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Novel 3D Cubic Topology in Hybrid Lead Halides with a Symmetric Aromatic Triammonium Exhibiting Water Stability

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Abstract:

The limitations of 3D perovskites are related to their narrow structural tunability of the organic cations and their moisture sensitivity. Herein, we report the new family of 3D cubic hybrid metal halides (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br), where T is 1,3,5-tris-(4-aminophenyl)benzene. The materials are synthesized through an *in-situ* N-alkylation of T and an efficient one-step solvothermal reaction containing ethanol, initiating a tunable synthetic avenue for the acquisition of structurally complex hybrid halides with luminophores. (T-Et₆)₃Pb₁₁X₃₁ consists of an unprecedented $Ia\bar{3}$ framework of [Pb₁₁X₃₁]⁹⁻ 1D chains embedded with (T-Et₆)³⁺ cations affording an overall 3D topology. The constituent [Pb₁₁X₃₁]⁹⁻ chains include exclusively octahedral lead halide units with clusters of face- and edge-sharing connectivity, giving rise to weak broad emission centered at ~660 nm observed at 78K. (T-Et₆)₃Pb₁₁I₃₁ demonstrates water stability for at least 7 days. Synthesis through ambient-pressure results in tunable structural variations of 0D structures rendering T₇Pb₃Br₂₇·DMF and T₂Sn₃Br₁₈·4H₂O·0.5Br₂, both of which feature blue PL emission at room temperature.

Introduction:

3D hybrid halide perovskites have become a prominent class of semiconductor research due to their attractive, tunable optoelectronic properties and low-temperature solution syntheses-processibility, which allow for a broad range of optoelectronic applications such as solar cells,¹⁻⁹ light emission,¹⁰⁻¹² radiation detection¹³⁻¹⁷ and lasing.¹⁸⁻¹⁹ The 3D halide perovskite structure has the general formula AMX_3 , composed of a 3D network of corner-sharing metal halide $[MX_6]^{4-}$ octahedra with the A-site cation occupying the center of the cuboctahedral cavities. A is one of the monovalent cations: Cs^+ , $CH_3NH_3^+$ (MA^+), $HC(NH_2)_2^+$ (FA^+) or recently $CH_3NH_2NH_2^+$ ²⁰⁻²¹ and $(CH_2)_2NH_2^+$,²² M is a divalent metal (Ge^{2+} , Sn^{2+} , Pb^{2+})²³ and X is a halide (Cl^- , Br^- , or I^-).²⁴⁻²⁵ Consequently, the compositional tailoring of 3D halide perovskites is limited to small, hydrophilic organic cations that render the material to being moisture sensitive.²⁶⁻³² Lastly, 3D halide perovskites crystallize in high-symmetry cubic space groups with phase transitions affording the tetragonal and orthorhombic polymorphs.³³⁻³⁶

Recently, a new class of 3D metal halide compounds have been investigated that incorporate diammonium cations larger than the A-site cation, affording a 3D network of both corner-sharing and edge-sharing connecting of $[MX_6]^{4-}$ octahedra.³⁷⁻⁴⁵ These compounds are referred to as perovskitoids as they display multiple attributes similar to 3D perovskites due to the corner-sharing $(M_2X_2X_{8/2})_{\infty}^{2-}$ frameworks, however they are lower in symmetry adapting mainly orthorhombic or monoclinic space groups.³⁸⁻⁴² Beyond the 3D perovskitoids, there is a meager amount of other octahedral structural motifs of 3D hybrid lead halide compounds reported with no design principles on how to rationally expand this phase space. Specifically, $(Et_2NHC_6H_4-CH_2C_6H_4NHEt_2)_{2n}(Pb_7I_{18})_n \cdot 4nH_2O$ is an open framework structure exhibiting photochromism that belongs to the monoclinic $C2/c$ space group, which displays edge-sharing $[PbI_6]^{4-}$ octahedra interlinking at a crystallographic inversion center to form incomplete cubane chains along the $[110]$ or $[1\bar{1}0]$ direction.⁴⁶ $(H_2DABCO)(Pb_2Cl_6)$ and $(H_3O)(Et_2-DABCO)_8(Pb_{21}Cl_{59})$ ($DABCO : \frac{1}{4}$ 1,4-diazabicyclo[2.2.2]-octane) are 3D structures belonging to the tetragonal space group $P4_32_12$ and monoclinic space group $P2_1/c$ respectively with corner-sharing $[PbCl_6]^{4-}$ octahedra forming nodes that demonstrate a high color rendering index of white-light emission.⁴⁷ Finally, $(HOOC(CH_2)_3NH_3)PbI_3$ is 3D structure displaying thermochromism that belongs to the orthorhombic space group $Imma$, which presents an inorganic unit of edge-sharing and face-sharing $[PbI_6]^{4-}$ octahedra that ultimately form a diamond-like 3D framework.⁴⁸

The 3D hybrid halide perovskite structure can be dimensionally reduced to layers of 2D structure,^{29, 43, 49-55} chains of 1D structure⁵⁶⁻⁶⁰ or 0D clusters of $[MX_6]^{4-}$ octahedra⁶¹⁻⁶⁴ through the incorporation of diverse organic cations. These organic cations are larger than the aforementioned A-site cations, permitting a vast compositional space of structural tunability for the synthesis of new hybrid halide materials for optoelectronic and technological applications^{52-53, 65-76} Despite the expandable phase space, the reported bulk, hybrid metal halide perovskite-related frameworks mainly features aliphatic or aromatic organic cations that are not optically active and do not contribute to the luminescent properties of the hybrid material.^{20-21, 49, 51, 60, 77-86} Whereas the incorporation of organic luminophores is comparatively a much more narrow phase space with insufficient structural design principles to guide the rational synthetic design of functional hybrid materials.^{66, 68, 87-92} In order to establish greater structural complexity in luminescent hybrid metal halides while significantly enhancing the moisture stability of the resultant compounds, it is desirable to template sophisticated hybrid halide compounds with optically active organic cations.^{66, 89-90, 92-94} Thus far, only a handful of low dimensional water-stable hybrid halide perovskites have been reported such as (1,8-octyldiammonium)Sn₂I₆ that is water stable for at least 15 hrs,⁶⁹ $[Pb_2Cl_2]^{2+}[^-O_2C(CH_2)_4CO_2^-]$ that is water stable for 24 hrs,⁹⁵ [N-methyladabconium]PbI₃ that is water stable for 1 month⁹⁶ and (4,4'-ethylenedipyridinium)Pb₂Br₆ that is water stable for 180 days.⁹³

Herein, we demonstrate that hybrid metal halides can acquire unusually high structural complexity and cubic symmetry by incorporating the symmetric triamine luminophore 1,3,5-tris-(4-aminophenyl)benzene, hereby symbolized T. We establish a new class of water-stable hybrid metal halide compounds with the T triammonium cation, where T is a π -electron rich molecule with a C_3 -symmetric propeller shape and inherent optical and high dielectric nature.⁹⁷ Through a one-step solvothermal synthesis in ethanol, the T cation *in-situ* ethylates all three amine sites to give the T-Et₆ trication, producing the cubic (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) compounds. The provided synthetic preparation provides a viable avenue to fine tune the organic luminophore and the inorganic lattice in the solid-state, yielding new hybrid structural motifs. (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) present an unprecedented framework of $[Pb_{11}X_{31}]^{9-}$ 1D chains inlaid with (T-Et₆)³⁺ cations that build altogether a 3D topology. The electronic structure of (T-Et₆)₃Pb₁₁I₃₁ shows the density of states' final relocalization resulting in essentially flat bands within the VB and CB. (T-Et₆)₃Pb₁₁I₃₁ presents an absorption edge at 1.9 eV with weak broad emission centered at ~660 nm at 78K.

Through ambient-pressure solution synthesis, adjustable structural variations of 0D structures with T^{3+} cations are acquired, yielding compounds $T_7Pb_3Br_{27}\cdot DMF$ and $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$. Owing to the incorporation of T^{3+} cations, $T_7Pb_3Br_{27}\cdot DMF$ and $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$ feature blue PL emission at room temperature. All four novel compounds exhibit moisture-stability. $(T-Et_6)_3Pb_{11}I_{31}$ is the only known 3D hybrid lead halide with water stability to our knowledge. Our work establishes the synthetic design of sophisticated and water-stable hybrid semiconductors with high-symmetry luminophores that render unique structural motifs, optoelectronic features, and moisture stability.

Experimental Section

All starting materials for synthesis were purchased commercially and were used without further purification. $Pb(CH_3COO)_2\cdot 3H_2O$ (99.9%), NaI, NaBr, Ethyl alcohol, 1,3,5-Tris(4-aminophenyl)benzene, hydroiodic acid (HI) (57 wt % in H_2O , distilled, stabilized, 99.95%), hydrobromic acid (ACS reagent, 48 wt % in H_2O) and hypophosphorous acid solution (50 wt % in H_2O) were purchased from Sigma-Aldrich and used as received.

Synthesis of $(T-Et_6)_3Pb_{11}I_{31}$: Lead acetate trihydrate (0.2 mmol, 75.9 mg), 1,3,5-Tris(4-aminophenyl)benzene (0.06 mmol, 20 mg), and NaI (0.2 mmol, 30 mg) were weighed and placed in a teflon chamber. 0.25 mL of HI and 5 mL of anhydrous ethanol were added, after which the teflon chamber was sealed inside a stainless-steel chamber. The reaction mixture was heated at $160^\circ C$ for 6 days and cooled for 24 hours. The teflon chamber was opened and found to have precipitated brown-yellow rod-like crystals.

