Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

"Green" Synthesis of Highly Luminescent Lead-Free $Cs_2Ag_xNa_{1-x}Bi_yIn_{1-y}Cl_6$ Perovskites

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Methods

Samples for structural and optical studies. Freshly produced precipitates were used to prepare homogeneous samples on various substrates which were selected to match each of the experimental methods. Glass and adhesive carbon tape on silicon were used for the characterization by X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX), and optical spectroscopy. To obtain homogeneously distributed layers of perovskites, 0.20 mL 2-propanol was added to the freshly synthesized and purified precipitates, and mixed until a homogeneous suspension was formed which was subsequently deposited onto the substrates by drop-casting. The suspension was left for drying under ambient conditions for 2-5 min forming a homogeneous layer.

Spectral characterization. Refrectance spectra were recorded using a BlackComet spectrometer (StellarNet Inc.) and a 75 W 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 $BaSO_4$, Alfa-Aesar). Absorption spectra were then calculated by dividing the reflectance spectra of the sample and the reference and subtracting the baseline. Additionally, absorption spectra were recorded for CANBIC during PL QY measurements on Quantaurus spectrometer. These spectra were identical to those detected using BlackComet spectrometer.

PL spectra were registered similarly to the reflectance spectra using BlackComet spectrometer in the range of 190-1000 nm using a UV LED (360-370 nm, Thorlabs) as an excitation source. The PL spectra were found to be identical to those registered during PL QY measurements on Quantaurus spectrometer. The CIE coordinate map and CCT were calculated by using Osram Color Calculator free software.

Photographs of luminescent CANBIC perovskites were registered at ambient conditions under illumination with UV lamp (350-370 nm).

Absolute PL QYs were determined using a Quantaurus-QY spectrometer (Hamamatsu) at room temperature. The sample was excited by the light from an in-built Xenon lamp with the excitation wavelength selected using a monochromator in 5 nm spectral bands. Ultra-pure $BaSO_4$ samples from Alfa-Aesar and Sigma-Aldrich were used as scattering references, both producing identical results. Three independently synthesized samples were measured at a set of excitation wavelengths and a distribution of PL QY values plotted to determine the average PL QY and standard deviation of the measurement. PL excitation spectra were additionally produced during these measurements.

Kinetic curves of PL decay were registered using a custom-designed setup based on a FluoTime300 luminescence spectrometer (Picoquant) equipped with 402 nm LDH-P-C-405B laser. The samples were excited by a 402 nm laser forwarded to the samples by an optical fiber and the PL signal collected in the range of 420-800 nm with excitation and emission slits set to 4 nm.

Raman spectra were detected on a WITec alpha700 confocal Raman microscope equipped with an UHTS 300 spectrometer in a spectral range of 100-1100 cm^{-1} and a resolution of 2 cm^{-1}. The samples were excited by a 532 nm laser with the maximal power of 7 mW.

The UV stability test was performed under ambient atmosphere by illuminating the CANBIC perovskite film on glass with a Smart UV source (MBJ, emission peak at 365 nm, nominal power 5 W) placed 10 cm above the CANBIC sample.

Structural characterization. XRD patterns were registered using a Panalytical X'pert powder diffractometer with filtered Cu K_α radiation ($\lambda = 1.54178$ Å) and an X'Celerator solid-state stripe detector in the Bragg-Brentano geometry in an angle range of 2θ = 5-100° with a step rate of 0.05° per min using 9 kV copper K_α irradiation. The samples were prepared by dropcasting of suspensions on glass and dried at ambient conditions. The XRD patterns were subjected to Rietvield refinement procedure using MAUD software.

SEM and cathodoluminescence imaging as well as EDX analysis were performed using a JEOL JSM-7610F Schottky field emission scanning electron microscope operating under 15-20 kV acceleration voltage. equipped with Deben Centaurus detector (for CL measurements) and X-Max 80 mm^2 silicon drift detector (Oxford Instruments and AZtec nanoanalysis software, for EDX measurements). The samples were prepared by drop-casting a suspension in 2-propanol onto polished adhesive carbon tape attached to a single-crystalline silicon plate and dried at ambient conditions. Cathodoluminescence images were registered at the lowest sensitivity of the detector.

