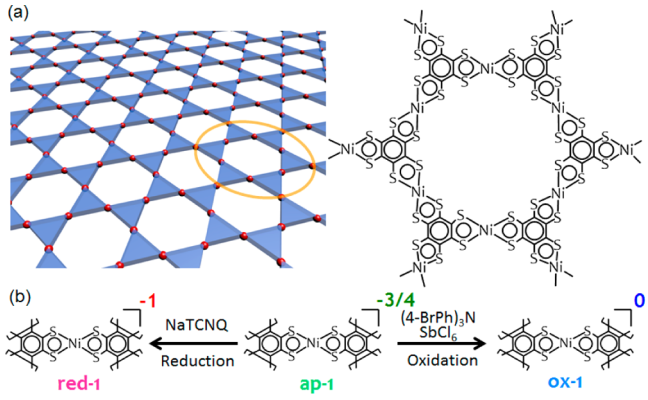

Figure 1. (a) Illustration of the chemical structure of the nickel bis(dithiolene) complex nanosheet. **1** corresponds to the stacked nanosheet. (b) Schematic illustration on redox control in **1**.

reported thus far are all inorganic materials. Bi_2Se_3[21−29] is a representative three-dimensional TI;[21−30] two-dimensional TIs (2D-TIs) are rarer, with the only known examples being a quantum well composed of HgTe/CdTe[31,32] and a Bi bilayer on Bi_2Te_3.[33,34] Besides, organic-based TI systems remain unexplored.

The authors predicted a two-dimensional network of Ph_3M (M = Pb or Bi) as a potential organic 2D-TI,[35] but it is hardly accessible. The authors also suggested a realizable candidate, the single-layer nickel bis(dithiolene) complex nanosheet (Figure 1a).[36] For this nanosheet to function as a 2D-TI, it requires precise control of its doping, so that the Fermi level locates in the gapped Dirac point. Herein, control in the oxidation state of the nickel bis(dithiolene) complex unit is equivalent to a modulation of the doping level: For example, an average oxidation number of −2/3 is suitable for a 2D-TI.[36]

The present report concentrates on two topics: the control of the oxidation state of the nickel bis(dithiolene) complex

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nanosheet (Figure 1b), which is important in making a 2D-TI, and the use of a sophisticated conductivity measurement method. Measurements are made employing the van der Pauw method using a four-probe set-up under the inspection of scanning electron microscopy (SEM), which gives a genuine electrical conductivity excluding a contact resistance. Associated with the conductivity measurement, photoelectron spectroscopy (PES) and first-principles calculations are conducted to investigate the band structure. Handling and size limitations lead to samples of stacked nanosheets (hereafter called **1**) being used in this series of studies.

To control the oxidation state, as-prepared **1** (**ap-1**) was oxidized using tris(4-bromophenyl)aminium hexachloroantimonate and reduced using NaTCNQ to give samples respectively labeled **ox-1** and **red-1**. The oxidation state was then investigated by X-ray photoelectron spectroscopy (XPS), where its S 2s peak sharply reflects the oxidation state of the bis(dithiolene) metal complex (Figure 2).[37] **Ap-1** showed an

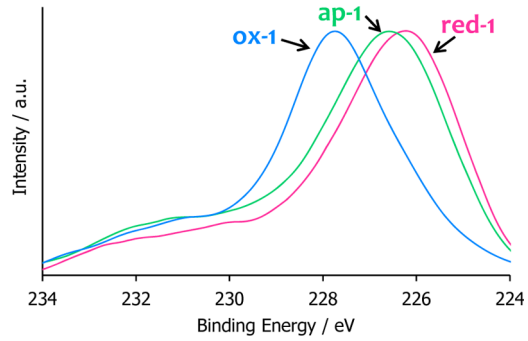

Figure 2. S 2s peak for the XPS of **1** (blue: **ox-1**; green: **ap-1**; red: **red-1**).

