

Supporting Information

Enabling White Color Tunability in Complex 3D-Printed Composites by using Lead-Free Self-Trapped Exciton 2D Perovskites/Carbon Quantum Dots Inks

Tawanwit Luangwanta,^{1,2} Silver-Hamil Turren-Cruz,^{1,3} Sofia Masi,¹ Samrat Das Adhikari,¹ Ileana Recalde,¹ Marcileia Zanatta,¹ Diego Iglesias,¹ Jhonatan Rodríguez-Pereira,⁴ Santi Gené-Marimon,⁵ Eugenia Martínez-Ferrero,⁵ Sulawan Kaowphong,² Emilio Palomares,^{5,6} Victor Sans,¹ Andrés F. Gualdrón-Reyes,^{1,7*} and Iván Mora-Seró^{1,*}*

¹Institute of Advanced Materials (INAM), Universitat Jaume I (UJI), Avenida de Vicent Sos Baynat, s/n, 12071 Castelló de la Plana, Castellón, Spain.

²Department of Chemistry, Center of Excellence in Materials Science and Technology, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

³Department of Physical Chemistry, Polish Academy of Sciences, Warsaw 01-224, Poland.

⁴Central European Institute of Technology, Brno University of Technology, Purkyňova 123, 612 00 Brno, Czech Republic.

⁵The Institute of Chemical Research of Catalonia – CERCA (ICIQ-CERCA) Tarragona, 43007, Spain.

⁶ICREA. Passeig Lluís Companys, 28. 08010 Barcelona. Spain.

⁷Facultad de Ciencias, Instituto de Ciencias Químicas, Isla Teja, Universidad Austral de Chile Valdivia, 5090000, Chile.

Corresponding authors: sero@uji.es, andres.gualdron@uach.cl, silver.turren@gmail.com

Experimental section

Synthesis of A₂SnX₄ perovskite microcrystals

OLA₂SnX₄ (X = Br, I) and PEA₂SnI₄ halide perovskites (HPs) were synthesized by using the hot-injection colloidal method, combining stoichiometrically oleic acid (OA)/oleylamine (OLA) and OA/phenethylamine (PEA) solutions and SnX₂-trioctylphosphine (TOP, 718165, 97%, Sigma-Aldrich) at high temperature, respectively. For the preparation of SnX₂-TOP, 0.35 g SnBr₂ (309257, Sigma-Aldrich) [0.43 g SnI₂ (T3449, >97.0 %, TCI)] were mixed with 1.5 mL TOP into a 20 mL three-neck flask at 160 °C under N₂ atmosphere for 1 h. Then, the resultant transparent solution was kept at 100 °C for subsequent use. For the preparation of OLA₂SnX₄ HPs, 0.4 mL of each OA (364525, 90 %, Sigma-Aldrich) and OLA (HT-OA100, 98 %, Sigma-Aldrich) were mixed with 20 mL 1-octadecene (1-ODE, O806, 90 %, Sigma-Aldrich) into a 50 mL three neck flask and dried under vacuum for 1 h at 100 °C. Then, the temperature of

OA/OLA solution was rapidly increased to reach 180 °C and 1 mL of preheated SnX₄-TOP solution was swiftly injected, obtaining a white precipitate. Similar procedure was conducted during the preparation of PEA₂SnI₄ by injecting 1 mL SnI₂ -TOP solution to a mixture of dried 0.4 mL OA/0.2 mL PEA (128945, 99 %, Sigma-Aldrich) in 20 mL 1-ODE at same temperature of reaction. In this line, a pale white precipitate was obtained. After injection, the flask containing the prepared materials was immediately added into an ice bath for 5 s to quench the reaction mixture. The crude was centrifugated three times with hexane (CHROMASOLV, 34859, 99.7%, Honeywell) at 5000 rpm for 5 min. Sn-HPs pellets was separated from supernatant and redispersed with hexane at 50 mgmL⁻¹.

