DOI: 10.1002/anie.200800603

Open-Framework Materials

# Wavelength-Dependent Photochromic Inorganic–Organic Hybrid Based on a 3D Iodoplumbate Open-Framework Material**

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Organically templated inorganic open-framework materials have been fueled by intriguing architectures and topologies as well as fascinating physical properties.[1,2] These materials can be structurally classified into two subclasses:[1,3] the zeotype materials, in which all polyhedra of the wall are exclusively tetrahedral, and the frameworks built from mixed polyhedra. However, 3D open-framework materials constructed from purely octahedral units have not been obtained so far for these materials, although these have been observed in a few metal–organic frameworks[4] and purely inorganic materials.[5,6]

Photochromic materials have received considerable attention for their potential applications in information display devices, high-density memory, and other high-tech areas. While purely organic[7] or inorganic[8] photochromic materials have been known for a long time, much attention has recently been dedicated to the development of photochromic inorganic–organic hybrids because of the novel and intriguing properties arising from the interactions between both organic and inorganic components. Structurally well-defined hybrids will give us better insight into these interactions. However, few hybrids based on transition-metal oxides and polyoxometalates have been explored with simultaneous characterization of their structure and photochromism.[9] Less attention has been paid to the photochromic hybrids based on metal halide semiconductors,[10] although the charge transfer between organic and inorganic components has been observed in these systems.[11]

We obtained a yellow prismatic hybrid crystal $(\mathrm{EDAMP})_{2n}(\mathrm{Pb_7I_{18}})_n\cdot 4n\,\mathrm{H_2O}$ (**1**; $\mathrm{EDAMP} = \mathrm{Et_2NHC_6H_4\text{-}CH_2C_6H_4NHEt_2}$) through a synchronous process of in situ N-alkylation and assembly under solvothermal conditions. This material represents a new subclass of 3D inorganic open-framework materials built from purely octahedral units and behaves as a quantum-wire array. More interestingly, the compound shows interesting wavelength-dependent photochromism. The structure of the same single crystal was characterized before (**1**, yellow) and after visible irradiation ($\lambda = 550$ nm; **2**, olive green), as well as after further UV irradiation ($\lambda = 300$ nm, **3**, dark green).

In traditional organic syntheses, N-alkylated products are obtained from the reaction of organic amines and alkyl iodides under alkaline conditions, whereas alkyl iodides are obtained from alcohols activated by HI under acidic conditions. We demonstrate herein a new one-step approach to form N-alkylated products (i.e. the alkylated DAMP compound in **1**) through in situ N-alkylation of organic amines and alcohols under acidic conditions by using a solvothermal technique. The existence of alkylated DAMP compound in **1** has been proved by $^1$H NMR and ESI-MS spectra (see the Supporting Information). This synchronous process can be expanded and a series of metal iodide hybrid frameworks can be realized by control of the alcohols (C1–C4), amines (aliphatic and aromatic), and metal salts (Pb, Bi, Sn). As for the metal–organic frameworks,[12] the solvo(hydro)thermal technique accompanying the in situ syntheses of organic species can provide a more convenient and effective route for the novel inorganic–organic hybrids than with traditional methods.

Single-crystal X-ray analyses reveal that compounds **1**, **2**, and **3** have the same crystal structures and only subtle differences in their organic species. Compound **1** exhibits a 3D inorganic open-framework structure, in which an incomplete cubane chain (ICC) acts as the building block of the inorganic framework. There are four crystallographically independent Pb atoms, which are all situated in a slightly distorted octahedral coordination environment. The incomplete cubane units, composed of edge-sharing $\mathrm{PbI_6}$ octahedra centered at Pb1, Pb2, and Pb3, interlink each other through a crystallographic inversion center to form ICCs extending along the [110] or $[1\bar{1}0]$ direction, in which neighboring incomplete cubanes are further consolidated by I2 and I3 atoms as shown in Figure 1a. This ICC is structurally similar to the inorganic chain in the 1D compound $(\mathrm{C_{10}H_7CH_2NH_3})_n(\mathrm{PbI_3})_n$ (**4**).[13] The Pb4 atom, located at the 4e position, is coordinated by two sets of I7, I8, and I9 atoms from the two crossed ICCs to complete an octahedral coordination environment (Figure 1b). The ICCs along the [110] and $[1\bar{1}0]$ directions stack respectively along the $[1\bar{1}0]$ and [110] directions to form intercrossing walls of the framework with an intercrossing angle of 72.1°. The walls are linked by Pb4 atoms to form a 3D open-framework structure as shown in Figure 1c and d, giving a non-interpenetrated $\mathrm{CdSO_4}$-type topology (Figure 1e). It is notable that the non-interpene-

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[**] We gratefully acknowledge financial support by the NSF of China (20571075, 20521101), the NSF for Distinguished Young Scientists of China (20425104), and the NSF of the Fujian Province (2006J0013).

