Supporting Information:

The capricious nature of iodine catenation in I_2 excess, perovskite-derived hybrid Pt(IV) compounds

E-mail:

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Experimental Information

The hydroiodic acid (HI, 57% wt/wt in aqueous solution, Spectrum) used for the following reactions did not contain the reducing stabilizer hypophosphorous acid (H₃PO₂). The free iodine in solution (that forms when hydroiodic acid is exposed to air) is needed for the (FA)₂PtI₆•2I₂ and (GUA)₈(PtI₆)₃[PtI₄(I₃)₂]•2I₂ preparations, and is also thought to be responsible for the oxidation of Pt²⁺ to Pt⁴⁺ during (DMA)₃PtI₆(I₃) preparation.

 $(FA)_2PtI_6 \bullet 2I_2$ was prepared by placing 50 mg of $(FA)_2PtI_6$ crystals in a sealed vial with a small amount of HI. The preparation of $(FA)_2PtI_6$ can be found in our previous publication.¹ If replicated, the amount of HI included should be just enough to cover all $(FA)_2PtI_6$ crystals. This mixture was left to recrystallize for at least one month, but can proceed longer if bronze $(FA)_2PtI_6$ crystals are still seen after that time. The originally bronze, metallic-looking $(FA)_2PtI_6$ crystals will become black crystals of $(FA)_2PtI_6 \bullet 2I_2$. We note that we were unable to prepare $(FA)_2PtI_6 \bullet 2I_2$ by exposing $(FA)_2PtI_6$ crystals to either iodine vapor or an iodine solution $(H_2O \text{ or organic solvent})$. Once the crystals of $(FA)_2PtI_6 \bullet 2I_2$ are filtered, do not wash with solvents as these will destroy the crystals. It was found best to gently dry them on filter paper, and leave for a few days to dry out.

 $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$ was prepared following the same procedure for the preparation of $(FA)_2PtI_6 \bullet 2I_2$. These crystals will also degrade with most solvents. The preparation of $(GUA)_2PtI_6$ can be found in our previous publication.¹

 $(DMA)_3PtI_6(I_3)$ was prepared by combining 99.30 mg DMAI (0.561 mmol, Sigma Aldrich, 98%) and 50 mg (0.187 mmol) PtCl₂ (Strem, 99.9%) in 8.0 g unstablized HI, and heated to dissolve any solid that initially formed. This solution was heated for 15 min. The solution then was slowly cooled to room temperature, where black plate habit crystals of $(DMA)_3PtI_6(I_3)$ form. These crystals were vacuum filtered, washed with diethyl ether, and vacuum-dried overnight.

Single crystal X-ray diffraction data was collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo K α X-ray source ($\lambda = 0.71073$ Å). The crystals were mounted on a cryoloop under Paratone-N oil and kept under nitrogen. Absorption correction of the data was carried out using the multiscan method as implemented in SADABS.² Subsequent calculations were carried out using SHELXTL.³ Structure determination was done using intrinsic methods. All hydrogen atom positions were omitted. Structure solution, refinement, and creation of publication data was performed using SHELXTL. Crystal structures were visualized using the VESTA software suite.⁴

Powder X-ray diffraction was performed on a Panalytical Empyrean Powder Diffractometer (Bragg-Brentano HD module, no monochromator) equipped with a Cu source $\lambda = 1.5418$ Å. Rietveld refinements were performed in the TOPAS software suite.⁵

A Shimadzu UV3600 UV-NIR Spectrometer was used to gather data in diffuse reflectance mode. The title compounds tested were suspended in $BaSO_4$ medium (*via* grinding). The reflectance spectra were Kubelka-Munk transformed for relative absorbance spectra.

Thermogravimetric analysis (TGA) on all compounds was conducted using a TA Instruments Discovery instrument. A rate of 25 cm³/min dry nitrogen purge was employed with a temperature ramp rate of 10°C/min. The maximum temperature of the experiment was 900°C.

Differential scanning calorimetry (DSC) measurements were performed using a TA Q2000 calorimeter. Samples (2 mg to 10 mg each) were hermetically sealed inside TZero aluminum pans. Samples were first cooled to -150° C, then heated at 10 °C/min. This was repeated for three cycles.

