Supporting Information

**Colloidal Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ Nanocrystals:** Undercoordinated Surface Cl Ions Limit their Light Emission Efficiency

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**EXPERIMENTAL SECTION**

**Chemicals.** Bismuth(III) acetate [Bi(ac)$_3$, 99.99%], cesium carbonate (Cs$_2$CO$_3$, 99%), silver acetate [Ag(ac), 99.99%], sodium acetate [Na(ac), 99%], indium(III) acetate [In(ac)$_3$, 99.99%], benzyol chloride (99%), oleylamine (C$_{18}$B, 70%), oleic acid (C$_{18}$A, 90%), hexane (anhydrous, 95%), ethyl acetate (EtAc, 99.9%), dioctyl ether (DOE, 99%), octanoic acid (C$_8$A, ≥99%), decanoic acid (C$_{10}$A, 98%), dodecanoic acid (C$_{12}$A, 98%), myristic acid (C$_{14}$A, 99%), palmitic acid (C$_{16}$A, 99%), phenylacetic acid (PhAc, 99%), octylamine (C$_8$B, 99%), decylamine (C$_{10}$B, 99%), dodecylamine (C$_{12}$B, 98%), tetradecylamine (C$_{14}$B, 95%), hexadecylamine (C$_{16}$B, 98%), dimethyl sulfoxide-d (DMSO-d$_6$, 99.9%) and chloroform-d (CDCl$_3$, 99.8%) were purchased from Sigma-Aldrich.
**Synthesis of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs.** Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs were prepared following an approach developed by our group with minor changes. In a typical synthesis, 0.25 mmol of Cs$_2$CO$_3$, 0.15 mmol of Ag(ac), 0.1 mmol of Na(ac), 0.25 mmol of In(ac)$_3$, 2.5 μmol of Bi(ac)$_3$, and 3.77 mmol of the desired carboxylic acid were mixed with 4 mL of DOE into a 20 mL glass vial under air (Scheme 1). The mixture was heated up to 90 °C under vigorous stirring for 15 min to dissolve the metal cation precursors. Then, 1.25 mmol of the desired alkylamine was added into the flask and the temperature was increased up to 120 °C. At this point, a solution of 1.72 mmol of benzoyl chloride in 600 μL of DOE was swiftly injected to trigger the reaction, which was immediately quenched by immersing the flask in an ice-water bath. The product was centrifuged at 4500 rpm for 5 min and the precipitate was dispersed in 3 mL of hexane for further characterizations.

**Transmission Electron microscopy (TEM).** The samples were prepared by dropping dilute solutions of NCs onto carbon film-coated 200 mesh copper grids for TEM measurements, which were carried out on a JEOL JEM-1011 transmission electron microscope operating at an acceleration voltage of 100 kV.

**X-ray diffraction (XRD).** XRD patterns were collected on a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and PIXcel3D 2x2 area detector operating at 45 kV and 40 mA. The patterns were collected in air at room temperature using a Parallel-Beam (PB) geometry and the symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution onto a zero-background silicon wafer. XRD patterns were processed using the HighScore software.

**Elemental analysis.** The elemental analysis was performed via energy dispersive X-ray spectroscopy (EDS) on a JEOL JSM-7500FA SEM-Analytical field-emission scanning electron microscopy (SEM) with an Oxford X-Max 80 system equipped with an 80 mm$^2$ silicon drift detector (SDD). To detect the small concentration of Bi inside the Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs, inductively coupled plasma mass spectrometry (ICP-MS) was preferred. This was carried out using an iCAP-TQ triple quadrupole spectrometer (ThermoFisher Scientific). The instrument was set with the following parameters to analyze the samples: plasma power 1550 W; spray chamber temperature 2.7°C; cool flow 14 l/min; aux flow 0.8 l/min. To prepare the sample for the analysis, 2 μL of the as-synthesized samples were diluted in 2 mL of hexane, then 10 μL of these diluted samples were dissolved in 100 μL of nitric acid (HNO$_3$ 60% v/v). The solution was further diluted by 10 mL of Milli-Q water and analyzed.

**UV–vis Absorption, PL and PLQY Measurements.** UV–vis absorption spectra were recorded using a Varian Cary 300 UV–vis spectrophotometer. PL and PLQY measurements were performed on an Edinburgh FLS920 spectrophotometer equipped with a Xenon lamp Xe900 and an integrating sphere. PL excitation and emission spectra were corrected taking into account the lamp and setup response. For absolute Quantum Yield measurements we used a correction file specifically calibrated for the integrating sphere, grating and detector employed. The samples were diluted to reach an optical density of 0.1 at the wavelength of excitation (340 nm).