XPS measurements (courtesy of Prof. Dietrich R.T. Zahn and Dr. Volodymyr Dzhagan, Chemnitz University of Technology) were performed with an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Scientific) equipped with a monochromatic Al K_α (1486.7 eV) source. A pass energy of 200 eV was used for survey spectra and 20 eV for high-resolution core-level spectra (providing a spectral resolution of 0.5 eV). Spectra deconvolution and quantification were performed using the Avantage Data System (Thermo Scientific).

Tables

Table S1. Selected literature reports on highly-luminescent microcrystalline In/Bi-based double perovskites

Structure	Additional dopants	PL QY (%)	Reference
CANBIC	-	86	10.1038/s41586-018-0691-0
	-	**92**	**Present work**
	-	89.9	10.1021/acs.chemmater.0c02463
	Ni, Ce	98.4-98.6	
CANBIC-SiO_2	-	57.3	10.1039/d1dt01325d
CANIC	Bi+Sb	41	10.1021/acsami.1c07809
CABIC	-	52.4	10.1039/d1dt04047b
CNIC	Sb	75.9	10.1021/acs.jpclett.0c00330
	Bi+Sb	77	10.1021/acsenergylett.1c01442

Figures

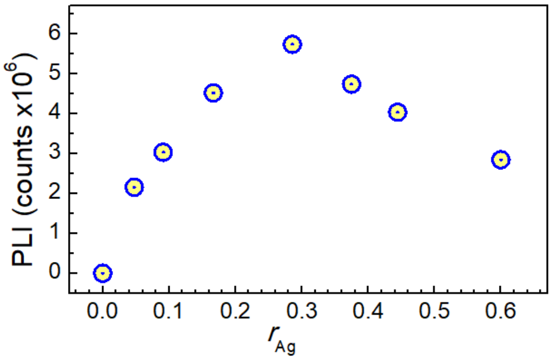

Figure S1. Integral PL intensity (PLI) of CANBIC perovskites produced at $y = 0.02$, 22 °C, [Cs]:[In] = 2.2 and different r_{Ag}.

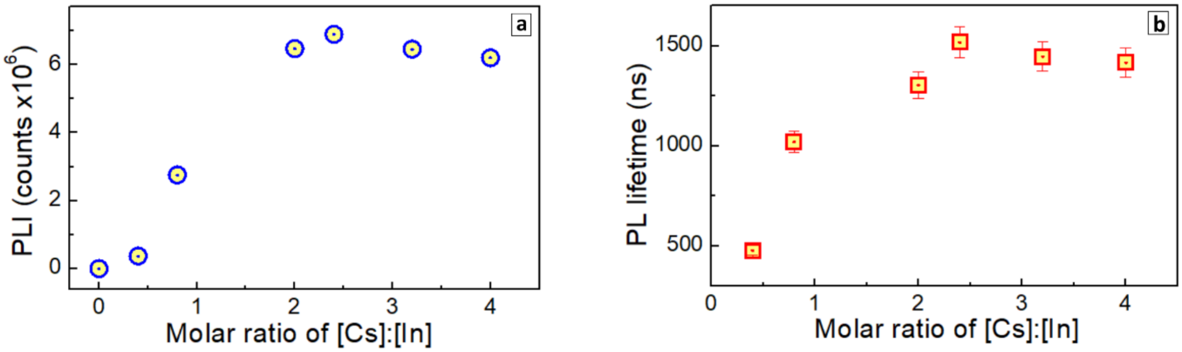

Figure S2. Integral PL intensity (PLI) (a) and PL lifetime (b) of CANBIC perovskites produced at $y = 0.02$, $r_{Ag} = 0.3$ and diferent molar ratio of [Cs]:[In] at 22 °C