Synthesis of $(T-Et_6)_3Pb_{11}Br_{31}$: Lead acetate trihydrate (0.2 mmol, 75.9 mg), 1,3,5-Tris(4-aminophenyl)benzene (0.06 mmol, 20 mg), and NaBr (0.2 mmol, 20.5 mg) were weighed and placed in a teflon chamber. 0.25 mL of HBr and 5 mL of anhydrous ethanol were added, after which the teflon chamber was sealed inside a stainless-steel chamber. The reaction mixture was heated at $160^\circ C$ for 6 days and then cooled for 24 hours. The teflon chamber was opened and found to have precipitated orange block crystals along with yellow needle crystals.

Synthesis of $T\cdot 3HBr$: 1,3,5-Tris(4-aminophenyl)benzene (0.15 mmol, 50 mg) was added to 2 mL HBr and heated at $200^\circ C$. A clear yellow solution was formed, and the solution became white over a continual heating period. The reaction mixture was allowed to cool to room temperature,

afterwards the cooled mixture was vacuum filtered and dried under vacuum. The solid yield after drying was 57.2 mg.

Synthesis of $T_7[PbBr_6]_3Br_9 \cdot DMF$: PbO (1 mmol, 223 mg) was dissolved in 5 mL HBr by heating to boiling at 200°C under constant magnetic stirring until a clear solution was obtained. 1,3,5-Tris(4-aminophenyl)benzene (0.06 mmol, 20 mg) and 1 mL DMF were added to the reaction mixture. A cloudy white precipitate crashed out, which turned pale cloudy pink upon continuous heating. The hotplate and stirring were then turned off, and the reaction solution was cooled to room temperature; Clear, thin needle crystals precipitated from the mixture. The reaction mixture was vacuum filtered and dried under vacuum.

Synthesis of $T_2Sn_3Br_{18} \cdot 4H_2O \cdot 0.5Br_2$: $SnCl_2 \cdot 2H_2O$ (1 mmol, 225.64 mg) was dissolved in a mixture of 4 mL HBr and 2 mL H_3PO_2 by heating to boiling at 200°C under constant magnetic stirring until a clear solution was obtained. 1,3,5-Tris(4-aminophenyl)benzene (0.1 mmol, 35 mg) was added to the reaction mixture. A cloudy yellow precipitate crashed out. The hotplate and stirring were then turned off, and the reaction solution was cooled to room temperature; Tiny yellow-clear needle crystals precipitated from the mixture. The reaction mixture was vacuum filtered and dried under vacuum.

Results and Discussion:

Synthetic Aspects:

Attempts to synthesize various dimensionality (1D, 2D or 3D) lead halide compounds incorporating the triamine molecule, T, through the classic solution synthesis at ambient-pressure by employing hydrohalic acid would not yield any crystalline product. The solubility of T in HX solvent is limited so DMF was added to the synthesis under heating and stirring. In the case of the HI/DMF solution, yellow crystals of $DMA Pb_3$ (DMA: dimethylamine) form as a result of the hydrolysis of DMF in heated hydroiodic acid that is known in the literature.⁹⁸⁻⁹⁹ In the case of the HBr/DMF solution, a new colorless compound incorporating T is formed with formula $T_7Pb_3Br_{27} \cdot DMF$ that has a 0D structure as verified by single crystal X-ray diffraction (See *Crystal Structure* Section below). Lastly, in order to obtain other hybrid metal halide compounds incorporating T, solution synthesis at ambient pressure was undertaken using $SnCl_2 \cdot 2H_2O$ and T in a HBr/ H_3PO_2 solution that yielded light-yellow needle crystals of the 0D structure

$T_2Sn_3Br_{18} \cdot 4H_2O \cdot 0.5Br_2$. Details of the syntheses of $T_7Pb_3Br_{27} \cdot DMF$ and $T_2Sn_3Br_{18}$ are in the *Experimental Section*.

Brown-yellow crystals of $(T-Et_6)_3Pb_{11}I_{31}$ and orange-yellow crystals of $(T-Et_6)_3Pb_{11}Br_{31}$ (**Figure 1D** and **Figure 1E**) were successfully obtained from solvothermal treatment of T, $Pb(CH_3COO)_2 \cdot 3H_2O$ and NaX (X=I, Br) in ethanol and HX (X=I, Br) at 160°C for 6 days. Details of the exact syntheses are in the *Experimental Section*. $Pb(CH_3COO)_2 \cdot 3H_2O$ is the source of Pb^{2+} and NaX (X=I, Br) is the source of X^- halide anion in the syntheses. Hydroiodic acid (HI) and hydrobromic acid (HBr) are employed respectively to protonate the triamine molecule T in a ratio 20:1 solvent to HX, overall leading to the creation of an acidic environment for the solvothermal synthesis. As a result of the acidic synthetic conditions,⁷³ the triamine molecule T undergoes a one-step, *in situ* N-diethylation reaction with the excess ethanol solvent to form the N-hexa-ethylated species $(T-Et_6)^{3+}$ (**Scheme 1**). It is noteworthy that the solvothermal conditions along with the obtained N-hexa-ethylated species $(T-Et_6)^{3+}$ serve a critical role in the self-assembly of the acquired $(T-Et_6)_3Pb_{11}X_{31}$ (X=I, Br) products. Single crystal X-ray diffraction (**Figure 1**) and NMR spectroscopy (**Figure S17**) verify the existence of the $(T-Et_6)^{3+}$ molecule in compounds $(T-Et_6)_3Pb_{11}X_{31}$ (X=I, Br). The reproducibility of the synthesis of $(T-Et_6)_3Pb_{11}X_{31}$ (X=I, Br) was confirmed where after multiple repetitions of the solvothermal reactions, all the experimental powder X-ray diffraction (PXRD) patterns match the simulated pattern of $(T-Et_6)_3Pb_{11}I_{31}$ (**Figure S6**). Therefore, the solvothermal synthetic technique can provide efficient routes to hybrid metal halide compounds that significantly enriches the phase space of perovskite-related compounds beyond the limited currently known structure types.

Powder X-ray diffraction verified the acquisition of the titled compounds with a small impurity phase present at $2\theta=9^\circ$ that could not be identified (**Figure S1** and **Figure S2**). Under the microscope, there is no apparent secondary phase that can be identified for the case of $(T-Et_6)_3Pb_{11}I_{31}$. The synthesis of $(T-Et_6)_3Pb_{11}Br_{31}$ yielded a distinct secondary phase of yellow needles. Single crystal X-ray diffraction analysis showed this phase is a cubic 3D assembly of lead halide chains templated by the T-Et₆ trications.

Description of Crystal Structures:

Compounds with 3D Cubic Topology

(T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) represent a unique structure type and new class of hybrid lead halide compounds with 3D cubic topology formed from purely octahedral units of 1D lead halide chains (**Figure 1**). The 3D topology of (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) consists of the complex [Pb₁₁X₃₁]⁹⁻ 1D chain that serves as the building block of the inorganic framework. The [Pb₁₁X₃₁]⁹⁻ chain features 5 consecutive face-sharing [PbX₆]⁴⁻ units connected to a cluster of 6 edge-sharing [PbX₆]⁴⁻ units (**Figure 1B**). The [Pb₁₁X₃₁]⁹⁻ chains do not bond to each other but instead weave a 3D tangled network that can be analogized to fabric weaves (**Figure 1A**). The 3D topology in (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) has cubic symmetry (*Ia* $\bar{3}$ space group in this case) that is unique. To our knowledge, there are no reports of hybrid lead halide compounds with high-symmetry cubic space groups, besides the well-known family of 3D hybrid lead halide perovskites, which belong to the cubic space group *Pm* $\bar{3}$ *m* and feature purely 3D corner-sharing motifs of [PbI₆]⁴⁻ octahedra.¹⁰⁰ For this new structure type of (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br), the high cubic symmetry is directed by the novel organic molecule (T-Et₆)³⁺ and their three-fold symmetry (**Scheme 1**). It is important to make a distinction between the dimensionality of structural units and overall topology of the structure. (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) are hybrid compounds consisting of secondary units of organic and inorganic chains. The organic framework of (T-Et₆)³⁺ cations embedded within the homogeneous cubic packing of the inorganic [Pb₁₁X₃₁]⁹⁻ 1D chains produces the resultant, hybrid compounds (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) that form an overall 3D topology. The topology of the structure without chain overlaps can only be represented in 3D space, thus this crystal structure has 3D (but 1-periodic) topology based on 1D structural units.

The triamine-based molecules' high symmetry and greater ability for electrostatic interactions leads to the unique, high symmetry self-assembly of the result hybrid organic-inorganic network. The four [Pb₁₁X₃₁]⁹⁻ chains run along the [1,0,0], [0,1,0], [0,0,1] and [1,1,1] directions and are all related to each other by symmetry. O'Keeffe et al., have developed an analytical description of homogenous packings of cubic cylinder motifs,¹⁰¹⁻¹⁰² where the term "cylinder packing" refers to the infinite packings of 1D cylinder motifs in which each cylinder relates to all the others by crystallographic symmetry operations. The (T-Et₆)₃Pb₁₁X₃₁ structures belong to the non-bundle <111> cylinder packings¹⁰² (Type No.1) with 4 cylinder chains [Pb₁₁X₃₁]⁹⁻ within the unit cell.¹⁰² The 4 cylinder chains can be described based on the body diagonal cylinder lengths that fall within one cubic unit cell, where along the [111] direction in the (T-Et₆)₃Pb₁₁X₃₁ structures there are one full [Pb₁₁X₃₁]⁹⁻ chain and 6 halves chains resulting in 4

chains altogether. Furthermore, the symmetry in O’Keeffe et al.,¹⁰² is an idealized (highest) symmetry for the non-bundle $\langle 111 \rangle$ cylinder packings that can be lowered in real chemical systems. As a result, the $(\text{T-Et}_6)_3\text{Pb}_{11}\text{X}_{31}$ structures that crystallize in the $Ia\bar{3}$ space group correspond to the Type 1 $\langle 111 \rangle$ cylinder packing with idealized $Ia\bar{3}d$ space group¹⁰².