average oxidation number of −3/4 for the nickel bis(dithiolene) unit.[15] The S 2s envelope could be deconvoluted into three peaks, corresponding to the shake-up peak often found in the dithiolene-type compound,[38,39] the −1 oxidation state for the nickel bis(dithiolene) unit, and the zero oxidation state, respectively (Figure S1). The S 2s envelope shifted toward higher binding energies upon oxidation, whereas reduction decreased the binding energy. The deconvolution of the S 2s peak suggests that the nickel bis(dithiolene) complex unit was monovalent, being in the 0 and −1 states in **ox-1** and **red-1**, respectively (Figures S2 and S3). These results suggest that an electrochemical doping channel is available in the nickel bis(dithiolene) complex nanosheet.

Our previous work had reported the electrical conductivity of pelletized samples of **1** measured using a primitive two-electrode set-up.[15] Here we employed an upgraded measurement technique. Each single microflake of **ox-1** and **ap-1** was subjected to the van der Pauw method under the control of SEM[40] (Figures 3a,b, S4, and S5). This measurement excluded resistances derived from the contact between the probe and the sample and also the grain boundary of the sample, thereby giving the intrinsic conductivity. **Ox-1** showed an electrical conductivity of 1.6×10^2 S cm^{-1} at 300 K, which is, to the best of our knowledge, the highest value for coordination polymers:[41−45] A two-dimensional Cu(I) 4-hydroxythiophenolate network features an electrical conductivity of 1.2×10^2 S cm^{-1},[41] whereas a recently reported metal−organic framework or porous coordination polymer (MOF or PCP) comprising the nickel bis(diimine) complex motif (with the

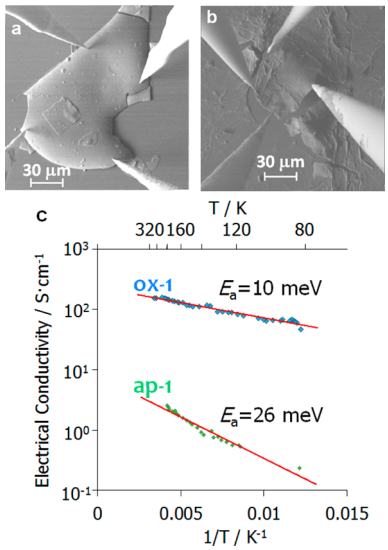

Figure 3. (a,b) SEM images for the van der Pauw measurement of **ox-1** and **ap-1**, respectively. (c) Temperature dependence of the electrical conductivity for **ox-1** and **ap-1**. Sample thickness: 1 μm. The conductivity contains an error of 10%.

same electronic structure as the bis(dithiolene) complex motif) has been reported to possess a conductivity of 4.0×10 S cm^{-1} at room temperature.[45] **Ap-1**, however, showed a conductivity that was smaller by 2 orders of magnitude (2.8 S cm^{-1} at 300 K). Figure 3c shows the temperature dependence of the conductivity, which decreased slightly with falling temperature. The linear relationship between the logarithm of the conductivity with respect to the reciprocal of the temperature in the Arrhenius plot gives the activation energy (E_a) of each sample (**ox-1**: 10 meV; **ap-1**: 26 meV). The E_a of **ox-1** appears quite small for a coordination polymer.

To reveal the origin of the observed high electrical conductivity and small activation energy, **ap-1** was subjected to PES. **Ap-1** on highly oriented pyrolytic graphite (HOPG) exhibited a Fermi edge even at 300 K: The Fermi edge was more prominent at 17 K (Figure 4). This result suggests a metallic nature. The band structure of **1** is also reproduced in first-principles calculation (Figure 5). The structure is based on