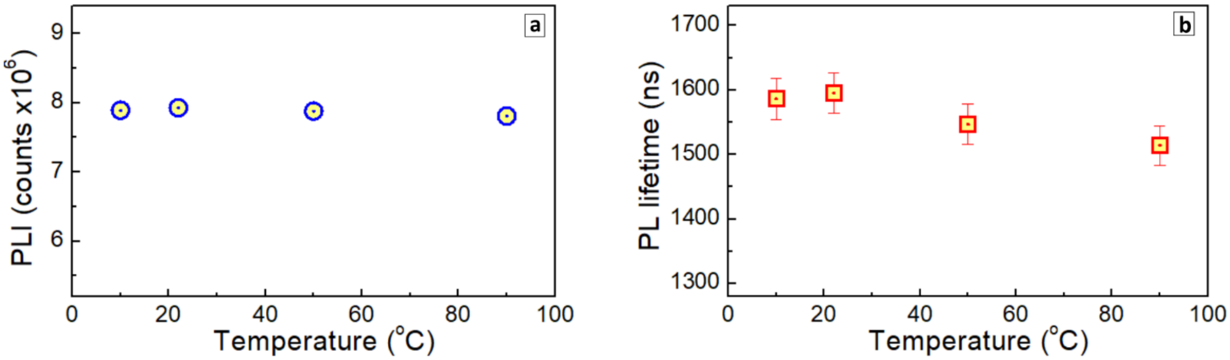

Figure S3. Integral PL intensity (PLI) (a) and PL lifetime (b) of CANBIC perovskites produced at $y = 0.02$, $r_{Ag} = 0.3$, [Cs]:[In] = 2.2 and different temperature

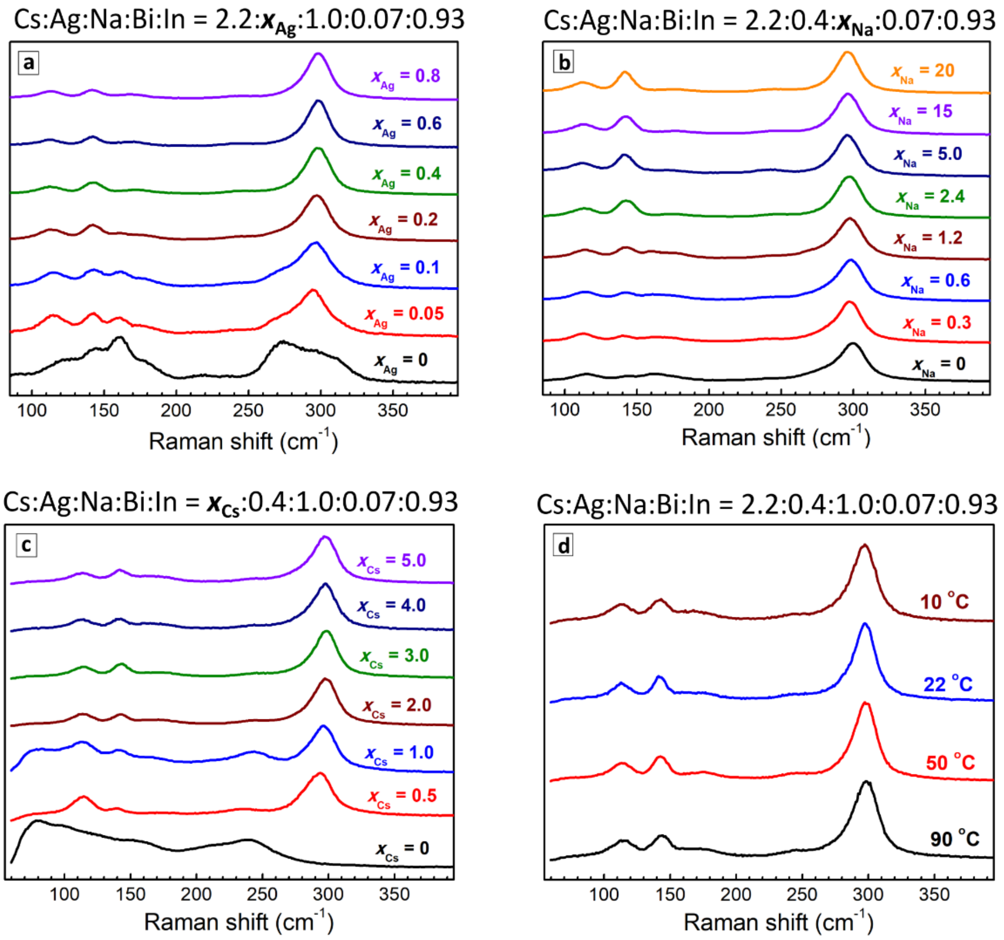

Figure S4. Raman spectra of CANBIC perovskites produces with variation of concentration of various components and the temperature of the synthesis. *Acknowledgement*: The authors thank Prof. Dietrich R.T. Zahn and Dr. Volodymyr Dzhagan (Semiconductor Physics, Chemnitz University of Technology) for providing these Raman data.

