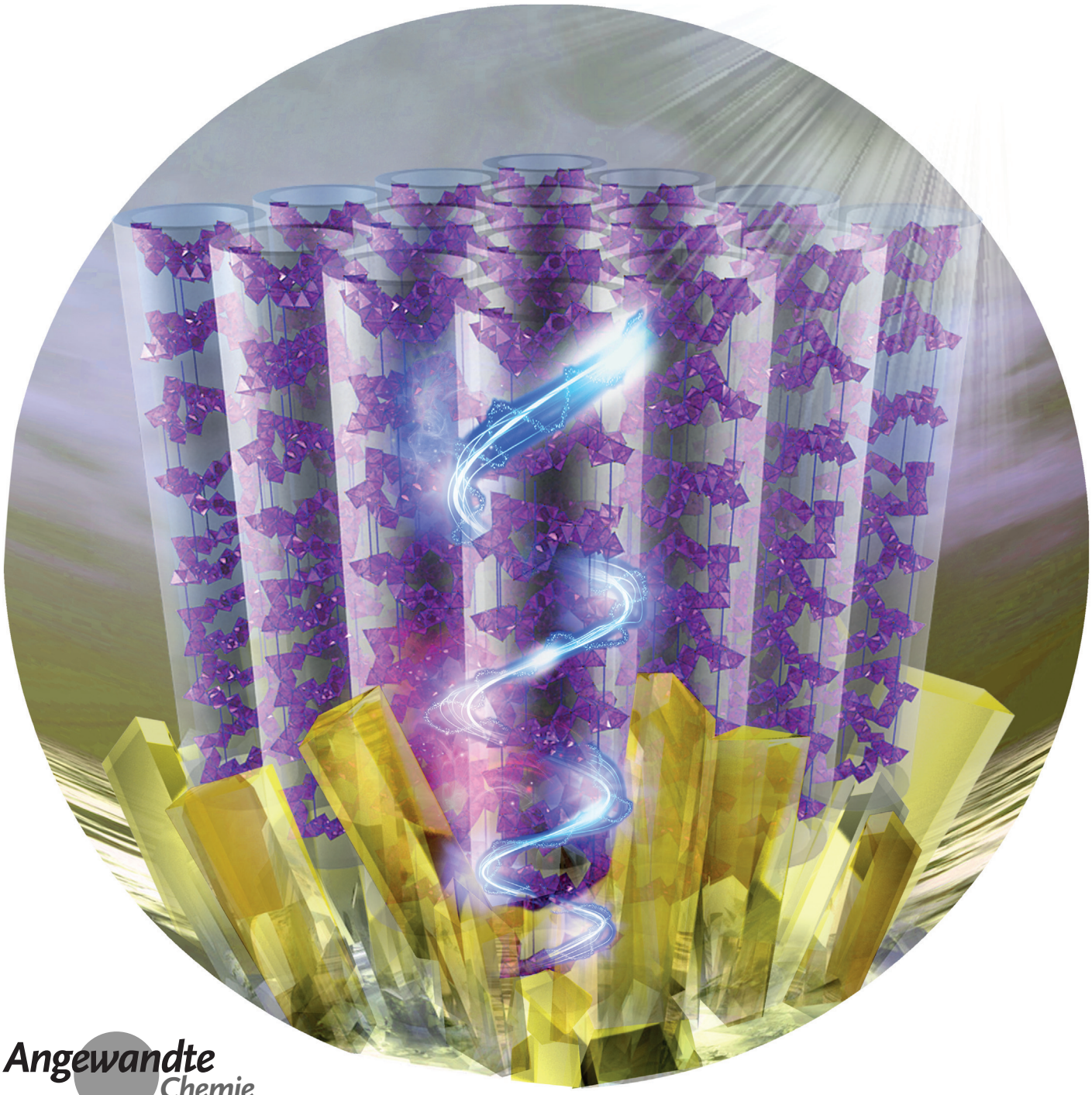
Inorganic Nanotubes

Deutsche Ausgabe: DOI: 10.1002/ange.201507083
Internationale Ausgabe: DOI: 10.1002/anie.201507083

Semiconductive Nanotube Array Constructed from Giant $[Pb^{II}_{18}I_{54}(I_2)_9]$ Wheel Clusters

Guan-E Wang, Gang Xu, Bin-Wen Liu, Ming-Sheng Wang, Ming-Shui Yao, and Guo-Cong Guo**

