Electronic Supplementary Material (ESI) for RSC Advances.

Terpyridine-Derived Perovskite Single Crystals with Tunable Structure and Electronic Dimensionality

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Contents

Experimental section

2,2:6,2-terpyridine (Tpy, J&K, >98%), PbI_2 (Aladdin, 99.9%), HI (Aladdin, 55.0 - 58.0%, with ≤1.5 % H_3PO_2 stabilizer), acetonitrile (Aladdin, 99.9%).

Growth of Tpy_2PbI_6 Single Crystals

0.233g Tpy and 0.0215 g PbI_2 were dissolved in a hydrothermal kettle containing 1mL of water, 2 mL of HI solution and 3 mL of acetonitrile. The mixture was placed on a heating table, heated to 170 °C and held at this temperature for 10hs to completely dissolve the starting materials. The solution was then cooled from 170 to 110 °C at a rate of 4 °C/h, from 110 °C to 60 °C at a rate of 1 °C/h and last from 60 to 30 °C at a rate of 2 °C/h. Finally, the black crystal was obtained.

Growth of $Tpy_4Pb_5I_{18}$ Single Crystals

0.233g Tpy and 0.215g PbI_2 were dissolved in a hydrothermal kettle containing 1mL of water, 2 mL of HI solution and 3 mL of acetonitrile. The mixture was placed on a heating table, heated to 140 °C and held at this temperature for 10hs to completely dissolve the starting materials. The solution was then cooled from 140 to 110 °C at a rate of 4 °C/h, from 110 °C to 60 °C at a rate of 1 °C/h and last from 60 to 30 °C at a rate of 2 °C/h. Finally, the red crystal was obtained.

Growth of $Tpy_2Pb_3I_6$ Single Crystals

0.233g Tpy and 0.215g PbI_2 were dissolved in a hydrothermal kettle containing 1mL of water, 0.4 mL of HI solution and 3 mL of acetonitrile. The cooling process was the

same as above. Finally, the yellow crystal was obtained.

Characterizations

The determination of unit-cell parameters and data collections were performed on XtaLAB Synergy-i using the scan technique with Mo Kα radiation (λ = 0.71073Å), for data collection at a temperature of 100(1) K. The single crystal structure was resolved and refined by SHELXT and OLEX2. [1-3] All H atoms were placed in geometrically calculated positions and refined using a riding model with C—H = 0.97 (methylene) and 0.96 Å (methyl), with Uiso(H) = 1.2Ueq(C) or 1.5 Ueq (methyl C). X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) spectra were measured with Thermo K-Alpha+. The single crystal structure was resolved and refined by SHELXT and OLEX2. [1-3] All H atoms were placed in geometrically calculated positions and refined using a riding model with C—H = 0.97 (methylene) and 0.96 Å (methyl), with Uiso(H) = 1.2Ueq(C) or 1.5 Ueq (methyl C). X-ray photoelectron spectroscopy (XPS) and Ultraviolet photoelectron spectroscopy (UPS) spectra were measured with Thermo K-Alpha+. All XPS spectra were shifted to account for sample charging using inorganic carbon at 284.80 eV as a reference. UPS spectra were used the HeI (21.22eV) emission line. Due to unresolved probable disorder, similarity and rigid-bond restraints were necessary for the anisotropic displacement parameters of the single crystal. UV-vis spectra were measured by placing the corresponding thin films in a double-beam spectrophotometer equipped with an integrating sphere (UV-3600PLUS220/230VC, SHIMADZU).

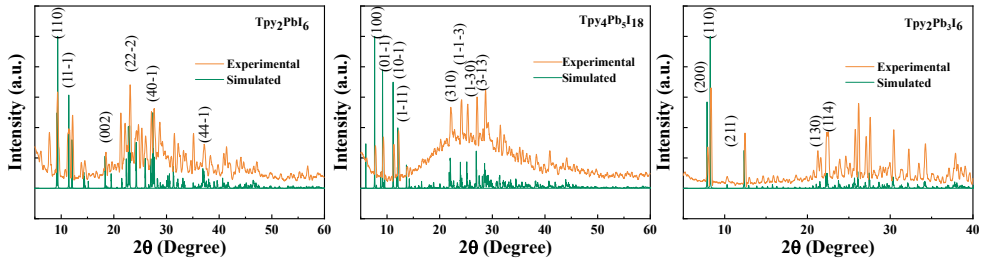

Fig. S1 XRD patterns of as-prepared 0D Tpy_2PbI_6, 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals.

