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$[(H_2en)_7(C_2O_4)_2]_n(Pb_4I_{18})_n \cdot 4nH_2O$, a New Type of Perovskite Co-templated by Both Organic Cations and Anions

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A novel inorganic–organic hybrid $[(H_2en)_7(C_2O_4)_2]_n(Pb_4I_{18})_n \cdot 4nH_2O$ has been synthesized by employing an organic anionic–cationic co-template. It shows a new type of perovskite structure, featuring an unprecedented staircase-like inorganic network. The title compound exhibits an intriguing semiconducting property with $E_g = 2.47$ eV and strong photoluminescence arising from band-edge transitions.

Inorganic–organic hybrids templated with organic cations have attracted considerable attention, including metal halides,[1] chalcogenides,[2] and phosphates.[3] The prospect of creating new materials for display and storage technologies provides a great motivation for research on the metal-halide-based hybrids.[4] In particular, a variety of perovskite inorganic–organic hybrids with corner-sharing octahedra have been explored, generally formulated as $(M_nX_{3n+1})^{(n+1)-}$ and $(M_nX_{3n+2})^{(n+2)-}$ (M = divalent main-group metal; X = halide).[1,5] In addition to balancing the charge from the inorganic component, the organic component also acts as a structure-directing agent. It has been demonstrated that the organic component with tunable charge, size, and shape can have a great effect on the structures and properties of hybrids, such as photoconductivity, luminescence, nonlinear optical properties, and thermal transition.[6] Except for a few examples of hybrids templated with metal–organic complexes,[7] where we showed a new type of magnetic semiconducting hybrid based on iodoplumbate,[7a] most of the hybrids employ single or mixed ammonium cations as templates and tend to form N–H···X hydrogen bonds between the inorganic and organic components.[8] Recently, the hybrids templated with bifunctional ammionium cations, for example, (hydroxyethyl)ammonium $[(HO(CH_2)_2NH_3)^+]$[6c] and aminocarboxylic acid $[(HO_2C(CH_2)NH_3)^+]$ cations,[9] have been reported. In addition, Mitzi et al. have described the intercalation of neutral solvent molecules into the organic cation in a perovskite inorganic–organic hybrid.[10] However, the templates in all of these hybrids are limited to organic cations; organic anions have never been invited into hybrid structures probably because their negative charge is thought to repel inorganic components and would thus make the structure unstable. To overcome this problem, we propose a new approach to introducing organic anions into the hybrid through supramolecular interactions between organic anions and cations, which forms an organic anionic–cationic co-template structure. Novel perovskite hybrid structures can be expected to emerge upon the use of such a co-template because of its

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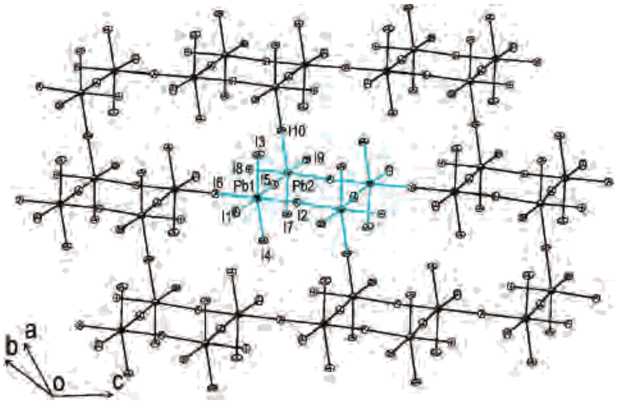

Figure 1. View of the 2-D staircase-like sheet in **1** with the cyan tetranuclear representing the Pb_4I_{18} building block.

characteristic structural features. Herein we report a novel inorganic−organic hybrid $[(H_2en)_7(C_2O_4)_2]_n(Pb_4I_{18})_n \cdot 4nH_2O$ (**1**; en = ethylendiamine)[11] with a new type of perovskite, synthesized by using an organic anionic−cationic co-template.