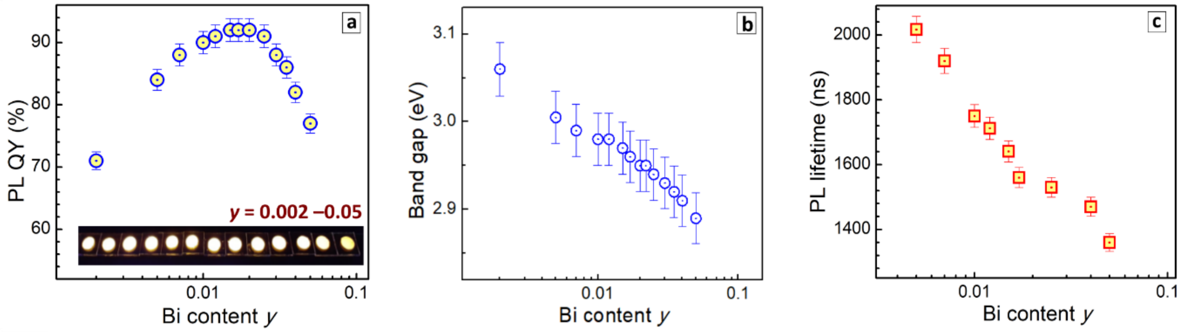

Figure S5. PL QY (a), bandgap (b), and PL lifetime (c) of CANBIC perovskites produced at x = 0.4 and different y at 22 °C. Insert in (a): a photograph of CANBIC samples with varied y (increasing from left to right) taken under UV illumination (350-370 nm). Red dashed line in (b) shows bandgap of undoped CANIC perovskite.

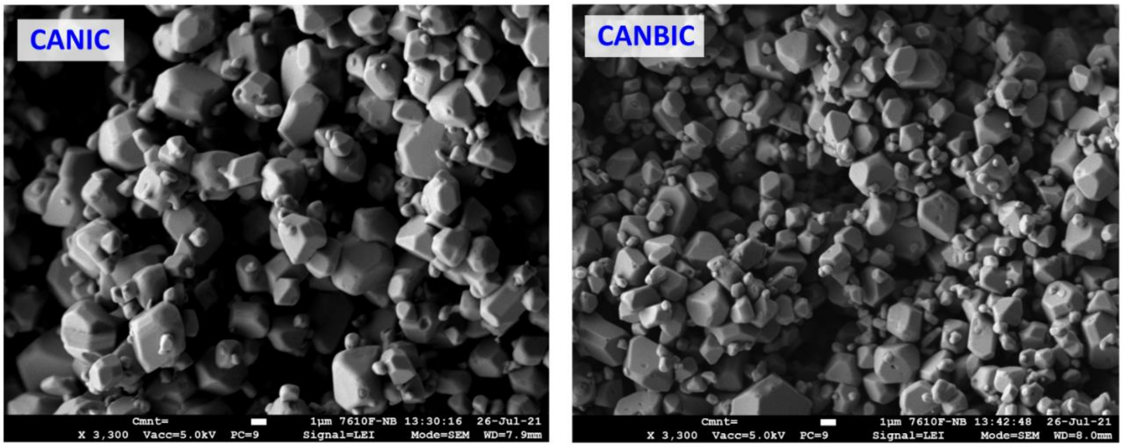

Figure S6. Survey SEM images of CANIC and Bi-doped CANBIC (2% Bi) perovskites.

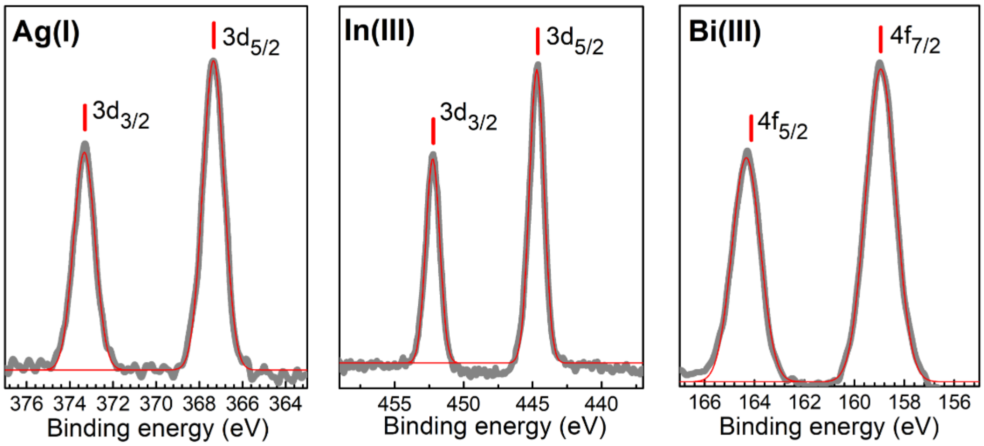

Figure S7. High-resolution X-ray photoelectron spectra of CANBIC perovskite (5%Bi) in the range of Ag3d, In3d, and Bi4f electron binding energies. Gray curves represent experimental spectra, red and blue lines – fits with Gaussian profiles. *Acknowledgement*: The authors thank Prof. Dietrich R.T. Zahn and Dr. Volodymyr Dzhagan (Semiconductor Physics, Chemnitz University of Technology) for providing XPS data.

