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2018

Li, X., Do, T. T. H., del Águila, A. G., Huang, Y., Chen, W., Xiong, Q., & Zhang, Q. (2018). A 3D haloplumbate framework constructed from unprecedented Lindqvist-like highly coordinated [Pb₆Br₂₅]₁₃- nanoclusters with temperature-dependent emission. *Chemistry - An Asian Journal*, 13(21), 3185-3189. doi:10.1002/asia.201801292

<https://hdl.handle.net/10356/144106>

<https://doi.org/10.1002/asia.201801292>

This is the accepted version of the following article: Li, X., Do, T. T. H., del Águila, A. G., Huang, Y., Chen, W., Xiong, Q., & Zhang, Q. (2018). A 3D haloplumbate framework constructed from unprecedented Lindqvist-like highly coordinated [Pb₆Br₂₅]₁₃- nanoclusters with temperature-dependent emission. *Chemistry - An Asian Journal*, 13(21), 3185-3189. doi:10.1002/asia.201801292, which has been published in final form at 10.1002/asia.201801292. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy [<https://authorservices.wiley.com/authorresources/Journal-Author>]

A 3D Haloplumbate Framework Constructed From Unprecedented Lindqvist-like Highly-Coordinated $[\text{Pb}_6\text{Br}_{25}]^{13-}$ Nanoclusters with Temperature-Dependent Emission

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Abstract: Searching novel haloplumbate building units to construct three-dimensional (3-D) frameworks is very important and highly desirable because such materials would possess new physical properties and potential applications. Here, by employing tetrakis(N-imidazole)methylene)methane (TIMM) as a structure-directing agent, the first 3-D haloplumbate framework constructed from unprecedented Lindqvist-like highly-coordinated $[\text{Pb}_6\text{Br}_{25}]^{13-}$ nanoclusters has been successfully prepared under hydrothermal condition, where all Pb^{2+} centres in $[\text{Pb}_6\text{Br}_{25}]^{13-}$ nanoclusters adopt seven-/eight- coordinated configurations. The as-obtained material is a wide-gap semiconductor (~3.1 eV) and can be stable up to 320 °C. More importantly, this material has been demonstrated to show temperature-dependent emission. Our results could provide a new strategy to explore novel metal-halide open-framework materials.

The design and fabrication of novel inorganic open-framework materials has attracted sustainable interests, owing to their intriguing architectures/topologies, fascinating physical properties, and potential applications in various areas such as ion exchange, industrial catalysis, molecular separation, and proton-conduction.^[1] Among these materials, So far, the most representative example is zeolite, which is built from inorganic MO_4 tetrahedra through sharing vertexes and still influences our daily life in all respects.^[2-3] Besides, chalcogenide framework materials based on supertetrahedral clusters have also gained considerable investigations due to their unique electric properties.^[4] Another kind of classic inorganic open-framework materials is polyoxometalate-based architectures because of their excellent catalytic properties.^[5] However, compared with the above-mentioned well-known materials, the effort to explore the chemistry of metal-halide-based open frameworks is much less. Such gap strongly encourages us to contribute our research in this direction.

As an important subclass of metal-halide materials, lead-halide perovskites (haloplumbates) have raised a great deal of research interests not only due to their potential applications in optoelectronic devices,^[6] but also due to their fascinating structural diversity.^[7] One common methodology to approach new haloplumbates is to employ inorganic alkali/alkali-earth cations, various protonated/N-alkylated organic species (e.g. bipyridine, imidazole and triazole), or diverse organic amines as structure-directing agents, to assemble lead-halide polyhedral together under hydrothermal/solvothermal conditions. However, most reported haloplumbate structures are low-dimensional, including isolated 0-D clusters,^[8] 1-D chains,^[9] or 2-D layers.^[10] It is still very challenge to obtain 3-D framework structures. Till now, the number of 3-D haloplumbates is very limited.^[11] Therefore, it is highly desirable to develop novel feasible strategies to construct 3-D haloplumbate frameworks for new optoelectronic applications.

In this research, for the first time, we employed a multi-imidazole molecule tetrakis(N-imidazole)methylene) methane (TIMM) as a structure-directing agent to approach 3-D haloplumbate frameworks, mainly based on the following considerations: 1) TIMM should be a good precursor to form charge-balance cations after protonated; 2) the high charge capacity of the protonated $[\text{H}_4\text{TIMM}]^{4+}$ species may allow lead ions and halogen anions to *in situ* form novel clusters; and 3) the protonated $[\text{H}_4\text{TIMM}]^{4+}$ species can act as structure-directing templates to form new extended structures.

