J. Am. Chem. Soc. **2000,** *122,* 8789−8790 8789

The First Covalent Organic−Inorganic Networks of Hybrid Chalcogenides: Structures That May Lead to a New Type of Quantum Wells

Xiaoying Huang and Jing Li*

Department of Chemistry, Rutgers University
Camden, New Jersey 08102

Huaxiang Fu

Department of Physics, Rutgers University
Camden, New Jersey 08102

Received June 22, 2000

Rigidity and stability, in addition to superior electronic, magnetic, and optical properties, have made inorganic frameworks highly attractive in the search for new, functional materials,[1] while organic and coordination compounds built upon molecular building-blocks hold great promises for processability, flexibility, structural diversity, and geometrical control, such as size, shape, and symmetry.[2] Incorporation of the two counterparts into a single structure may generate organic−inorganic hybrid composites that enhance or combine the useful properties of both components, as found in zeolites and other mesoporous oxides.[3] For example, an intensively pursued area in the miniaturization of electronic devices is the investigation of composite materials that combine the semiconducting functionality of the inorganic constituent with the lower weight and volume of the organic component.[1,4] Many examples have been reported in which organic species enter the inorganic structures through either ionic bonding or relatively weak H-bonding and van der Waals interactions. However, organic−inorganic covalent architectures with explicit bonding directions are much needed, but rare.[5] The novel periodic mesoporous organosilicas (PMOs) recently reported have shed light on the preparation of hybrid materials of this type.[6] The ability to change or modify physical properties, such as optical absorption edges, is of equal significance to the synthesis of new materials. This can be achieved, for example, by controlling the alloy composition[7] and the size of confined systems such as quantum dots (QD)[8] and quantum well (QW).[9] Currently, semiconductor dots are preferred because a very large variation is achievable in these systems.[10] However, it is a great challenge to generate uniform and periodic lattices of dots.[11] Here, we report a new type of covalently bonded hybrid composites that not only possess a uniform and periodic structure, but simultaneously offer a significant variation of optical properties.

The three novel compounds, [α-ZnTe(en)$_{1/2}$] (**I**), [β-ZnTe(en)$_{1/2}$] (**II**), and [ZnTe(pda)$_{1/2}$](**III**), represent the first examples of chalcogenide-based hybrid materials of which uniform structures are formed via direct, covalent bonds between the inorganic host (the II−VI semiconductor ZnTe) and the organic spacers. **I** and **II** were synthesized in ethylenediamine (en) and **III** in 1,3-propanediamine (pda). Both en and pda serve as solvents and as a source of bifunctional ligands.[12] **I**−**III** are stable in air for a long period of time. Upon heating they are converted to ZnTe by separating out the organic component, L.[12] The formation of the title compounds is, therefore, reversible: ZnTe + L (solvent) ↔ ZnTe(L)$_{1/2}$, L = en, pda. The conversion between the two groups of compounds may also be achieved under mild conditions: (**I**, **II**) ↔ **III**.[12] X-ray diffraction analysis reveals that the crystal structure of **I** is a three-dimensional network[13] containing 2D [ZnTe] slabs and en molecules, as illustrated in Figure 1a. The [ZnTe] slabs stack along the *c*-axis and are interconnected by en molecules, each bridged to two Zn metal centers from the adjacent slabs. As shown in Figure 1b, the inorganic slab is a puckered 6^3 (honeycomb) net formed by alternating, three-coordinated Zn and Te. It may also be regarded as a "slice" from the zinc blende[14] or wurtzite[15] structure of ZnTe. To achieve a stable tetrahedral coordination, each Zn atom in the layer forms its fourth bond with a nitrogen from the solvent molecule, en. Note that this compound is unique in that the en molecules enter the M_xQ_y (Q = S, Se, Te) chalcogenide frameworks via a rare bridging coordination to the metal centers. To the best of our knowledge, such a coordination mode has not been previously reported for a chalcogenide-based structure. Structure **II** is a polymorph of **I**. Its crystal structure[16] (Figure 2) is closely related to **I** in that the local coordination of the metal and chalcogen atoms is similar in both networks. The differences lie in the topology of the 6^3 nets (Figures 1b and 2b) and the relative orientation and connectivity

---

[1] Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286*, 945.