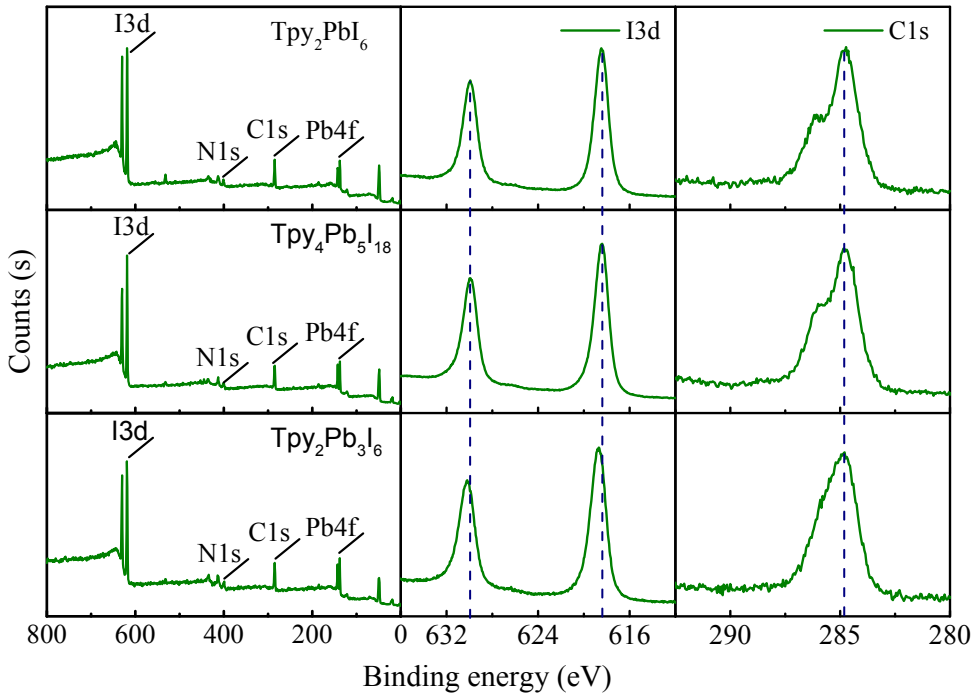

Fig. S2 Region XPS spectra of I3d and C1s and the full XPS spectra in Tpy_2PbI_6, $Tpy_4Pb_5I_{18}$ and $Tpy_2Pb_3I_6$ perovskite single crystals.

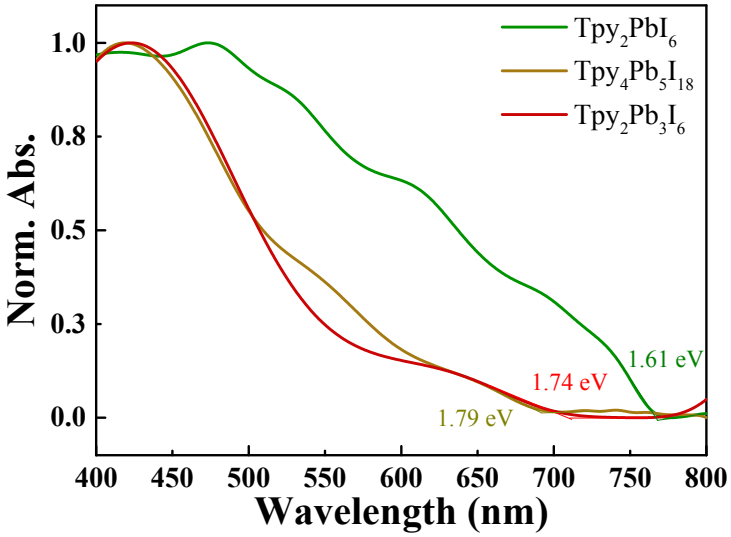

Fig. S3 UV-vis spectra of 0D Tpy_2PbI_6, 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals.

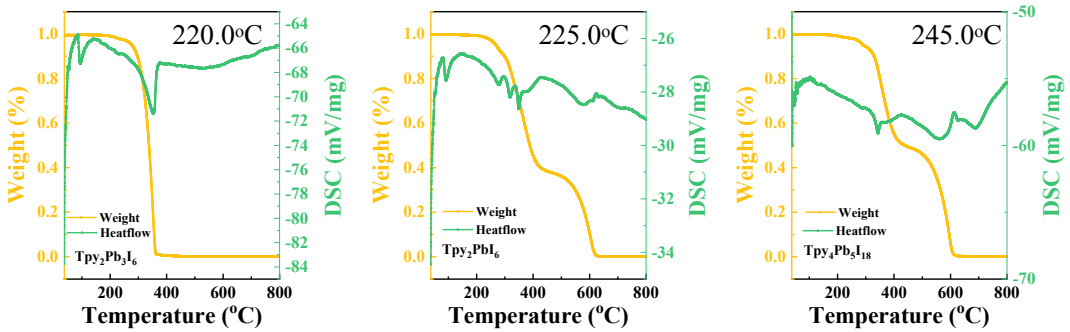

Fig. S4 TGA/DSC curves of the as-prepared 0D Tpy_2PbI_6, 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals.