Herein, we report an unprecedented 3-D haloplumbate $(\text{H}_4\text{TIMM})\text{Pb}_7\text{Br}_{18}$ (**1**), constructed from unusual Lindqvist-like $[\text{Pb}_6\text{Br}_{25}]^{13-}$ nanoclusters, which connect to each other through sharing faces and edges. More importantly, all Pb^{2+} ions in **1** adopt uncommon highly-coordinated geometries (seven-coordinated and eight-coordinated). To the best of our knowledge, **1** represents not only the first example of a 3-D haloplumbate framework constructed from highly-coordinated Pb^{2+} ions, but also the first haloplumbate containing unusual $[\text{Pb}_6\text{Br}_{25}]^{13-}$ nanoclusters.

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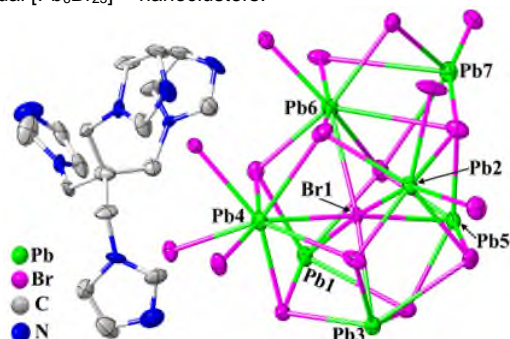


Figure 1 View of the asymmetric unit of **1**, the displacement ellipsoids are drawn at 80% probability level, all hydrogen atoms and lattice water guests are omitted for clarity.

Under hydrothermal condition, colourless block crystals of **1** (Figure S1) were obtained in 25% yield (based on TIMM) by reacting PbBr_2 , HBr and TIMM in water. The as-obtained **1** is very stable in air, water, or common organic solvents such as methanol, ethanol, and acetone. SCXRD structural analysis reveals that **1** crystallizes in the orthorhombic space group $Pbca$ (CCDC: 1853384), and its asymmetric unit consists of seven independent Pb^{2+} ions, eighteen Br anions and one protonated $[\text{H}_4\text{TIMM}]^{4+}$ cation (Figure 1). One of the most intriguing structural characteristics in **1** is the coordination geometries of Pb^{2+} ions, which adopt highly-coordinated slightly-distorted configurations. Three of them (Pb2, Pb5, Pb7) are seven-coordinated while the rest (Pb1, Pb3, Pb4, Pb6) are eight-coordinated (Figure S2). It is worthy to point that seven/eight-coordinated Pb^{2+} ions are very rare in haloplumbate chemistry.^[12] Generally, most Pb^{2+} ions in the reported haloplumbates tend to form six-coordinated configuration. A detailed search in CCDC database indicates that the reported seven- or eight-coordinated Pb^{2+} ions in the haloplumbates normally co-exist with six-coordinated Pb^{2+} ions.^[12] The haloplumbates completely made from highly-coordinated Pb^{2+} ions (both seven- and eight-coordinated) is unprecedented and **1** is the first example in this system.

The second intriguing structural characteristic in **1** is the presence of a novel Lindqvist-like $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster (Figure 2a). The Lindqvist-type clusters are a kind of classical polyoxometalate structures based on MO_6 ($M=\text{V}^{\text{V}}, \text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}, \text{Nb}^{\text{V}}, \text{Ta}^{\text{V}}$) octahedra with formula of $[\text{M}_6\text{O}_{19}]^{2-/8-}$ (Figure S3).^[13] The basic structural feature of Lindqvist-type clusters is that six M atoms are integrated by a $\mu_6\text{-O}$ atom to form a $[\mu_6\text{-OM}_6]$ octahedron (Figure S3). In $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster, six Pb^{2+} ions are linked together by one $\mu_6\text{-Br}$ anion, forming a $[\mu_6\text{-BrPb}_6]$ octahedral core (Figure 2b). The core is further stabilized by eight $\mu_3\text{-Br}$ bridges and sixteen terminal Br anions, resulting in a slightly-distorted Lindqvist-like cluster with a size of about $1.21 \times 1.21 \times 1.21 \text{ nm}^3$. The bond lengths for Pb-Br_c , Pb-Br_b and Pb-Br_t ($\text{Br}_c = \mu_6\text{-Br}$; $\text{Br}_b = \mu_3\text{-Br}$; $\text{Br}_t = \text{terminal Br ligand}$) fall in the range of $2.975 \sim 3.466$, $2.895 \sim 3.888$, $2.865 \sim 3.432 \text{ \AA}$, respectively. It is noteworthy to note that there are several differences between $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster and classical $[\text{M}_6\text{O}_{19}]^{2-/8-}$ clusters: 1) the coordination geometries of Pb^{2+} ions in $[\text{Pb}_6\text{Br}_{25}]^{13-}$ are obviously different from metal cations in classical $[\text{M}_6\text{O}_{19}]^{2-/8-}$ clusters; 2) the $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster is stabilized by eight μ_3 -bridges, while in the $[\text{M}_6\text{O}_{19}]^{2-/8-}$ clusters, twelve μ_2 -bridges are employed to form the structure; and 3) the number of terminal ligands in the periphery of $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster is sixteen, while only six in $[\text{M}_6\text{O}_{19}]^{2-/8-}$. To the best of our knowledge, such a Lindqvist-like $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster has never been reported in haloplumbate chemistry.

