

Supporting Information

In(III)-Dictated Formation of Double $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{Fe}_y\text{In}_{1-y}\text{Cl}_6$ Perovskites

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Methods and Instruments

Synthesis of CANFIC perovskites. Double $\text{Cs}_2\text{Ag}_x\text{Na}_{1-x}\text{Fe}_y\text{In}_{1-y}\text{Cl}_6$ (CANFIC) perovskites were precipitated from highly acidic aqueous solutions at RT and in an air-open atmosphere. The constituent trivalent cations (Fe, In) and monovalent cations (Cs, Ag, and Na) were separated into two precursors (denoted further as precursors #1 and #2) to avoid any side reactions between the metal salts and hydrolytic processes. In the optimized synthetic procedure the nominal Fe-to-In ratio γ was varied by introducing different amounts of BiCl_3 and InCl_3 to precursor #1, while precursor #2 contained constant amounts of AgNO_3 and sodium acetate (NaAc). Below an exemplary synthesis protocol is provided in detail for the particular case of CANFIC perovskite with 5%In.

Precursor #1 was prepared by adding 95.0 μL 1.0 M aqueous FeCl_3 solution (containing 6 M HCl to suppress Fe^{3+} hydrolysis) and 5.0 μL aqueous InCl_3 solution (containing 4 M HCl to suppress In^{3+} hydrolysis) to 600 μL concentrated (12 M, 37 w.%) aqueous HCl solution.

Precursor #2 was prepared by adding to 100 μL aqueous 1 M AgNO_3 solution consecutively and under intense stirring 30 μL concentrated aqueous NH_4OH solution (13.4 M, 25 w.%), 25 μL aqueous 4.0 M NaAc solution (Ac – acetate), and 100 μL aqueous 4 M CsAc solution. The presence of excessive cesium and sodium chlorides over stoichiometric amounts is a necessary condition for the formation of pure perovskite CANFIC phases.

Precursor #2 was rapidly added to precursor #1 resulting in the precipitation of the CANFIC product at intense stirring. The as-precipitated CANFIC suspensions were left in a closed vial (with Parafilm layer) for 12-15 h (overnight) with no reflux to achieve deeper crystallization of the target CANFIC phase and

reduce the number of phases-admixtures.

The supernatant solutions were separated and discarded, and 1.0 mL 2-propanol was added to each vial with microcrystalline CANFIC to remove unreacted residuals of precursors. The mixture was subjected to centrifugation at 3000 rpm, the precipitate separated, and the purification procedure was repeated once more. Final powders were dried at RT and relative humidity of 40-50% and kept in the dark under ambient conditions. The mass yield of the final product was 83% of the theoretical value.

Details of the preparation of stock solutions are provided below.

- (1) aqueous 1.0 M InCl_3 solution in 4.0 M HCl: 2.21 g InCl_3 dissolved in 3.33 mL 12.0 M (37%) HCl with ca. 2 min stirring and deionized (DI) water added after complete dissolution to reach the total volume of 10 mL;
- (2) aqueous 1.0 M FeCl_3 solution in 6.0 M HCl: 2.70 g $\text{FeCl}_3 \times 6\text{H}_2\text{O}$ dissolved in 5 mL 12.0 M (37%) HCl with ca. 10 min stirring and DI water added after complete dissolution to reach the total volume of 10 mL;
- (3) aqueous 1.0 M AgNO_3 solution: 1.70 g AgNO_3 dissolved in 9.0 mL DI water with ca. 2 min stirring and DI water added after complete dissolution to reach the total volume of 10 mL;
- (4) aqueous 4.0 M NaAc solution: 5.44 g $\text{NaAc} \times 3\text{H}_2\text{O}$ dissolved in 6.0 mL DI water with ca. 2 min stirring and DI water added after complete dissolution to reach the total volume of 10 mL;
- (5) aqueous 4.0 M CsAc solution: 7.68 g CsAc dissolved in 7.0 mL DI water with ca. 2 min stirring and DI water added after complete dissolution to reach the total volume of 10 mL.