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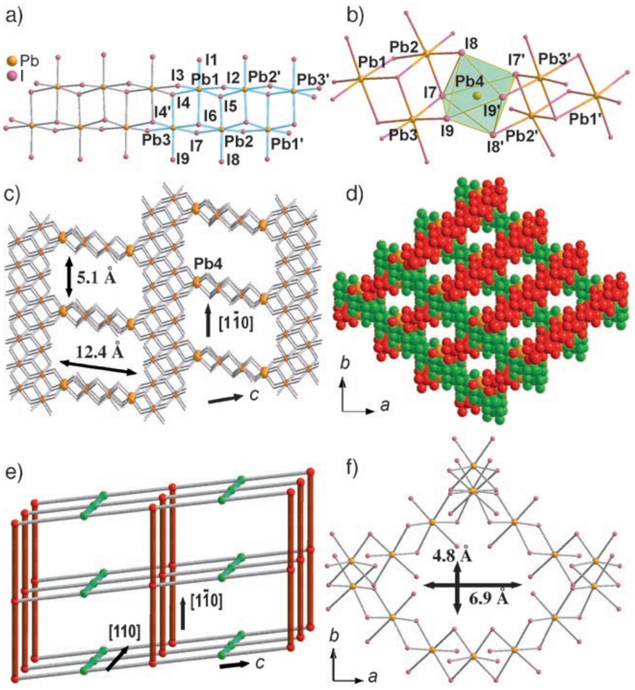


***Figure 1.*** a) The incomplete cubane chain. b) Coordination environment of Pb4 atom. c) ICCs linked by Pb4 atoms to form an open-framework structure with 1D 14-ring channels along the [110] and [1$\bar{1}$0] directions. Pb: yellow; I: pink. d) The packing of **1** along the *c* axis with the cations and lattice water molecules omitted for clarity. Red and green: ICCs extending along the [110] and [1$\bar{1}$0] directions, respectively; orange: Pb4 atoms. e) Perspective view of the $CdSO_4$-type topology in **1** with the crystallographic inversion center of neighboring incomplete cubanes as nodes of the topological framework. The green and red lines represent the chains, whereas the gray lines represent the bridging Pb4 atoms. f) The 16-ring channels along the *c* axis.

trated $CdSO_4$ network in **1** is quite rarely observed because of its intrinsically low packing density.[14]

The inorganic framework has 1D 14-ring channels running along the [110] and [1$\bar{1}$0] directions. These channels are approximately rectangular in shape and have dimensions of approximately $5.1 \times 12.4$ Å$^2$ without considering internal van der Waals radii (Figure 1c). Furthermore, the crossed ICCs stack along the *c* axis to give 1D 16-ring channels (Figure 1d), which are elliptical and have an opening of $4.8 \times 6.9$ Å$^2$ (Figure 1f). The perpendicular channels along the [110], [1$\bar{1}$0], and [001] directions merge to form a 3D tunnel network, which accommodates the EDAMP ions and lattice water molecules. The guest molecules occupy 45.0% of the crystal volume in **1** as calculated by the program PLATON.[15]

It is difficult to synthesize metal–halide open-framework materials.[16] Heretofore, the known examples are only three zeotype materials based on mixed transition-metal halides[17] and one based on mixed-valent tin iodide.[18] Compound **1** is the first example of a 3D iodoplumbate open-framework material. More importantly, the 3D open-framework structure of **1**, in which all the polyhedra of the wall are exclusively octahedral, can be classified as a new structural subclass of the organically templated inorganic open-framework materials.