On the other hand, from a symmetry viewpoint, the $Ia\bar{3}$ cubic space group (T_h) corresponds to a slightly lower symmetry than the $\text{Pm}\bar{3}m$ space group (O_h) lacking essentially four-fold axes. Nevertheless, the crystallographic structure exhibits three-fold symmetry axes, as this symmetry operation finds its origin in each sub-network of 1D $[\text{Pb}_{11}\text{X}_{31}]^{9-}$ lead halide chains. Indeed, the sub-network of 1D lead halide chains is related to the trigonal R space group, where the triamine-based molecules maintain this symmetry. The electronic properties of the whole structure may be indeed understood by considering firstly those of each sub-network of 1D lead halides, and then the coupling between the four $[\text{Pb}_{11}\text{X}_{31}]^{9-}$ chains in the composite structure (vide infra, see **S.I.** Section 3.5 *Electronic Calculations*).

Significantly, halide atoms I5 and Br5 in the structure have a very rare octahedral coordination where they are sitting in the center of a Pb-X fragment with a NaCl-type motif (**Figure 1C**). Of the other known examples of an iodine atom in octahedral coordination within a hybrid lead halide $[\text{Pb}_6\text{I}_{19}]$ cluster is the example with viologen molecules¹⁰³⁻¹⁰⁴ of 1D structures such as $(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{Pb}_2\text{I}_6$ where $\text{C}_{12}\text{H}_{14}\text{N}_2$ is methylviologen and the Pb^{2+} features both octahedral and trigonal prismatic coordination within the inorganic framework¹⁰³, as well as $(\text{C}_4\text{H}_9\text{N})_8\text{Pb}_{18}\text{I}_{44}$ ¹⁰⁵. Overall, between the two analogues compounds $(\text{T-Et}_6)_3\text{Pb}_{11}\text{X}_{31}$ ($\text{X}=\text{I}, \text{Br}$) bromide compound $(\text{T-Et}_6)_3\text{Pb}_{11}\text{Br}_{31}$ unit cell dimensions are 0.792 Å smaller and its volume is 2706.39 Å³ smaller than $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ (**Table 1**). Additionally, there is notable elongation of the Pb-X bond lengths within the $[\text{Pb}_{11}\text{X}_{31}]^{9-}$ framework with an average bond length of Pb-I equal to 3.213 Å and even more dramatic elongation for the bromide compound with an average bond length of Pb-Br equal to 3.086 Å (**Table 2**). In comparison the average Pb-X length in 3D halide perovskites is around 3.15 Å for Pb-I bonds and 2.97 Å for Pb-Br bonds.²⁴

Viewing the crystal structure $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ along the [100] direction (**Figure 2A**) demonstrates how the $[\text{Pb}_{11}\text{X}_{31}]^{9-}$ 1D chain intercross at various orientations, where the $[\text{Pb}_{11}\text{I}_{31}]^{9-}$ chains shaded with the same color are directed in the same orientation. The contact distance between the $[\text{Pb}_{11}\text{I}_{31}]^{9-}$ chains is 4.486 Å for $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ (**Table 2**), as shown in **Figure 2B**. The

molecular three-fold axis of the organic cations $(\text{T-Et}_6)^{3+}$ coincides with the three-fold axis of the unit cell. The shortest nitrogen-iodine distance in $(\text{T-Et}_6)\text{Pb}_{11}\text{I}_{31}$ is $\text{N3-I2} = 3.701 \text{ \AA}$ implying a significant $\text{I}\cdots\text{H}$ hydrogen bonding. The closest contact of a nitrogen atom on the $(\text{T-Et}_6)^{3+}$ molecule to an aromatic carbon atom from an adjacent $(\text{T-Et}_6)^{3+}$ molecule is 4.803 \AA . The closest distance of aromatic carbon atoms from adjacent $(\text{T-Et}_6)^{3+}$ cations 5.623 \AA , indicating that π - π stacking is not apparent. On the other hand, for the $(\text{T-Et}_6)_3\text{Pb}_{11}\text{Br}_{31}$ compound, the contact distance between the $[\text{Pb}_{11}\text{Br}_{31}]^{9-}$ chains is 4.852 \AA , a slightly larger distance than in the iodide analog despite the smaller unit cell dimension and volume of $(\text{T-Et}_6)_3\text{Pb}_{11}\text{Br}_{31}$ (**Table 2**). However, the nitrogen-bromide distance is smaller with $\text{N1-Br3} = 3.488 \text{ \AA}$ consistent with significant $\text{Br}\cdots\text{H}$ hydrogen bonding, and the closest contact of a nitrogen atom on the $(\text{T-Et}_6)^{3+}$ molecule to an aromatic carbon atom from an adjacent $(\text{T-Et}_6)^{3+}$ molecule is 1.596 \AA . Due to the cubic symmetry, the contact angle between $[\text{Pb}_{11}\text{X}_{31}]^{9-}$ chains in both $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ and $(\text{T-Et}_6)_3\text{Pb}_{11}\text{Br}_{31}$ are identical at 70.53° .

Reversible-cycle differential scanning calorimetry (DSC) was performed on $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ crystal sample in the temperature range of -50°C to 120°C to identify any phase transitions. Temperature-dependent phase transitions are a frequent phenomenon in hybrid halide perovskites. From the DSC measurements, it was possible to identify a reversible-phase transition for $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ that presents an endothermic peak at -24°C (**Figure S8**). The sharp shape of the transition peaks presents the characteristic of a first-order transition.

Compounds with 0D Topology

The crystal structures of 0D compounds $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ and $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{Br}_2$ containing the T molecule were obtained from the solution synthesis on a hotplate at ambient pressure (**Figure 3**). Single crystal X-ray diffraction demonstrates that $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ is essentially a double salt with T^{3+} cations between the isolated $[\text{PbBr}_6]^{4-}$ octahedra and with bromine atoms coordinated to DMF molecules such as the chemical formula can also be described as $\text{T}_7[\text{PbBr}_6]_3[\text{Br}]_9\cdot\text{DMF}$. The PXRD of the experimental pattern of the $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ crystals matches the simulated pattern derived from the single crystal X-ray structure (**Figure S4**). Furthermore, $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{Br}_2$ is also a 0D structure featuring isolated tin bromide octahedra with T^{3+} cations between with Sn^{4+} oxidation state. Additionally, in $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{Br}_2$, the bromide atoms of the $[\text{SnBr}_6]^{2-}$ octahedra are coordinated to water molecules and the Br_2 moiety

forms hydrogen bonds with the ammonium groups of the T^{3+} cations. The experimental PXRD pattern of $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$ crystals matches the simulated pattern, verifying the phase acquisition (**Figure S5**). Interestingly, higher dimensionality compounds than 0D could not be acquired through the solution synthesis at ambient-pressure, suggesting that the bonding of such large hydrocarbon amines have weak electrostatic interaction with the lead-halide frameworks, despite the beneficial attributes of π -conjugation, aromaticity, and polyamine groups. In the case of the solvothermal synthesis, the additive effect of high vapor pressure which results in the full ethylation of the amino groups on the T molecule proves to be critical in acquiring the 3D compounds $(T-Et_6)_3Pb_{11}X_{31}$ ($X=I, Br$).

Stability:

A limiting factor in the development of 3D hybrid halide perovskite devices for optoelectronic applications is their long-term stability under operating conditions. Introducing more hydrophobic and bulky organic cations endows enhanced stability in the resultant lower-dimensional congeners of 2D perovskites and even lower dimensional 1D- and 0D-related frameworks.^{29, 32, 52-53} Thus, there is broad interest in hybrid lead halide compounds with moisture stability. The $(T-Et_6)_3Pb_{11}X_{31}$ ($X=I, Br$) with its bulky, hydrophobic $(T-Et_6)^{3+}$ cations and 3D topology provides a rare example of a water stable system. Crystals of $(T-Et_6)_3Pb_{11}I_{31}$ retain their structural integrity after being exposed to ambient air in the dark for three months, as it can be seen in the PXRDs of **Figure 4A**. Moreover, $(T-Et_6)_3Pb_{11}I_{31}$ crystals were added to a vial with water and after 7 days the collected PXRD pattern showed no structural decomposition (**Figure 4B**). Moreover, the 0D compounds $T_7[PbBr_6]_3\cdot [Br]_9\cdot DMF$ and $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$ also maintain their structural integrity upon prolonged exposure to ambient air upon PXRD observation.

Optical Properties:

The optical bandgaps of the synthesized compounds are extrapolated from the absorption onset based on the optical absorption spectra shown in **Figure 5** and **Figure S11**, which were measured at room temperature. They are estimated by extrapolating from the absorption edges, a slope perpendicular to the x axis. Compound $(T-Et_6)_3Pb_{11}I_{31}$ exhibits one absorption edge with estimated bandgap 1.72 eV. The protonated triamine $T\cdot 3HBr$ feature two absorption edges with an estimated bandgap 2.24 eV. The 0D compound $T_7Pb_3Br_{27}\cdot DMF$ displays three absorption edges

with an estimated bandgap 2.75 eV. $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$ displays two absorption edges with estimated bandgap 2.40 eV. Summary of the optical properties of the materials are outlined in **Table 3**. Weak absorption may be due to the observed absorption being dominated not by a band edge transition but rather it is highly convoluted owing to the presence of the organic component. The absorption spectrum of the protonated amine is presented in **Figure 5** and this spectrum shows considerable spectral overlap with the metal halide compounds presented here, complicating an assignment of peaks with the current data. To further our understanding of this new structural family of hybrid metal halides will require more detailed investigations of their optical properties in a separate study.