**NMR measurements.** For these analyses, the samples of PhAc-C18B require a different washing step: (i) the crude solution (5 ml) was centrifuged at 6000 rpm for 5 min. (2) The
precipitate was redispersed with 1 ml of anhydrous CHCl₃ shaking vigorous to get a turbid brown solution; (3) The turbid solution was left to sediment for 2 hours and the transparent supernatant was collected; (4) EtAc (1 times in volume) was added to supernatant resulting in a turbid dispersion that was centrifuged at 4500 rpm for 5 min; (5) the precipitate was redispersed in CHCl₃ (1 ml) and reprecipitated with the addition of EtAc (1 times in volume) and centrifugation at 4500 rpm for 5 min; (6) the precipitate was collected and redispersed in 0.6 ml of CDCl₃. All NMR spectra were acquired at 300 K on a Bruker Advance III 400 MHz spectrometer, equipped with a Broad Band Inverse probe (BBI). ¹H NMR spectra were accumulated after an automatic 90° optimization on each sample tube, with 120 transients, 65526 digit points, no steady scans, at a fixed receiver gain (1 or 64 according to sample concentration), over a spectral width of 20.55 ppm (offset at 6.18 ppm). An apodization function equivalent to 0.3 Hz was applied to the FIDs before Fourier transform. All spectra were referred to the residual non-deuterated solvent signal, at 7.26 ppm or at 2.50 ppm, for CDCl₃ and DMSO-d₆ respectively. 2D Nuclear Overhauser effect spectroscopy (¹H-¹H NOESY): the experiment (noesygpph, Bruker library) was acquired in CDCl₃ with 64 scans, a relaxation delay of 2s, a mixing time of 350 ms, by using 2048 data points in the direct dimension and 256 increments.

**Computational Methodology.** For the classical molecular dynamics (MD) simulations the interactions between atoms/ions were modelled by a CHARMM force field. In particular, the interactions between the inorganic core ions Cs, Ag, In, Cl and carboxylate/ammonium headgroup atoms were modeled by only non-bonded interactions, the Lennard-Jones and the Coulomb potentials. The corresponding parameters were fitted using an adaptive rate Monte Carlo optimization algorithm as described in the literature and implemented in our own developed auto-FOX code. Here, radial distribution functions (rdf) between pairs of atoms are initially computed at a higher level of theory, by performing ab-initio DFT molecular dynamics for 10 ps. Then, these rdfs are fitted at the lower level methodology, in our case a classical force-field, using the rate adaptive algorithm. This approach has been successful to obtain parameters for CdSe nanocrystals capped with oleate ligands and more recently also for perovskite nanocrystals (publications to be released soon). The forcefield parameters describing the oleylammonium and phenylacetate ligands were taken using the MATCH algorithm, which obtains the parameters by comparison of chemical fragments as present in the literature. Finally, a starting nanocrystal of 6nm was prepared by randomly displacing 80% of surface Cl by Phenylacetate and 50% of Cs ions by oleylammonium. This was done using the nano-CAT set of tools developed by us.

The classical MD simulations on our nanocrystal model consisted of three successive steps. (1) an initial structure relaxation by a steepest-descent minimization. (2) a 1.5 ns equilibration run in vacuum at constant volume and temperature (300K) allowing the ligands to diffuse on the NC surface. In both stages, the position of the inorganic core atoms, i.e. Cs, Ag, In and Cl, were restrained to a fixed position using a very stiff harmonic potential to maintain the NC integrity. (3) Finally, a production run of 10 ns at 300K, still in vacuum, where also the inorganic core were allowed to relax. All simulations were performed using GROMACS.
For the electronic structure calculations, we have carried out atomistic simulations at the density functional theory level using the PBE exchange–correlation functional and a double-ζ basis set plus polarization functions on all atoms as implemented in the CP2K 6.1. All structures have been optimized in vacuum. Scalar relativistic effects were incorporated as effective core potential functions in the basis set. Spin–orbit coupling effects were not included, but their impact on the relaxed structural properties was demonstrated to be negligible for similar systems. More details on how the models were built is found in the main text.