Figure 2 shows the UV/Vis absorption spectrum of **1**. The peak at 402 nm (3.1 eV) for the 3D compound **1** is very close to that at 401 nm (3.1 eV) for the 1D compound **4**,[13] which seems to be inconsistent with the rule that the energy gap decreases as the dimensionality increases.[19] Ab initio calculations performed to understand the observed spectrum for the 3D inorganic skeleton in **1** and the ICC in **4** gave the same energy gap of 2.6 eV. In terms of the partial density of states (DOS) analyses (Figure 3), the absorption peaks for the inorganic parts in **1** and **4** are both assigned as charge transitions from I 5p occupied orbitals to Pb 6p–I 5p unoccupied antibonding orbitals. Moreover, the DOS analyses show that the contribution of Pb4 atoms in **1** to the conducting band is significantly smaller than that of the other Pb atoms, which indicates that the band gap of **1** is mainly determined by the contribution of ICCs. The results from experiment and calculation both show that the energy gap of the 3D inorganic skeleton in **1** is consistent with that of the ICC in **4**, indicating that charge transfer in **1** mainly occurs within rather than between the ICCs, although the ICCs are linked by Pb4 atoms. To our knowledge, few compounds with high-dimensional infinite structure exhibit solely the properties of their 1D building blocks, other than some single-chain magnets.[20] The ICCs in **1** and **4**, which are conceptually derived from a specific cut of the 2D bulk $PbI_2$ network along a certain direction (see the Supporting Information),[21] can be regarded as a quantum wire.[22] The inorganic open-frame-

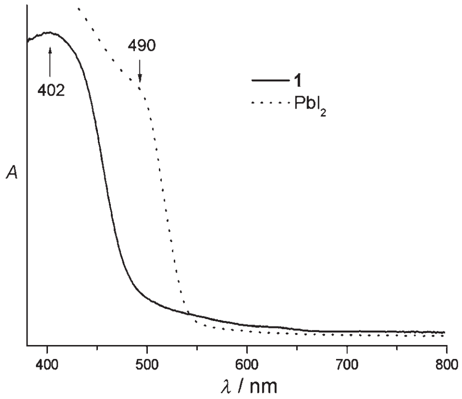


***Figure 2.*** UV/Vis spectra of bulk $PbI_2$ and **1** at room temperature.

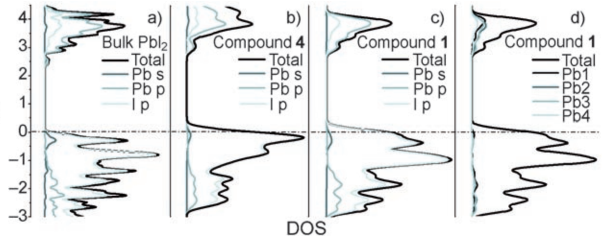


***Figure 3.*** Total and partial densities of states plots of $PbI_2$ (a), the ICC in **4** (b), and the inorganic skeleton in **1** (c and d) with the Fermi level set as zero.

work structure in **1** can thus be considered as an ordered and periodic quantum-wire array, which may present important opportunities for the generation of electronic and optoelectronic devices ranging from ultrafast optical switching to ultradense memories.[23]

The title compound also shows an interesting wavelength-dependent photochromic response. In fact, the yellow compound **1** is rather sensitive to light and turns slightly green upon irradiation by sunlight for several hours. As shown in the left inset of Figure 4, when yellow **1** is stimulated by Vis irradiation (550 nm), olive green **2** was obtained with two new absorption bands appearing at 583 and 629 nm. After radiation for 240 min, the two bands reach a maximum and no further color change visible to the naked eye and no new absorption band are observed. Interestingly, when compounds **1** or **2** are irradiated at 300 nm, dark-green **3** is obtained and another new absorption band at 498 nm shows up in addition to the bands at 583 and 629 nm. Their intensities increase with the duration of UV irradiation and reach a maximum after 360 min (Figure 4). The absorption thresholds of the three bands are progressively red-shifted with increasing irradiation time. Wavelength-dependent absorption spectra also indicate that the band at 498 nm can be triggered only by the light below 500 nm (right inset in Figure 4). Reversion of the color for **2** and **3** can be accomplished by heating at 100 °C. In addition, the photochromic transformation can be observed in air as well as in a high-vacuum environment, implying the coloration–decoloration is not the result of a surface oxidation reaction.[24]