Apart from the novel $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster, another interesting structural characteristic in **1** is the further assembly of these nanoclusters.

As shown in Figures 2c-2d, there are two kinds of linking modes between two adjacent clusters. Two thirds of Pb^{2+} ions (Pb1, Pb3, Pb4, Pb6) connect to the neighbouring clusters through sharing three bridging Br ions (sharing faces), and the rest of Pb^{2+} ions (Pb2, Pb5) link to the surrounding symmetry-related clusters through two bridging Br ions (sharing edges).

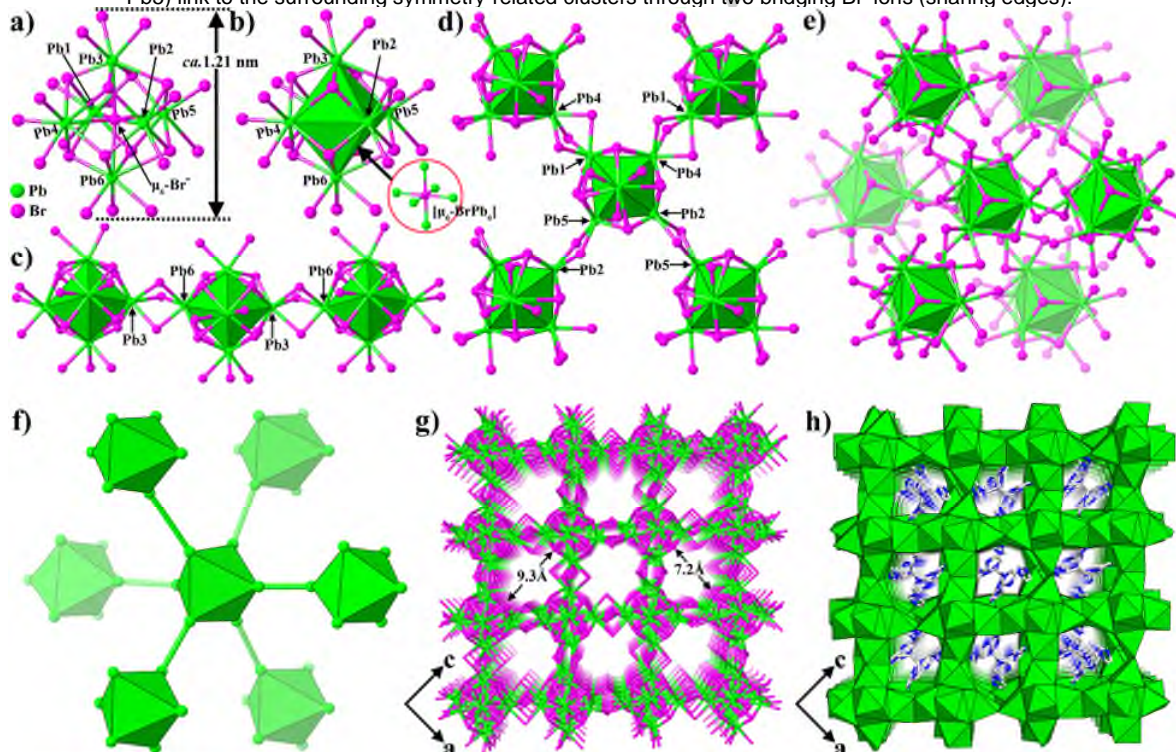


Figure 2 a)-b) Ball-stick and polyhedral of Lindqvist-like $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster. c)-d) View of the linking detail of $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster with adjacent ones. e)-f) View of the linking style of $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster, showing that each $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster connects to six neighboring clusters. g)-h) View of the 3-D framework structure of **1** along the b axis. Colour code: octahedra in b)-f) are $[\mu_6\text{-BrPb}_6]$; polyhedra in h) are PbBr_7 and PbBr_8 ; carbon and nitrogen atoms in f) are grey and blue.