Aqueous solutions of HCl (37%, 12.0 M) and NH_4OH (25%, 13.4 M) were used as supplied. All stock solutions were kept in closed vessels in the dark at room temperature.

Samples for structural/spectral studies. Glass or adhesive carbon tape on silicon were used as substrates for spectral characterization, X-ray diffraction (XRD), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), respectively. To produce the samples, 0.20 mL 2-propanol is added to freshly synthesized and purified CANFIC precipitate, mixed till the formation of a homogeneous suspension, deposited on the substrates by drop-casting, and left for drying for 2-5 min under ambient conditions forming a dense and homogeneous layer.

Structural characterization. XRD patterns of CANFICs were registered using a Panalytical X'pert powder diffractometer with filtered $\text{Cu } K_\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and an X'Celerator solid-state stripe detector in the Bragg-Brentano geometry in an angle range of $2\theta = 5\text{-}100^\circ$ with a step rate of 0.05° per min. The XRD patterns were subjected to a Rietveld refinement procedure using MAUD software.

SEM and EDX analysis were performed using a JEOL JSM-7610F Schottky field emission scanning electron microscope operating under 15-20 kV acceleration voltage and equipped with an X-Max 80 mm^2 silicon drift detector (Oxford Instruments) and AZtec nanoanalysis software. EDX spectra were collected for at least five different spots of each sample and the results were averaged.

Spectral characterization. Diffuse reflectance spectra of CANFICs were recorded using a BlackComet spectrometer (StellarNet Inc.) and a 75W Xenon lamp (Thorlabs) as an excitation source. The spectra were registered with an optical Y-fiber probe in identical geometry for samples and a reference (ultra-pure BaSO₄, Alfa-Aesar). The light transmittance through the samples was found to be zero. The reflectance spectra were transformed into absorption spectra using the Kubelka-Munk formula and BaSO₄ as a scattering reference.

Raman spectra were registered on a WITec alpha700 confocal Raman microscope equipped with a UHTS 300 spectrometer and a 532-nm laser.

Tables

Table S1. Composition of CANFIC perovskites with varied nominal Fe/In ratio y

y	y_a	x	x_a	Composition (expected: Cs ₂ Ag _{0.50} Na _{0.50} Fe _{y} In _{1-y} Cl ₆)
1.00	1.00	0.50	0.64	Cs _{2.25} Ag _{0.64} Na _{0.36} FeCl _{6.5}
0.99	0.99	0.50	0.62	Cs _{2.05} Ag _{0.62} Na _{0.38} Fe _{0.99} In _{0.01} Cl _{6.22}
0.98	0.98	0.50	0.61	Cs _{2.12} Ag _{0.61} Na _{0.39} Fe _{0.98} In _{0.02} Cl _{6.13}
0.97	0.97	0.50	0.60	Cs _{2.13} Ag _{0.60} Na _{0.40} Fe _{0.97} In _{0.03} Cl _{6.15}
0.95	0.96	0.50	0.59	Cs _{1.94} Ag _{0.59} Na _{0.41} Fe _{0.96} In _{0.04} Cl _{5.82}
0.90	0.89	0.50	0.53	Cs _{1.97} Ag _{0.53} Na _{0.47} Fe _{0.89} In _{0.11} Cl _{5.88}
0.80	0.82	0.50	0.50	Cs _{2.06} Ag _{0.50} Na _{0.50} Fe _{0.82} In _{0.18} Cl _{5.89}
0.70	0.66	0.50	0.45	Cs _{2.02} Ag _{0.45} Na _{0.55} Fe _{0.66} In _{0.34} Cl _{6.03}
0.50	0.48	0.50	0.43	Cs _{1.97} Ag _{0.43} Na _{0.57} Fe _{0.48} In _{0.52} Cl _{5.62}
0.30	0.26	0.50	0.41	Cs _{1.97} Ag _{0.41} Na _{0.59} Fe _{0.26} In _{0.74} Cl _{5.44}
0.10	0.10	0.50	0.41	Cs _{2.04} Ag _{0.41} Na _{0.59} Fe _{0.10} In _{0.90} Cl _{5.32}
0	0	0.50	0.40	Cs _{1.98} Ag _{0.40} Na _{0.60} InCl _{5.28}

Note: in all cases the cation ratio was ([Fe]+[In]) : [Ag] : [Na] = 1 : 1 : 1, $x = [Ag]/([Ag]+[Na])$.