Dedicated to Prof. Thomas C. W. Mak on the occasion of his 80th birthday



Abstract: *Crystalline nanotube array would create great opportunity for novel electrical application. Herein we report the first example of a metal halide based crystalline nanotube array which is constructed from an unprecedented giant $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel cluster, as determined by synchrotron X-ray diffraction. The electrical properties of the single crystal were studied and the present compound shows typical semiconductivity and highly anisotropic conductivity.*

As a classical nanotubular material, carbon nanotubes have shown great success in research into fuel cells, battery, supercapacitors, lightweight electrical conductors, flexible electronics, and heaters since the 1990s.[1] Other interesting properties and applications of nanotubular materials, such as superconductivity, thermal electricity, ferroelectric, optical nonlinearity, photoluminescence, gas storage, are expected, if they can be synthesized with various inorganic elements.[2] Prompted by this potential, diverse inorganic nanotubes made from, for example, zinc oxide, silica, silicon, alumina, titania have been prepared.[3] These inorganic nanotubes are normally formed by rolling up exfoliated mono- or multilayer sheets of a layered compound. Therefore, they have large size distributions and are arranged in forms of fully or partially disordered arrays.[4] Besides above mentioned inorganic nanotubes, there is another kind of nanotubular material in extended solids, which is often negatively charged and assembled into crystal arrays through Coulomb interaction, hydrogen bonding, and other weak interactions. This kind of nanotube has the advantages of high quality and quantity yield, well-defined size, as well as a highly ordered array, which are extremely desired properties for future applications. Several crystalline inorganic nanotube arrays are known, including $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$,[5] $Na_2V_3O_7$,[6] $SbPS_4$,[7] $Na_2EuSiSe_4$,[8] $(C_4H_{12}N)_{14}[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$,[9] $Ba_5[(UO_2)(PO_4)_3(B_5O_9)].nH_2O$,[4] $(H_3O)_2K[(H_3O)@([18]crown-6)][(UO_2)_3(SeO_4)_5](H_2O)_4$,[10] $[Ni(1,2\text{-}PDA)_3]_2(HOCH_2CH_2CH_2NH_3)_3(H_3O)_2[Ge_7O_{14}X_3]_3$ (X = F, OH).[11] However, they are limited to oxides and chalcogenides. It is still a big challenge to prepare well-defined inorganic nanotube arrays with other elements. Moreover, most of these reports only disclosed the structural details of the compounds. Studies of their physical properties, such as the conductivity of crystalline nanotube array, have not been developed, but are extremely desired for their further application.

Inorganic–organic hybrids have become a research focus recently not only due to their unique long-range structure ordering crystalline features, but also owing to their superb light-harvesting and unique electrical properties.[12] Solar-cell devices fabricated with a metal-halide-based inorganic–organic hybrid have given power-conversion efficiency increases from 3.8% to 19.3% within only four years.[13] In the metal-halide-based inorganic–organic hybrids, the inorganic component offers rich structural possibilities including discrete cluster,[14] chain,[15] two-dimensional layer,[16] and three-dimensional framework,[17] which is the main structure factor dominating the interesting electrical, optical, and magnetic properties in hybrids. Hybrid materials with new metal-halide-structures that may bring novel physical properties attract more and more research interest.

Herein, we report the first example of metal-halide-based crystalline nanotube array, $(Pr_2DABCO)_{21}[Pb^{II}_{18}I_{54}(I_2)_9]$-$[Pb^{II}_2I_9]_2I_5{\cdot}13H_2O$ (**1**) (DABCO = 1,4-diazabicyclo-[2.2.2]octane, Pr = *n*-propyl). The crystal structure of **1** was determined by synchrotron X-ray diffraction and reveals that iodoplumbate nanotube array is composed by unprecedented $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel clusters connecting to each other through I–I covalent bonds (Figure 1). The electrical properties of **1** measured on a single-crystal were also studied and show significantly anisotropic semiconductive behavior.

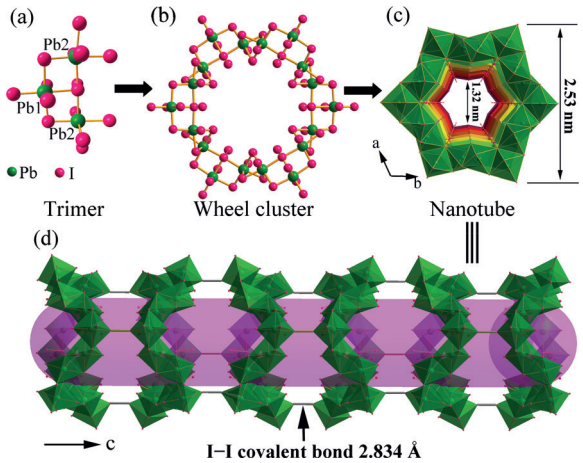


Figure 1. a) The Pb_3I_{13} trimers in the wheel cluster; b) The $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel cluster viewed along the *c* direction; c) The 1D nanotube in **1** viewed along the *c* direction. d) The 1D nanotube in **1**.