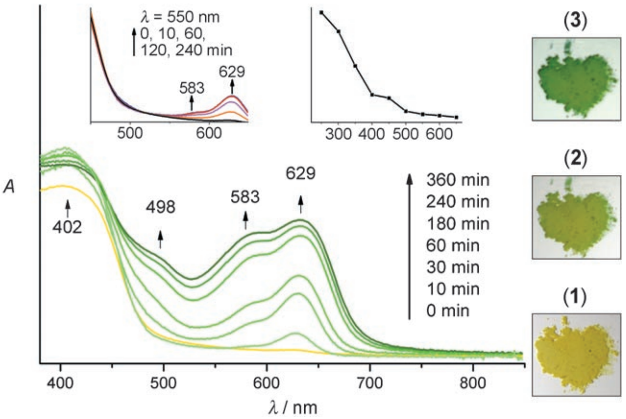
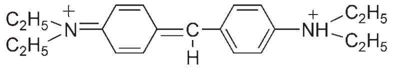


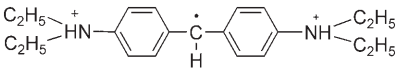
*Figure 4.* Spectral and color changes of the title compound upon repeated irradiation at 300 nm at 25 °C. Left inset: Spectral changes of the compound upon repeated irradiation at 550 nm at 25 °C. Right inset: Plot of absorbance at 498 nm after irradiation at various wavelengths for 10 min. The powder samples of **1**, **2**, and **3** are shown on the right.

Electron paramagnetic resonance (EPR) measurements show that 1) before irradiation (**1**), no EPR signal is detected; 2) after irradiation at 550 nm (**2**), also no EPR signal is observed; 3) after irradiation at 300 nm (**3**), a symmetric EPR signal is observed with *g* value of 2.0014 and enhances with the irradiation duration; 4) after color conversion by heating, there is still no signal for **2** and the EPR signal for **3** disappears (see the Supporting Information), suggesting that the photoresponsive behavior should result from the production of one type of free radicals induced by irradiation.

As an analogue of EDAMP$^{2+}$, Am (Am = $Me_2NC_6H_4CH_2C_6H_4NMe_2$) is known to produce an amine radical cation or central carbon radical, depending on temperature, after γ-irradiation.[25] Accordingly, a preliminary mechanism is proposed for the intricate photochromism of the title compound. First, for inorganic–organic hybrids, a radical would be produced when electrons transfer from the valence band of the inorganic component to the LUMO of the organic component.[7,26] This transfer can also be realized even under the irradiation by lower energy light (Vis and UV; see the Supporting Information). A very small absorption band at around 630 nm is also observed for **1**, corresponding to the inorganic–organic interaction. After the irradiation at 550 nm, the EDAMP$^{2+}$ ion in **1** firstly may transform into the amine radical cation, which is unstable at the room temperature and promptly transforms into a diamagnetic carbonium ion (Scheme 1) to form olive green **2**,[25] agreeing with the absence of EPR signal for **2**. In contrast to **1**, the bond lengths C31–C21 (1.460 Å) and C34–N21 (1.456 Å) in **2** are significantly shortened, and the ring (C31–C36) is seriously distorted (the mean plane deviation of the ring increases from ±0.0038 to ±0.0134 Å; see the Supporting Information). Upon irradiation at 300 nm, the EDAMP$^{2+}$ in **1** transforms into a central carbon radical cation (Scheme 2) to form dark-green **3**, which is stable at the room temperature, as confirmed by the EPR spectra. The C14-C21-C31 bond angle in **3** is 115.3°, which is significantly larger than those in **1** (113.3°) and **2** (113.5°) and is consistent with the suggestion that the formation of a radical on the C21 atom leads to a slight transition of sp$^3$-bonded phase into sp$^2$-bonded. The detailed mechanism is being investigated by theoretical calculations.



*Scheme 1.* Carbonium ion in **2**.



*Scheme 2.* Carbon-centered radical cation in **3**.

In summary, an unprecedented 3D iodoplumbate hybrid open-framework material built from exclusively octahedral units was obtained by in situ N-alkylation under solvothermal conditions. This material represents a new structural subclass of the organically templated inorganic open-framework compounds. The 3D compound **1** exhibits the properties for its 1D ICC building blocks to behave as an ordered and periodic quantum-wire array. More interestingly, the compound also exhibits a wavelength-dependent photochromic response because of the formation of a radical under irradiation.