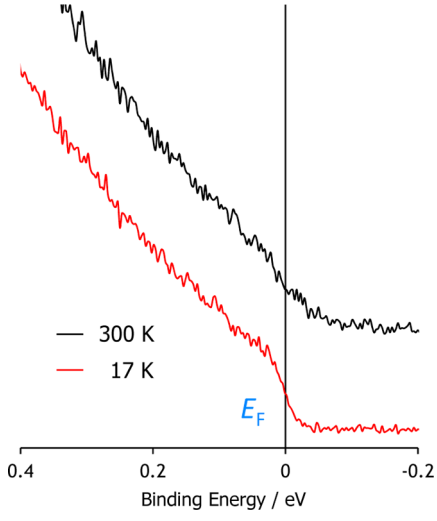

Figure 4. PES of **ap-1** acquired at 300 and 17 K.

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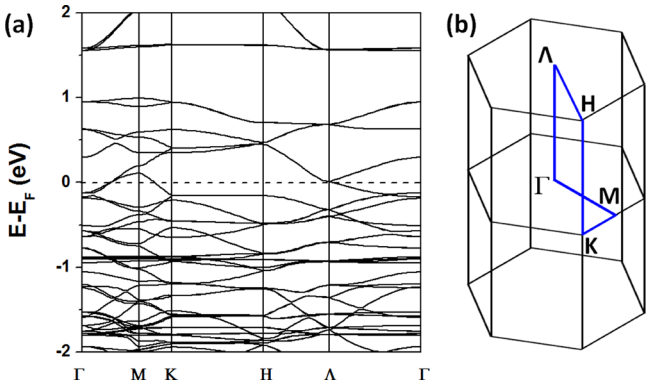

Figure 5. (a) First-principles band structure of **ox-1**. (b) Corresponding first Brillouin zone and high-symmetry k-points.

that suggested by powder X-ray diffraction analysis,[15] and the oxidation number of the nickel bis(dithiolene) unit considered herein is zero (i.e., **ox-1**). The band structure also indicates a metallic nature (Figure 5).

Both PES and the band calculation suggest that **ox-1** and **ap-1** are metallic, although the van der Pauw conductivity measurement revealed semiconductive behavior with small E_a. This discrepancy might stem from a structural disorder in the sample. Particularly, **ap-1** contained Na^+ as a countercation, which could have amplified the structural confusion.