The solvothermal reaction of PbI_2, $K_2C_2O_4 \cdot H_2O$, and en (molar radio 1:1:15) in a solution of concentrated HI and ethanol at 120 °C for 2 days led to the yellow prismatic crystals of the title compound.[12] It is important to keep a sufficient quantity of HI in the solution with a pH value about 1. In addition, the reactant $K_2C_2O_4 \cdot H_2O$ cannot be replaced by $H_2C_2O_4$ because the concentrated HI solution disfavors the formation of $C_2O_4{}^{2-}$ anions from $H_2C_2O_4$.

The structure of the title compound is composed of three structural units: unique 2-D staircase-like sheets $(Pb_4I_{18})_n{}^{10n-}$, organic anionic−cationic co-templates, and lattice water molecules. There are two crystallographically independent Pb atoms, which are both situated in a slightly distorted octahedral coordination environment. The Pb1, Pb2, Pb1($-x$, $2 - y$, $1 - z$), and Pb2($-x$, $2 - y$, $1 - z$) octahedra corner-share with each other to form a coplanar $Pb_4I_{16}I_{4/2}$ tetramer, which acts as the building block of the inorganic sheet. The Pb_4I_{18} tetramers corner-share through the equatorial μ_2-I6 atoms to form a nearly coplanar step of the staircase extending along the c direction. The steps interlink through the axial μ_2-I10 atoms to form a staircase-like sheet as shown in Figure 1. The Pb−I bond lengths are 3.0475(7)−3.4621(9) Å, in agreement with those found in other perovskite iodoplumbate based hybrids.[13,14] Interestingly, the Pb−I−Pb bond angles [176.04(1) and 180.0°] in **1** are obviously higher than those in all $(PbI_4)_n{}^{2n-}$ hybrids[6c,14] (e.g., the reported highest Pb−I−Pb bond angle is 173.7°[14]), which partly results from the absence of hydrogen-bonding interactions between the inorganic and organic components in **1**.[14,15] In general, the traditional organic cationic templates favor the formation of a distinct family of ⟨100⟩- or ⟨110⟩-oriented perovskites.[1] However, the new type of inorganic perovskite in **1** cannot be obtained by cutting the 3-D perovskite structure along a certain crystallographic direction.

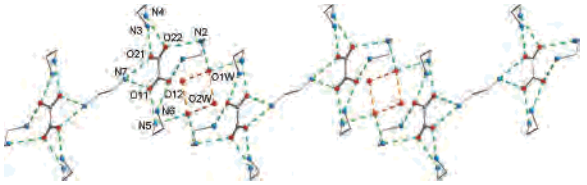

Figure 2. 1-D chain formed by co-templates and planar tetranuclear water clusters through N−H···O and O−H···O hydrogen bonds (dash lines representing hydrogen bonds).

Supramolecular assembly is an efficient route to crystal engineering with designed structures and properties of materials. In the title compound, the hydrogen-bonding interactions occur among the organic ions, stabilizing the co-template structure. As shown in Figure 2, the co-template consists of two oxalate group anions and seven protonated en cations, wherein each oxalate group is “chelated” by three protonated en cations through N−H···O hydrogen bonds to form a sub-co-template cation. The co-template can be regarded as a protonated en bridging two sub-co-template cations through N−H···O hydrogen bonds. Four lattice water molecules form a planar tetranuclear water cluster with a crystallographic inversion center through O−H···O hydrogen bonds.[16] The cationic co-templates and tetranuclear water clusters interlink alternately through N−H···O hydrogen bonds to form a cationic 1-D supramolecular chain, which is located between the inorganic sheets (Figure 3).