Figures

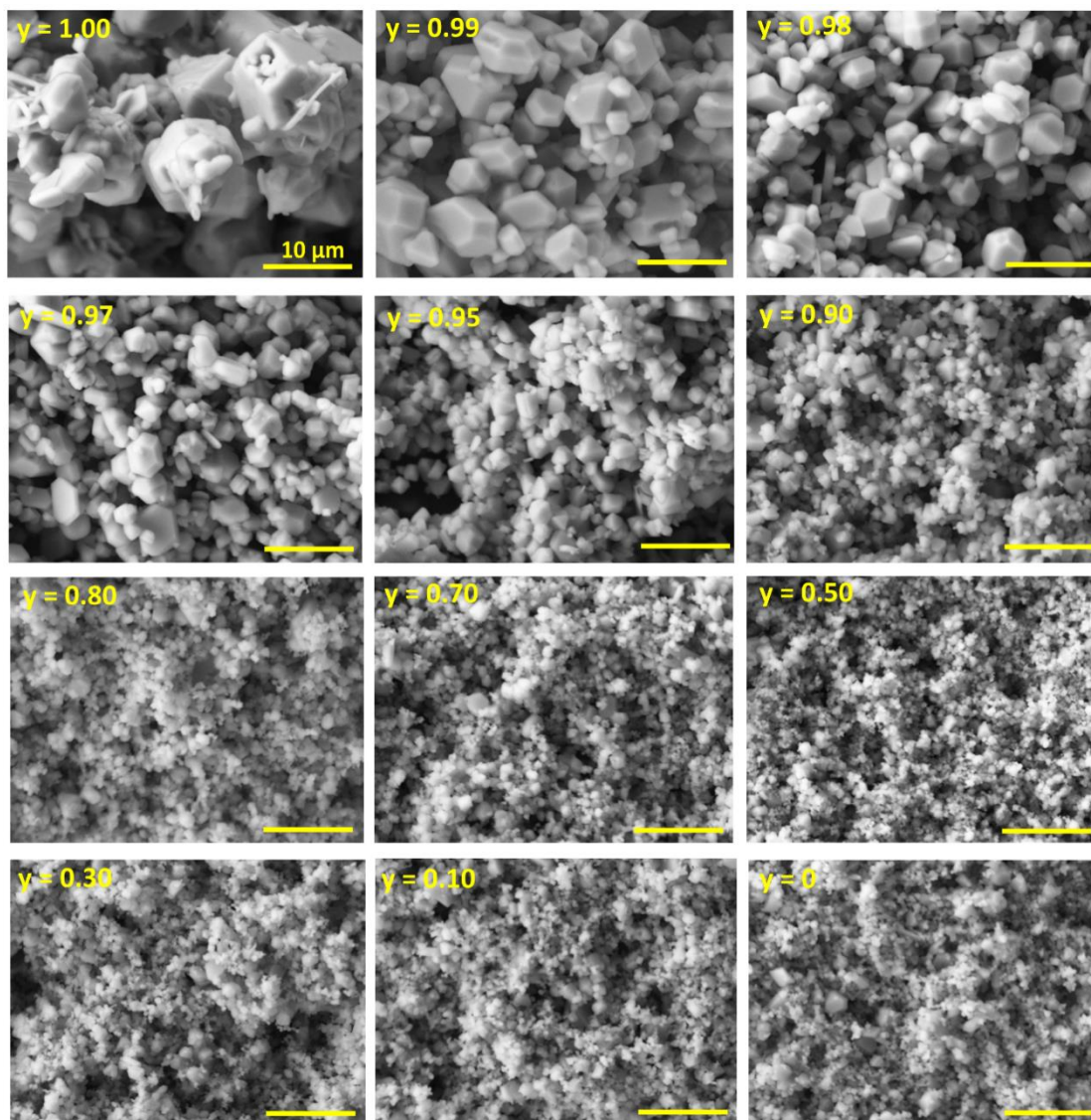


Figure S1. SEM images of CANFICs synthesized at different nominal Fe fractions γ .

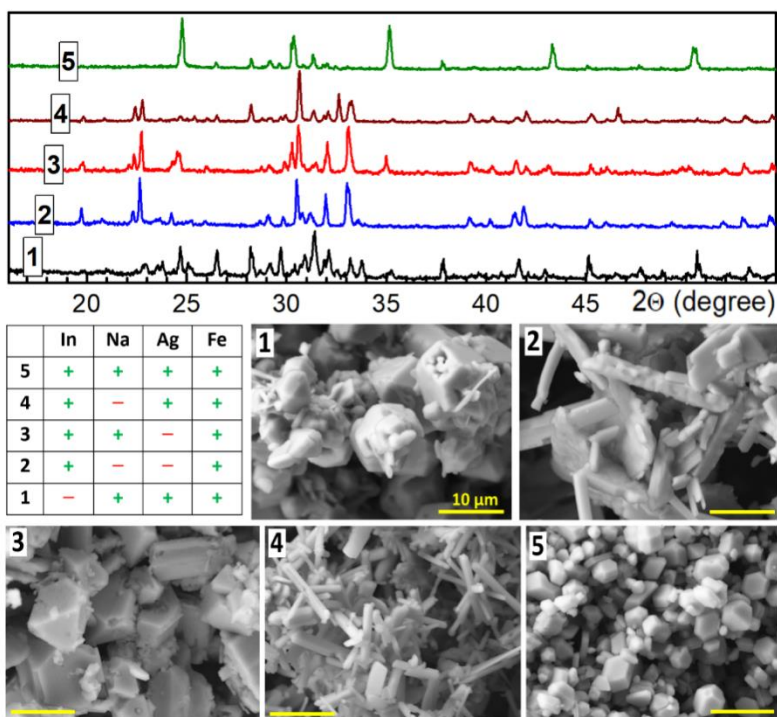


Figure S2. Upper part - XRD patterns (upper part) and SEM images (lower part) of CANFIC products synthesized in the absence of one or two metal constituents (curves 1-4) and with all three metals present (5). Curve 1 – no In, 2 – no Na and Ag, 3 – no Ag, 4 – no Na (see table in lower part).