The photoluminescence (PL) emission spectra of the 3D triamine lead halides (**Figure 6**) and 0D triamine lead halide compounds (**Figure 7**) were collected at room temperature. The photoluminescence properties of the pure triamine molecule T (**Figure S9 A,B**) and the protonated triamine T·3HBr species (**Figure S9 C,D**) are given in the **S.I**. The protonated triamine T·3HBr species shows a red-shift in the emission properties as compared to the T species consistent with what is observed in the absorption data (**Figure S9**). Further details on the optical properties of amino substituted triphenylbenzene derivatives with a 3-fold symmetry (like ours) has been reported elsewhere.¹⁰⁶

Compound $(T-Et_6)_3Pb_{11}I_{31}$ did not display any measurable photoluminescence at room temperature; however, emission was observed at 78 K (**Figure 6A**). Two peaks are observed at this temperature, a strong narrow emission centered at 750 nm, and a weak broad emission at higher energy centered at ~660 nm, thus indicating a more complex PL mechanism with some of this luminescence arising from traps. Further assignment of this high-energy emission band is beyond the scope of this work and a more detailed study on the temperature-dependent optical properties of this compound is required. The narrow, low energy emission peak displays slow biexponential recovery kinetics with a fast 51 ns and a slow 1.3 μ s component (**Figure 6B**). The observed emission at 750 nm at low temperature is found well below the estimated optical bandgap of the material (1.72 eV); however, we note that the band gap is measured at RT whereas the emission is measured at 78 K.

The $T_7[PbBr_6]_3[Br]_9\cdot DMF$ compound (**Figure 7**) displays blue emission at 404 nm when excited at 330 nm. When excited at 405 nm, the compound displays broad emission centered at ~520 nm. These two bands are assigned to different origins with the high-energy narrow band

assigned to localized $[\text{PbBr}_6]^{4-}$ -based emission and the low energy broad band to T-based emission. Furthermore, photoluminescence excitation spectra support that these two luminescence features have distinct origins. The excitation spectrum monitoring the 404 nm-centered emission shows two strong bands at ~ 290 and ~ 350 nm that are consistent with the reported electronic transitions in isolated $[\text{PbBr}_6]^{4-}$ octahedra in the 0D Cs_4PbBr_6 material further supporting our assignment of this emission.¹⁰⁷⁻¹⁰⁸ The excitation spectrum monitoring the 520 nm-centered emission shows one broad band centered at ~ 400 nm that tails into the visible and supports our assignment that these two emissions share separate electronic origins. We suspect that this emission arises from the T^{3+} species within the $\text{T}_7[\text{PbBr}_6]_3[\text{Br}]_9 \cdot \text{DMF}$ material as it shares similar emission characteristics to that $\text{T} \cdot 3\text{HBr}$. Both features display fast recombination dynamics with lifetimes of <1 , 1.8, 8.1 ns for the 404 nm band and <1 , 1.5, 4.4 ns for the 520 nm band (the first component is IRF limited and cannot be further determined).

The luminescence properties of the 0D tin compound, $\text{T}_2\text{Sn}_3\text{Br}_{18} \cdot 4\text{H}_2\text{O} \cdot 0.5\text{Br}_2$, are presented detailed in the Supporting Information (**Figure S10**). This compound displays a single very broad luminescence feature centered at ~ 710 nm with a FWHM of 200 nm. This emission is long-lived and shows triexponential decay dynamics with lifetimes of 2.2 ns, 138 ns, and 1.4 μs , with an average decay time of 1.2 μs . The excitation spectrum corresponding to this emission shows a strong feature at ~ 350 nm that is consistent with absorption in isolated $[\text{SnBr}_6]^{2-}$ octahedra.¹⁰⁹ Based on the breadth and long lifetime of this feature, we assign it to self-trapped excitonic emission, which is further consistent with reports of luminescence in the 0D Cs_4SnBr_6 system.¹⁰⁹

Valence Band Maximum (VBM) Energy:

Photoemission yield spectroscopy in air (PYSA) was utilized to measure the absolute VBM energy of the materials in order to derive the band energy diagrams of the studied materials (**Figure 8**).¹¹⁰⁻¹¹¹ The position of the VBM in the band energy diagrams was determined through the PYSA measurements, while the conduction band minimum (CBM) was determined by subtracting the corresponding band gap values (based on the absorption edge) from the measured VBM energies. The VBM of $\text{T} \cdot 3\text{HBr}$ a smaller value of -5.77 in comparison to -5.57 of T. 0D compounds $\text{T}_7\text{Pb}_3\text{Br}_{27} \cdot \text{DMF}$ and $\text{T}_2\text{Sn}_3\text{Br}_{18} \cdot 4\text{H}_2\text{O} \cdot 0.5\text{Br}_2$ have close VBM values of -5.64 and -5.55

respectively. Given the similar range in value of the VBM for (T-Et₆)₃Pb₁₁I₃₁ (-5.62) to the 0D compounds, the reduced bandgap of this cubic compound is a result of the lowest unoccupied molecular orbital (LUMO) of the component (T-Et₆)³⁺ cations. Since the hydrogen bond donor amine-groups are electronically isolated from the aromatic moieties of the T-based molecules, the lower energy LUMO in (T-Et₆)₃Pb₁₁I₃₁ can be attributed to supramolecular effects.

Electronic Properties:

Rationalization of the electronic structure of (T-Et₆)₃Pb₁₁I₃₁ is provided by computational investigations based on density functional theory (DFT, see **S.I.**). The large cubic crystal structure, with unit cell dimension greater than 30 Å, is considered using the corresponding primitive cell in which the entangled [Pb₁₁I₃₁]⁹⁻ chains are now along (1,0,0), (0,1,0), (0,0,1) and (1,1,1), and that counts half the number of atoms. However, the resulting simulation cell remains too large (1212 atoms) to allow treatments beyond plain DFT, such as hybrid functionals, that would offer, for instance, a better description of the material's band gap.

The calculated band structure of (T-Et₆)₃Pb₁₁I₃₁ (**Figure 9A**) shows a band gap of 2.27 eV and essentially flat bands around the Fermi level with bandwidths of the order of 1 meV (**Figure S12**). Such a low dispersion, detrimental to charge carrier transport properties, can be expected when the corner-sharing connectivity of perovskites is substituted by face-sharing octahedra.⁸² The valence band maximum (VBM, **Figure 9B**) is distributed over the inorganic chains and illustrates the three-fold symmetry imposed by the $Ia\bar{3}$ space group. On the other hand, the conduction band minimum (CBM, **Figure 9C**) involves the π -system of organic cations (**Figure S13**) and no visible contribution from the lead and iodide atoms. This is confirmed looking at the sharp peak of (T-Et₆) states above the band gap in the projected density of states (pDOS, **Figure 9D** and **S14**). In addition, we observe that the VBM (**Figure 9B**) is formed by the contributions of the iodide dangling bonds found in the 6 edge-sharing octahedra cluster part of the inorganic network.

To explore further the electronic structure of (T-Et₆)₃Pb₁₁I₃₁, we carried out a crystal orbital Hamilton population (COHP) bonding analysis (**Figure 9E**).¹¹² We find a weak antibonding interactions between [Pb₁₁I₃₁]⁹⁻ chains, that are less than 5 Å apart, close to the Fermi level. This coupling also appears when considering the band structures of a sub-network of 1D halide chains, that present strictly non-dispersive bands (**Figure S15**). Then, when we add the sub-networks of

1D halide chains one after the other, we can see the energy dispersion increase. More importantly, the COHP analysis shows a significant bonding interaction between the inorganic network and T-Et₆ cations that are in close contact with the [Pb₁₁I₃₁]⁹⁻ chains (black line, **Figure 9E**). This strong coupling between the inorganic and organic moieties greatly affects the band structure and one can see that the cations tend to relocalize the valence states close to the Fermi level (**Figure S16**). Our computed bandgap (2.27 eV) is greater than the measured absorption edge (1.90 eV) and the low-temperature PL peak (1.65 eV). Since the GGA functional used here should lead to a significant bandgap underestimation, we can infer that the optical features cannot be assigned to band-to-band transitions but rather attributed the 0D character of the electronic density of states that may induce in turn a strong localization of excitonic resonance in the lattice.