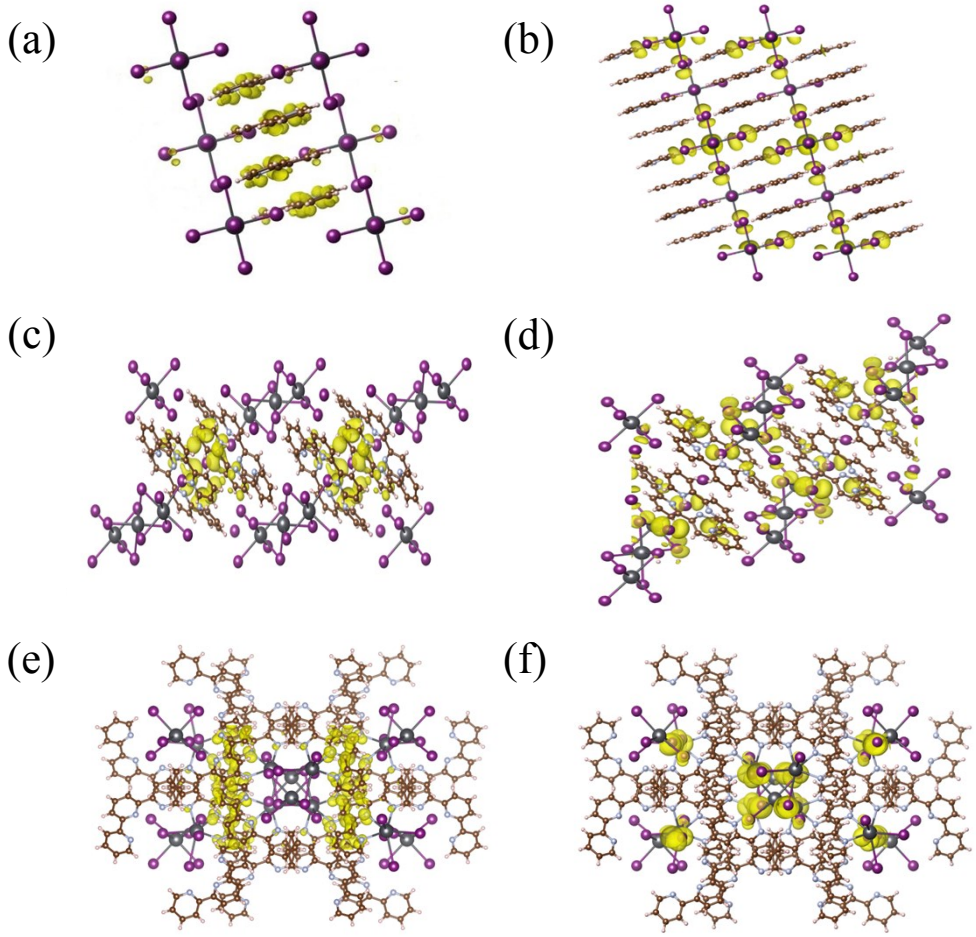

Fig. S5 LUMO-associated charge distribution and HOMO-associated charge distribution of the as-prepared 0D Tpy_2PbI_6, 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals.

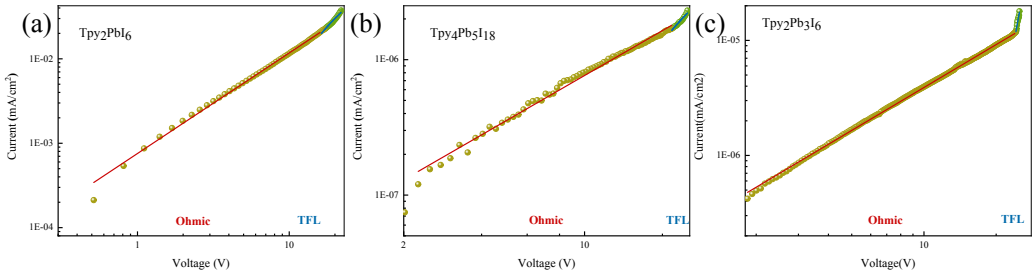

Fig. S6 Dark current-voltage curves of (a) 0D Tpy_2PbI_6 (b) 1D $Tpy_4Pb_5I_{18}$ and (c) 1D

$Tpy_2Pb_3I_6$single crystals. Trap density (Ntrap) and carrier mobility (μ) are evaluated based on space-charge-limited current (SCLC).

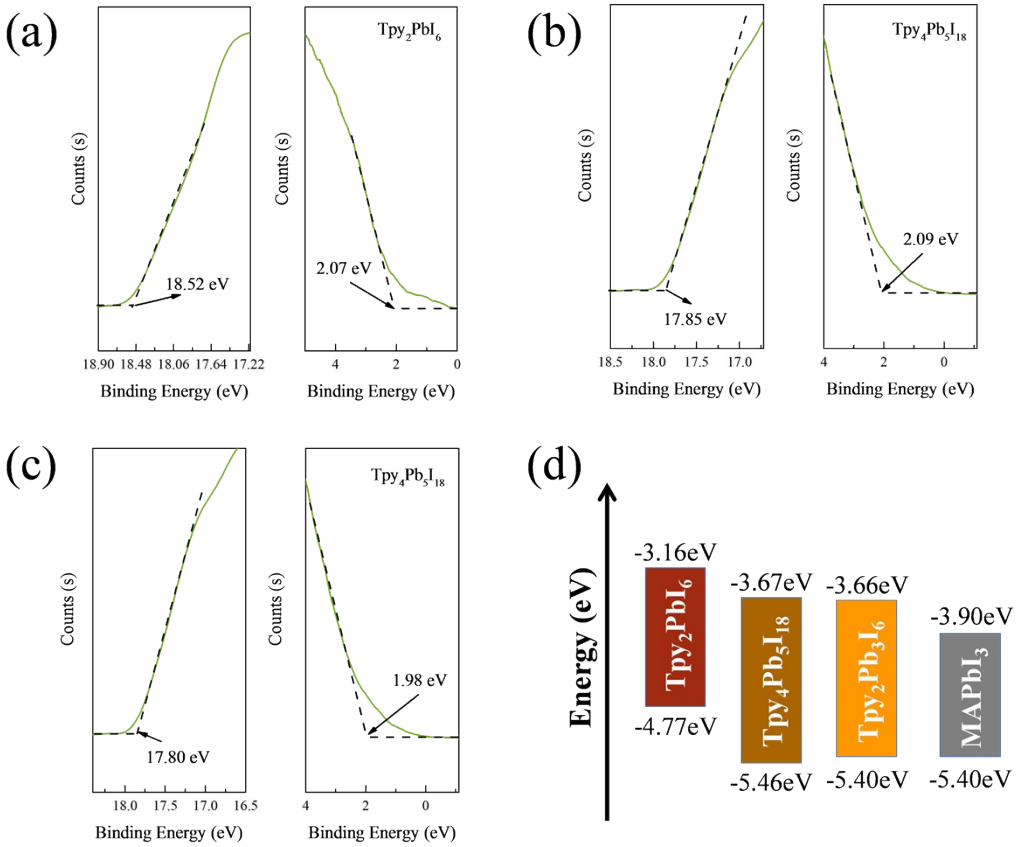

Fig. S7 (a-c) UPS cutoff spectra of 0D Tpy_2PbI_6 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals. (d) Calculated band gap alignment of 0D Tpy_2PbI_6 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ single crystals.

Table S1. Details of X-ray crystallographic parameters of 0D Tpy_2PbI_6, 1D $Tpy_4Pb_5I_{18}$ and 1D $Tpy_2Pb_3I_6$ Single Crystals.