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**Table S1.** SEM-EDS and ICP elemental analyses of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs synthesized using different carboxylic acid-alkylamine combinations.
|                | %   | 1.93 | 0.67 | 0.46 | 5.34 |
|----------------|-----|------|------|------|------|
| C16A+C14B      | 1.05% | 1.93 | 0.67 | 0.46 | 5.34 |
| C16A+C16B      | 1.30% | 2.12 | 0.7  | 0.5  | 6.02 |
| C16A+C18B      | 1.70% | 2.1  | 0.7  | 0.5  | 6.3  |
| C18A+C8B       | 1.10% | 1.9  | 0.7  | 0.21 | 5.2  |
| C18A+C10B      | 0.86% | 2    | 0.55 | 0.4  | 5.76 |
| C18A+C12B      | 0.97% | 2.12 | 0.52 | 0.53 | 6.09 |
| C18A+C14B      | 1.05% | 2.07 | 0.72 | 0.46 | 5.55 |
| C18A+C16B      | 1.30% | 2.02 | 0.67 | 0.37 | 5.4  |
| C18A+C18B      | 1%    | 2.2  | 0.7  | 0.51 | 6.2  |
| PhAc+C18B      | 1.30% | 2.3  | 0.65 | 0.62 | 6.0  |
Figure S1. a) Size distribution histogram and b) absorption and PL spectra of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs synthesized by employing PhAc and oleylamine (Cit8B).
Figure S2. $^1$H NMR spectra in CDCl$_3$ of (a) mixture of PhAc acid and oleylamine (C$_{18}$B) (mole ratio = 1:1), and (b) PhAc+C$_{18}$B Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs (the same spectrum reported in Figure 1c); diagnostic peaks are assigned.
Figure S3. $^1$H-$^1$H 2D NOESY spectrum in CDCl$_3$ of mixture of PhAc and oleylamine (C18B) (mole ratio = 1:1), as free ligands, all the cross peaks show positive (blue) sign, indicating a fast correlation time ($\tau_c$) for both species in solution.
**Figure S4.** $^1$H NMR spectrum in CDCl$_3$ of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs made with PhAc and oleylamine (OAm in this figure) and not subjected to the cleaning step with EtAc. It is possible to detect here the presence of free ligands and of the amide formed by the condensation of PhAc and OAm (PhAc-OAm amide), diagnostic peaks are assigned. The corresponding NOESY spectrum was shown in Figure S5.
Figure S5. $^1$H-1H 2D NOESY spectrum in CDCl$_3$ of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs made with PhAc and oleylmaine (OAm in this figure) and not subjected to the cleaning step with EtAc. Ligands dynamically interacting with the NCs’ surface return negative sign (red) cross peaks due to a long correlation time ($\tau_c$), whereas impurity such as PhAc-OAm amide returns positive sign (blue) cross peak, indicating a fast correlation time($\tau_c$), similar to that of free molecules in solution. PhAc-OAm amide, therefore, is not bound to the NC surface.
Figure S6. $^1$H NMR spectrum of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs after their dissolution in DMSO-d6. The ratio between the integrated areas of the peaks at 3.3 ppm (23, representative of the PhAc) and at 2.5 ppm (2, representative of the oleylamine) is 1.15:1.
Estimate of the number of surface sites passivated by PhAc and C18B
A cubic NC having a side of 24.4 nm (and surface terminated by CsCl) the surface area is 3572.16nm$^2$ and it is characterized by 13256 Cl and 13254 Cs surface sites.

The NMR analysis yielded a number of PhAc species per NC of 10575 and a number of C18B species per NC of 6932. The resulting surface coverage is 4.92 ligands/nm$^2$ with 80% of Cl surface sites are occupied by PhAc and 52% of Cs surface sites occupied by C18B.

Figure S7. Time-average radial distribution functions obtained from the MD simulations at room temperature of a ∼6.0 nm Cs$_2$AgInCl$_6$ NC capped with 82% PhAc / 54% C18B, corresponding to the probability of finding: (red) PhAc ligands around a given PhAc ligand; (green) C18B ligands around a given C18B ligand; (blue) PhAc ligands around a given C18B ligand or viceversa. For each curve, the dashed line indicates the radial distance at the initial maximum which characterizes the average distance between nearest-neighbor ligands. The distances between ligands are calculated using the positions of their head groups (carbon atoms of the anchoring carboxylate groups and nitrogen atoms of the anchoring ammonium groups for PhAc and C18B, respectively). The figure shows that the relative distance between PhAc and OLAM is shorter than pairs of PhAc and OLAM combinations indicating that the two types of ligands are intermixed.
**Figure S8.** TEM images of Bi-doped Cs$_{2}$Ag$_{1-x}$Na$_x$InCl$_6$ NCs synthesized with different combinations of alkylamines and carboxylic acids. Scalebars are 50nm.
Figure S9. (a-e) XRD patterns of samples obtained with different combinations of alkylamines and carboxylic acids. (f) XRD patterns of hexadecilamine (C16B), tetradecylamine (C14B), hexadecanoic acid (C16A) and tetradecanoic acid (C14A). The impurity peaks present in some of the products in (a-e) can be attributed to the presence
of either alkylamines and/or carboxylic acids shown in (f) which could not be washed away from the nanocrystals.