Electronic structure calculations for (FA)₂PtI₆•2I₂ were performed with the Vienna Ab initio Simulation Package (VASP),⁶⁻⁹ which implements the KohnSham formulation of density functional theory (DFT) using a plane wave basis set and the projector augmented wave formalism.^{10,11} The generalized gradient approximation was employed using the exchange and correlation functional of Perdew, Burke, and Ernzerhof (GGAPBE).¹² The plane

wave basis set cutoff energy (800 eV) and k-point mesh density (~1500 k-points per reciprocal atom for convergence of the charge density, ~40,000 k-points per reciprocal atom for computing the density of states, all Γ -centered Monkhorst-Pack sampling)¹³ were chosen based on convergence of the total energy. Structure relaxation was performed, including van der Waals corrections (DFT-D3 method of Grimme,¹⁴ to a force tolerance of 4 meVÅ¹. The relaxed structure preserved the space group symmetry observed in experiment. The Brillouin zone path was that of Setyawan and Curtarolo.¹⁵ The electrostatic potential was visualized on isosurfaces of the valence charge density with custom python code using the improved marching cubes algorithm of Lewiner and coworkers as implemented in the skimage package.¹⁶

Material descriptions

All structures reported were solved via single crystal X-ray diffraction with relevant crystallographic data summarized in Tables S1 and S2, and structures with 95% elipsoids in Figures S1 - S4. The CCDC deposition numbers are 1864903 – 1864907.

The B alerts in the low and room temperature data sets for $(FA)_2PtI_6 \bullet 2I_2$ data originate from the close $I_2 - I^-$ anion distances. We discuss this in the main text as the formation of a 1D polyiodide chain.

The B alerts in the 100 K data set for $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2]\bullet 2I_2$ pertain to the close I_2 to I^- anions distances which we describe as secondary bonding associations in the main text.

The B alerts in both $(DMA)_3PtI_6(I_3)$ data sets come from the omitted hydrogen atoms which were not included due to the disorder of the organic cation atom sites. Hydrogens were included on the N site of the ordered DMA cation. There is one B alert in the 100 K data set which is due to secondary bond associations between I_3^- to I^- anions.

Empirical Formula	$[CH(NH_2)_2]PtI_6 \bullet 2I_2$		$[C(NH_2)_3]_8(PtI_6)_3[PtI_4(I_3)_2]\bullet 2I_2$
Crystal habit, color	block, black		block, black
Crystal system	tetragonal	tetragonal	triclinic
Space group (#)	$P4_2/mnm$ (136)	$P4_2/mnm$ (136)	P1 (2)
Volume (Å ³)	1178.6(4)	1200.3(16)	2176(3)
<i>T</i> (K)	100	270	108
a (Å)	12.340(2)	12.379(7)	12.768(9)
b (Å)	12.340(2)	12.379(7)	13.016(9)
c (Å)	7.728(1)	7.833(5)	14.52(1)
α (°)	90	90	110.55(2)
β (°)	90	90	102.74(2)
γ (°)	90	90	93.87(2)
Ζ	2	2	1
$ ho$ (g mol $^{-1}$)	1554.23	1554.23	5321.86
Dens. $(g \text{ cm}^{-3})$	4.379	4.328	4.061
Abs. (mm^{-1})	19.040	18.698	17.793
F_{000}	1316	1336	2272
Reflections (unique)	6507 (1005)	3456 (995)	9573 (4834)
R_{int}	0.0258	0.0574	0.1981
R_1	0.0217	0.0337	0.0817
wR_R	0.0412	0.0408	0.1936
∂F ($e A^{-3}$)	1.117 & -6.062	1.132 & -1.266	4.382 & -4.836
GOF	1.102	1.208	0.939

Table S1: Crystallographic Data for $(FA)_2PtI_6 \bullet 2I_2$ and $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$

Empirical Formula	$[NH_2(CH_3)]$	$\overline{H_2(CH_3)_2]_3PtI_6(I_3)}$	
Crystal habit, color	block, black		
Crystal system	monoclinic	monoclinic	
Space group (#)	C2/m (12)	C2/m (12)	
Volume (Å ³)	1342.5(1)	1414.3(3)	
Т (К)	100	264	
a (Å)	16.768(9)	17.012(2)	
b (Å)	7.666(4)	7.8309(9)	
c (Å)	10.656(6)	10.837(2)	
α (°)	90	90	
β (°)	101.46(2)	101.705(8)	
γ (°)	90	90	
Z	2	2	
$ ho$ (g mol $^{-1}$)	1475.47	1475.47	
Dens. (g cm $^{-3}$)	3.650	3.465	
Abs. (mm^{-1})	15.570	14.779	
F_{000}	1272	1272	
Reflections (unique)	3470 (2107)	4293 (2297)	
R_{int}	0.0980	0.1329	
R_1	0.0634	0.0580	
wR_R	0.1348	0.0791	
∂F ($e A^{-3}$)	3.384 & -5.871	3.407 & -1.727	
GOF	1.062	1.533	

Table S2: Crystallographic Data for $(DMA)_3PtI_6(I_3)$.