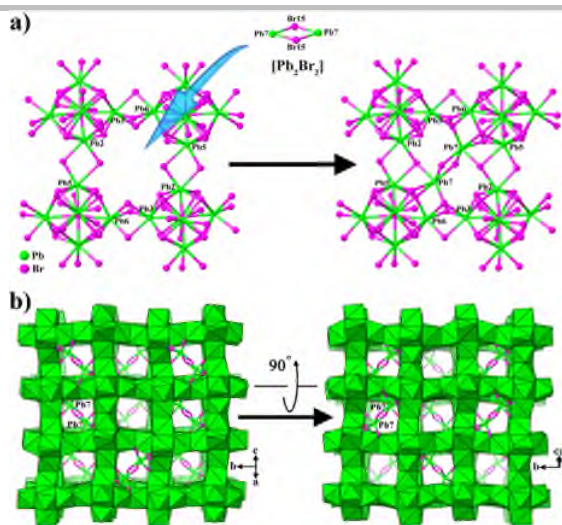


Figure 3 a) View of the insertion of a $[\text{Pb}_2\text{Br}_{12}]^{8-}$ fragment into the diagonal position of four-membered window generated by interconnecting four $[\text{Pb}_6\text{Br}_{25}]^{13-}$ clusters. b) View of the 3-D framework of **1** along the directions perpendicular to b axis. Polyhedra code: PbBr_7 and PbBr_8 , green.

Each $[\text{Pb}_6\text{Br}_{25}]^{13-}$ cluster totally connects six neighbouring ones through two types of linking modes in different directions (Figures 2e–2f). As a result, these six-connected $[\text{Pb}_6\text{Br}_{25}]^{13-}$ clusters self-assemble into a 3-D anionic framework with PCU-type topology (Figures 2g and S4). Generally, frameworks with PCU-type topology have 1-D channels in three mutually perpendicular directions. However, the framework of **1** only possesses 1-D channels along b axis. This is because additional $[\text{Pb}_2\text{Br}_2]$ fragments, formed by two symmetric Pb^{7+} ions and two $\mu_2\text{-Br}$ anions, insert into the diagonal position of square windows in the directions perpendicular to b axis (Figure 3a). Consequently, there is no obvious channel on the framework along the directions except b axis (Figure 3b). The protonated $[\text{H}_4\text{TlMM}]^{4+}$ cations, which occupy 36.0% of the total crystal volume,^[14] locate at the 1-D channels of the 3-D framework (Figure 2h). These positive organic species not only serve as charge-balance cations for the anionic framework, but also act as templates to direct the formation of the final structure. Due to the presence of four methylene arms on the skeleton, the $[\text{H}_4\text{TlMM}]^{4+}$ cation can easily adjust its conformation to meet the steric requirement of the framework during the self-assembly process. Apart from the electrostatic interactions, there are also abundant C–H...Br, N–H...Br hydrogen bond interactions between $[\text{H}_4\text{TlMM}]^{4+}$ cations and the anionic framework (Table S1), which may be helpful to stabilize the framework. To date, although more than 700 cases of haloplumbates have been reported in CCDC database, the number of haloplumbates with 3-D framework structures is no more than eight.^[11] Accordingly, **1** not only is the first 3-D framework structure based on novel Lindqvist-like $[\text{Pb}_6\text{Br}_{25}]^{13-}$ clusters, but also represents a new 3-D framework type in haloplumbates.

The purity of the as-prepared **1** have been examined by powder X-ray diffraction (PXRD) analysis through comparing the as-prepared sample with the simulated one based on SCXRD result (Figure S5). Thermogravimetric analysis of **1** shows no weight loss in the range of 30–320 °C, indicating that **1** has a high thermal stability and there is no guest solvent molecules in crystal lattices (Figure S6).