The remarkable structural feature of **1** is to incorporate organic anions $(C_2O_4)^{2-}$ into organic cations $(H_2en)^{2+}$ through supramolecular interactions to form a co-template. It is worth noting that the organic anions can attract more organic cations to form co-template structures with higher positive charge. As a result, the inorganic component will have to increase its negative charge in order to satisfy the neutrality requirement and may thus yield new types of perovskite structures in hybrids. Up to now, the charge of the $(Pb_7I_{18})_n{}^{10n-}$ ion is the highest one among the reported bivalent metal halide hybrids. Furthermore, in comparison with the traditional templates, the co-template may form in different sizes and diversity of shape through the selection of organic anions and cations as well as the modulation of their supramolecular interactions, which will favor the formation of a diverse

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(11) Crystal data for the title compound: $T = 123(2)$ K, triclinic, space group $P\bar{1}$, $C_9H_{39}I_9N_7O_6Pb_2$, $a = 12.083(4)$ Å, $b = 13.678(4)$ Å, $c = 14.004(5)$ Å, $\alpha = 105.314(2)°$, $\beta = 112.061(2)°$, $\gamma = 104.900(2)°$, $V = 1897.3(11)$ Å^3, $Z = 2$, $\mu = 16.216$ mm^{-1}, 14 255 reflections measured, 6448 independent reflections ($R_{\text{int}} = 0.0292$), 5500 reflections with $I > 2\sigma(I)$, R1 = 0.0368, wR2 = 0.0874.

(12) A mixture of PbI_2 (0.5 mmol, 231 mg), $K_2C_2O_4 \cdot H_2O$ (0.5 mmol, 92 mg), concentrated hydriodic solution HI (45%; 1.5 mmol, 3 mL), en (7.5 mmol, 0.5 mL), and 2 mL of ethanol was heated at 120 °C for 2 days in a sealed 25-mL Teflon-lined stainless steel vessel. Upon cooling at 3 °C/h to room temperature, the yellow prism crystals of **1** were obtained in 50% yield (based on PbI_2). Thermogravimetric analysis (Figure S2 in the Supporting Information) of **1** showed a weight loss of 1.7% corresponding to the loss of four water molecules in the temperature range 25−105 °C, and compound **1** decomposes above 276 °C. A probable process of decomposition is shown in electrospray ionization. Elem anal. Calcd for **1**: C, 5.70; H, 2.07; N, 5.17. Found: C, 5.45; H, 2.25; N, 4.98. IR (KBr): 3434.65, vs; 2918, m; 1618, s; 1569, m; 1493, s; 1299, s; 1023, m; 997, m; 968, w; 772, m; 458, m.

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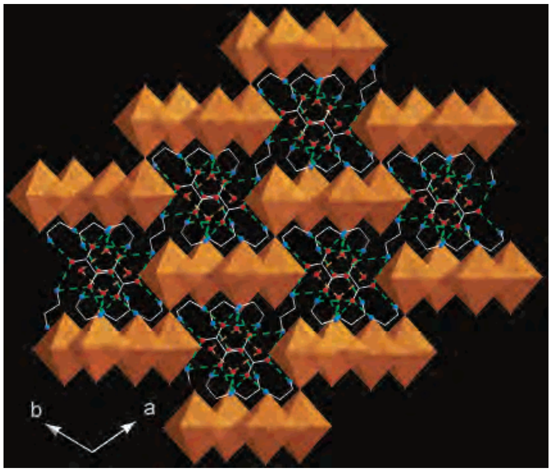

Figure 3. 2-D view of the staircase-like structure of **1** along the *c* axis with cationic organic chains located between the sheets.

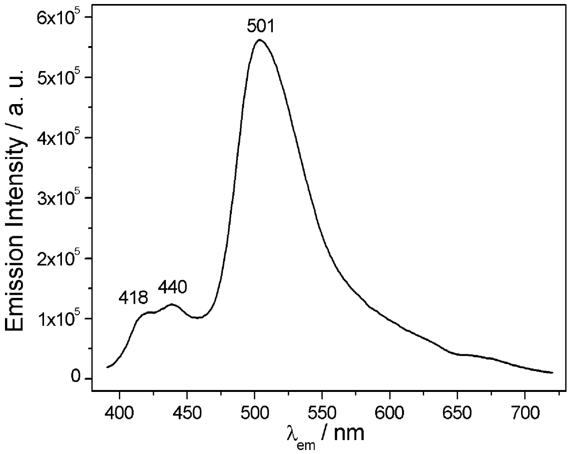

Figure 4. Solid-state emission spectrum of **1** (λ_{ex} = 371 nm) at room temperature.

configuration of an inorganic component and thus properties of the hybrid.