Figure S1: Crystal structure of $(FA)_2PtI_6 \bullet 2I_2$ at 100 K with displacement ellipsoids (95% probability). (a) Depiction of the 1D chains forming between the iodide on the $[PtI_6]^{2-}$ octahedra and I_2 molecules. Hydrogen bonding columns that form between the FA cations and the I_2 molecules are displayed with dashed lines. The pertinent bond lengths are: I_2 molecule 2.77 Å; I_2 – I^- 3.29 Å; N-H···I₂ 3.0 Å. (b) Side view of the 2D sheets that are found parallel to the *ab* plane.



Figure S2: Crystal structure of $(FA)_2PtI_6 \bullet 2I_2$ at 260 K with displacement ellipsoids (95% probability). (a) Depiction of the 1D chains forming between the iodide on the $[PtI_6]^{2-}$ octahedra and I_2 molecules. Hydrogen bonding columns that form between the FA cations and the I_2 molecules are displayed with dashed lines. The pertinent bond lengths are: I_2 molecule 2.76 Å; I_2-I^- 3.32 Å; N-H···I₂ 3.05 Å. (b) Side view of the 2D sheets that are found parallel to the *ab* plane.



Figure S3: Crystal structure of $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2]\bullet 2I_2$ at 100 K with displacement ellipsoids (95% probability). (a) Depiction of the $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2]\bullet 2I_2$ structure with organic cations omitted. (b) Top down view of the *cb*-plane of $(GUA)_2PtI_6\bullet I_2$, demonstrating the secondary iodide bonding network that forms between **2** and **3**. The I₃ moieties of **3** run perpendicular to the *b*-axis, and link with **2**. The I₂ molecules seen in between **1** and **2** in this view are the I₂ molecules that link **3** along the *a*-axis seen in (c). (c) Top down view of the secondary bonding axis in the *ab*-plane, which forms between I₂ molecules and the four equatorial I⁻ iodides of **3**.



Figure S4: Crystal structure of $(DMA)_3PtI_6(I_3)$ at 100 K [(a) and (b)] and 264 K [(c) and (d)] with displacement ellipsoids (95% probability). (a) View of $(DMA)_3PtI_6(I_3)$ down the *b*-axis. (b) View of $(DMA)_3PtI_6(I_3)$ depicting the hydrogen bonding interactions between DMA cations and $[PtI_6]^{2-}$ octahedra, as well as the arrangement of I_3^- anions relative to the nearby $[PtI_6]^{2-}$ octahedra. The distance between apical $[PtI_6]^{2-}$ iodides and nearby I_3^- is 3.49 Å. (c) View of $(DMA)_3PtI_6(I_3)$ down the *b*-axis. (d) View of $(DMA)_3PtI_6(I_3)$ depicting the hydrogen bonding interactions between DMA cations and $[PtI_6]^{2-}$ octahedra, as well as the arrangement of I_3^- anions relative to the nearby $I_6(I_3)$ depicting the hydrogen bonding interactions between DMA cations and $[PtI_6]^{2-}$ octahedra, as well as the arrangement of I_3^- anions relative to the nearby $[PtI_6]^{2-}$ octahedra. The distance between DMA cations and $[PtI_6]^{2-}$ octahedra, as well as the arrangement of I_3^- anions relative to the nearby $[PtI_6]^{2-}$ octahedra. The distance between DMA cations and $[PtI_6]^{2-}$ octahedra, as well as the arrangement of I_3^- anions relative to the nearby $[PtI_6]^{2-}$ octahedra. The distance between apical $[PtI_6]^{2-}$ iodides and nearby I_3^- is 3.56 Å.

Proposed hydrogen bonding network of $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$

The following figures illustrate the proposed hydrogen bonding network that exists in $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$. Due to the overall small contribution to the SXRD dataset that the N and C atoms provide, it is difficult to say that the reported GUA cation positions are definitive. However, the hydrogen bonding network that forms using the isotropic positions of the N atoms and their respective H atoms, looks uncannily similar to the network seen in the parent compound of $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$, $(GUA)_2PtI_6$. Namely, each of the six hydrogens of the GUA cations point towards nearby I^- on $[PtI_6]^{2-}$ octahedra. In order to deconstruct this complex network of hydrogen bonding, Figures S5-S7 describe the suspected hydrogen bonding network formed by the four crystallographically distinct GUA cations. The cations are labeled GUA1 through GUA4, and coincide with the .cif atom labels as such GUA1 = C1, N1, H1a, H1b, N2, H2a, H2b, N3, H3a, H3b, etc in sequential order. GUA2 and GUA4 are included together to emphasize that their bonding preferences are the same, i.e. the hydrogen bonding network forms only with the Pt octahedra 1 and **2**. Interestingly, unlike the hydrogen bonding network that forms in $(FA)_2PtI_6 \bullet 2I_2$, the proposed network exists exclusively with $[PtI_6]^{2-}$, except for the GUA3 cation (Figure S7) which bonds with one of the I_3 molecules. The network has been drawn with a H \cdots I maximum of 3.3 Å, so as to account for other favorable, yet weaker, hydrogen bonding positions of the GUA cations.