## Experimental Section

**1**: All chemicals were used as purchased without further purification. A mixture of PbI$_2$ (0.5 mmol, 231 mg) and DAMP (0.5 mmol, 99 mg) was heated with HI ($\geq$45 %, 4 mL) and CH$_3$CH$_2$OH (3 mL) in a 25 mL teflon-lined stainless-steel autoclave at 160 °C for 2 days. Upon cooling to room temperature at 3 K h$^{-1}$, yellow prismatic crystals of **1** were obtained in 65 % yield (based on PbI$_2$).

Crystals of olive green compound **2** were obtained by irradiating crystals of yellow compound **1** with visible light (550 nm) from a Xe arc lamp with a UV cutoff filter. Crystals of dark green compound **3** were obtained by irradiating crystals of either **1** or **2** with UV light (300 nm) from a Xe arc lamp with a UV cutoff filter. The olive-green crystals of **2** and dark-green crystals of **3** are both stable and can persist longer than one month in air in the dark. The crystals of **2** and **3** turn completely into yellow crystals of **1** upon heating at 100 °C in air. CCDC-640447 (**1**), CCDC-675754 (**2**), and CCDC-675755 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: February 6, 2008

**Keywords:** iodoplumbates · open-framework materials · organic–inorganic hybrid composites · photochromism

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[1] a) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268; b) G. Férey, C. Mellon-Draznieks, C. Serre, F. Millange, *Acc. Chem. Res.* **2005**, *38*, 217.

[2] a) *Atlas of Zeolite Framework Types* (Eds: C. Baerlocher, W. M. Meier, D. H. Olson), Elsevier, London, **2001**; b) P. Feng, X. Bu, N. Zheng, *Acc. Chem. Res.* **2005**, *38*, 293; c) A. Corma, M. J. Diaz-Cabbanas, J. L. Jorda, C. Martinez, M. Moliner, *Nature* **2006**, *443*, 842; d) R. F. Lobo, *Nature* **2006**, *443*, 757.

[3] G. Férey, *Chem. Mater.* **2001**, *13*, 3084.

[4] A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* **2006**, 4780.

[5] R. Ghosh, X. Shen, J. C. Villegas, Y. Ding, K. Malinger, S. L. Suib, *J. Phys. Chem. B* **2006**, *110*, 7592.

[6] R. E. Sykora, T. E. Albrecht-Schmitt, *Inorg. Chem.* **2003**, *42*, 2179.

[7] a) S. Takami, L. Kuroki, M. Irie, *J. Am. Chem. Soc.* **2007**, *129*, 7319; b) A. Natarajan, C. K. Tsai, S. I. Khan, P. McCarren, K. N. Houk, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2007**, *129*, 9846; c) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778.

[8] a) B. W. Faughnan, D. L. Staebler, Z. J. Kiss, in *Applied Solid State Science*, *Vol. 2* (Eds: R. Wolfe, C. J. Kriessman), Academic Press, New York, **1971**, pp. 107; b) K. Bange, *Solar Energy Mater. Solar Cells* **1999**, *58*, 1; c) M. Irìe, *Chem. Rev.* **2000**, *100*, 1685; d) T. He, J. N. Yao, *Photochem. Photobiol. C* **2003**, *4*, 125; e) G. H. Brown, *Photochromism*, Wiley-Interscience, New York, **1971**; f) H. Du, H. Bouas-Laurent, *Photochromism. Molecules and Systems*, Elsevier, Amsterdam, **1990**.

[9] a) T. He, J. N. Yao, *Prog. Mater. Sci.* **2006**, *51*, 810; b) T. Yamase, *Chem. Rev.* **1998**, *98*, 307; c) M. T. Pope, *Heteropoly and Isopoly Oxometaltes*, Springer, New York, **1983**.

[10] G. Xu, G.-C. Guo, M.-S. Wang, Z.-J. Zhang, W.-T. Chen, J.-S. Huang, *Angew. Chem.* **2007**, *119*, 3313; *Angew. Chem. Int. Ed.* **2007**, *46*, 3249.

[11] J. Fujisawa, N. Tajima, *Phys. Rev. B* **2005**, *72*, 125201.

[12] J.-P. Zhang, S.-L. Zheng, X.-C. Huang, X.-M. Chen, *Angew. Chem.* **2004**, *116*, 208; *Angew. Chem. Int. Ed.* **2004**, *43*, 206.