In conclusion, the oxidation state of **1** was controlled via chemical oxidation and reduction, which fixed the valence of the nickel bis(dithiolene) complex unit at 0 and −1, respectively. The electrical conductivity of a single microflake of **1** was evaluated using the van der Pauw method under the control of SEM; it showed a very high conductivity of 1.6×10^2 S cm^{-1} at 300 K. The metallic nature of **1** was confirmed by PES and first-principles calculations. This work establishes a remarkable area of progress in coordination polymer chemistry and will be a sound step toward the realization of an organic 2D-TI.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, deconvolution of the S 2s peaks in XPS, close-ups of typical SEM images for **ox-1** and **ap-1** showing flat and smooth textures, and typical *V*−*I* plots for **ox-1** and **ap-1** in the van der Pauw measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) 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.
(2) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 10451−10453.
(3) Geim, A. K.; Novoselov, K. S. *Nat. Mater.* **2007**, *6*, 183−191.
(4) Geim, A. K. *Science* **2009**, *324*, 1530−1534.
(5) Lin, Y. M.; Dimitrakopoulos, C.; Jenkins, K. A.; Farmer, D. B.; Chiu, H.-Y.; Grill, A.; Avouris, Ph. *Science* **2010**, *327*, 662.
(6) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. *Phys. Rev. Lett.* **2010**, *105*, 136805.
(7) Zande, A. M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y.-M.; Lee, G.-H.; Heinz, T. F.; Reichman, D. R.; Muller, D. A.; Hone, J. C. *Nat. Mater.* **2013**, *12*, 554−561.
(8) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M. *Nano Lett.* **2011**, *11*, 5111−5116.
(9) Butler, S. Z.; Hollen, S. M.; Cao, L.; Cui, Y.; Gupta, J. A.; Gutierrez, H. R.; Heinz, T. F.; Hong, S. S.; Huang, J.; Ismach, A. F.; Johnston-Halperin, E.; Kuno, M.; Plashnitsa, V. V.; Robinson, R. D.; Ruoff, R. S.; Salahuddin, S.; Shan, J.; Shi, L.; Spencer, M. G.; Terrones, M.; Windl, W.; Goldberger, J. E. *ACS Nano* **2013**, *7*, 2898−2926.
(10) Niyogi, S.; Bekyarova, E.; Hong, J.; Khizroev, S.; Berger, C.; Heer, W.; Haddon, R. C. *J. Phys. Chem. Lett.* **2011**, *2*, 2487−2498.
(11) Yazyev, O. V.; Louie, S. G. *Nat. Mater.* **2010**, *9*, 806−809.
(12) Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C. *Nat. Photonics* **2010**, *4*, 611−622.
(13) Bao, Q.; Loh, K. P. *ACS Nano* **2012**, *6*, 3677−3694.
(14) Grigorenko, A. N.; Polini, M.; Novoselov, K. S. *Nat. Photonics* **2012**, *6*, 749−758.
(15) 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.
(16) Hoshiko, K.; Kambe, T.; Sakamoto, R.; Takada, K.; Nishihara, H. *Chem. Lett.* **2014**, *43*, 252−253.
(17) Murakami, S.; Nagaosa, N.; Zhang, S. C. *Phys. Rev. Lett.* **2004**, *93*, 156804.
(18) Hasan, M. Z.; Kane, C. L. *Colloquium: topological insulators. Rev. Mod. Phys.* **2010**, *82*, 3045−3067.
(19) Wang, Z. F.; Liu, Z.; Liu, F. *Phys. Rev. Lett.* **2013**, *110*, 196801.
(20) Kong, D.; Cui, Y. *Nat. Chem.* **2011**, *3*, 845−849.
(21) Moore, J. E.; Balents, L. *Phys. Rev. B* **2007**, *75*, 121306.
(22) Hsieh, D.; Qian, D.; Wray, L.; Xia, Y.; Hor, Y. S.; Cava, R. J.; Hasan, M. Z. *Nature* **2008**, *452*, 970.
(23) Fu, L.; Kane, C. L.; Mele, E. *Phys. Rev. Lett.* **2007**, *98*, 106803.
(24) Xia, Y.; Qian, D.; Hsieh, D.; Wray, L.; Pal, A.; Lin, H.; Bansil, A.; Grauer, D.; Hor, Y. S.; Cava, R. J.; Hasan, M. Z. *Nat. Phys.* **2009**, *5*, 398−402.
(25) Hong, S. S.; Kundhikanjana, W.; Cha, J. J.; Lai, K.; Kong, D.; Meister, S.; Kelly, M. A.; Shen, Z.-X.; Cui, Y. *Nano Lett.* **2010**, *10*, 3118−3122.