**Figure S10.** Absorption spectra and PL emission curves of Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs obtained with different combinations of alkylamines and carboxylic acids.
**Table S2.** PLQY values and mean NC size measured for Bi-doped Cs$_2$Ag$_{1-x}$Na$_x$InCl$_6$ NCs synthesized using different carboxylic acid-alkylamine combinations.

| Sample     | PLQY (%) | Mean Size (nm)    |
|------------|----------|-------------------|
| C10A-C8B   | 22       | 16.1 ± 1.7        |
| C10A-C10B  | 25       | 14.4 ± 3.1        |
| C10A-C12B  | 14       | 17.4 ± 2.9        |
| C10A-C14B  | 20       | 21.1 ± 4.5        |
| C10A-C16B  | 23       | 50.2 ± 14.5       |
| C10A-C18B  | 23       | 14.3 ± 1.7        |
| C12A-C8B   | 26       | 20.5 ± 2.1        |
| C12A-C10B  | 37       | 12.5 ± 1.2        |
| C12A-C12B  | 26       | 13.1 ± 1.9        |
| C12A-C14B  | 15       | 17.2 ± 2.9        |
| C12A-C16B  | 30       | 14.1 ± 2.9        |
| C12A-C18B  | 26       | 9.9 ± 1.1         |
| C14A-C8B   | 27       | 23.2 ± 5.3        |
| C14A-C10B  | 26       | 19.3 ± 3.4        |
| C14A-C12B  | 25       | 10.5 ± 1.2        |
| C14A-C14B  | 16       | 13.7 ± 2.6        |
| C14A-C16B  | 17       | 19.2 ± 2.9        |
| C14A-C18B  | 24       | 14.2 ± 1.5        |
| C16A-C8B   | 4        | Heavily aggregated|
| C16A-C10B  | 16       | Heavily aggregated|
| C16A-C12B  | 0        | Heavily aggregated|
| C16A-C14B  | 0        | Heavily aggregated|
| C16A-C16B  | 0        | Heavily aggregated|
| C16A-C18B  | 16       | 8.9 ± 1.1         |
| C18A-C8B   | 23       | 17.8 ± 2.5        |
| C18A-C10B  | 25       | 18.0 ± 2.3        |
| C18A-C12B  | 17       | 16.5 ± 3.8        |
| C18A-C14B  | 21       | 14.5 ± 1.5        |
| C18A-C16B  | 21       | 13.0 ± 1.5        |
| C18A-C18B  | 21       | 12.0 ± 0.9        |
Figure S11. Variation of the PL emission of DP NCs obtained with C12A-C10B and exposed to different ligand pairs.
Figure S12. (left) Electronic structure of a \( \sim 3.0 \) nm \( \text{Cs}_{324}\text{Pb}_{216}\text{Cl}_{756} \) NC model optimized at the DFT/PBE level of theory after the removal of four CsCl ion pairs around a Cl ion. This Cl ion although coordinated by only one nearby ion (the Pb below it), contributes to the formation of “shallow” trap states, well within the valence band. This is in strike contrast with the double perovskite nanocrystal presented in the main text. (right) Relaxed structure of the NC model illustrating the one-coordinated Cl surrounding.
Figure S13. a) Transient absorption spectra for the representative high PLQY sample. The three major bleach features, corresponding to the transition involving electronic states deep in the conduction band and the localized exciton, are clearly visible. A broad photoinduced absorption (PIA) covers the entire spectral region, superimposing a strong negative background. Overlapped to this negative PIA signal, which arises immediately after photoexcitation (0 ps) and has fully evolved within approximately 1.45 ps (grey thin lines), there is the simultaneous rise of the bleach features mentioned above. The PIA signal might be due to the presence of very dense optically inactive states within the valence band (VB) and conduction band (CB) that become accessible after photoexcitation only. b)
Pump-probe dynamics in the first few picoseconds at the three main feature (E = 1.95 eV, 2.6V and 3.45 eV, as highlighted in the first panel). The similar rise time of approximately 0.5 ps of these transitions indicates that they share a common state which, in our case, it is most probably connected to the hole since the dynamics in the CB does not contribute significantly to the signal. c) Pump-probe dynamics of representative low PLQY samples (15%) at E = 3.1eV. This novel transition is most probably related to transitions involving surface trap states. The immediate signal rise time indicates that an ultrafast hole trapping takes place followed by a recovery of the signal, and thus a depletion of this state, within a few picoseconds only.