Yellow platelike crystals of **1** were synthesized by solvothermal reaction of a mixture of PbI_2, DABCO, HI, and *n*-propanol (more details shown in Supporting Information, Table S1–S3). Because of huge electron-number disparity between inorganic iodoplumbate and organic Pr_2DABCO^{2+}, it is difficult to determine the structure of the organic part in **1** with a normal lab X-ray instrument. Therefore, synchrotron X-ray diffraction was applied and the single-crystal structure of **1** was revealed successfully. Compound **1** crystallizes in a hexagonal space group, $P6_3/mcm$, with five structural units: a 1D nanotube built from unique giant $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel clusters, isolated $(Pb^{II}_2I_9)^{5-}$ clusters, I^- ions, propylated $(Pr_2DABCO)^{2+}$ dications, and lattice water molecules. The valence of Pb is confirmed to be 2+ by XPS (X-ray photoelectron spectroscopy) measurement. The asymmetric unit of **1** is shown in Figure S1. The phase purity of **1** is verified by elemental analysis and powder X-ray diffraction (PXRD) determination (Figure S2).

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507083.

To design and synthesize inorganic wheel-like clusters is an attractive research frontiers owing to their aesthetically pleasing structure,[18] unique chemical and physical properties, as well as diverse potential applications, such as magnetism,[19] nanotechnology[20] and redox activity.[21] Wheel clusters shows much structural diversity and tunability: many metals can be used, such as, V, Mo, Cr, W, Nb; the size of these wheel-clusters can be tuned to a great extent from relative small (Ti_8) and (Ln_8),[22] to very large (Mo_{150})[23] and (Mo_{154}).[24] Up to now, the wheel clusters are limited in polyoxometalates and chalcogenides. The inorganic part of **1** shows unique 18-membered metal wheel cluster $[Pb^{II}_{18}I_{54}(I_2)_9]$. As shown in Figure 1, there are two crystallographically independent Pb atoms in the wheel cluster, Pb1 and Pb2, both of which are coordinated by six I atoms and situated in a slightly distorted octahedral coordination environment. The bond lengths of Pb–I fall in the range of 3.051(3)–3.468(6) Å with an average value of 3.263(3) Å, reasonable for Pb ions in iodoplumbates.[25] Two Pb2-centered octahedra edge-sharingly connect to one Pb1 octahedron on the opposite side to form a Pb_3I_{13} trimer (Figure 1 a), which acts as the building block of the wheel. Through face-sharing connection between Pb2 octahedra, six Pb_3I_{13} trimers link with each other end-to-end to form a closed wheel cluster $[Pb^{II}_{18}I_{54}(I_2)_9]$ in D_3 symmetry, with an outer diameter of 2.53 nm and the inner diameter of about 1.32 nm (Figure 1 c). Notably, $[Pb^{II}_{18}I_{54}(I_2)_9]$ is the first metal halide wheel cluster.

A discrete wheel cluster has the possibility to be used as a building block to construct nanotubular structures. For example, carbon nanotubes have been shown to be synthesized from carbon nanorings.[26] However, nanotubes have never been constructed from metal halides. As shown in Figure 1 c, d, compound **1** is an unprecedented iodoplumbate nanotube, which is assembled from $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel clusters. The $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheels are linked with each other in a face-to-face manner by I–I covalent bonds to form the $[Pb^{II}_{18}I_{54}(I_2)_9]_n$ nanotube along the *c* axis with a crystallographic 6_3 screw axis running through the center of the nanotube. The I–I distance between neighboring $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheels is 2.838(8) Å, which falls in the reasonable distance for I–I covalent bonding (2.70–3.20 Å).[27] The Iodoplumbate nanotube inherits the geometric configuration of the $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel in that the opening window of its 1D channel is the same as that of $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel (Figure 1 c). The nanotubes are assembled in hexagonal-type symmetry and result highly ordered crystalline nanotube array (Figure 2).

