# **Supplementary Information**

# Spontaneous anion-exchange synthesis of optically active mixedvalence Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> perovskite from layered CsAuCl<sub>4</sub> perovskite

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#### (A) Experimental section

### (1) Chemicals

The following chemicals for the synthesis were used as received without further purification: Cesium chloride (CsCl, Sigma-Aldrich, 99.9%), gold chloride (AuCl<sub>3</sub>, Sigma-Aldrich, 99.9%), hydroiodic acid (HI, 55% solution), and de-ionized (DI) water.

#### (2) Synthesis Procedure

**CsAuCl<sub>4</sub> with x = 0, 25, 50, 68, 75 and 100 µl of HI:** For the synthesis of CsAuCl<sub>4</sub> via precipitation reaction method, firstly, 0.2M solutions of CsCl and AuCl<sub>3</sub> in DI water were prepared. Now, aq. solution of CsCl is added dropwise into AuCl<sub>3</sub> solution at ice-cold temperature (5-10°C) keeping the stirring intact. An immediate yellow precipitate, CsAuCl<sub>4</sub>, was formed which was collected via centrifugation (8000 rpm for 5 min) and dried in a vacuum desiccator for further characterizations like XRD, diffuse reflectance, XPS etc. In the next step, the precipitate formed (CsAuCl<sub>4</sub>) is used as it is without any separation or filtration. This precipitate was dissolved when extra 5 ml DI water is added to it to form an ionic solution containing Cs<sup>+</sup>, Au<sup>+</sup>/Au<sup>3+</sup> and Cl<sup>-</sup> ions. To this ionic solution, 55% solution of HI is added in steps of 25, 50, 68, 75 and 100 µl. The product at the end of each reaction was collected using centrifugation (8000 rpm for 5 min). The supernatant was discarded and the process was repeated for three times. The final precipitate was allowed to dry in a vacuum desiccator. As can be seen from the images in Figure S1, the color of the sample changes from yellow (x = 0 to 50 µl) to brown (x = 68 and 75 µl) to black (x = 100 µl).



**Figure S1:** (a-e) Digital image of  $CsAuCl_4$  compound (x = 0 µl) and different HI concentration (x = 50, 68, 75 and 100 µl) treated compounds. (a) is  $CsAuCl_4$  phase, (b)-(d) has mixed phases while (e) represents  $Cs_2Au_2I_6$  phase, without any trace of impurity phases.

In case of other halides (Cl or Br), the suggested method did not render the similar results. For instance, if  $CsAuCl_4$  is treated with hydrobromic acid (HBr), then a simple anion-exchange reaction happened which resulted in the formation of  $CsAuBr_4$ , whereas, on

treating CsAuCl<sub>4</sub> with hydrochloric acid (HCl), the phase remained the same (no change in the phase was observed).

#### (B) Characterization Technique:

Rigaku X-ray diffractometer was used in order to obtain X-ray diffraction patterns at 40 kV and 40mA. The diffractometer used Cu-K $\alpha$  (K $\alpha$  = 1.5406 Å) monochromatic radiation and Scintillator NaI, Dtex detector and the patterns were recorded in the range 2 $\theta$  = 10°-50°. Lattice parameters of these patterns were obtained by Rietveld refinement using FullProf software. The crystal structures were visualized using VESTA (Visualization of electronic and structural analysis). In order to find out the oxidation state of Au, X-ray photoemission spectroscopy (XPS) was carried where the XPS spectra were calibrated to 284.7 eV in accordance with the C 1s of aliphatic carbon taken as reference. The bandgaps were found out from UV-Vis diffuse reflectance spectra obtained using Perkin Elmer, Lambda 950 UV-Vis spectrometer.

From Rietveld refinement, the lattice parameters obtained were a = 14.07 Å, b = 6.25 Å, c = 9.59 Å,  $\alpha = 90^{\circ}$ ,  $\beta = 115^{\circ}$  and  $\gamma = 90^{\circ}$  for CsAuCl<sub>4</sub> and a = 8.28 Å, b = 8.28 Å, c = 12.08Å,  $\alpha = 90^{\circ}$ ,  $\beta = 90^{\circ}$  and  $\gamma = 90^{\circ}$  for Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>.