Conclusions

Understanding how to acquire and tune novel structural motifs in functional hybrid materials with high structural complexity is necessary for predictive materials synthesis of well-defined structure-property relationships with technological relevance. The cubic lead halide frameworks of (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) based on the C₃-symmetric propeller-shaped triamine T: 1,3,5-tris-(4-aminophenyl)benzene form in ethanol by an efficient *in situ* N-diethylation and one-step reaction through solvothermal synthesis. These materials constitute a new structural class of hybrid lead halides with 3D topology. (T-Et₆)₃Pb₁₁X₃₁ (X=I, Br) consist of a unique structural motif of embedded (T-Et₆)³⁺ cations and [Pb₁₁X₃₁]⁹⁻ 1D chains composed of solely octahedral lead halide units with face- and edge-sharing connectivity. The octahedral lead halide subunits feature rare octahedral coordination environment of I5 and Br5 atoms within a Pb-X network with NaCl-type cell. The highly periodic structural class (T-Et₆)₃Pb₁₁X₃₁ expands current descriptive crystal chemistry with its homogenous cubic packing that can serve a basis for exploration of porous materials and for post-synthetic transformations in the solid state yielding multifunctional materials. The piece-by-piece electronic structure of (T-Et₆)₃Pb₁₁I₃₁ shows the weak interaction between chains, which eventually lead to flat valence bands because of the interaction between the chains and the organic cations from the conduction band. (T-Et₆)₃Pb₁₁I₃₁ exhibits an absorption onset at 1.72 eV with weak broad emission at centered at ~660 nm at 78K. In particular, the water stability of (T-Et₆)₃Pb₁₁I₃₁, due to the hydrophobic (T-Et₆)³⁺ cations, initiates a new synthetic strategy in the rational design of environmentally robust hybrid halides. Additionally, the synthetic exploration of hybrid metal halides based on T³⁺ cations demonstrates adjustable structural

variations of 0D structures through ambient-pressure solution synthesis, ensuing compounds $T_7Pb_3Br_{27}\cdot DMF$ and $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$. Despite their simple structural motifs of isolated $[MX_6]$ octahedra ($M=Pb^{2+}$, Sn^{4+}) with T^{3+} cations in between, both $T_7Pb_3Br_{27}\cdot DMF$ and $T_2Sn_3Br_{18}\cdot 4H_2O\cdot 0.5Br_2$ feature blue PL emission at room temperature as a result of embodying luminophore T. This study introduces the fundamental structural design principles for creating novel, periodic hybrid materials using metal halide compounds that incorporate highly symmetric luminophores with enhanced moisture stability. The connectivity modes of the metal-halide octahedra can be directed through tuning the organic and inorganic components, thereby enabling the fine-tuning of the electronic structure and optoelectronic properties of the resulting materials.

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Associated Content:

Supporting Information

Methods, complementary syntheses, additional structural and characterization data: nanoindentation data, single crystal and powder X-ray diffraction, electronic structure and dielectric calculations, optical data, NMR spectroscopy, SEM and microscope images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

X-ray crystallographic data for $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$, CCDC 2216515

X-ray crystallographic data for $(\text{T-Et}_6)_3\text{Pb}_{11}\text{Br}_{31}$, CCDC 2216514

X-ray crystallographic data for $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$, CCDC 2216512

X-ray crystallographic data for $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{Br}_2$, CCDC 2216513

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The authors declare no competing financial interest.

Figures:

Scheme 1. In situ N-Diethylation of T Luminophore

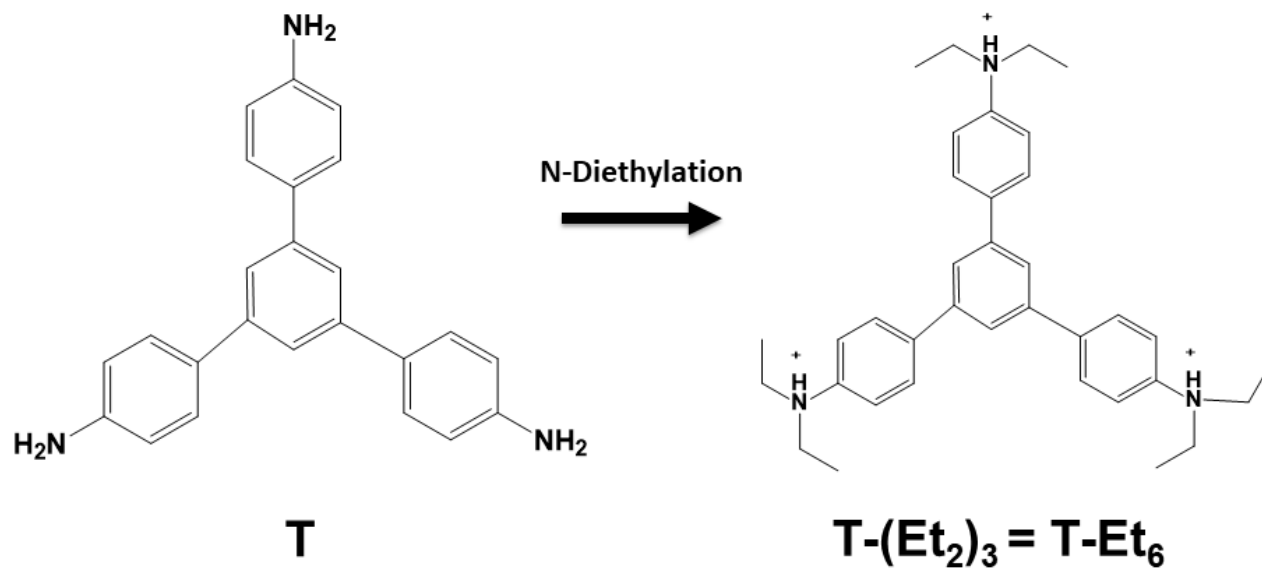


Table 1. Crystal Data and Structure Refinement for Novel (T-Et₆)₃Pb₁₁X₃₁ compounds

	(T-Et ₆) ₃ Pb ₁₁ I ₃₁	(T-Et ₆) ₃ Pb ₁₁ Br ₃₁
Empirical formula	C ₁₀₈ H ₁₁₇ N ₉ Pb ₁₁ I ₃₁	C ₁₀₈ H ₁₁₇ N ₉ Pb ₁₁ Br ₃₁
Crystal system	cubic	cubic
Space group	<i>Ia</i> $\bar{3}$	<i>Ia</i> $\bar{3}$
Crystal Shape and Color	Brown-Yellow Rod	Orange-Yellow Block
Unit cell dimensions (Å)	a = 32.78380(10)	a = 31.9220(2)
	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
Volume (Å ³)	35235.3 (3)	32529.0(6)
Z	8.00016	8.0016
Density (g/cm ³)	2.931	2.567
Independent reflections	8579 [R _{int} = 0.0459]	6710 [R _{int} = 0.0543]
Completeness to $\theta = 25.242^\circ$	99.9%	99.9%
Data k/ restraints / parameters	8579 / 7 / 204	6710 / 0 / 145
Goodness-of-fit	1.035	1.055
Final R indices [I > 2 σ (I)]	R _{obs} = 0.0494, wR _{obs} = 0.1235	R _{obs} = 0.0798, wR _{obs} = 0.2478
R indices [all data]	R _{all} = 0.0790, wR _{all} = 0.1394	R _{all} = 0.1366, wR _{all} = 0.2785

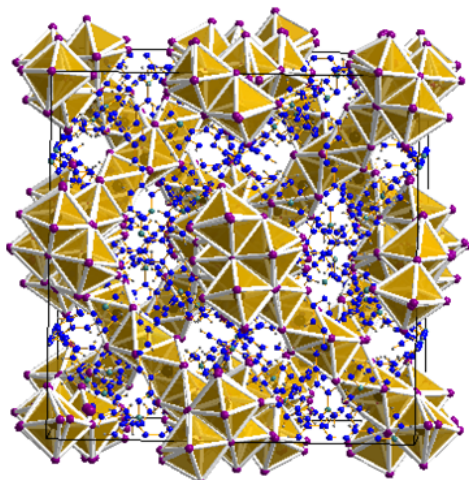
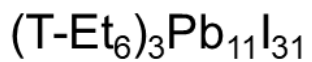
Table 2. Summary of structural parameters of novel (T-Et₆)₃Pb₁₁X₃₁ compounds

	(T-Et ₆) ₃ Pb ₁₁ I ₃₁	(T-Et ₆) ₃ Pb ₁₁ Br ₃₁
Average Pb-X Bond Length (Å)	3.213 Å	3.086 Å
Distance between 1D [Pb ₁₁ X ₃₁] ⁹⁻ Chains (Å)	4.486 Å	4.852 Å
Angle between 1D [Pb ₁₁ X ₃₁] ⁹⁻ Chains (°)	70.53 °	70.53 °

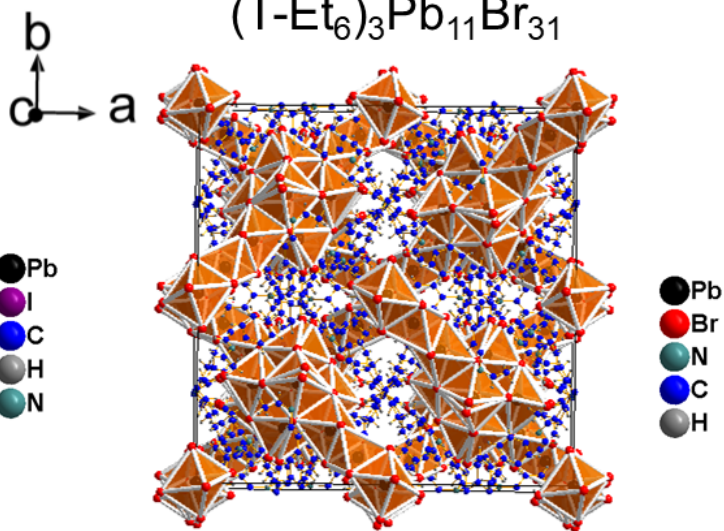
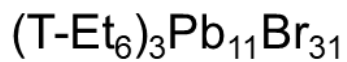
Table 3. Summary of optical properties of studied compounds

Compound	Extrapolated Bandgap (eV)	VBM (eV)	CBM (eV)
T	-	5.57	2.50
T·3HBr	2.24	5.77	2.40
(T-Et ₆) ₃ Pb ₁₁ I ₃₁	1.72	5.62	1.75
T ₇ Pb ₃ Br ₂₇ DMF	2.75	5.64	2.20
T ₂ Sn ₃ Br ₁₈ ·4H ₂ O·0.5Br ₂	2.40	5.55	2.45