In addition to the $[Pb^{II}_{18}I_{54}(I_2)_9]_n$ nanotube, discrete $(Pb^{II}_2I_9)^{5-}$ dimers constructed by face sharing (PbI_6) octahedra are another iodoplumbates component in **1**, which together with the $(Pr_2DABCO)^{2+}$ ions works as co-templates and surround the $[Pb^{II}_{18}I_{54}(I_2)_9]_n$ nanotube (Figure 2 and Figure S3). Discrete I^- anions reside in the nanotube. As shown in Figure 2, the organic dications and water filled the space between the nanotubes. All these components in **1** form complex weak interactions with each other by hydrogen-bonding and electrostatic interactions, to stabilize the packing of crystal **1** (Figure S3).

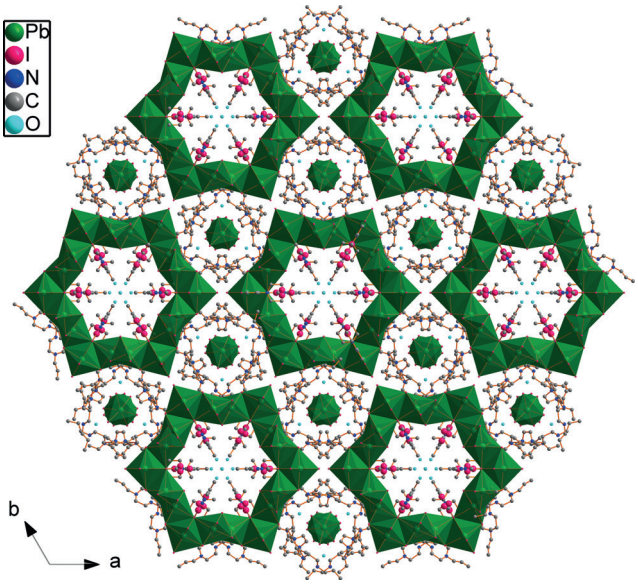

Figure 2. The packing of **1** viewed along the *c* direction. Coordination spheres of Pb atoms are shown as polyhedra for clarity.

On heating, compound **1** gradually releases all of its guest water molecules below 120 °C, and then is stable up to about 200 °C without weight loss (Figure S4). As shown in Figure S2, the PXRD pattern of the sample treated at 180 °C for 2 h is almost the same as the synthesized **1**, demonstrating the crystal structure of **1** is maintained until at least 180 °C.

The electrical properties of **1** were investigated with a direct current two-terminal method on several single-crystal samples (Figure 3 a). As shown in Figure 3 b,c,d and e, the conductivities of **1** along both the *a* and *c* directions have positive temperature effect, demonstrating its semiconductive features. Under room temperature, compound **1** has conductivities of 0.9×10^{-10} and 0.8×10^{-9} S cm^{-1} along the *a* and *c* axis, respectively; while at 180 °C, the conductivities reach to their highest values of 1.5×10^{-8} and 0.9×10^{-6} S cm^{-1} along the *a* and *c* axis, respectively. The activation energy of conductivity along the *a* and *c* direction are 0.28 and 0.54 eV, respectively. All of the values fall in the range of typical semiconductive materials and are comparable to other crystalline inorganic–organic hybrids.[12f,28]

Compound **1** shows very significantly anisotropic charge-transport behavior. Under room temperature, the conductivity of **1** along the *c* axis is about one order of magnitude higher than that along the *a* axis, which further increases to about two orders of magnitude at 180 °C. The conductivity of **1** also shows anisotropic temperature effect: from room temperature to 180 °C, the conductivity of **1** along the *c* axis increases with the value of about three orders of magnitude, while the conductivity along the *a* axis increases only by approximately two orders of magnitude. These observations are consistent with its structure as a iodoplumbate nanotube extended along the *c* axis. Normally, the conductive properties of metal-halide-based hybrid material arise from the extended inorganic structure in the crystal. The $[Pb^{II}_{18}I_{54}(I_2)_9]_n$ nanotube is the only extended inorganic component and stretches along