Crystal type / Parameter	Tpy_2PbI_6	$Tpy_4Pb_5I_{18}$	$Tpy_2Pb_3I_6$
CCDC NO.	2081449	2081451	2081450

Formula weight	1439.16 g/mol	4255.24 g/mol	1849.50 g/mol
Crystal system	monoclinic	triclinic	orthorhombic
Space group	C 1 2/m 1	P -1	P b c n
Unit-cell dimensions	a = 13.0069(3) Å b = 14.6783(3) Å c = 10.1587(3) Å α = 90° β = 107.854°(3) γ = 90°	a = 12.8492(2) Å b = 12.89296(18)Å c =15.7151(2)Å α = 86.4469° (11) β = 70.5166° (13) γ = 72.3962°(13)	a = 22.4598(5) Å b = 12.1864(2) Å c = 14.4057(3) Å α = 90° β = 90° γ = 90°
Volume	1846.09(8) $Å^3$	2337.22(6) $Å^3$	3942.90(15) $Å^3$
Z	2	1	4
ρ(calculated)	2.589 g/cm3	3.023 g/cm3	3.116 g/cm3
Absorption coefficient	9.616	14.958	17.506
F(000)	1296	1854	3232
Crystal size max/mid/min	0.2×0.2×0.1mm^3	0.2×0.2×0.1mm^3	0.2×0.2×0.1mm^3
Radiation	MoKα(λ=0.71073)	MoKα(λ=0.71073)	MoKα(λ=0.71073)
Index ranges	-16≤h≤16, -18≤k≤16, -13≤l≤13	-15≤h≤16, -16≤k≤16, -19≤l≤20	-28≤h≤28, -15≤k≤15, -17≤l≤18
Reflections collected	18696	44481	30343
Independent reflections	2095[Rint=0.029, Rsigna=0.0349]	9900 [Rint=0.0325, Rsigna=0.0530]	4243 [Rint=0.0273, Rsigna=0.0452]
Data/restraints/ parameters	2095/0/110	9900 /0/445	4243/0/208
Final R indexes [I>=2σ(I)]	R1=0.0292, wR2=0.0687	R1=0.0329, wR2=0.0614	R1=0.0273, wR2=0.0445
Final R indexes [all data]	R1=0.0349, wR2=0.0709	R1=0.0535, wR2=0.0666	R1=0.0452, wR2=0.0489
Goodness-of-fit on F^2	1.073	0.983	1.085
Largest difference map peak/hole	1.271/-1.405e $Å^{-3}$	0.762/-1.246e $Å^{-3}$	1.116/-1.323e $Å^{-3}$

Table S2. Details of atoms occupation situation of Tpy_2PbI_6.

Atom	**x**	**y**	**z**	**Occ.**	**U**	Site	**Sym.**
Pb01	0.5	0.5	0.5	1	0.03974	2c	2/m
I002	0.75977	0.5	0.52831	1	0.04605	4i	m
I003	0.43368	0.5	0.17671	1	0.05428	4i	m
I004	0.5	0.27497	0.5	1	0.06287	4h	2
N005	0.8614	0.5	0.9641	1	0.0384	4i	m
N006	0.8166	0.6494	0.8118	1	0.0498	8j	1
C007	0.8562	0.6616	0.9493	1	0.0439	8j	1
C008	0.8773	0.579	1.0351	1	0.0421	8j	1

C009	0.928	0.5	1.248	1	0.068	4i	m
H009	0.951182	0.500001	1.344175	1	0.082	6	
C00A	0.8767	0.75	0.995	1	0.0568	8j	1
H00A	0.903454	0.761902	1.089304	1	0.068	8j	1
C00B	0.9112	0.5819	1.1786	1	0.0579	8j	1
H00B	0.92224	0.637045	1.225971	1	0.069	8j	1
C00C	0.8181	0.8051	0.7629	1	0.0649	8j	1
H00C	0.805684	0.85275	0.699706	1	0.078	8j	1
C00D	0.7972	0.717	0.7194	1	0.0626	8j	1
H00D	0.769343	0.704138	0.625533	1	0.075	8j	1
C00E	0.8579	0.8211	0.9016	1	0.0625	8j	1
H00E	0.872392	0.880593	0.933613	1	0.075	8j	1
H006	0.798	0.6	0.778	1	0.056	8j	1

Table S3. Bond length of Tpy_2PbI_6.

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
Pb01	I002	3.3020(5)	C008	C00B	1.388(7)
Pb01	I002	3.3019(5)	C009	H009	0.93
Pb01	I003	3.1294(4)	C009	C00B	1.377(7)
Pb01	I003	3.1294(4)	C009	C00B	1.377(7)
Pb01	I004	3.3030(5)	C00A	H00A	0.93
Pb01	I004	3.3031(5)	C00A	C00E	1.381(8)
N005	C008	1.348(6)	C00B	H00B	0.93
N005	C008	1.348(6)	C00C	H00C	0.93
N006	C007	1.345(6)	C00C	C00D	1.366(8)
N006	C00D	1.335(7)	C00C	C00E	1.364(8)
N006	H006	0.80(6)	C00D	H00D	0.93
C007	C008	1.469(8)	C00E	H00E	0.93
C007	C00A	1.376(7)			

Table S4. Bond Angles of Tpy_2PbI_6.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I002	Pb01	I002	180	N005	C008	C007	115.0(4)
I002	Pb01	I004	90	N005	C008	C00B	122.4(5)
I002	Pb01	I004	90	C00B	C008	C007	122.6(5)
I002	Pb01	I004	90	C00B	C009	H009	119.2
I002	Pb01	I004	90	C00B	C009	H009	119.2
I003	Pb01	I002	87.887(12)	C00B	C009	C00B	121.7(7)
I003	Pb01	I002	87.887(12)	C007	C00A	H00A	119.8
I003	Pb01	I002	92.112(12)	C007	C00A	C00E	120.4(5)
I003	Pb01	I002	92.113(12)	C00E	C00A	H00A	119.8
I003	Pb01	I003	180	C008	C00B	H00B	121.3
I003	Pb01	I004	90	C009	C00B	C008	117.4(6)