The optical response of the haloplumbate structures have

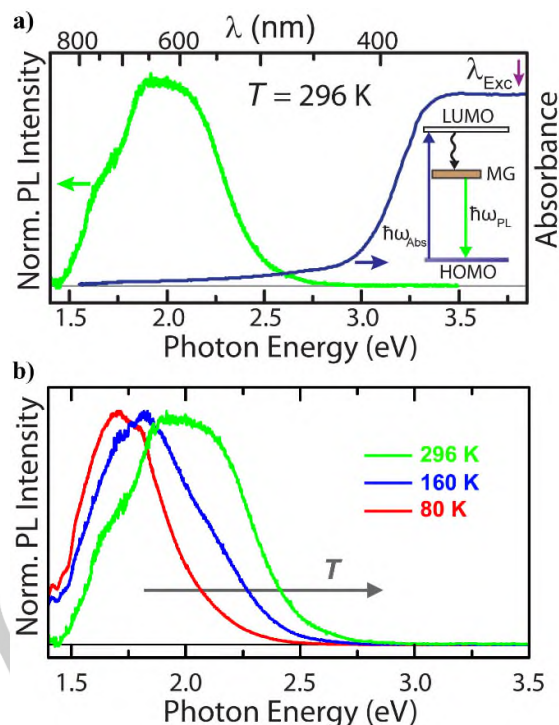


Figure 4 a) Normalized absorption (blue curve) and photoluminescence (green curve) spectra taken at room temperature ($T = 296$ K). Inset: Energy scheme explaining the optical response of **1**. The optical bandgap is defined by the energy difference between the HOMO and the LUMO. Photoluminescence originates from mid-gap states (MG). b) Selected PL spectra taken at various temperatures, from left to right, of 80 K (red curve), 160 K (light-blue curve) and 296 K (green curve).

been investigated by means of photoluminescence spectroscopy and continuum-light (UV-Visible) experiments, which can provide important information on their internal electronic transitions. When the sizes of the studied single crystals are macroscopic, the absorbance (A) can be obtained from the reflectance (R) and the transmittance (T_r) as $A(h\nu) = 1 - R(h\nu) - T_r(h\nu)$, where ($h\nu$) is photon energy (Figure S7). The calculated absorbance spectrum at room temperature ($T = 296$ K) is shown by the blue curve in Figure 4a. At low energies (long wavelengths), light absorption is weak. At energies of ~ 3.0 eV ($\lambda \sim 400$ nm), the absorption drastically increases and then saturates. The steep increment defines the lowest energy required (*i.e.*, bandgap) to photo-excite electrons from the highest-occupied (HOMO) to the lowest-unoccupied (LUMO) molecular orbitals (see inset at Figure 4a). From the quantitative analysis (Figure S8), we concluded that the optical bandgap is ~ 3.1 eV. This energy is comparable to other wide-bandgap semiconductors, such as GaN,¹⁵ ZnO,¹⁶ lead-halide with perovskite lattices¹⁷ and organic compounds.¹⁸

Photoexciting the haloplumbates with higher-energy laser (larger than the bandgap (λ_{Exc})) results in a broadband emission. A normalized photoluminescence spectrum, taken at room temperature, is shown by the green curve in Figure 4a. The photoluminescence band is centred at ~ 2.0 eV, corresponding to a shift of ~ 1 eV to lower energies with respect to the bandgap. Although semiconductors can exhibit large energy differences between the absorption onset and the photoluminescence spectral position (so-called Stokes shift),¹⁹ the pronounced shift can hardly be explained by the assistance of vibrational (phonon)

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modes to the optical transition. We believe that the broadband luminescence originates from the states located within the bandgap of the structure (mid-gap (MG) states), whose precise microscopic origin is not clear yet. As these states locate at the bandgap, they might experience similar responses under external stimuli, such as temperature.²⁰ Figure 4b shows normalized photoluminescence spectra at selected temperatures of $T = 80$ K (red curve), $T = 160$ K (light-blue curve) and $T = 296$ K (green curve). With increasing temperature, the photoluminescence spectral position shifts to higher energies (blue-shift). This blue-shift has been observed in lead-halide semiconductors with perovskite crystal structures.²¹⁻²³ Moreover, the photoluminescence peak shift is reversible as a function of temperature.

In summary, an unprecedented 3-D haloplumbate framework, which exhibits several unique structural features, has been successfully constructed under hydrothermal condition. The deliberate choice of a flexible multi-imidazole molecule TIMM as a structure-directing agent is crucial for the formation of the framework structure. The optical spectroscopy study reveals that **1** is a wide-gap semiconductor with the optical bandgap of ~ 3.1 eV. Interestingly, **1** exhibits broad light emission centred at the red region of the electromagnetic spectrum. The large energy difference between absorption and optical emission, highly minimizes re-absorption effects that might be potentially interesting for applications in luminescent-like light concentrators. This work will not only enrich the structural diversity of inorganic open-framework materials, but also provide a new perspective towards the development of unique haloplumbate architectures with interesting photoelectric properties.