A



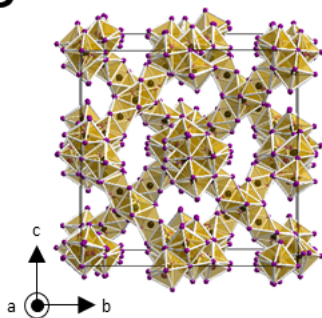
$a = 32.7838(1) \text{ \AA}; V = 35235.29(32) \text{ \AA}^3$



$a = 31.9220(2) \text{ \AA}; V = 32529.0(6) \text{ \AA}^3$

B

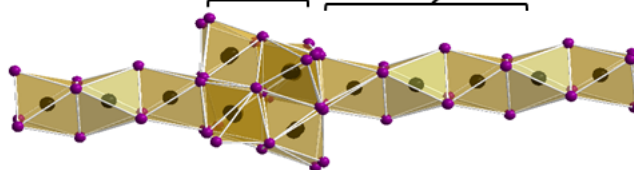
Inorganic network



= 4 x

Cluster of 6 edge-sharing octahedra with 1 I⁻ at the center of a Pb-octahedra

5 face-sharing octahedra chain



4 entangled chains along $(-1, 1, 1)$, $(1, -1, 1)$, $(1, 1, -1)$ and $(1, 1, 1)$

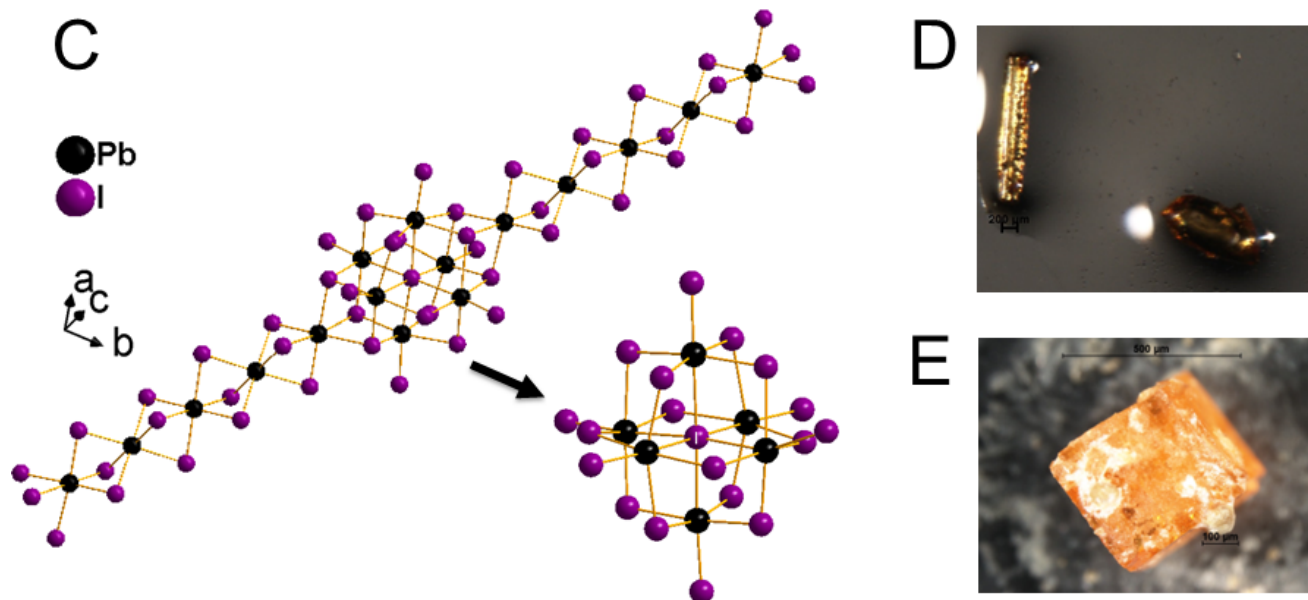


Figure 1. (A) Unit cell of crystal structures $(T-Et_6)_3Pb_{11}I_{31}$ and $(T-Et_6)_3Pb_{11}Br_{31}$ with 3D cubic topology viewed along the c-axis denoting the unit cell dimensions and volume respectively (B) Polyhedral view of $(T-Et_6)_3Pb_{11}I_{31}$ decomposed into its fundamental $[Pb_{11}I_{31}]^{9-}$ entanglement chain featuring 5 consecutive face-sharing $[PbI_6]^4$ units connected to a cluster of 6 edge-sharing $[PbI_6]^4$ units (C) View of repeating unit of $[Pb_{11}I_{31}]^{9-}$ chain highlighting the octahedral coordination environment of I5 atom within a NaCl-type $[Pb_6I_{19}]$ cluster along the ab plane (D) Microscope image of $(T-Et_6)_3Pb_{11}I_{31}$ crystal (E) Microscope image of $(T-Et_6)_3Pb_{11}Br_{31}$ crystal.

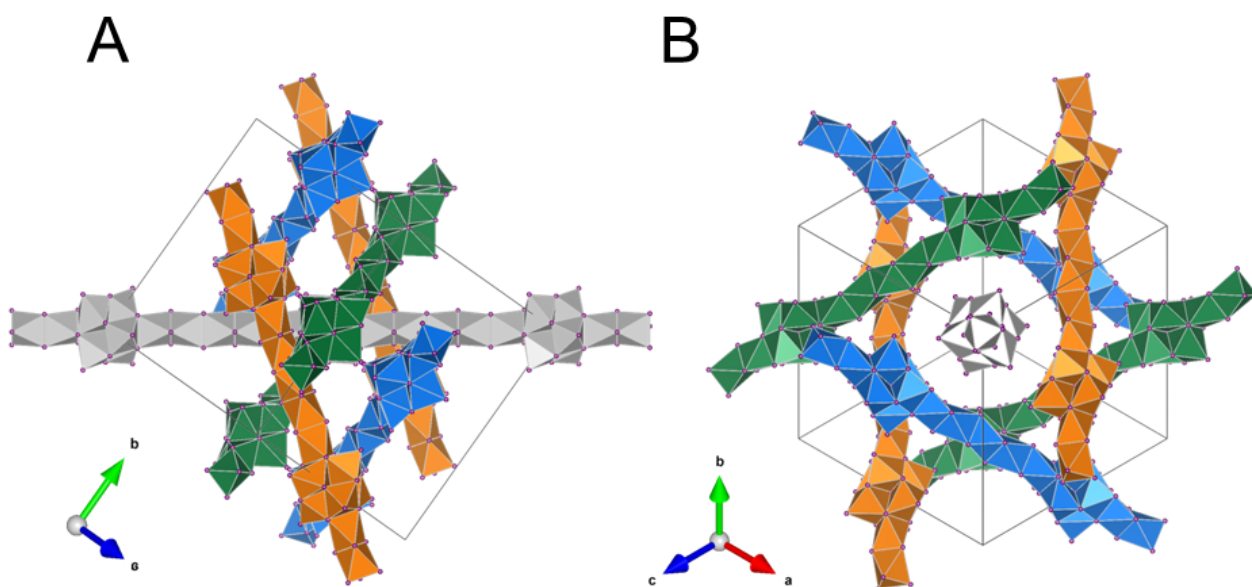


Figure 2. View of the different orientations of the distinct 1D $[\text{Pb}_{11}\text{I}_{31}]^{9-}$ entanglement chains in the $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ unit cell where the organic cations have been omitted in the depiction. The 1D $[\text{Pb}_{11}\text{I}_{31}]^{9-}$ chains with the same color are directed in the same orientation. **(A)** View from $[100]$ direction. Altogether the entanglement of the 1D $[\text{Pb}_{11}\text{I}_{31}]^{9-}$ chains gives rise to the 3D topology of compound $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$. **(B)** View along the $[111]$ direction where the distance between two distinct chains is 4.486 \AA and the angle between the chains is 70.53° .