Synthesis of carbon quantum dots (CQDs)

The synthesis of CQDs of hexadecylamine (HDA) was performed by following the hot injection procedure reported elsewhere.¹ In this way, 1.5 g 1-hexadecylamine (HDA) and 15mL of 1-ODE were added into a 100 mL three-neck flask and stirred during 30 min under inert conditions at room temperature. Afterwards, the solution was heated up to 300 °C. Once the reaction achieved this temperature, 1g citric acid was rapidly added and the solution was kept under stirring during 3 h. Here, the solution was cooled down at room temperature. As-prepared CQDs were isolated with acetone, and the solution was centrifuged 4500 rpm for 20 min. Then, the supernatant was discarded and the solid obtained was washed three times with methanol. Finally, blue-emitting CQDs were dispersed in hexane at a concentration of 50 mgmL⁻¹. For further characterization and fabrication of composites, different mixtures of 6 mgmL⁻¹ CQDs and Y mgmL⁻¹ OLA₂SnX₄ and PEA₂SnI₄ (Y = 1.4, 1.6, 1.7, 1.9 and 2.1) were prepared to obtain the corresponding OLA₂SnX₄/CQDs and PEA₂SnI₄/CQDs mixtures with cool-, neutral- and warm white light tonalities. Then, corresponding photographs of luminescent pure 2D perovskites dispersions, A₂SnX₄/CQDs mixtures and CQDs colloidal solutions were obtained under UV illumination (365 nm) with a portable UV lamp.

Fabrication of stable and luminescent A₂SnX₄/CQDs-polymer composite films

For the preparation of A₂SnX₄/CQDs polymeric composite films, isobornyl acrylate (IBA, Sigma-Aldrich) and butylacrylate (BA, Sigma-Aldrich) monomers were used as the matrix in the specimens, while 1,4-Butanediol diacrylate and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, Sigma-Aldrich) (DBA, Sigma-Aldrich) were used as crosslinker agent and UV-initiator, respectively, without further purification. In opaque vials, native PEA₂SnI₄, CQDs and the corresponding PEA₂SnI₄/CQDs inks were dried under vacuum and stirring cycles. The vacuum was carried out at 40 °C to remove the solvent, and vortex stirring allowed to homogenize of semi-wet nanoparticles inside the entire vial. Stable and highly luminescent UV-curing 3D structures were obtained from an acrylic matrix (BA+ IBA) with 85 mol%

IBA, in presence of 15 wt% of crosslinker, 1.2 wt% of UV-initiator and 2% wt of luminescent materials. The acrylic mixture containing the inks were kept under constant magnetic stirring for 10 min. Then, the obtained dispersions were placed in refrigeration for at least 15 min prior to cure.

The prepared chilled formulations of acrylic monomers with the inks were used to prepare white, orange, and blue luminescent composite 3D structures. The coloured formulations were deposited in cylindrical moulds and in a printer tank, designed for an Elegoo Mars Pro 2 stereolithography (SLA) 3D printer, to obtain cubic networks of different dimensions, and 3D reliefs figures. The orange solution was used to make "3D-Mario" structures, while the blue acrylic solution to prepare small "3D-dinosaurs" and neutral white solution was used to prepare "3D-phantom" structures. The Elegoo Mars 2 Pro printer was equipped with a 405nm LED light source and a 2560x1620 Liquid Crystal display. 3D structures were designed using Hyperganic Core software and exported as .stl files to be sliced in ChituBox software. The UV light is responsible for hardening the acrylic mixture in the thin layers that are deposited on the printing platform, thus forming the printed object.

The cylindrical structures in form of pellets were cured at 40 °C during 60 min in a UV-Fore Cure unit, 405 nm light, with heating system curing control (Formlabs, USA) working in static conditions. The printing parameters were adjusted for the starting acrylic monomeric formulation, for each of the colored composite formulations; and taking into account the 3D structure to be printed. Printing parameters were set as follows: layer thickness 0.1mm, lifting distance 7mm, lifting speed 80mm/s, retraction speed 80mm/s. The light exposure time for the layers was 15 s for the cubic networks, 17 s for the lower layers; and for neutral white, orange and blue 3D figures, 20, 17 and 40 s, respectively, respectively. All the colored formulations suffered 4 s of pre-polymerization in the printer tank in order to make the 3D printing effective. Once the 3D structures were printed, the object was extracted from the platform, washed with isopropyl alcohol and UV-cured at 40 °C during 40 min.