Acknowledgements

Q.Z acknowledges financial support from AcRF Tier 1 (RG 111/17, RG 2/17, RG 114/16, RG 8/16) and Tier 2 (MOE 2017-T2-1-021), Singapore. Q.X. gratefully acknowledges the funding support from Singapore Ministry of Education via AcRF Tier 1 grants (RG 113/16 and RG 194/17).

Keywords: Haloplumbate • Semiconductor • Photoluminescence • Lindqvist-like • Highly-coordinated

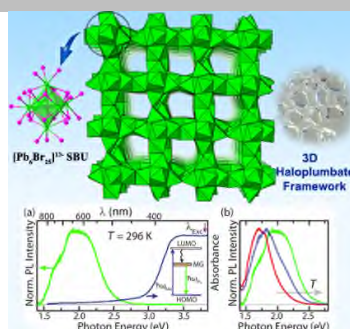
- [1] a) V. Vattipalli, A. M. Paracha, W. Hu, H. Chen, W. Fan, *Angew. Chem. Int. Ed.* **2018**, *57*, 3607-3611; b) K. Ding, A. Corma, J. A. Macia-Agullo, J. G. Hu, S. Kramer, P. C. Stair, G. D. Stucky, *J. Am. Chem. Soc.* **2015**, *137*, 11238-11241; c) W. W. Xiong, Q. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 11616-11623.
- [2] J. Cejka, A. Corma, S. Zones, Zeolites and Catalysis: Synthesis, Reactions and Applications, Wiley-VCH, Weinheim, **2010**, ISBN: 978-3-527-32514-6.
- [3] a) C. Zhang, E. Kapaca, J. Li, Y. Liu, X. Yi, A. Zheng, X. Zou, J. X. Jiang, J. H. Yu, *Angew. Chem. Int. Ed.* **2018**, *57*, 6486-6490; b) A. Corma, F. Rey, J. Rius, M. J. Sabater, S. Valencia, *Nature* **2004**, *431*, 287-290.
- [4] a) H. Li, A. Laine, M. O'Keeffe, O. M. Yaghi, *Science* **1999**, *283* (5405), 1145-1147; b) Q. Zhang, X. Bu, J. Zhan, T. Wu, P. Feng, *J. Am. Chem. Soc.* **2007**, *129*, 8412-8413; c) T. Wu, L. Wang, X. Bu, V. Chau, P. Feng, *J. Am. Chem. Soc.* **2010**, *132*, 10823-10831; d) Y. Liu, P. D. Kanhere, C. L. Wong, Y. Tian, Y. Feng, F. Boey, T. Wu, H. Chen, T. J. White, Z. Chen, Q. Zhang, *J. Solid-state Chem.* **2010**, *183*, 2644-2649; e) T. Wu, X. Wang, X. Bu, X. Zhao, L. Wang, P. Feng, *Angew. Chem. Int. Ed.* **2009**, *48*, 7204-7207; f) Q. Zhang, T. Wu; X. Bu, T. Tran, P. Feng, *Chem. Mater.*, **2008**, *20*, 4170-4172.
- [5] a) T. Boyd, S. G. Mitchell, D. Gabb, D. L. Long, Y. F. Song, L. Cronin, *J. Am. Chem. Soc.*, **2017**, *139*, 5930-5938; b) S. G. Mitchell, C. Streb, H. N. Miras, T. Boyd, D. L. Long, L. Cronin, *Nat. Chem.* **2010**, *2*, 308; c) D. Liu, Y. Lu, H. Q. Tan, W. L. Chen, Z. M. Zhang, Y. G. Li, E. B. Wang, *Chem. Commun.* **2013**, *49*, 3673-3675; d) J. Gao, S. Cao, Q. Tay, Y. Liu, L. Yu, K. Ye, P. C. S. Mun, Y. Li, G. Rakesh, S. C. J. Loo, Z. Chen, Y. Zhao, C. Xue, Q. Zhang, *Sci. Report* **2013**, *3*, 1853.
- [6] a) J. Burschka, N. Pellet, S. J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin, M. Gratzel, *Nature* **2013**, *499*, 316-319; b) L. L. Mao, Y. L. Wu, C. C. Stoumpos, B. Traore, C. Katan, J. Even, M. R. Wasielewski, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, *139*, 11956-11963; c) N. Wang, W. Liu, Q. Zhang, *Small Methods*, **2018**, *2*, 1700380; d) D. Cortecchia, S. Neutzner, A. R. S. Kandada, E. Mosconi, D. Meggiolaro, F. D. Angelis, C. Soci, A. Petrozza, *J. Am. Chem. Soc.* **2017**, *139*, 39-42; e) Z. Zhuang, C. Peng, G. Zhang, H. Yang, J. Yin, H. Fei, *Angew. Chem. Int. Ed.* **2017**, *56*, 14411-11416; f) N. Wang, K. Zhao, T. Ding, W. Liu, A. S. Ahmed, Z. Wang, M. Tian, X. W. Sun, Q. Zhang, *Adv. Energy Mater.* **2017**, *7*, 1700522; g) P.-Y. Gu, N. Wang, C. Wang, Y. Zhou, G. Long, M. Tian, W. Chen, X. W. Sun, M. G. Kanatzidis, Q. Zhang, *J. Mater. Chem. A* **2017**, *5*, 7339-7344.