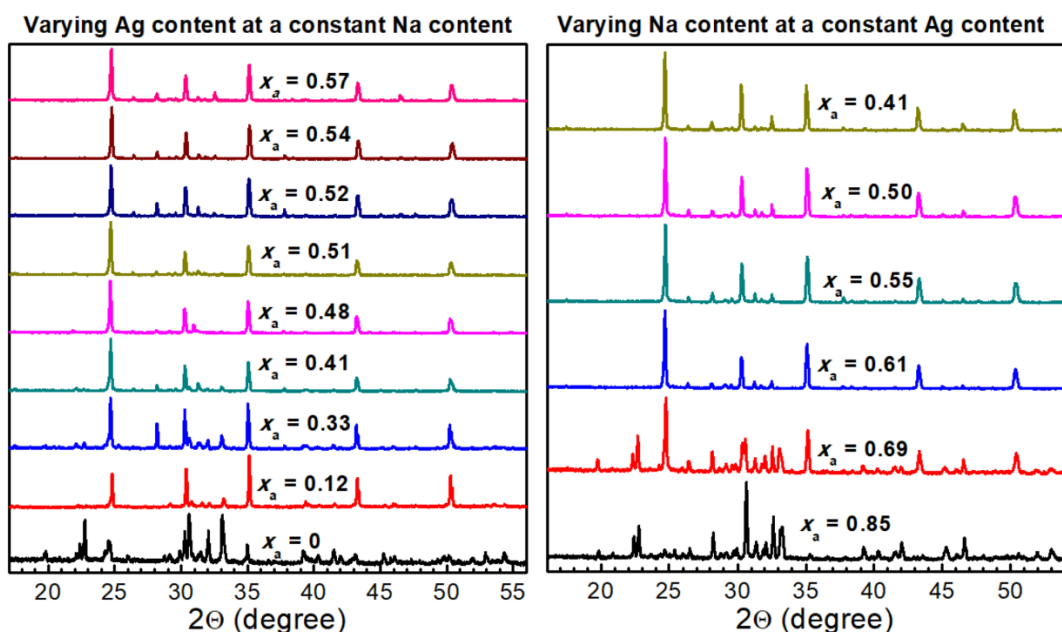


Figure S3. XRD patterns of CANFICs produced at different actual Ag fractions in two regimes: by varying Ag content at a constant Na content (left figure) and by varying Na content at a constant Ag content (right figure). Constant Ag(Na) content corresponds to 100% of stoichiometric quantity with respect to Fe+In. $\gamma = 0.95$ in all cases.

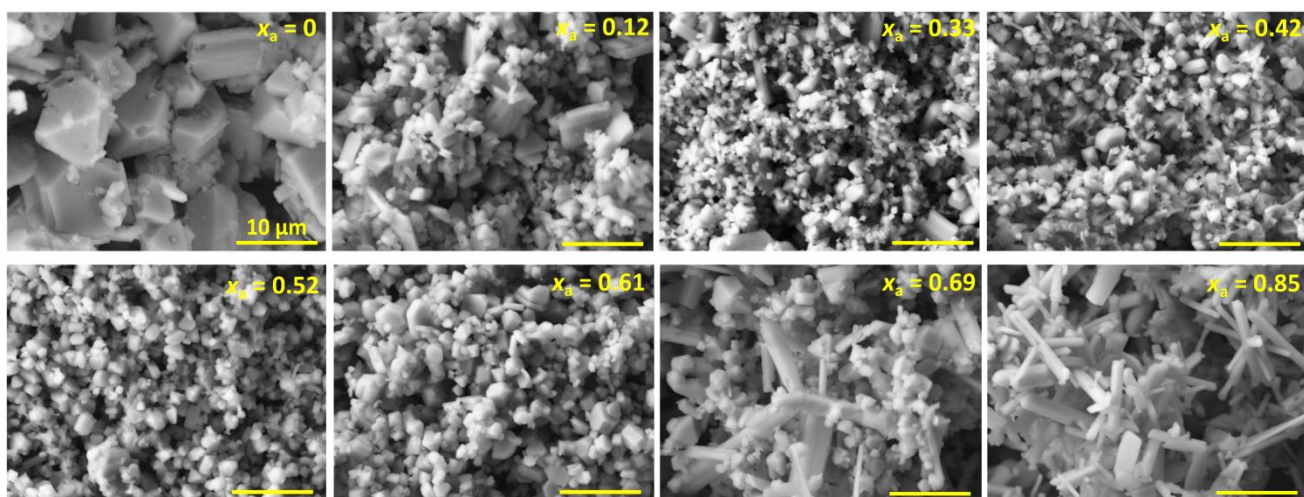


Figure S4. SEM images of CANFICs synthesized at different actual Ag fractions x_a .