Characterization of the A_2SnX_4 /CQDs mixtures and polymeric composites

The morphology of the OLA_2SnX_4 , PEA_2SnI_4 HPs and CQDs was analyzed through high-resolution transmission electron microscopy (HRTEM) by using a LaB6 Jeol JEM 2100plus, with applied bias of 200 kV. The average particle size of perovskite and CQDs was obtained from the TEM images with ImageJ software. X-ray diffraction (XRD) profiles of the materials were obtained by using a D4 Endeavor diffractometer from Bruker-AXS, using a $Cu K\alpha$ radiation source ($\lambda = 1.54056 \text{ \AA}$). Steady state- and time-resolved photoluminescence (TRPL) measurements were conducted on inks and polymeric composite materials through Hamamatsu Absolute QY Measurement System C9920-02, equipped with an integrating sphere and a photoluminescence spectrophotometer (Fluorolog 3-11, Horiba). An excitation wavelength (λ_{exc}) of 350 nm was used to perform the steady state PL of pure A_2SnX_4 , CQDs and the A_2SnX_4 /CQDs

mixtures. TRPL measurements were carried out at 405 nm pulsed laser (NanoLED-405L, <100 ps of pulse width, 1 MHz frequency). For liquid samples, the concentration of the composites was fixed to 2 mgmL⁻¹ in hexane, using a quartz cuvette of 10 x 10 mm. The absolute photoluminescence quantum yield (PLQY) of the perovskites was estimated through the Absolute QY Measurement System C9920-02, with an integrating sphere, under an excitation wavelength of 350 nm. The concentration of the pure A₂SnX₄, CQDs and the A₂SnX₄/CQDs samples was fixed to 2 mgmL⁻¹ in hexane. Before conducting the measurements, absorbance was fixed in an interval range around 0.4-0.5, being these values adequate to achieve suitable PLQY in the samples. For all the optical characterization, the samples were kept under visible light and room conditions. Surface chemical composition and electronic state of PQDs were determined by X-ray Photoelectron Spectroscopy (XPS, ESCA-2R, Scienta-Omicron). Here, pure A₂SnX₄, CQDs and the A₂SnX₄/CQDs inks were deposited by drop-casting on Ti sheets heated at 50°C, under ambient conditions, obtaining the corresponding layers. Spectra were recorded using monochromatic Al K α = 1486.6 eV. The following sequence of spectra were recorded: survey spectra, C 1s, O 1s, N 1s, Sn 3d, I 3d. Binding energy scale was referenced to adventitious carbon (284.8 eV). CasaXPS processing software (Casa software Ltd) was used to analyze the data and the quantitative analysis was made using sensitivity factors provided by the manufacturer. Nuclear Magnetic Resonance (NMR) spectroscopy was performed on PNCs solutions using a Bruker Avance III HD spectrometer operating at a ¹H frequency of 400 MHz, at 298 K. ¹H spectra were processed in MestReNova software.

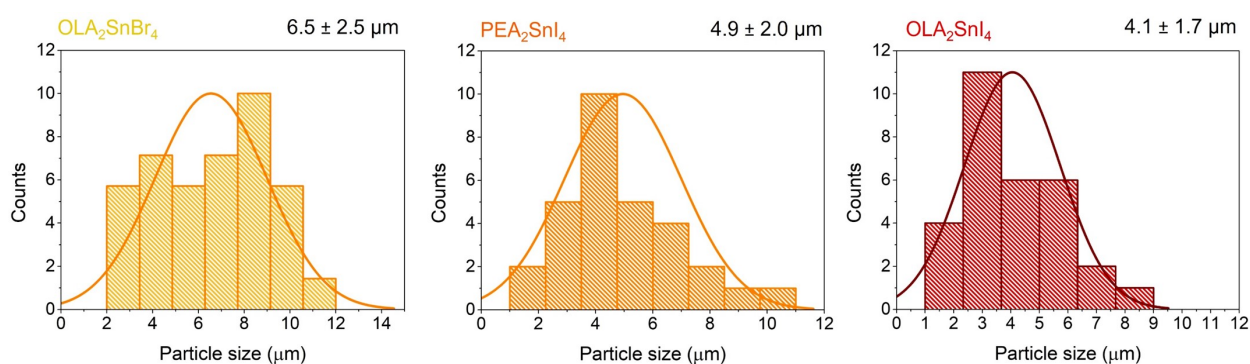


Figure S1. Particle size distribution obtained from TEM images for pure OLA₂SnX₄ (X = Br, I) and PEA₂SnI₄ microcrystals