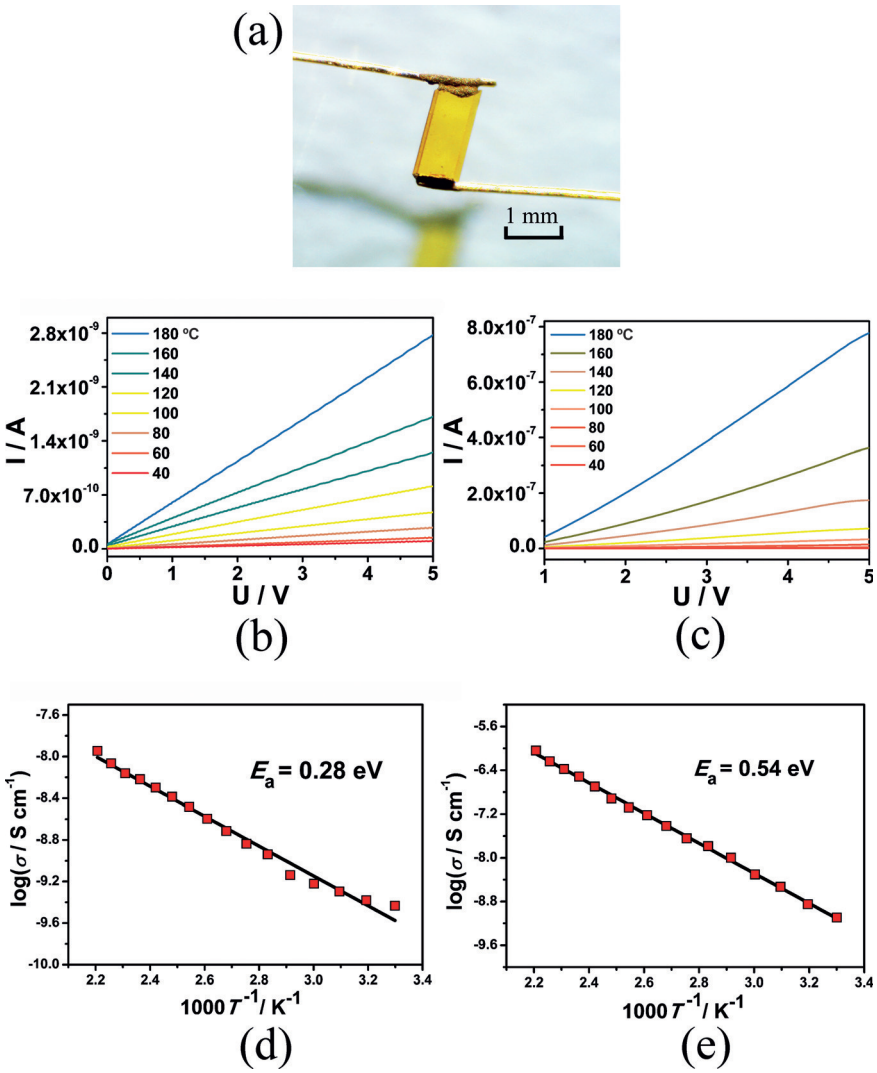

Figure 3. Photograph of the single crystal of **1** for electrical study (a); Temperature-dependent *I–V* curve for **1** along the *a* direction (b) and *c* direction (c); Arrhenius plots of **1** along the *a* direction (d) and *c* direction (e), E_a is the activation energy.

the *c* axis, and can thus act as a better charge-transport channel than other discrete components in **1**.

In conclusion, we report the first example of metal-halide-based crystalline inorganic nanotube array which is constructed from an unprecedented giant $[Pb^{II}_{18}I_{54}(I_2)_9]$ wheel cluster. The present result may from a bridge between wheel clusters and nanotubes which are two fascinating but distinct fields of research. The electrical properties based on the single-crystal of **1** were investigated, and the result shows that compound **1** is typical semiconductor and has high anisotropic conductivity.

Experimental Section

A mixture of PbI_2 (0.5 mmol, 0.231 g), DABCO (DABCO = 1,4-diazabicyclo[2.2.2]-octane) (0.5 mmol, 0.056 g), *n*-propanol (5 mL), and concentrated HI (1.0 mL, 45%) was heated at 160 °C for 3 days in a sealed 25 mL Teflon-lined stainless steel vessel. Upon cooling at 3 °C h^{-1} to room temperature, yellow sheet-like crystals of **1** (yield based on PbI_2, 60%) were obtained. Elemental Analysis (%): Calcd: C 14.47, N 2.81, H 2.78; Found: C 14.86, N 2.98, H 2.86. The EDS measurements confirmed the presence of Pb and I in an approximate molar ratio of 1:4.33. CCDC 1414085 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

NSF of China (51402293, 21401193, 21471149, 91222204), and the NSF of Fujian Province (2014J01065, 2014J05025). We are grateful to Mr. Zeng-Qiang Gao for the single-crystal intensity data collection on Beijing Synchrotron Radiation Facility (BSRF).

Keywords: semiconductors · inorganic–organic hybrid composites · lead · nanotube arrays · wheel clusters

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 514–518
Angew. Chem. **2016**, *128*, 524–528

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Received: July 30, 2015
Published online: November 9, 2015