**Figure S2:** Rietveld refinement of the PXRD pattern of  $CsAuCl_4$ . The result shows that the refined fit of  $CsAuCl_4$  adopts monoclinic structure with C2/c space group symmetry.

XRD profile for the compound (25  $\mu$ l HI addition) shows two dominant peaks at 2 $\theta$  = 38.13° and 44.40° corresponding to Au metal and other smaller peaks match to AuI phase as shown

in Figure S3(a), whereas, prominent AuI is formed as the concentration of HI is increased to 50  $\mu$ l. At 68  $\mu$ l, the peaks corresponding to Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> are prominent with subdued impurity peaks of AuI, Figure S3(b). The critical value of HI which is added in order to achieve pure phase of Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> is 100  $\mu$ l (Figure S4).



**Figure S3:** XRD profile for the compound for (a) x = 25 and 50 µl of added HI showing two dominant peaks at  $2\theta = 38.13^{\circ}$  and  $44.40^{\circ}$  corresponding to Au metal and other small peaks match to AuI phase and (b) x = 68 µl of added HI showing the mixed phase of Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> and AuI.



**Figure S4:** Rietveld refinement of the PXRD pattern of  $Cs_2Au_2I_6$ . The result shows that the refined fit of  $Cs_2Au_2I_6$  adopts tetragonal structure with *I4/mmm* space group symmetry.

If we increase the concentration of HI beyond the threshold value i.e. 100  $\mu$ l, phase pure Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> appears to be formed without a trace of impurity peaks in the XRD data, as can be seen in the Figure S5.



**Figure S5:** XRD profiles for the  $Cs_2Au_2I_6$  compound obtained with the addition of x = 100, 200 and 500 µl concentration of of HI. Pure  $Cs_2Au_2I_6$  phase is formed without a trace of impurity peaks as seen in the XRD data.



**Figure S6:** SEM images of (a) CsAuCl<sub>4</sub> and (b)  $Cs_2Au_2I_6$  showing uniform rod-shaped geometry. EDS shows the atomic ratios of Cs/Au and Cl/Au to be 1.14 and 3.99 for (c) CsAuCl<sub>4</sub> whereas, the atomic ratios of Cs/Au and I/Au came out to be 0.9 and 2.8 for (d) Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>, respectively, which is consistent with the crystallographic composition.

Figure S7 shows the XPS spectra obtained at room temperature which are calibrated to 284.7 eV in accordance with the C 1s of aliphatic carbon taken as reference.<sup>1</sup> The spin-orbit components for Cs 3d present at binding energies of ~ 724.4 eV ( $3d_{5/2}$ ) and ~ 738.4 eV ( $3d_{3/2}$ ) indicate that Cs is present in +1 (Cs<sup>+</sup>) oxidation state in CsAuCl<sub>4</sub> and Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>. The spectrum for Cl 2p shows spin-orbit split at binding energies of ~ 199.0 eV ( $2p_{3/2}$ ) and ~ 200.6 eV ( $3d_{1/2}$ ) indicating presence of Cl in -1 (Cl<sup>-</sup>) oxidation state in CsAuCl<sub>4</sub>. The peaks at ~ 619.1 eV ( $3d_{5/2}$ ) and ~ 630.6 eV ( $3d_{3/2}$ ) indicate that I belongs to -1 (I<sup>-</sup>) oxidation state in Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>.



**Figure S7:** XPS spectra corresponding to (a) C 1s, (b) Cs 3d, (c) Cl 2p and (d) I 3d of CsAuCl<sub>4</sub> and Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>. The spin-orbit components for Cs 3d, Cl 2p and I 3d indicate that Cs, Cl and I are present in +1 (Cs<sup>+</sup>), -1(Cl<sup>-</sup>) and -1(I<sup>-</sup>) oxidation states in CsAuCl<sub>4</sub> and Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> respectively.