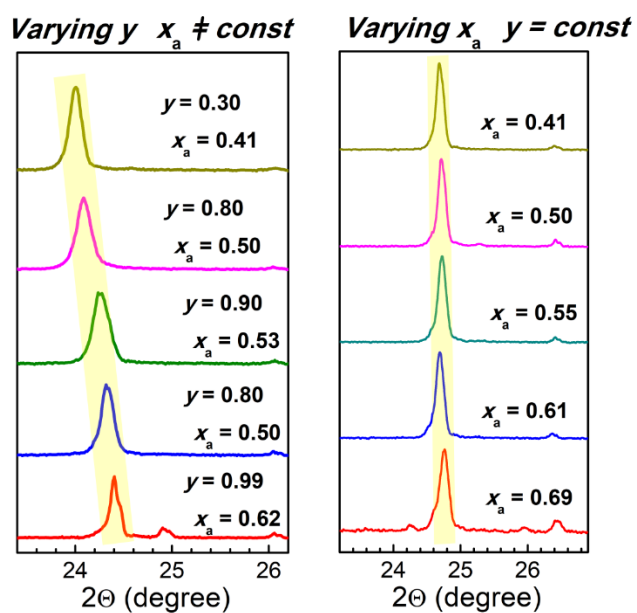


Figure S5. Fragments of XRD patterns of CANFIC perovskites produced varied y and x_a (left panel) and varied x_a and constant y (right panel).

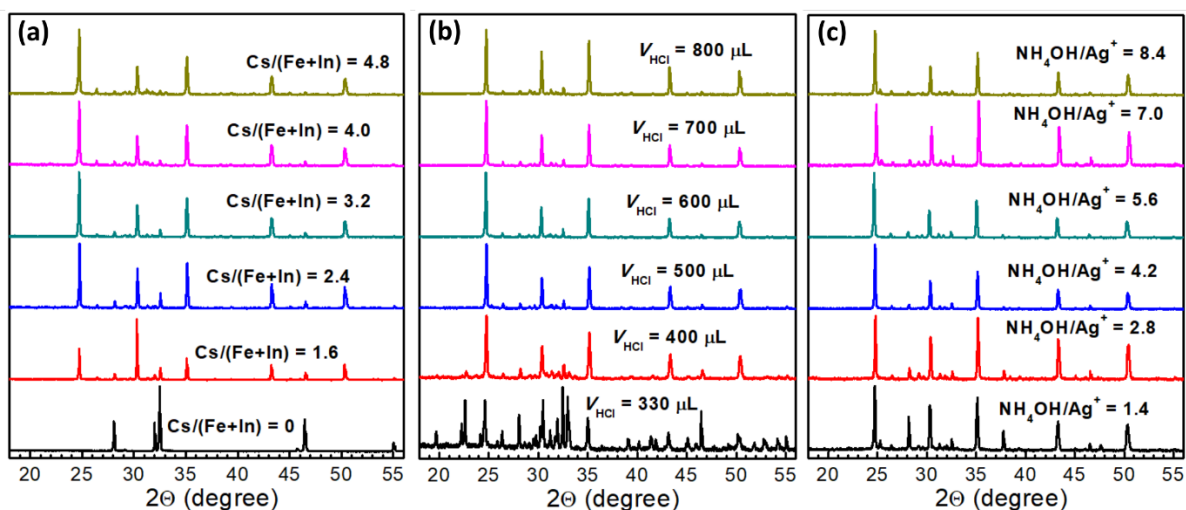


Figure S6. XRD patterns of CANFICs produced at varied Cs to Fe+In fraction (a), the varied volume of concentrated (12 M) HCl added to the precursors (b), and the varied ratio of $\text{NH}_4\text{OH}/\text{Ag}^+$ (c). $\gamma = 0.95$ in all cases.