Figure S5: View of the hydrogen bonding network that forms between GUA1 and 1, 2, and 3. The hydrogen bonding that occurs between GUA1 and 3 occurs between two of the four equitorial I^- , not any of the I atoms of the I_3 moiety, which is excluded for clarity.



Figure S6: View of the hydrogen bonding network that forms between GUA2/GUA4 and the Pt species, **1** and **2**. This network illustrates that even though **1** and **2** are not linked via a secondary iodide bonding network, that they are extensively coupled via the hydrogen bonding network.



Figure S7: View of the hydrogen bonding network that forms between GUA3, and the Pt species, **1** and **3**. GUA3 forms one hydrogen bond with the terminal I atom of the I_3 moiety.

Powder X-ray Diffraction



Figure S8: Rietveld refinements of the title compounds.

Table S3: Refined lattice parameters of title compounds.

Forumla	$(FA)_2PtI_6\bullet 2I_2$	$(\text{GUA})_8(\text{PtI}_6)_3[\text{PtI}_4(I_3)_2]\bullet 2I_2$	$(DMA)_3PtI_6(I_3)$
a (Å)	12.402	12.683	17.030
b (Å)	12.402	13.045	7.840
c (Å)	7.865	14.628	10.841
α (°)	90	109.54	90
β (°)	90	102.81	101.75
γ (°)	90	94.11	90

Experimental laboratory PXRD data was Rietveld refined (without atomic occupancy) using room temperature single crystal diffraction as the structural comparison (Figure S8). The refinements indicate that the each bulk sample has unit cell parameters close to single crystal diffraction dimensions (Table S3 refined data, Tables S1 and S2 for single crystal data).

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of the title compounds are presented in Figures S9 - S11. The degradation profiles of $(FA)_2PtI_6 \bullet 2I_2$ and $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$ are quite similar, in that they show a multistep evolution including the release of I_2 near 100 °C until 300 °C. The degradation profile of $(DMA)_3PtI_6(I_3)$ occurs in one step near 210 °C.



Figure S9: TGA data for (FA)₂PtI₆•2I₂ from room temperature to 900°C.



Figure S10: TGA data for $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$ from room temperature to 900°C.



Figure S11: TGA data for $(DMA)_3PtI_6(I_3)$ from room temperature to 900°C.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry of the title compounds are presented in Figures S12 - S14. All materials display no observable first order phase transition.



Figure S12: DSC data for $(FA)_2PtI_6 \bullet 2I_2$ between $-150 \degree C$ and $25 \degree C$.



Figure S13: DSC data for $(GUA)_8(PtI_6)_3[PtI_4(I_3)_2] \bullet 2I_2$ between $-150 \degree C$ and $75 \degree C$.



Figure S14: DSC data for $(DMA)_3PtI_6(I_3)$ between $-150 \degree C$ and $150 \degree C$.

Band Structure and Density of States

Band structure and density of states for the compound $(FA)_2PtI_6\bullet 2I_2$ are illustrated in Figure S15. Clearly noted is the disperse conduction band, which is due to iodine/iodide

proximity, as well as the position of the empty I_2 states which lie above the Pt d e_g levels.



Figure S15: Band structure and density of states for the compound $(FA)_2PtI_6 \bullet 2I_2$.

Electrostatic potential examination

Visualized in Figure S16(a) is the crysal structure of $(FA)_2PtI_6\bullet 2I_2$, (b) the electron localization function, and (c) the electrostatic potential visualized on isosurfaces of the valence charge density for $(FA)_2PtI_6\bullet 2I_2$. We believe that Figure S16(c) is a an insightful way to view the electrostatic potential, as it shows how electro-/nucleo-philic the "surface" of each molecule is, rather than a slice through the interior of atoms. It is noted that the hydrogens on the FA cation are quite electrophilic (especially the N–H), hence their tendency to be hydrogen bond donors. Most interestingly, there is an electrophilic region along the I₂-axis which points towards the iodide of the $[PtI_6]^{2-}$ octahedra which is a part of the extended I chain. We believe this observation, in addition to the overall structural signatures (bond angles and distances) of each component moiety, is partial evidence for the existence of the σ -holes on the I₂ molecules, consistent with halogen bonding.¹⁷⁻¹⁹



(c) electrostatic potential on (valence) charge density isosurface



Figure S16: (a) The crystal structure of $(FA)_2PtI_6\bullet 2I_2$, (b) the electron localization function, and (c) the electrostatic potential visualized on isosurfaces of the valence charge density for $(FA)_2PtI_6\bullet 2I_2$. The color legend indicates the degree of negative electrostatic potential.

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