I003	Pb01	I004	90	C009	C00B	H00B	121.3
I003	Pb01	I004	90	C00D	C00C	H00C	120.9
I003	Pb01	I004	90	C00E	C00C	H00C	120.9
I004	Pb01	I004	180	C00E	C00C	C00D	118.2(6)
C008	N005	C008	118.7(6)	N006	C00D	C00C	120.0(6)
C007	N006	H006	122(4)	N006	C00D	H00D	120
C00D	N006	C007	124.1(5)	C00C	C00D	H00D	120
C00D	N006	H006	114(4)	C00A	C00E	H00E	119.7
N006	C007	C008	116.7(4)	C00C	C00E	C00A	120.6(5)
N006	C007	C00A	116.7(5)	C00C	C00E	H00E	119.7
C00A	C007	C008	126.6(5)				

Table S5. Details of atoms occupation situation of $Tpy_4Pb_5I_{18}$.

Atom	x	y	z	Occ.	U	Site	Sym.
Pb01	1.000	0.500	1.000	1	0.038	1c	-1
Pb02	0.835	0.097	0.710	1	0.040	2i	1
Pb03	0.927	0.284	0.862	1	0.039	2i	1
I004	0.941	0.302	0.658	1	0.049	2i	1
I005	0.815	0.548	0.893	1	0.044	2i	1
I006	1.080	0.711	0.930	1	0.050	2i	1
I007	0.739	-0.102	0.763	1	0.049	2i	1
I008	0.624	0.192	0.636	1	0.050	2i	1
I009	1.167	0.343	0.822	1	0.053	2i	1
I00A	1.028	0.027	0.815	1	0.059	2i	1
I00B	0.500	0.500	0.500	1	0.059	1h	-1
I00C	0.682	0.237	0.899	1	0.059	2i	1
I00D	1.000	0.000	0.500	1	0.066	1b	-1
N00E	0.712	0.489	0.599	1	0.031	2i	1
N00F	0.805	0.336	0.467	1	0.039	2i	1
N00G	0.458	0.920	0.712	1	0.040	2i	1
N00H	0.522	0.474	0.721	1	0.049	2i	1
N00I	0.433	1.052	0.847	1	0.069	2i	1
C00J	0.674	0.555	0.674	1	0.035	2i	1
N00K	0.638	0.918	0.563	1	0.056	2i	1
H00K	0.626	0.948	0.614	1	0.068	2i	1
C00L	0.262	1.024	0.938	1	0.058	2i	1
H00L	0.205	0.988	0.952	1	0.069	2i	1
C00M	0.840	0.426	0.451	1	0.038	2i	1
C00O	0.799	0.505	0.529	1	0.035	2i	1
C00P	0.720	0.637	0.680	1	0.046	2i	1
H00P	0.693	0.680	0.733	1	0.055	2i	1
C00Q	0.910	0.262	0.322	1	0.058	2i	1

H00Q	0.934	0.206	0.279	1	0.069	2i	1
C00R	0.377	0.916	0.791	1	0.041	2i	1
C00S	0.334	1.156	0.981	1	0.073	2i	1
H00S	0.328	1.209	1.021	1	0.087	2i	1
C00U	0.806	0.653	0.606	1	0.056	2i	1
H00U	0.837	0.709	0.608	1	0.067	2i	1
C00V	0.913	0.435	0.367	1	0.054	2i	1
H00V	0.939	0.496	0.353	1	0.065	2i	1
C00W	0.576	0.534	0.745	1	0.037	2i	1
C00X	0.480	0.849	0.646	1	0.042	2i	1
C00Y	0.423	0.770	0.657	1	0.055	2i	1
H00Y	0.441	0.720	0.610	1	0.066	2i	1
C5	0.847	0.587	0.529	1	0.050	2i	1
H5	0.905	0.598	0.478	1	0.060	2i	1
C7	0.948	0.351	0.301	1	0.062	2i	1
H7	0.997	0.356	0.244	1	0.075	2i	1
C9	0.356	0.997	0.859	1	0.043	2i	1
C13	0.430	0.447	0.777	1	0.064	2i	1
H13	0.396	0.405	0.755	1	0.076	2i	1
C14	0.724	0.933	0.491	1	0.074	2i	1
H14	0.769	0.976	0.495	1	0.088	2i	1
C15	0.591	0.806	0.481	1	0.075	2i	1
H15	0.548	0.761	0.479	1	0.090	2i	1
C17	0.388	0.482	0.865	1	0.061	2i	1
H17	0.324	0.465	0.905	1	0.073	2i	1
C18	0.253	1.105	0.998	1	0.071	2i	1
H18	0.189	1.123	1.051	1	0.085	2i	1
C21	0.571	0.857	0.561	1	0.047	2i	1
C22	0.837	0.256	0.407	1	0.049	2i	1
H22	0.809	0.196	0.422	1	0.058	2i	1
C24	0.424	1.129	0.903	1	0.088	2i	1
H24	0.480	1.165	0.889	1	0.106	2i	1
C25	0.535	0.570	0.836	1	0.055	2i	1
H25	0.572	0.611	0.856	1	0.066	2i	1
C27	0.675	0.822	0.404	1	0.096	2i	1
H27	0.687	0.790	0.349	1	0.115	2i	1
C28	0.743	0.885	0.410	1	0.076	2i	1
H28	0.801	0.894	0.359	1	0.091	2i	1
C32	0.441	0.544	0.895	1	0.066	2i	1
H32	0.413	0.568	0.955	1	0.080	2i	1
C1	0.318	0.840	0.807	1	0.057	2i	1
H1	0.264	0.838	0.863	1	0.068	2i	1
C8	0.340	0.768	0.738	1	0.066	2i	1

H8	0.299	0.718	0.747	1	0.079	2i	1
H00I	0.489	1.041	0.796	1	0.022	2i	1
H00F	0.762	0.329	0.513	1	0.060	2i	1
H00H	0.545	0.444	0.658	1	0.090	2i	1

Table S6. Bond length of $Tpy_4Pb_5I_{18}$.