[2] Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acct. Chem. Res.* **1998**, *31*, 474. Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. Zaworotko, M. J. Crystal Engineering of Coordination Polymers. In *Electrical and Optical Polymer Systems*; Wise, D. L., Cooper, T. M., Gresser, J. D., Trantolo, D. J., Wnek, G. E., Eds.; Marcel Dekker: New York, 1998; Chapter 25, pp 871−901. O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3.

[3] Smith, J. V. *Chem. Rev.* **1988**, *88*, 149. Kressge, C. T.; Leonowicz, M. E.; Roth, W. J. Vartuni, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. Mann, S.; Ozin, G. *Nature* **1996**, *382*, 313. Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152.

[4] Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. *Nature* **1994**, *370*, 354. Era, M.; Hattori, T.; Taira T.; Tsutsui, T. *Chem. Mater.* **1997**, *9*, 8 and references herein.

[5] Halasyamani, P. S.; Drewitt, M. J.; O'Hare, D. *Chem. Commun.* **1997**, 867. Rujiwatra, A.; Kepert, C. J., Rosseinsky, M. J. *Chem. Commun.* **1999**, 2307. Hagrman, P. J.; Hagrman, D. E.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. Alberti, G.; Brunet, E.; Dionigi, C.; Juanes, O.; de la Mata, M. J.; Rodríguez-Ubis, J. C.; Vivani, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 8, 3351.

[6] Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611. Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867. Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302.

[7] Zunger, A.; Mahajan, S. In *Handbook of Semiconductors*; Elsevier: Amsterdam, 1994; Vol. 3B, 1399.

[8] Lisensky, G. C.; Penn, R. L.; Murphy, C. J.; Ellis, A. B. *Science* **1990**, *248*, 840. Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

[9] Bastard, G.; Mendez, E. E.; Chang, L. L.; Esaki, L. *Phys. Rev. B* **1982**, *26*, 1974.

[10] Alivisatos, A. P. *MRS Bull.* **1998**, *23*, 18.

[11] Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.

[12] All reactions were carried out in 23 mL acid digestion bombs unless otherwise specified. All reaction products were washed with 30 and 95% ethanol and dried in anhydrous ethyl ether. All three compounds were formed phase-pure. Brownish column-like crystals of **I** were collected after 0.272 g of $ZnCl_2$ (2 mmol) and 0.128 g of Te (1 mmol) reacted in en (6 mL) at 200 °C for 3 days (yield: 77.5%). Reactions of $Zn(NO_3)_2 \cdot 6H_2O$ (0.595 g), Te (0.128 g) and en (6 mL) in a mole ratio of 2:1:90 at 190 °C for 3 days afforded the brownish platelike crystals of **II** (yield: 92.4%). Brownish thin platelike crystals of **III** were obtained by reactions of $Zn(NO_3)_2 \cdot 6H_2O$ (0.595 g), Te (0.128 g) and pda (5 mL) in a mole ratio of 2:1:60 at 200 °C for 3 days (yield: 91.3%). A mixture of 0.0175 g **I** and **II** in 0.30 mL of pda sealed in an evacuated Pyrex tube was heated at 190 °C for 8 days and was converted completely to **III**; 0.0580 g of **III** in 5 mL of en solution reacted at 200 °C for 4 days resulted in a mixture of **I** and **II**. Thermogravimetric analyses of **I**−**III** were performed on a computer controlled TA Instrument 2050TGA analyzer. 23.498, 8.917, and 12.814 mg powder samples of **I**, **II**, and **III**, respectively, were loaded into alumina pans and heated with a ramp rate of 10 °C/min from room temperature to 410 °C. The residues were examined by powder X-ray diffraction immediately after the TGA experiment. The title compounds can also be obtained by heating ZnTe directly in en and pda at 200 °C for 3 days.

[13] Crystal data of **I**: $C_2H_8N_2Te_2Zn_2$, $M = 446.04$, orthorhombic, space group *Pbca*, $a = 7.061(1)$ Å, $b = 6.927(1)$ Å, $c = 17.524(4)$ Å, $V = 857.1(3)$ Å^3, $Z = 4$, $F(000) = 792$, $D_c = 3.457$ g·cm^{-3}, μ(Mo Kα) = 12.184 mm^{-1}, 38 variables refined on F^2 with 713 observed reflections collected at 295 K ($\theta_{max} = 26.0$ °) with $I \geq 2\sigma(I)$ yielding R1 = 0.0351, wR2 = 0.0716, GOF = 1.183.

[14] Jumpertz, E. A. *Z. Elektrochem.* **1955**, 419.

[15] Aminoff, G. *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.* **1923**, *58*, 203.