- [7] a) C. Zhou, Y. Tian, M. Wang, A. Rose, T. Besara, N. K. Doyle, Z. Yuan, J. C. Wang, R. Clark, Y. Hu, T. Siegrist, S. Lin, B. Ma, *Angew. Chem. Int. Ed.* **2017**, *56*, 9018-9022; b) C. C. Stoumpos, M. G. Kanatzidis, *Acc. Chem. Res.* **2015**, *48*, 2791-2802; c) S. M. Islam, C. D. Malliakas, D. Sarma, D. C. Maloney, C. C. Stoumpos, O. Y. Kontsevoi, A. J. Freeman, M. G. Kanatzidis, *Chem. Mater.* **2016**, *28*, 7332-7343; d) L. Ming, W. X. Tao, W. L. Chen, *Coord. Chem. Rev.* **2009**, *253* 2787-2804; e) L. Mao, Y. Wu, C. C. Stoumpos, M. R. Wasielewski, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, *139*, 5210-5215.
- [8] a) L. M. Zhao, W. T. Zhang, K. Y. Song, Q. Q. Wu, Y. Li, H. H. Li, Z. R. Chen, *CrystEngComm*, **2018**, *20*, 2245-2252; b) G. Liu, J. Liu, Z. Sun, Z. Zhang, L. Chang, J. Wang, X. Tao, Q. Zhang, *Inorg. Chem.*, **2016**, *55*, 8025-8030; c) X. W. Lei, C. Y. Yue, J. C. Wei, R. Q. Li, Y. Lia, F. Q. Mi, *Dalton Trans.* **2016**, *45*, 19389-19398.
- [9] a) C. Sun, M. X. Du, J. G. Xu, F. F. Mao, M. S. Wang, G. C. Guo, *Dalton Trans.* **2018**, *47*, 1023-1026; b) G. E. Wang, G. Xu, M. S. Wang, J. Sun, Z. N. Xu, G. C. Guo, *J. Mater. Chem.* **2012**, *22*, 16742-16744; c) G. E. Wang, G. Xu, P. X. Li, S. H. Wang, M. S. Wang, G. C. Guo, J. S. Huang, *CrystEngComm* **2013**, *15*, 2579-2582; d) G. N. Liu, J. R. Shi, X. J. Han, X. Zhang, K. Li, J. Li, T. Zhang, Q. S. Liu, Z. W. Zhang, C. Li, *Dalton Trans.* **2015**, *44*, 12561-12575.
- [10] a) E. R. Dohner, A. Jaffe, L. R. Bradshaw, H. I. Karunadasa, *J. Am. Chem. Soc.* **2014**, *136*, 13154-13157; b) E. R. Dohner, E. T. Hoke, H. I. Karunadasa, *J. Am. Chem. Soc.* **2014**, *136*, 1718-1721; c) A. Lemmerer, D. G. Billing, *CrystEngComm* **2012**, *14*, 1954-1966; d) G. E. Wang, X. M. Jiang, M. J. Zhang, H. F. Chen, B. W. Liu, M. S. Wang, G. C. Guo, *CrystEngComm*, **2013**, *15*, 10399-10404.
- [11] a) Z. J. Zhang, S. C. Xiang, G. C. Guo, G. Xu, M. S. Wang, J. P. Zou, S. P. Guo, J. S. Huang, *Angew. Chem. Int. Ed.* **2008**, *47*, 4149-4152; b) C. Sun, M. S. Wang, P. X. Li, G. C. Guo, *Angew. Chem. Int. Ed.* **2017**, *56*, 554-558; c) G. E. Wang, G. Xu, M. S. Wang, L. Z. Cai, W. H. Li, G. C. Guo, *Chem. Sci.* **2015**, *6*, 7222-7226; d) G. F. Liu, P. Y. Gu, L. Niea, Q. Zhang, *Chem. Commun.* **2017**, *53*, 12365-12368; e) G. F. Liu, J. Liu, X. Tao, D. S. Li, Q. Zhang, *Inorg. Chem. Front.* **2016**, *3*, 1388-1392; f) C. Peng, Z. Zhuang, H. Yang, G. Zhang, H. Fei, *Chem. Sci.* **2018**, *9*, 1627-1633.
- [12] a) G. F. Wang, L. Chen, X. J. Song, Y. Z. Li, X. T. Chen, Z. L. Xue, *Polyhedron* **2014**, *81*, 550-554; b) G. Mahmoodi, V. Stilinovic, A. Bauza, A. Frontera, A. Bartyzel, C. Ruiz-Perez, A. M. Kirillov, *RSC Adv.* **2016**, *6*, 60385-60393; c) S. P. Zhao, Y. J. She, C. Xue, X. Q. Huang, R. Y. Huang, H. Xu, *Inorg. Chem. Commun.* **2014**, *44*, 96-100; d) D. G. Billing, A. Lemmerer, *CrystEngComm* **2009**, *11*, 1549-562.
- [13] a) Y. L. Wu, X. X. Li, Y. J. Qi, H. Yu, L. Jin, S. T. Zheng, *Angew. Chem. Int. Ed.* **2018**, *57*, 8572-8576; b) A. Bayagud, J. Zhang, R. N. N. Khan, J. Hao, Y. Wei, *Chem. Commun.* **2014**, *50*, 13150-13152; c) L. B. Fullmer, R. H. Mansergh, L. N. Zakharov, D. A. Keszler, M. Nyman, *Cryst. Growth Des.* **2015**, *15*, 3885-3892.
- [14] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7-13.
- [15] B. Monemar, *Phys. Rev. B* **1974**, *10*, 676-681.
- [16] V. Srikant and D. R. Clarke, *J. Appl. Phys.* **1998**, *83*, 5447-5451.