Figure S8 shows the crystal structure of these compounds visualized using VESTA (Visualization of electronic and structural analysis). In the crystal structure of CsAuCl<sub>4</sub>, it can be seen that Au is coordinated by four chloride ions forming a squareplanar geometry [AuCl<sub>4</sub>]<sup>-</sup> (Figure S8(a)). The measured bond length for Au-Cl comes out to be 2.2718(14) Å and 2.2835(14) Å in the equatorial position, showing a very small deviation from being a perfect square.<sup>2</sup> In contrast, the crystal structure of Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> (Figure S8(b)) is formed by two types of arrangements: Au1 atom forms a perfectly square planar arrangement with four I1 atoms whereas Au2 atom is wellcoordinated linearly by two I2 atoms. The calculated bond length of 2.650Å for Au1-I1 and 2.578Å for Au2-I2 comes to be in good agreement with [AuI<sub>4</sub>]<sup>-</sup> (2.646Å) and [AuI<sub>2</sub>]<sup>-</sup> (2.586Å) in the mixed-valence compound Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub>.<sup>3</sup> It is well noted here that CsAuCl<sub>4</sub> features only Au<sup>III</sup> in a square planar arrangement whereas  $Cs_2Au_2I_6$  features both monovalent Au<sup>I</sup> and trivalent Au<sup>III</sup> species in the nearest neighbour environment. Also, in  $Cs_2Au_2I_6$ , if the second nearest neighbours are taken then it can be easily seen that each Au atom is surrounded by six I<sup>-</sup> atoms, hence forming two kind of octahedrons:  $[Au^{III}(I1)_4(I2)_2]$  (elongated) and  $[Au^I(I2)_2(I1)_4]$  (compressed) due to the difference in bond length along the axial and equatorial planes.<sup>4</sup> This results in the formation of the quaternary system, namely double perovskite structure.



**Figure S8:** Refined crystal structure of (a)  $CsAuCl_4$  and (b)  $Cs_2Au_2I_6$  using VESTA. In the crystal structure of  $CsAuCl_4$ , it can be seen that Au is coordinated by four chloride ions forming a square-planar geometry  $[Au^{3+}Cl_4]$ -whereas, the square planar  $[Au^{3+}I_4]$ - (II) and linear  $[Au^{1+}I_2]$ - (I) networks due to the disproportionation in valency of Au can be seen in  $Cs_2Au_2I_6$ . This mixed valence of Au in  $Cs_2Au_2I_6$  results in the elongation and compression  $AuX_6$  octahedra.

The optical properties of  $CsAuCl_4$  and  $Cs_2Au_2I_6$  are studied by obtaining diffuse reflectance curves and then using the equation that articulates absorbance as a function of reflectance which is given by Kubleka-Munk (K-M)<sup>5</sup> equation:

$$F(R_{\infty}) = K/S = (1 - R_{\infty})^2/2R_{\infty}$$

where,  $R_{\infty}$  is reflectance and K and S are the absorption and scattering coefficient of the sample, respectively.<sup>6</sup> Only when the scattering coefficient is independent of the incident photon wavelength, the diffuse reflectance spectrum matches closely with the absorption spectrum. In our studies, this condition is satisfied for bulk samples since the wavelength of the interacting photons is less than the average grain size of the absorbing materials making S

independent of the wavelength.<sup>7, 8</sup> The Urbach energy is calculated for CsAuCl<sub>4</sub> and Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> (Figure S9) by using the equation:

$$A \propto e^{E/E}U$$

where A is absorbance, E is excitation energy and  $E_U$  is the Urbach energy.<sup>9</sup>



**Figure S9:** Urbach energies calculated experimentally for  $CsAuCl_4$  (x = 0 µl HI) and  $Cs_2Au_2I_6$  (x = 100 µl HI). The inverse of the slope obtained from the graph between Ln(A) and photon energy gives the value of Urbach energy.