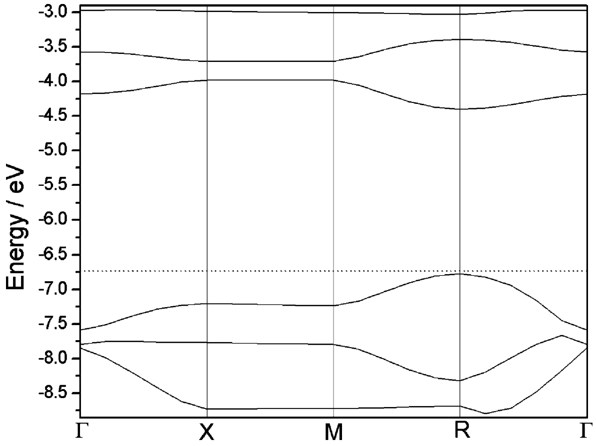

Figure 5. Calculated electronic band structure of the inorganic sheet $(Pb_4I_{18})_n^{10n-}$ in **1**.

As shown in Figure 4, compound **1** exhibits a strong photoluminescent emission band at 501 nm and relatively weak photoluminescent emission shoulder peaks at 418 and 440 nm upon photoexcitation at 371 nm. The emission band at 501 nm is close to the energy gap of 2.47 eV (503 nm) obtained from the optical absorption data of **1** (Figure S1 in the Supporting Information). To understand the structure–property relationship, an electronic band-structure calculation[17] is performed for the $(Pb_4I_{18})_n^{10n-}$ sheet in **1**. Its highest occupied molecular orbital and lowest unoccupied molecular orbital positions in Figure 5 give a direct gap of 2.33 eV at the R point, close to the experimental one for **1**, suggesting the near-edge adsorption of the $(Pb_4I_{18})_n^{10n-}$ inorganic sheet. The calculation shows that the title compound is a direct band-gap material, which supports the observation of strong luminescent properties. The agreement of the calculated energy gap with the observed emission band suggests that the photoluminescent emission band at 501 nm can be assigned to the transition between the valence band and the conductive band of the inorganic sheet. The calculated value of the energy gap of **1** is intermediate between those of the one-layer (2.85 eV) and three-layer (2.19 eV) perovskite structures and comparable to that of a two-layer perovskite structure (2.37 eV),[18] which suggests that the energy band of the staircase-like perovskite structure in **1** may exhibit the feature of the energy band of the two-layer perovskite structure. The shoulder peaks of **1** can be assigned to the internal transition of the oxalate group because similar emissions at 421 and 438 nm are also found in the emission spectrum of the pure $K_2C_2O_4 \cdot H_2O$ complex upon the same photoexcitation wavelength (Figure S3 in the Supporting Information). It is exciting that the hybrid can inherit and reflect the properties of incorporated organic anions.

In summary, the strategy of co-templating through the integration of organic anions with organic cations offers a feasible and convenient avenue of introducing different types of organic anions into inorganic–organic hybrids. The present work suggests that the organic anions can effectively modulate the charge, size, and shape of co-templates, which will benefit the formation of new types of inorganic perovskites in the hybrids as well as new functional hybrids. This strategy can be extended to the field of inorganic–organic hybrids with cationic templates. Works in these directions are underway.

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Supporting Information Available: Thermogravimetric analysis curve, solid-state optical absorption spectrum, solid-state excitation spectra, the calculated density of state of the inorganic sheet in **1**, the solid-state emission spectrum of $K_2C_2O_4 \cdot H_2O$, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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