10.1021/ja002224n CCC: $19.00 © 2000 American Chemical Society
Published on Web 08/24/2000

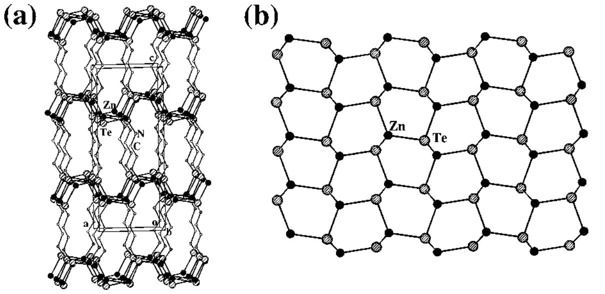

Figure 1. (a) View of structure **I** shown along the *b*-axis with the unit cell outlined. The large solid circles are Zn, shaded circles Te, and small open and singly shaded circles C and N, respectively. (b) The 2D [ZnTe] slab projected along the *c*-axis.

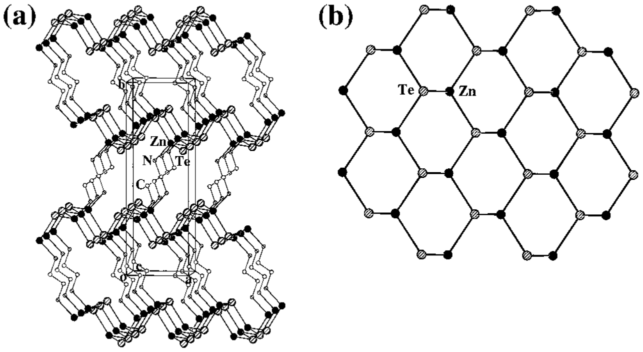

Figure 2. (a) View of **II** along the *c*-axis. The same labeling scheme as in Figure 1 is used here. (b) The [ZnTe] slab projected along the *b*-axis.

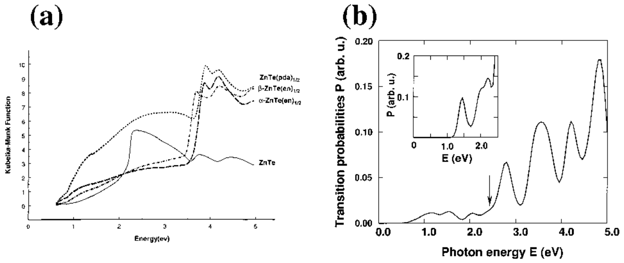

Figure 3. (a) Optical absorption spectra for I, II, III, and bulk ZnTe. (b) The calculated transition probability spectrum for **I**. The arrow indicates the onset energy at which an abrupt increase of absorption occurs. Some minor absorption takes place below this onset energy because of the energy levels of Te dangling bonds and some organic states inside the intrinsic band gap. In the inset, the theoretical transition probability spectrum of bulk ZnTe is shown.

between the inorganic slabs and organic pillars in the two structures. For **III**, its ZnTe slab is topologically similar to that of **I,** while the relative orientation of the slabs and the connectivity between the slabs and the pda molecules are different.[17] The synthesis of **III** demonstrates that organic spacers of different length can be incorporated into the same inorganic bulk.

The optical absorption spectra of the three compounds, measured by diffuse reflectance experiments,[18] are depicted in Figure 3a. The new absorption edges of 3.5, 3.3, and 3.4 eV were found for **I**, **II**, and **III**, respectively, compared to the value of 2.1 eV measured by the same method for bulk ZnTe (Figure 3a),[19] indicating a very large blue shift (1.2−1.4 eV) of the absorption edge. In addition, some new distinguishable peaks appear above 4.0 eV in the spectra of all three phases. To confirm this large blue shift, we have calculated the band structure and transition probability spectra using density functional theory within local density approximation (LDA).[20] Our calculated band gap of bulk ZnTe is 1.2 eV, which is smaller than the experimental value of 2.1 eV due to the well-known "band gap problem" of the LDA.[21] This systematic error of 0.9 eV is demonstrated[22] to be transferable when we change from bulk ZnTe to hybrid compounds. The calculated transition probability[23] for **I** is shown in Figure 3b. We see that the onset of effective transition edge indeed shifts from 1.2 eV for bulk ZnTe (see the inset of Figure 3b) to 2.5 eV for **I**. Both the observed blue shift of absorption edge and the new distinguishable absorption peaks can be explained by quantum confinement effect (QCE). The change of kinetic energy due to the QCE will increase the band gap and the energy separation of allowed transitions near the absorption edge.[24] The latter makes the near-edge absorption more resolvable. Note that such a large blue shift of 1.3 eV of optical absorption edge can be achieved only for very small, chemically grown, colloidal dots (for example, CdSe or InP dots[11,25]) in which a uniform structure would be virtually impossible. By contrast, all of our hybrid compounds here have uniform and periodic structures.