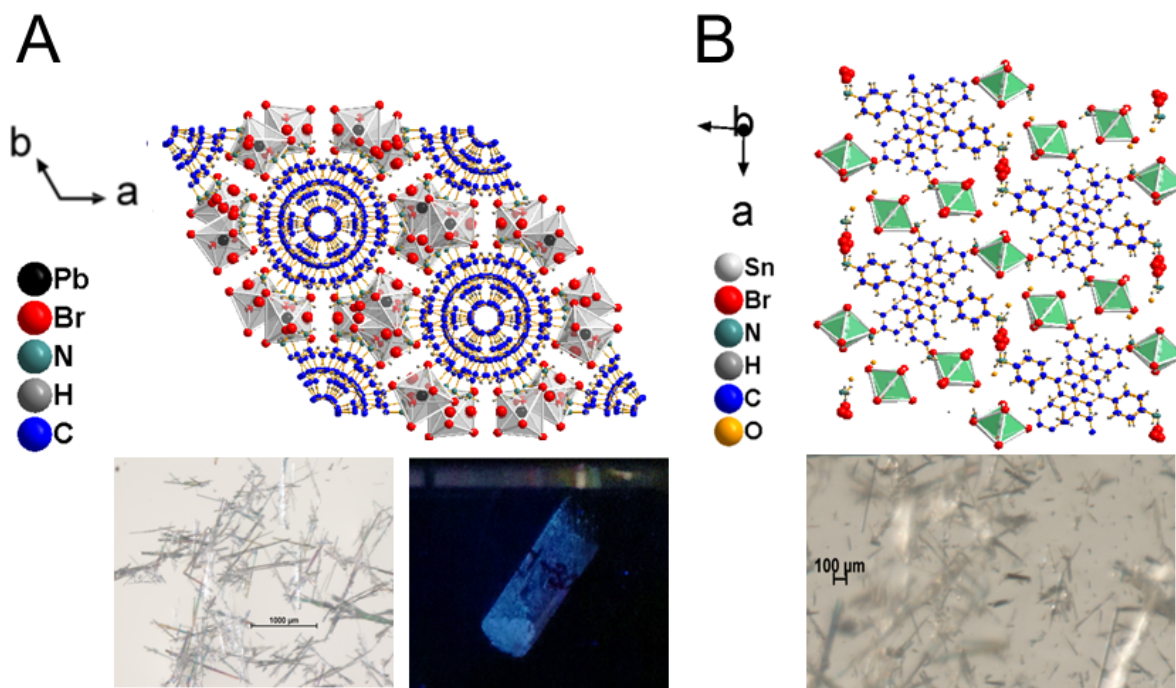


Figure 3. Crystal structure of 0D structures obtained through solution synthesis at ambient-pressure along with microscope image of crystals **(A)** $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ that belongs to $R-3c$ space group with unit cell dimensions $a = b = 29.014(2) \text{ \AA}$, $c = 34.682(4) \text{ \AA}$ and $\gamma = 120^\circ$. Microscope image of $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ crystals, followed by picture of vial of dried $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ crystalline powder under UV illumination in the dark. **(B)** $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}\cdot 0.5\text{Br}_2$ that belongs to $P2_1/n$ space group with unit cell dimensions $a = 17.436(15) \text{ \AA}$, $b = 7.362(6) \text{ \AA}$, $c = 30.01(3) \text{ \AA}$ and $\beta = 94.163(10)^\circ$.

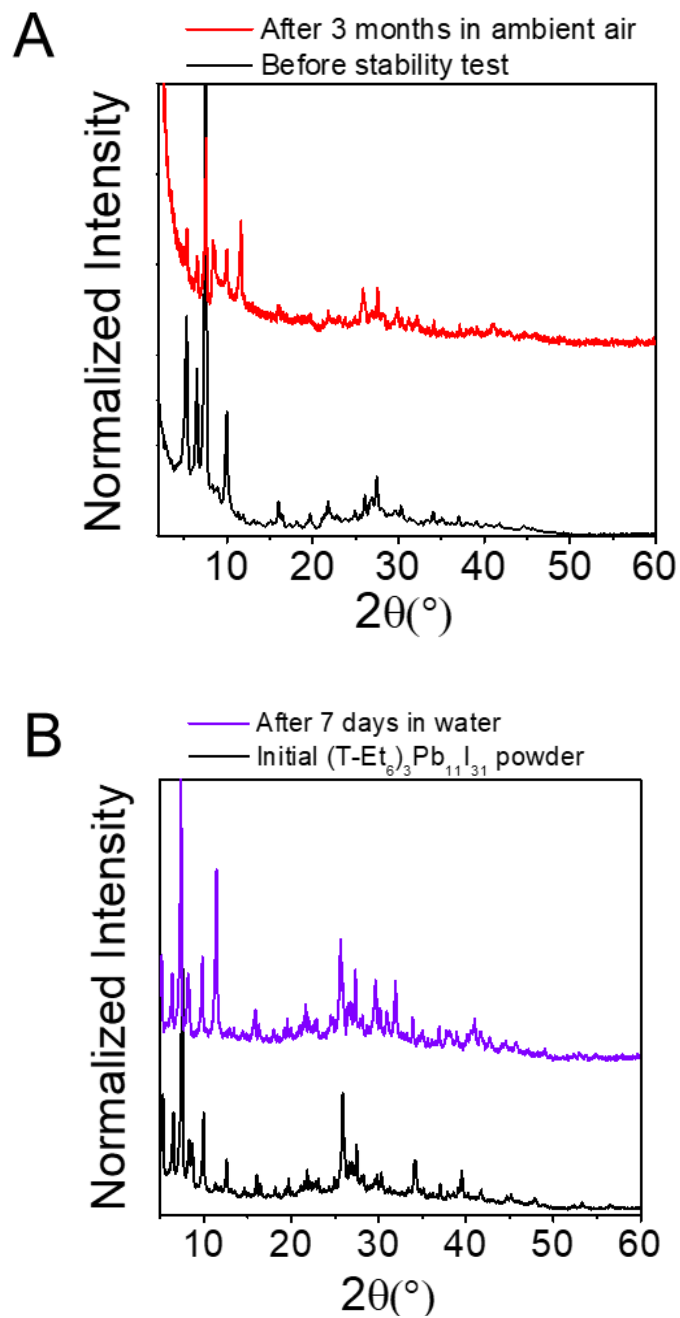


Figure 4. (A) PXRD pattern of (T-Et₆)₃Pb₁₁I₃₁ crystals before and after 3 months stored in ambient air. (B) PXRD pattern of (T-Et₆)₃Pb₁₁I₃₁ crystals before and after 7 days in water.

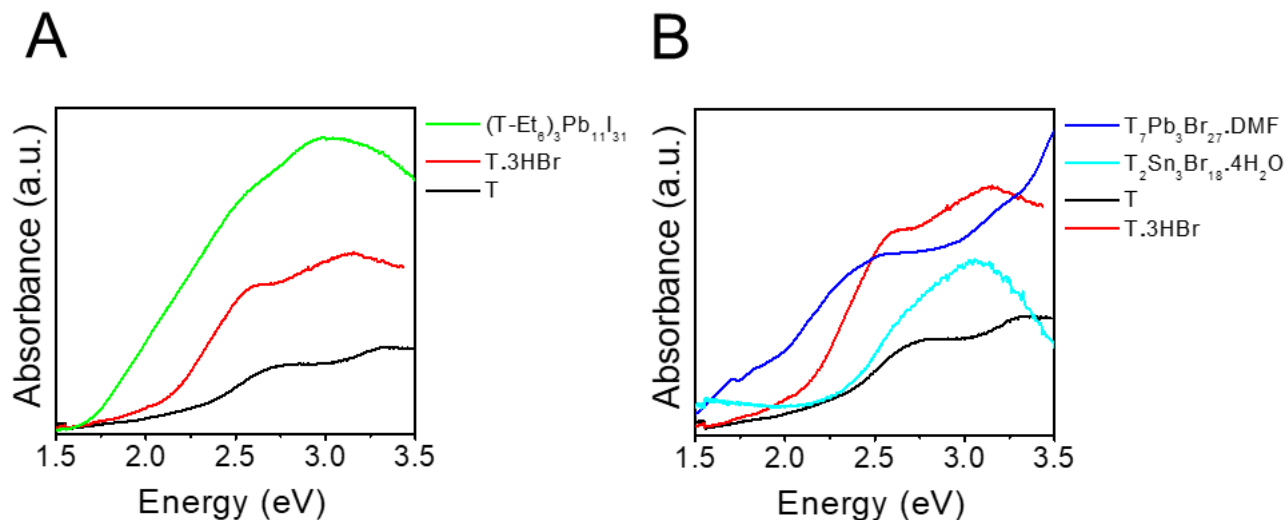


Figure 5. Solid-state optical absorption spectra of compounds **(A)** $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ alongside T and T.3HBr, **(B)** $\text{T}_7\text{Pb}_3\text{Br}_{27}\cdot\text{DMF}$ and $\text{T}_2\text{Sn}_3\text{Br}_{18}\cdot 4\text{H}_2\text{O}$ alongside T and T.3HBr.

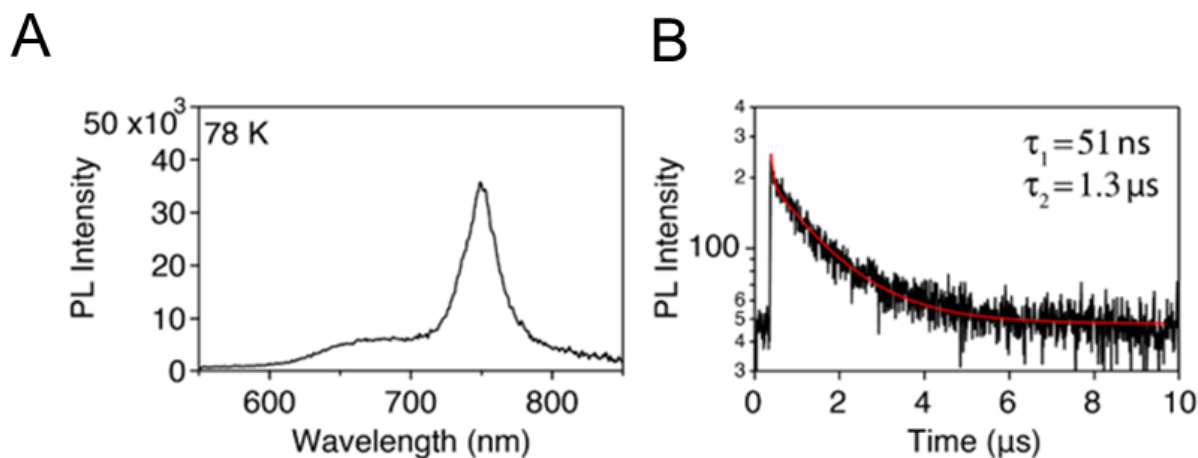


Figure 6. Steady-state PL emission spectrum for $(\text{T-Et}_6)_3\text{Pb}_{11}\text{I}_{31}$ at 78 K **(A)** followed by the time-resolved PL dynamics at 78 K **(B)**. The compound shows biexponential recovery dynamics with lifetimes of 51 ns and 1.3 μs .