[13] G. C. Papavassiliou, G. A. Mousdis, C. P. Raptopoulou, A. Terzis, *Z. Naturforsch. B* **1999**, *54*, 1405.

[14] a) V. Niel, A. L. Thompson, C. Munoz, A. Galet, A. E. Goeta, J. A. Real, *Angew. Chem.* **2003**, *115*, 3890; *Angew. Chem. Int. Ed.* **2003**, *42*, 3760; b) X.-Y. Wang, H.-Y. Wei, Z.-M. Wang, Z.-D. Chen, S. Gao, *Inorg. Chem.* **2005**, *44*, 572.

[15] L. A. Spek, *PLATON*, *Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, **1999**.

[16] a) D. B. Mitzi, *Prog. Inorg. Chem.* **1999**, *48*, 1; b) H. Li, Z. Chen, L. Guo, K. Ding, J. Li, C. Huang, Z. Cai, *Aust. J. Chem.* **2007**, *60*, 595; c) N. Louvain, W. Bi, N. Mercier, J. Buzré, C. Legein, G. Corbel, *Dalton Trans.* **2007**, 965.

[17] a) J. D. Martin, K. B. Greenwood, *Angew. Chem.* **1997**, *109*, 2162; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2072; b) J. D. Martin, A. M. Dattelbaunm, T. A. Thornton, R. M. Sullivan, J. Yang, M. T. Peachey, *Chem. Mater.* **1998**, *10*, 2669.

[18] J. Guan, Z. Tang, A. M. Guloy, *Chem. Commun.* **2005**, 48.

[19] a) E. A. Axtell, J.-H. Liao, Z. Pikramenou, M. G. Kanatzidis, *Chem. Eur. J.* **1996**, *2*, 656; b) G. C. Papavassiliou, *Prog. Solid State Chem.* **1997**, *25*, 125.

[20] Y.-Z. Zheng, M.-L. Tong, W.-X. Zhang; X.-M. Chen, *Angew. Chem.* **2006**, *118*, 6458; X.-M. Chen, *Angew. Chem.* **2006**, *118*, 6458; *Angew. Chem. Int. Ed.* **2006**, *45*, 6310.

[21] The bulk PbI$_2$ exhibits experimental and calculated energy gaps of 2.5 eV (490 nm) and 2.3 eV (539 nm), respectively (Figure 2). A blue shift is observed in the energy gap of the ICC in **4** relative to the energy gap of bulk PbI$_2$ as a result of the quantum confinement effect (QCE). The structure of PbI$_2$ is adopted from: V. K. Agrawal, G. K. Chadha, G. C. Trigunayat, *Acta Crystallogr. Sect. A* **1970**, *26*, 140.

[22] a) T. Umebayashi, K. Asai, T. Kondo, A. Nakao, *Phys. Rev. B* **2003**, *67*, 155405; b) X. Y. Huang, J. Li, Y. Zhang, A. Mascarenhas, *J. Am. Chem. Soc.* **2003**, *125*, 7049; c) M. Shimizu, J.-I. Fujisawa, J. Ishi-Hayase, *Phys. Rev. B* **2005**, *71*, 205306; d) A. Damin, F. X. L. Xamena, C. Lamberti, B. Civalleri, C. M. Zicovich-Wilson, A. Zecchina, *J. Phys. Chem. B* **2004**, *108*, 1328.

[23] T. L. Reinecke, P. A. Knipp in *Festkörperprobleme/Advances in Solid State Physics*, *Vol. 36* (Eds: R. Helbing), Vieweg, Wiesbaden, **1997**, pp. 105.

[24] Y. Suenaga, H. Konaka, T. Sugimoto, T. Kuroda-Sowa, M. Maekawa, M. Munakata, *Inorg. Chem. Commun.* **2003**, *6*, 389.

[25] a) O. V. Kolninov, V. V. Kolesnikova, *High Energy Chem.* **2001**, *35*, 328; b) O. V. Kolninov, V. V. Kolesnikova, V. K. Milinchuk, *Nucl. Instrum. Methods Phys. Res. Sect. B* **1999**, *151*, 330.

[26] A. Bose, P. He, C. Liu, B. D. Ellman, R. J. Twieg, S. D. Huang, *J. Am. Chem. Soc.* **2002**, *124*, 4.