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- [17] M. Saba, F. Quochi, A. Mura, G. Bongiovanni, *Acc. Chem. Res.*, **2016**, *49*, 166-173.
- [18] J. C.S. Costa, R. J.S. Taveira, C. F.R.A.C. Lima, A. Mendes, L. M.N.B.F. Santos, *Opt. Mater.* **2016**, *58*, 51-60.
- [19] F. Meinardi, F. Bruni, S. Brovelli, *Nat. Rev. Mater.* **2017**, *2*, 17072(1-9).
- [20] a) A. Dey, P., D. Kabra, *Adv. Optical Mater.* **2018**, *6*, 1800109; b) O. Nazarenko, M. R. Kotyrba, S. Yakunin, M. Aebli, G. Raino, B. M. Benin, M. Wörle, M. V. Kovalenko, *J. Am. Chem. Soc.* **2018**, *140*, 3850-3853.
- [21] V. D'Innocenzo, G. Grancini, M. J. P. Alcocer, A. R. S. Kandada, S. D. Stranks, M. M. Lee, G. Lanzani, H. J. Snaith, A. Petrozza, *Nat. Commun.* **2014**, *5*, 3586(1-6).
- [22] N. Sestu, M. Cadelano, V. Sarritzu, F. Chen, D. Marongiu, R. Piras, M. Mainas, F. Quochi, M. Saba, A. Mura, G. Bongiovanni, *J. Phys. Chem. Lett.* **2015**, *6*, 4566-4572.
- [23] T. T. H. Do, A. G. Águila, C. Cui, J. Xing, Z. Ning, Q. Xiong, *Phys. Rev. B* **2017**, *96*, 075308(1-9).
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The first 3-D haloplumbate framework constructed from unprecedented Lindqvist-like highly-coordinated $[\text{Pb}_6\text{Br}_{25}]^{13-}$ nanoclusters was successfully obtained. The as-prepared material is a wide-gap semiconductor, and shows an interesting temperature-dependent photoluminescence.



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A 3D Haloplumbate Framework Constructed From Unprecedented Lindqvist-like Highly-Coordinated $[\text{Pb}_6\text{Br}_{25}]^{13-}$ Nanoclusters with Temperature-Dependent Emission