In our synthesis process, cleaning is a very crucial step for final purity of the compound. A proper cleaning process requires washing the precipitate with DI water 2-3 times via centrifugation done at 8000 rpm for 5 minutes. Sometimes, it may take more iterations in cleaning and if not done properly, may leave behind minor impurity in the sample. A systematic ageing study for longer period (upto 200 days) is shown in Figure S10 for a sample which has small amount of Au impurity peak. XRD of the sample is taken at regular time interval which confirms no deterioration in the phase apart from a peak at  $2\theta = 38.19^{\circ}$ which corresponds to Au. The intensity of Au peak remains same for 90 days  $(I_{(220)}/I_{(111)} \sim$ 2.5 where I<sub>(hkl)</sub> is the intensity for (hkl) plane). After three months, the relative peak intensity of Au begins to increase slowly (Figure S10) as compared to the most intense (220) peak of the Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> phase ( $I_{(220)}/I_{(111)} \sim 1$  for 120 - 200 days) with all other XRD peaks belonging to Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> remaining intact. From this, we can infer that Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> structure is minimally degraded and remains stable for about six months and suggests that the presence of Au impurity does not affect rest of the Cs<sub>2</sub>Au<sub>2</sub>I<sub>6</sub> structure. This stability test is just to explain how crucial the cleaning process is, which if not done properly, may give rise to some impurity peaks.



**Figure S10:** (a) XRD of  $Cs_2Au_2I_6$  showing the ambience stability. The \* sign shows the peak corresponding to side phases of Au (111). (b) XRD data (Zoom-in) shows slight increase in the intensity of the peak at  $2\theta = 38.19^{\circ}$  giving  $I_{(220)}/I_{(111)} \sim 2.5$  for 0 - 90 days and  $I_{(220)}/I_{(111)} \sim 0.8$  for 120 - 200 days, where,  $I_{(hkl)}$  is the intensity corresponding to (hkl) plane.

# (C) Computational Details

For theoretical modelling of the reaction formation energies, Vienna Ab initio Simulation Package (VASP)<sup>10-12</sup> was used to perform the Density Functional Theory (DFT)<sup>13</sup> based abinitio calculations using plane-wave basis set and Projector Augmented Wave (PAW)<sup>14</sup> pseudopotentials with PBE exchange-correlation functional<sup>15</sup>. We used the Tetrahedron method with Blöchl corrections<sup>16</sup> for better accuracy in ground state energy values. A plane wave energy cut-off value of 500 eV was used for all the compounds. The conjugate gradient algorithm was used to optimize the cell volume, shape and atomic positions for all the structures with a force convergence tolerance of 0.01 eV/Å on each atom. A tolerance of 10<sup>-6</sup> eV was used for the convergence of self-consistent-field (scf) calculations. The Brillouin zone sampling was done using automated  $\Gamma$  (gamma) centred K point mesh. A fully converged K-point mesh was used for all the calculations. All the relevant compounds (see equations 1-4 given below) were simulated in their respective experimentally reported stable structures. The formation energy ( $\Delta E_f$ ) of the synthesis process was calculated as,

$$\Delta E_f = \sum_{j=1}^n p_j \mu_j - \sum_{i=1}^m r_i \mu_i$$

Where,  $\mu_j$  and  $\mu_i$  are the DFT ground state energies of the products and the reactants, respectively and  $p_j$  and  $r_i$  are their respective weight factors. Symbol `n' and `m' denote the total number of the products and reactants respectively.

The reactions used for calculating the formation enthalpy of  $CsAuCl_4$ ,  $CsAuI_4$  and  $Cs_2Au_2I_6$  are:

$$CsCl + AuCl_{3} \rightarrow CsAuCl_{4} \dots \dots (1)$$

$$CsAuCl_{4} + 4HI \rightarrow CsAuI_{4} + 4HCl \dots (2)$$

$$CsI + AuI + AuI_{3} \rightarrow Cs_{2}Au_{2}I_{6} \dots \dots (3)$$

$$2CH_{3}NH_{2} + 2RCOOH + 3PbI_{2} \rightarrow 2CH_{3}NH_{2}PbI_{3} + Pb(RCOO)_{2} \dots (4)$$

**Table S1:** Formation enthalpy  $(\Delta E_f)$  of various gold halide and hybrid perovskites.

Compound (Phase)	$\Delta E_f$ (meV/Formula unit)
CsAuCl <sub>4</sub> (Monoclinic)	-876
Cs <sub>2</sub> Au <sub>2</sub> Cl <sub>6</sub> (Tetragonal)	-1383
CsAuI <sub>4</sub> (Monoclinic)	290
Cs <sub>2</sub> Au <sub>2</sub> I <sub>6</sub> (Tetragonal)	-538
MAPbI <sub>3</sub> (Tetragonal)	-48217

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