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
Pb01	I005	3.2433(4)	C00P	H00P	0.93
Pb01	I005	3.2433(4)	C00P	C00U	1.366(8)
Pb01	I006	3.1998(4)	C00Q	H00Q	0.93
Pb01	I006	3.1998(4)	C00Q	C7	1.352(9)
Pb01	I009	3.2510(4)	C00Q	C22	1.369(8)
Pb01	I009	3.2510(4)	C00R	C9	1.452(8)
Pb02	I004	3.2615(5)	C00R	C1	1.374(8)
Pb02	I007	3.1255(5)	C00S	H00S	0.93
Pb02	I008	3.1802(5)	C00S	C18	1.348(10)
Pb02	I00A	3.2980(5)	C00S	C24	1.348(9)
Pb02	I00C	3.2501(5)	C00U	H00U	0.93
Pb02	I00D	3.3438(2)	C00U	C5	1.383(8)
Pb03	I004	3.1560(5)	C00V	H00V	0.93
Pb03	I005	3.2613(5)	C00V	C7	1.404(8)
Pb03	I006	3.2445(5)	C00W	C25	1.405(8)
Pb03	I009	3.2526(5)	C00X	C00Y	1.402(8)
Pb03	I00A	3.2135(5)	C00X	C21	1.480(8)
Pb03	I00C	3.2438(5)	C00Y	H00Y	0.93
N00E	C00J	1.347(6)	C00Y	C8	1.370(9)
N00E	C00O	1.339(6)	C5	H5	0.93
N00F	C00M	1.337(7)	C7	H7	0.93
N00F	C22	1.325(7)	C13	H13	0.93
N00F	H00F	0.76(5)	C13	C17	1.365(8)
N00G	C00R	1.338(7)	C14	H14	0.93
N00G	C00X	1.325(7)	C14	C28	1.361(9)
N00H	C00W	1.332(7)	C15	H15	0.93
N00H	C13	1.339(8)	C15	C21	1.362(8)
N00H	H00H	0.99(6)	C15	C27	1.380(10)
N00I	C9	1.337(8)	C17	H17	0.93
N00I	C24	1.330(8)	C17	C32	1.377(9)
N00I	H00I	0.86(5)	C18	H18	0.93
C00J	C00P	1.380(7)	C22	H22	0.93
C00J	C00W	1.459(8)	C24	H24	0.93
N00K	H00K	0.86	C25	H25	0.93
N00K	C14	1.351(7)	C25	C32	1.375(9)
N00K	C21	1.333(7)	C27	H27	0.93

C00L	H00L	0.93	C27	C28	1.375(10)
C00L	C9	1.388(8)	C28	H28	0.93
C00L	C18	1.398(9)	C32	H32	0.93
C00M	C00O	1.484(8)	C1	H1	0.93
C00M	C00V	1.366(7)	C1	C8	1.364(8)
C00O	C5	1.387(7)	C8	H8	0.93

Table S7. Bond Angles of $Tpy_4Pb_5I_{18}$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I005	Pb01	I005	180	C00J	C00P	H00P	120.9
I005	Pb01	I009	82.928(11)	C00U	C00P	C00J	118.2(6)
I005	Pb01	I009	97.073(11)	C00U	C00P	H00P	120.9
I005	Pb01	I009	97.072(11)	C7	C00Q	H00Q	120.3
I005	Pb01	I009	82.928(11)	C7	C00Q	C22	119.5(6)
I006	Pb01	I005	93.865(11)	C22	C00Q	H00Q	120.3
I006	Pb01	I005	93.866(11)	N00G	C00R	C9	115.0(6)
I006	Pb01	I005	86.135(11)	N00G	C00R	C1	123.0(6)
I006	Pb01	I005	86.134(11)	C1	C00R	C9	122.0(6)
I006	Pb01	I006	180	C18	C00S	H00S	121
I006	Pb01	I009	83.660(11)	C18	C00S	C24	118.1(7)
I006	Pb01	I009	83.659(11)	C24	C00S	H00S	121
I006	Pb01	I009	96.340(11)	C00P	C00U	H00U	119.8
I006	Pb01	I009	96.341(11)	C00P	C00U	C5	120.4(6)
I009	Pb01	I009	180	C5	C00U	H00U	119.8
I004	Pb02	I00A	81.587(13)	C00M	C00V	H00V	120.6
I004	Pb02	I00D	85.386(9)	C00M	C00V	C7	118.9(6)
I007	Pb02	I004	178.352(14)	C7	C00V	H00V	120.6
I007	Pb02	I008	85.009(13)	N00H	C00W	C00J	116.3(5)
I007	Pb02	I00A	96.765(13)	N00H	C00W	C25	117.2(6)
I007	Pb02	I00C	95.715(13)	C25	C00W	C00J	126.5(6)
I007	Pb02	I00D	94.920(10)	N00G	C00X	C00Y	122.8(6)
I008	Pb02	I004	96.622(13)	N00G	C00X	C21	115.5(6)
I008	Pb02	I00A	170.465(14)	C00Y	C00X	C21	121.7(6)
I008	Pb02	I00C	89.468(13)	C00X	C00Y	H00Y	121.2
I008	Pb02	I00D	88.108(10)	C8	C00Y	C00X	117.6(6)
I00A	Pb02	I00D	101.039(11)	C8	C00Y	H00Y	121.2
I00C	Pb02	I004	84.079(13)	C00O	C5	H5	121.1
I00C	Pb02	I00A	81.039(13)	C00U	C5	C00O	117.9(6)
I00C	Pb02	I00D	168.844(12)	C00U	C5	H5	121.1
I004	Pb03	I005	90.254(12)	C00Q	C7	C00V	120.2(6)
I004	Pb03	I006	174.075(13)	C00Q	C7	H7	119.9
I004	Pb03	I009	92.829(13)	C00V	C7	H7	119.9
I004	Pb03	I00A	84.568(13)	N00I	C9	C00L	116.4(6)