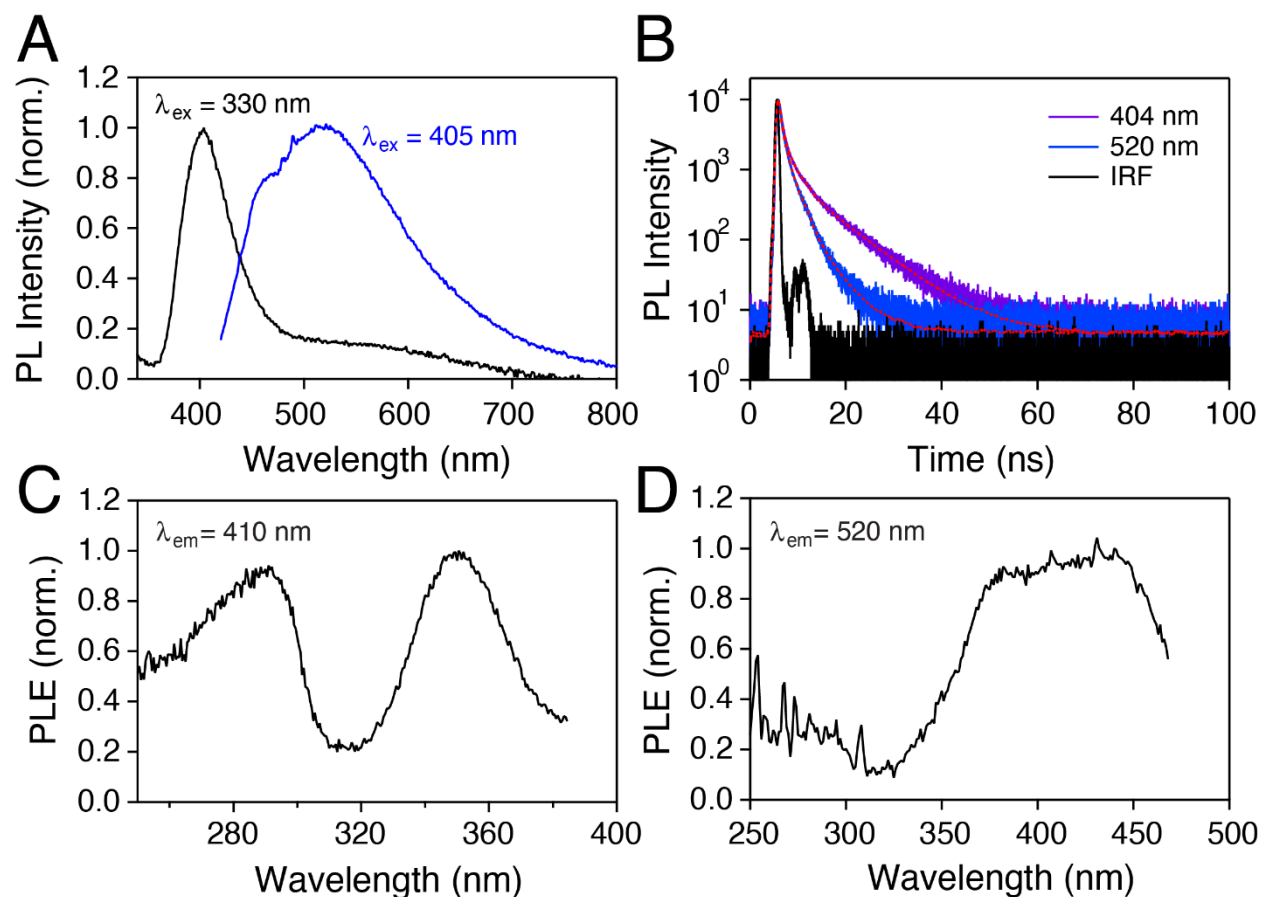


Figure 7. Steady-state and time-resolved PL emission and excitation spectra for $T_7Pb_3Br_{27}DMF$. **(A)** gives the room-temperature PL spectra for $T_7Pb_3Br_{27}DMF$ when excited at 330 and 405 nm. Two distinct emission bands are observed depending on excitation wavelength. **(B)** The time-resolved PL for the two bands is fitted to a triexponential (red dash line) with lifetimes of <1, 1.8, 8.1 ns for the 404 nm band and <1, 1.5, 4.4 ns for the 520 nm band. The fast component is IRF limited. The photoluminescence excitation spectra for the emission at 410 nm **(C)** and 520 nm **(D)** show distinct differences consistent with these two emission bands sharing separate origins.

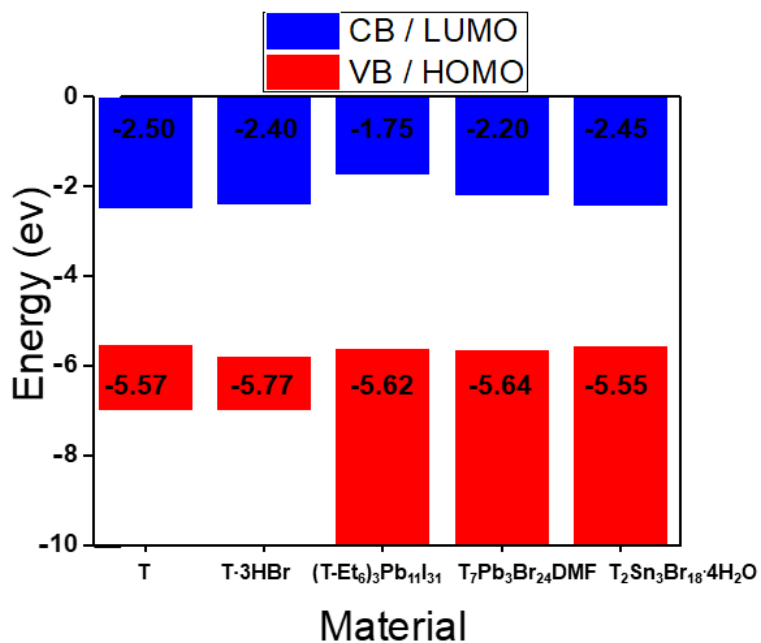


Figure 8. Band alignment diagram with valence band maximum energies determined from Photoemission Yield Spectroscopy in Air (PYSA) measurements of T, T·3HBr, 3D (T-Et₆)₃Pb₁₁I₃₁, 0D T₇Pb₃Br₂₇·DMF and 0D T₂Sn₃Br₁₈·4H₂O·0.5Br₂.

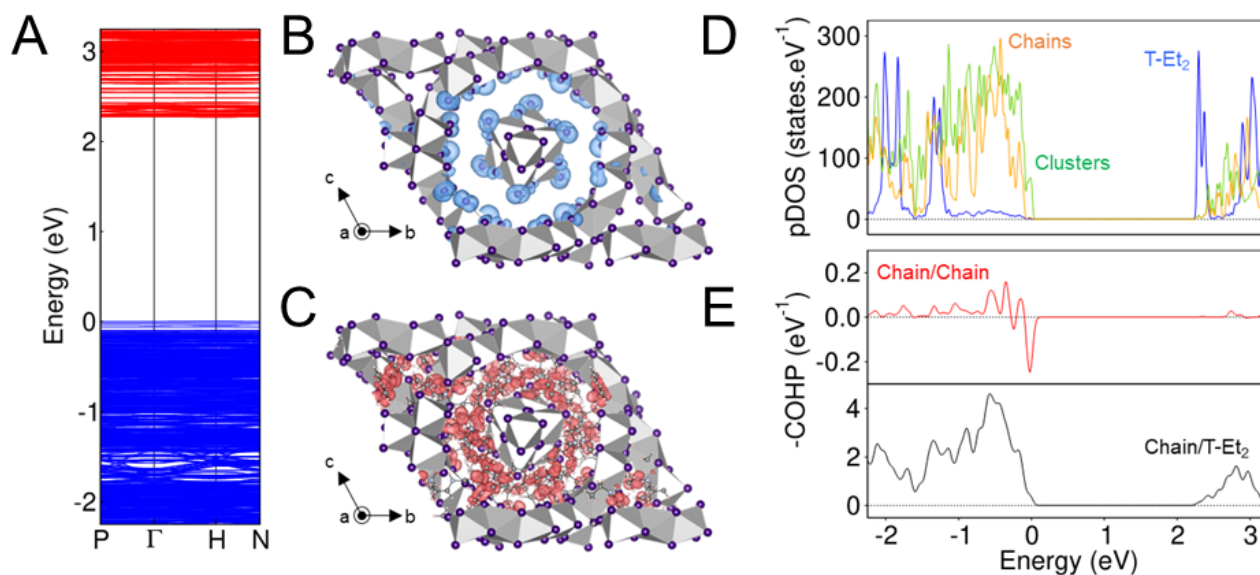


Figure 9. (A) DFT computed band structures of (T-Et₆)₃Pb₁₁I₃₁. (B) and (C) Partial charge densities taken at the valence band maximum (VBM, blue) and the conduction band minimum (CBM, red), respectively. For clarity, T-Et₆ cations are not depicted for the VBM that is distributed over [Pb₁₁I₃₁]⁹⁻ chains, while the CBM is composed by contributions of the T-Et₆ cations. Identical

images would be obtained looking along the other chain directions, i.e. (0,1,0), (0,0,1) and (1,1,1). **(D)** Density of states projected over T-Et₆ cations (blue), the 5 face-sharing octahedra chain (orange) and the 6 edge-sharing octahedra cluster (green). **(E)** Crystal orbital Hamilton population (COHP) bonding analysis showing a weak interaction between chains (red) and a strong interaction between the chains and the T-Et₆ cations. Bonding and anti-bonding interactions are represented by positive and negative values, respectively.

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