The formation of **I**−**III** has demonstrated that (a) the appropriate solvothermal conditions and strong donor solvents are powerful enough to break the 3D ZnTe lattice into slabs, (b) the direct, covalent bonding of organic ligands to ZnTe bulk has allowed the structural information of the organic species imprinted onto the inorganic framework, (c) such a covalent organic−inorganic network exhibits a drastic change in the optical properties, and (d) the uniform, periodic hybrid composites are generated in a controllable manner. It may be possible to vary the thickness of the inorganic layers and thus modify the optical properties as desired.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-9553066) is gratefully acknowledged.

Supporting Information Available: Tables of atomic coordinates of all atoms, isotropic and anisotropic thermal parameters, bond distances and angles, crystallographic data and ortep drawings for **I**−**III** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA002224N

---

(16) Crystal data of **II**: $C_2H_8N_2Te_2Zn_2$, $M = 446.04$, orthorhombic, space group *Pnnm*, $a = 5.660(1)$ Å, $b = 17.156(3)$ Å, $c = 4.336(1)$ Å, $V = 421.0(1)$ Å^3, $Z = 2$, $F(000) = 396$, $D_c = 3.518$ g·cm^{-3}, μ(Mo Kα) = 12.401 mm^{-1}, 25 variables refined on F^2 with 339 observed reflections collected at 295 K ($\theta_{max} = 26.0$ °) with $I \geq 2\sigma(I)$ yielding R1 = 0.0495, wR2 = 0.0816, GOF = 1.345.

(17) Crystal data of **III**: $C_3H_{10}N_2Te_2Zn_2$, $M = 460.07$, orthorhombic, space group *Cmc*2$_1$, $a = 20.169(4)$ Å, $b = 7.038(1)$ Å, $c = 6.882(1)$ Å, $V = 976.9(3)$ Å^3, $Z = 4$, $F(000) = 824$, $D_c = 3.128$ g·cm^{-3}, μ(Mo Kα) = 10.695 mm^{-1}, 31 variables refined on F^2 with 518 observed reflections collected at 295 K ($\theta_{max} = 26.0$ °) with I ≥ $2\sigma(I)$ yielding R1 = 0.0594, wR2 = 0.0750, GOF = 0.997.

(18) (a) Optical diffuse reflectance measurements of **I**, **II**, and **III** were performed on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. A similar procedure as previously described[18b] was used to collect and convert the data using the Kubelka−Munk function.[18c] (b) Li, J.; Chen, Z.; Wang, X.-X.; Proserpio, D. M. *J. Alloys Compd.* **1997**, 262−263, 28−33. (c) Wendlandt, W. WM.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience: A Division of John Wiley & Sons: New York, 1966.

(19) This is in good agreement with the previously reported band gap values, 2.1−2.3 eV. Pankove, J. I. *Optical Processes in Semiconductors*; Prentice-Hall: 1971. West, A. R. *Basic Solid State Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1999.

(20) Kohn, W.; Sham, L. J., *Phys. Rev.* **1965**, 140, A1133. Perdew, J.; Zunger, A., *Phys. Rev. B* **1981**, 23, 5048.

(21) Sham, L. J.; Schluter, M. *Phys. Rev. Lett.* **1983**, *51*, 1888. Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L., Jr. *Phys. Rev. Lett.* **1982**, *49*, 1691.

(22) Delerue, C.; Lannoo, M.; Allan, G. *Phys. Rev. Lett.* **2000**, *84*, 2457.

(23) Our calculated imaginary part of dielectric function for bulk ZnTe agrees well with the experimental results.

(24) Fu, H.; Zunger, A. *Phys. Rev. B* **1998**, *57*, R15064. Axtell, E. A.; Liao, J.-H.; Pikramenou, Z.; Kanatzidis, M. G. *Chem. Eur. J.* **1996**, *2*, 656.

(25) Nozik, A. J.; Micic, O. I. *MRS Bull.* **1998**, *23*, 24.