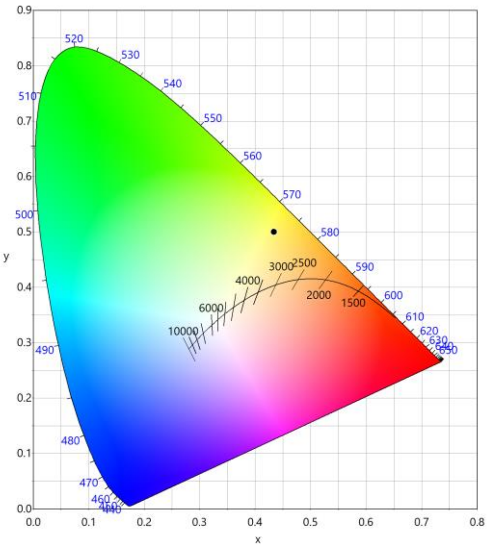

Figure S8. CIE color map showing the position of the emission color of CANBIC perovskite (y = 0.02, black point).

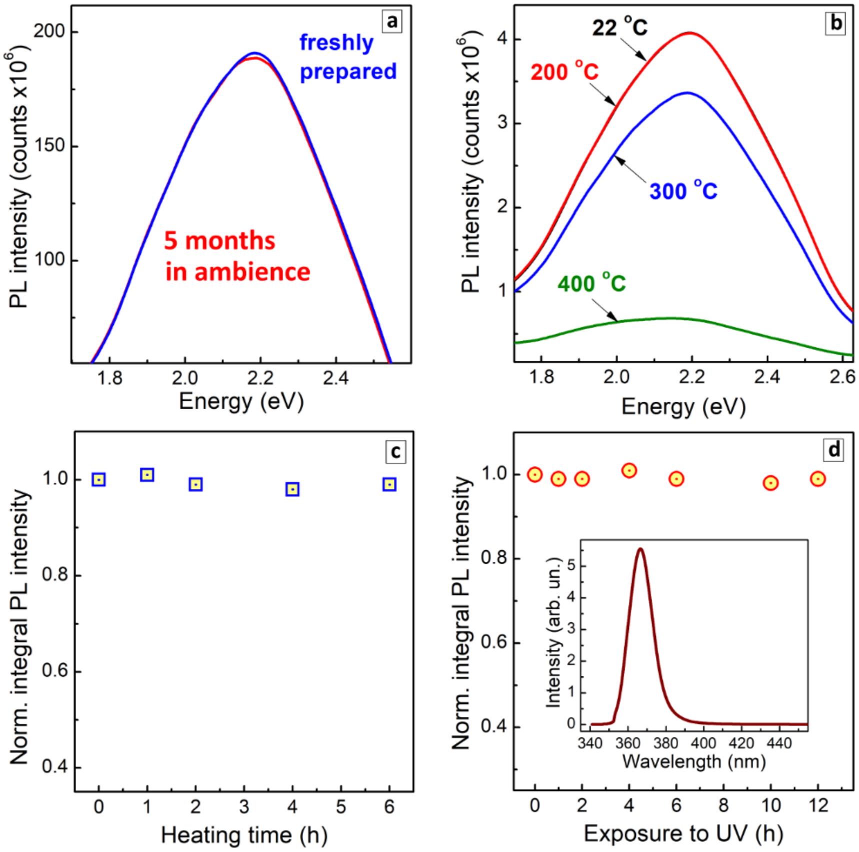

Figure S9. (a, b) PL spectra of CANBIC perovskite (y = 0.05) subjected to (a) prolonged (5 months) storage under ambient conditions in the dark; (b) heating at 200-400 °C for 30 min on air. (c, d) Integral PL intensity of the CANBIC perovskite as a function of the duration of heating at 150°C (c) and illumination with UV light (d). Insert in (d): emission spectrum of UV source used for the test.