(26) Hor, Y. S.; Richardella, A.; Roushan, P.; Xia, Y.; Checkelsky, J. G.; Yazdani, A.; Hasan, M. Z.; Ong, N. P.; Cava, R. J. *Phys. Rev. B* **2009**, *79*, 195208.
(27) Cha, J. J.; Williams, J. R.; Kong, D.; Meister, S.; Peng, H.; Bestwick, A. J.; Gallagher, P.; Goldhaber-Gordon, D.; Cui, Y. *Nano Lett.* **2010**, *10*, 1076−1081.
(28) Kong, D.; Dang, W.; Cha, J. J.; Li, H.; Meister, S.; Peng, H.; Liu, Z.; Cui, Y. *Nano Lett.* **2010**, *10*, 2245−2250.
(29) Zhang, Y.; He, K.; Chang, C.-Z.; Song, C.-L.; Wang, L.-L.; Chen, X.; Jia, J.-F.; Fang, Z.; Dai, X.; Shan, W.-Y.; Shen, S.-Q.; Niu, Q.; Qi, X.-L.; Zhang, S.-C.; Ma, X.-C.; Xue, Q.-K. *Nat. Phys.* **2010**, *6*, 584.
(30) Chen, Y. L.; Analytis, J. G.; Chu, J.-H.; Liu, Z. K.; Mo, S.-K.; Qi, X. L.; Zhang, H. J.; Lu, D. H.; Dai, X.; Fang, Z.; Zhang, S. C.; Fisher, I. R.; Hussain, Z.; Shen, Z.-X *Science* **2009**, *325*, 178−181.
(31) Bernevig, B. A.; Hughes, T. L.; Zhang, S. C. *Science* **2006**, *314*, 1757−1761.
(32) König, M.; Wiedmann, S.; Brüne, C.; Roth, A.; Buhmann, H.; Molenkamp, L. W.; Qi, X.-L.; Zhang, S.-C. *Science* **2007**, *318*, 766−770.
(33) Hirahara, T.; Bihlmayer, G.; Sakamoto, Y.; Yamada, M.; Miyazaki, H.; Kimura, S.-I.; Blügel, S.; Hasegawa, S. *Phys. Rev. Lett.* **2011**, *107*, 166801.
(34) Yang, F.; Miao, L.; Wang, Z. F.; Yao, M.-Y.; Zhu, F.; Song, Y. R.; Wang, M.-X.; Xu, J.-P.; Fedorov, A. V.; Sun, Z.; Zhang, G. B.; Liu, C.; Liu, F.; Qian, D.; Gao, C. L.; Jia, J.-F. *Phys. Rev. Lett.* **2012**, *109*, 016801.
(35) Wang, Z. F.; Liu, Z.; Liu, F. *Nat. Commun.* **2013**, *4*, 1471.
(36) Wang, Z. F.; Su, N.; Liu, F. *Nano Lett.* **2013**, *13*, 2842−2845.
(37) Sellmann, D.; Binder, H.; Häußinger, D.; Heinemann, F. W. *Inorg. Chim. Acta* **2000**, *300*−*302*, 829−836.
(38) Zhou, S.; Ichimura, K.; Inokuchi, H. *J. Mater. Chem.* **1995**, *5*, 1725−1729.
(39) Liu, S.-G.; Liu, Y.-Q.; Zhu, D.-B. *Synth. Met.* **1997**, *89*, 187−191.
(40) Hobara, R.; Nagamura, N.; Hasegawa, S.; Matsuda, I.; Yamamoto, Y.; Miyatake, Y.; Nagamura, T. *Rev. Sci. Instrum.* **2007**, *78*, 053705.
(41) Givaja, G.; Amo-Ochoa, P.; Garcıa, C. J. G.; Zamora, F. *Chem. Soc. Rev.* **2012**, *41*, 115−147.
(42) Low, K. H.; Roy, V. A. L.; Chui, S. S. Y.; Chan, S. L. F.; Che, C. M. *Chem. Commun.* **2010**, *46*, 7328−7330.
(43) Coronado, E.; Mascaros, J. R. G.; Garcia, C. J. G.; Laukhin, V. *Nature* **2000**, *408*, 447.
(44) Sun, D.; Luo, G.-G.; Zhang, N.; Xu, Q.-J.; Jin, Y.-C.; Wei, Z.-H.; Yang, C.-F.; Lin, L.-R.; Huang, R.-B.; Zheng, L.-S. *Inorg. Chem. Commun.* **2010**, *13*, 306−309.
(45) Sheberla, D.; Sun, L.; Blood-Forsythe, M. A.; Er, S.; Wade, C. R.; Brozek, C. K.; Aspuru-Guzik, A.; Dincă, M. *J. Am. Chem. Soc.* **2014**, *136*, 8859−8862.