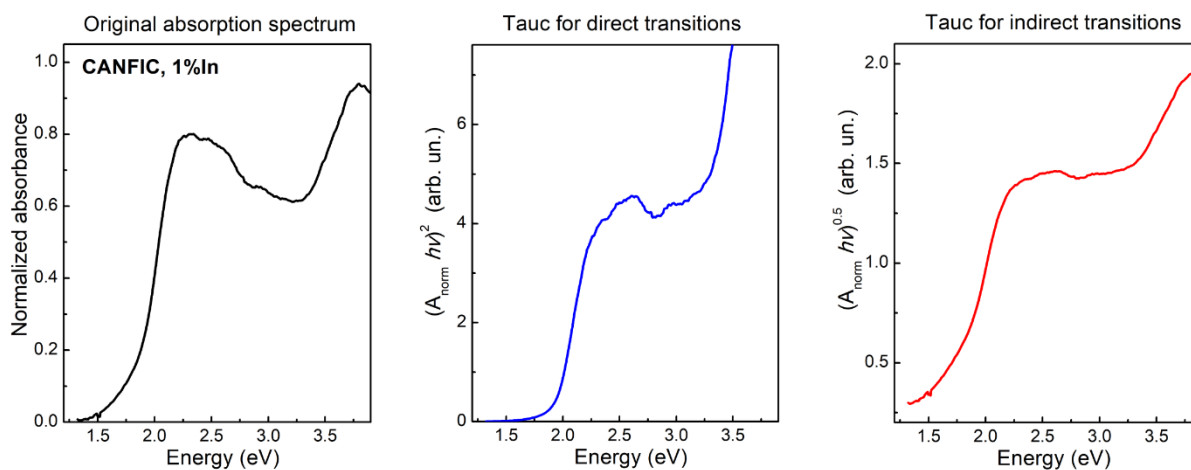


Figure S7. The normalized absorption spectrum of CANFIC perovskite (1% In) presented in the Tauc equation coordinates for direct and indirect interband electron transitions.

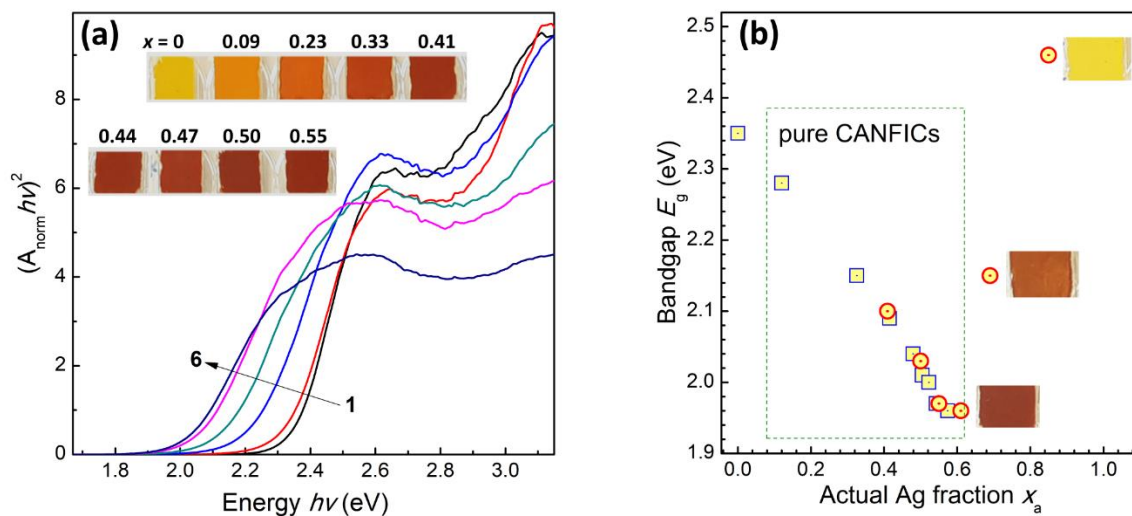


Figure S8. (a) Absorption spectra of CANFICs produced at different nominal Ag fractions $x = 0$ (curve 1), 0.09 (2), 0.23 (3), 0.33 (4), 0.47 (5), and 0.55 (6). (b) Bandgap E_g of CANFICs as a function of actual Ag fraction x_a . Nominal Fe fraction y is 0.95 in (a, b). Inserts show photographs of microcrystalline films with varied x on glass. Squares show a series with varied Ag content at a constant Na content, and circles – a series with varied Na content at a constant Ag content.