I004	Pb03	I00C	85.885(13)	N00I	C9	C00R	118.2(6)
I006	Pb03	I005	85.108(12)	C00L	C9	C00R	125.5(6)
I006	Pb03	I009	82.934(12)	N00H	C13	H13	120.6
I009	Pb03	I005	82.624(12)	N00H	C13	C17	118.7(7)
I00A	Pb03	I005	174.358(13)	C17	C13	H13	120.6
I00A	Pb03	I006	100.201(13)	N00K	C14	H14	121.2
I00A	Pb03	I009	99.832(14)	N00K	C14	C28	117.7(7)
I00A	Pb03	I00C	82.425(13)	C28	C14	H14	121.2
I00C	Pb03	I005	94.995(13)	C21	C15	H15	120.2
I00C	Pb03	I006	98.172(13)	C21	C15	C27	119.7(8)
I00C	Pb03	I009	177.297(14)	C27	C15	H15	120.2
Pb03	I004	Pb02	80.601(11)	C13	C17	H17	120.3
Pb01	I005	Pb03	78.626(10)	C13	C17	C32	119.3(7)
Pb01	I006	Pb03	79.505(10)	C32	C17	H17	120.3
Pb01	I009	Pb03	78.641(10)	C00L	C18	H18	119.2
Pb03	I00A	Pb02	79.210(12)	C00S	C18	C00L	121.5(7)
Pb03	I00C	Pb02	79.479(11)	C00S	C18	H18	119.2
Pb02	I00D	Pb02	180	N00K	C21	C00X	117.4(5)
C00O	N00E	C00J	117.7(5)	N00K	C21	C15	118.6(7)
C00M	N00F	H00F	122(5)	C15	C21	C00X	124.0(7)
C22	N00F	C00M	124.5(6)	N00F	C22	C00Q	118.8(6)
C22	N00F	H00F	113(5)	N00F	C22	H22	120.6
C00X	N00G	C00R	117.8(5)	C00Q	C22	H22	120.6
C00W	N00H	C13	125.0(6)	N00I	C24	C00S	120.5(8)
C00W	N00H	H00H	123(4)	N00I	C24	H24	119.7
C13	N00H	H00H	112(4)	C00S	C24	H24	119.7
C9	N00I	H00I	118(3)	C00W	C25	H25	120.4
C24	N00I	C9	124.6(7)	C32	C25	C00W	119.2(7)
C24	N00I	H00I	117(3)	C32	C25	H25	120.4
N00E	C00J	C00P	123.1(6)	C15	C27	H27	120.3
N00E	C00J	C00W	113.5(5)	C28	C27	C15	119.5(7)
C00P	C00J	C00W	123.4(6)	C28	C27	H27	120.3
C14	N00K	H00K	118	C14	C28	C27	120.4(7)
C21	N00K	H00K	118	C14	C28	H28	119.8
C21	N00K	C14	124.1(6)	C27	C28	H28	119.8
C9	C00L	H00L	120.5	C17	C32	H32	119.7
C9	C00L	C18	118.9(7)	C25	C32	C17	120.6(7)
C18	C00L	H00L	120.5	C25	C32	H32	119.7
N00F	C00M	C00O	116.2(5)	C00R	C1	H1	120.7
N00F	C00M	C00V	118.0(6)	C8	C1	C00R	118.7(7)
C00V	C00M	C00O	125.8(6)	C8	C1	H1	120.7
N00E	C00O	C00M	114.7(5)	C00Y	C8	H8	120
N00E	C00O	C5	122.8(6)	C1	C8	C00Y	120.0(7)

C5	C00O	C00M	122.5(6)	C1	C8	H8	120

Table S8. Details of atoms occupation situation of $Tpy_2Pb_3I_6$.

Atom	x	y	z	Occ.	U	Site	Sym.
Pb1	0.58940	0.34888	0.45787	1	0.03180	8d	1
Pb2	0.5	0.58256	0.25	1	0.04036	4c	.2.
I3	0.55724	0.63250	0.44941	1	0.0353	8d	1
I4	0.60842	0.25396	0.66613	1	0.03980	8d	1
I5	0.59790	0.38786	0.23840	1	0.04955	8d	1
N17	0.69641	0.4192	0.4929	1	0.0332	8d	1
N6	0.67482	0.2178	0.4171	1	0.0299	8d	1
C12	0.7426	0.3526	0.4775	1	0.0339	8d	1
C7	0.7316	0.2550	0.4201	1	0.0367	8d	1
C11	0.6631	0.1252	0.3713	1	0.0330	8d	1
C10	0.7072	0.0691	0.3233	1	0.0500	8d	1
H10	0.69821	0.00461	0.29181	1	0.06	8d	1
N19	0.55889	0.1580	0.3996	1	0.0355	8d	1
C9	0.7644	0.1097	0.3229	1	0.0544	8d	1
H9	0.7942	0.07425	0.28965	1	0.065	8d	1
C16	0.7041	0.5087	0.5457	1	0.0427	8d	1
H16	0.67171	0.55414	0.55741	1	0.051	8d	1
C8	0.7765	0.2024	0.3716	1	0.0495	8d	1
H8	0.81495	0.23056	0.37245	1	0.059	8d	1
C13	0.7981	0.3735	0.5151	1	0.0578	8d	1
H13	0.82971	0.32582	0.50462	1	0.069	8d	1
C15	0.7588	0.5355	0.5831	1	0.0566	8d	1
H15	0.76380	0.5992	0.61772	1	0.068	8d	1
C18	0.6008	0.0856	0.3749	1	0.0333	8d	1
C20	0.5020	0.1249	0.4008	1	0.0514	8d	1
H20	0.47272	0.17566	0.41620	1	0.062	8d	1
C14	0.8055	0.4652	0.5676	1	0.069	8d	1
H14	0.841	0.483	0.587	1	0.083	8d	1
C21	0.4851	0.0191	0.3804	1	0.0576	8d	1
H21	0.44516	-0.0011	0.38194	1	0.069	8d	1
C1	0.5863	-0.0221	0.3549	1	0.0470	8d	1
H1	0.61600	-0.072	0.33957	1	0.056	8d	1
C2	0.5279	-0.0553	0.3578	1	0.0561	8d	1
H2	0.51777	-0.1276	0.34446	1	0.067	8d	1

Table S9. Bond length of $Tpy_2Pb_3I_6$.

Atom	Atom	Length/ Å	Atom	Atom	Length/ Å
Pb1	I4	3.2436(4)	C10	C9	1.375(8)
Pb1	I5	3.2028(4)	N19	C18	1.338(6)

Pb1	N17	2.601(4)	N19	C20	1.339(6)
Pb1	N6	2.565(4)	C9	H9	0.93
Pb1	N19	2.566(4)	C9	C8	1.358(8)
Pb2	I3	3.2055(4)	C16	H16	0.93
Pb2	I3	3.2055(4)	C16	C15	1.379(8)
Pb2	I4	3.3702(4)	C8	H8	0.93
Pb2	I4	3.3702(4)	C13	H13	0.93
Pb2	I5	3.2393(4)	C13	C14	1.360(9)
Pb2	I5	3.2393(4)	C15	H15	0.93
N17	C12	1.336(6)	C15	C14	1.372(9)
N17	C16	1.341(6)	C18	C1	1.383(7)
N6	C7	1.354(6)	C20	H20	0.93
N6	C11	1.334(6)	C20	C21	1.377(7)
C12	C7	1.469(7)	C14	H14	0.86(6)
C12	C13	1.382(7)	C21	H21	0.93
C7	C8	1.384(7)	C21	C2	1.362(8)
C11	C10	1.387(7)	C1	H1	0.93
C11	C18	1.482(7)	C1	C2	1.372(8)
C10	H10	0.93	C2	H2	0.93

Table S10. Bond Angles of $Tpy_2Pb_3I_6$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
I5	Pb1	I4	163.348(12)	C10	C11	C18	122.1(5)
N17	Pb1	I4	79.40(9)	C11	C10	H10	120.3
N17	Pb1	I5	95.04(9)	C9	C10	C11	119.4(5)
N6	Pb1	I4	83.74(9)	C9	C10	H10	120.3
N6	Pb1	I5	79.74(9)	C18	N19	Pb1	119.8(3)
N6	Pb1	N17	63.78(13)	C18	N19	C20	118.4(4)
N6	Pb1	N19	63.92(13)	C20	N19	Pb1	121.5(3)
N19	Pb1	I4	90.83(10)	C10	C9	H9	120.5
N19	Pb1	I5	80.06(10)	C8	C9	C10	118.9(5)
N19	Pb1	N17	127.50(13)	C8	C9	H9	120.5
I3	Pb2	I3	158.111(16)	N17	C16	H16	119
I3	Pb2	I4	81.738(9)	N17	C16	C15	121.9(5)
I3	Pb2	I4	85.369(10)	C15	C16	H16	119
I3	Pb2	I4	85.368(10)	C7	C8	H8	120
I3	Pb2	I4	81.737(9)	C9	C8	C7	120.0(5)
I3	Pb2	I5	111.413(10)	C9	C8	H8	120
I3	Pb2	I5	85.010(10)	C12	C13	H13	120.7
I3	Pb2	I5	85.012(10)	C14	C13	C12	118.6(6)
I3	Pb2	I5	111.414(10)	C14	C13	H13	120.7
I4	Pb2	I4	107.526(14)	C16	C15	H15	121
I5	Pb2	I4	160.383(10)	C14	C15	C16	118.0(6)

I5	Pb2	I4	160.383(10)	C14	C15	H15	121
I5	Pb2	I4	85.643(10)	N19	C18	C11	117.3(4)
I5	Pb2	I4	85.643(9)	N19	C18	C1	121.0(5)
I5	Pb2	I5	85.810(16)	C1	C18	C11	121.6(5)
Pb1	I4	Pb2	91.468(9)	N19	C20	H20	118.6
Pb1	I5	Pb2	90.987(10)	N19	C20	C21	122.9(5)
C12	N17	Pb1	119.0(3)	C21	C20	H20	118.6
C12	N17	C16	119.2(5)	C13	C14	C15	120.7(6)
C16	N17	Pb1	119.8(3)	C13	C14	H14	119(4)
C7	N6	Pb1	119.3(3)	C15	C14	H14	120(4)
C11	N6	Pb1	119.5(3)	C20	C21	H21	120.7
C11	N6	C7	119.0(4)	C2	C21	C20	118.7(6)
N17	C12	C7	117.0(4)	C2	C21	H21	120.7
N17	C12	C13	121.6(5)	C18	C1	H1	120
C13	C12	C7	121.4(5)	C2	C1	C18	119.9(5)
N6	C7	C12	116.6(4)	C2	C1	H1	120
N6	C7	C8	121.0(5)	C21	C2	C1	119.1(6)
C8	C7	C12	122.4(5)	C21	C2	H2	120.5
N6	C11	C10	121.5(5)	C1	C2	H2	120.5
N6	C11	C18	116.4(4)				

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