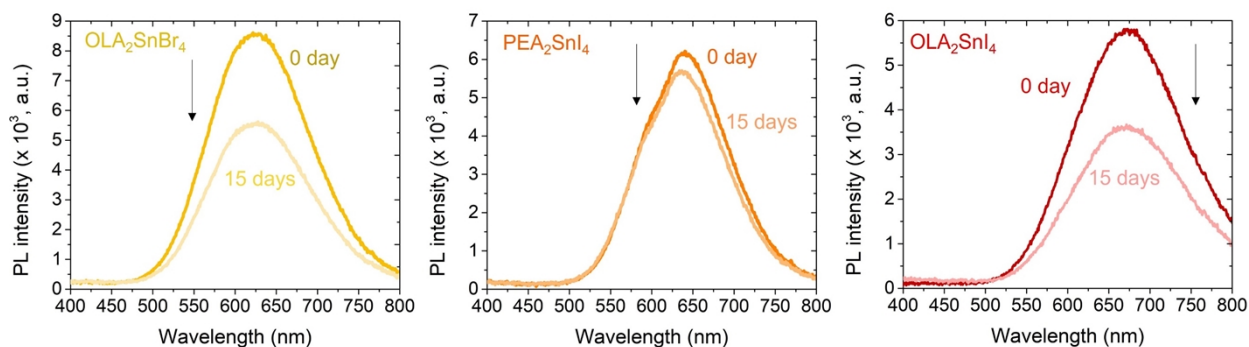


Figure S2. PL spectra of pure OLA_2SnX_4 ($X = \text{Br}, \text{I}$) and PEA_2SnI_4 microcrystals after 0 and 15 days of aging.

XRD patterns of A_2SnX_4 perovskite microcrystals

The characterization of the crystalline structure was performed through XRD measurements, where the typical XRD patterns for OLA_2SnX_4 and PEA_2SnI_4 perovskites were observed. The XRD peaks of the samples follow periodic small angle intervals, ascribed to the inorganic $[\text{SnX}_6]^{4-}$ stacking, describing a 2D structure. In this context, the 2θ increment for $\text{OLA}_2\text{SnBr}_4$, OLA_2SnI_4 and PEA_2SnI_4 were estimated to be $\sim 2.01^\circ$, 3.17° and 4.80° , respectively, as seen in Figure S1. By using the Bragg equation, we have calculated their corresponding periodic spacings (d) from these periodicity values to be ~ 4.4 , 2.8 and 1.8 nm, respectively. This value represents the separation of $[\text{SnX}_6]^{4-}$ layers by the presence of OLA^+ and PEA^+ organic spacers, typical from a Ruddlesden–Popper type structure. Additionally, the d -spacing of the OLA_2SnI_4 is smaller than that of the $\text{OLA}_2\text{SnBr}_4$. As it is reported by Haque et.al. for other type of A_2SnX_4 , the change of bromide by iodide anions promotes shift in the Bragg angles to higher values, with a slight decrease in d -spacing between the $[\text{SnX}_6]^{4-}$ octahedra layers. This is an indication of a decrease in the separation between the perovskite octahedra units. Considering that the Sn-I bond is larger than that of the Sn-Br one, we suggest that the arrangement of OLA^+ cations are compressed by the bigger size of $[\text{SnI}_6]^{4-}$ than $[\text{SnBr}_6]^{4-}$. However, the large difference between the d -spacings of both OLA_2SnX_4 allows to infer that a deficiency of A-site cations is presented into the iodide-based perovskite, mediating the closing up of the inorganic layers. In the case of PEA_2SnI_4 , the estimated d -spacing ~ 1.8 nm is larger than the value reported in the literature (~ 1.6 nm), coming from the 2D structure of the red-emitting PEA_2SnI_4 .² This feature is attributed to the face-to-face aromatic ring alignment between the PEA^+ cations, favoring the band-to-band transitions into the material. Therefore, we infer that the increase of the d -spacing for the STE-based PEA_2SnI_4 prepared in this work is caused by some modifications in the intramolecular packing of the PEA^+ cations arrays, promoting the octahedra distortion and the generation of the STE dynamics. These results allow to conclude the existence of different 2D A_2SnX_4 perovskites, which will be used for the preparation of the $\text{A}_2\text{SnX}_4/\text{CQDs}$ inks with diverse white-light emission tonalities.

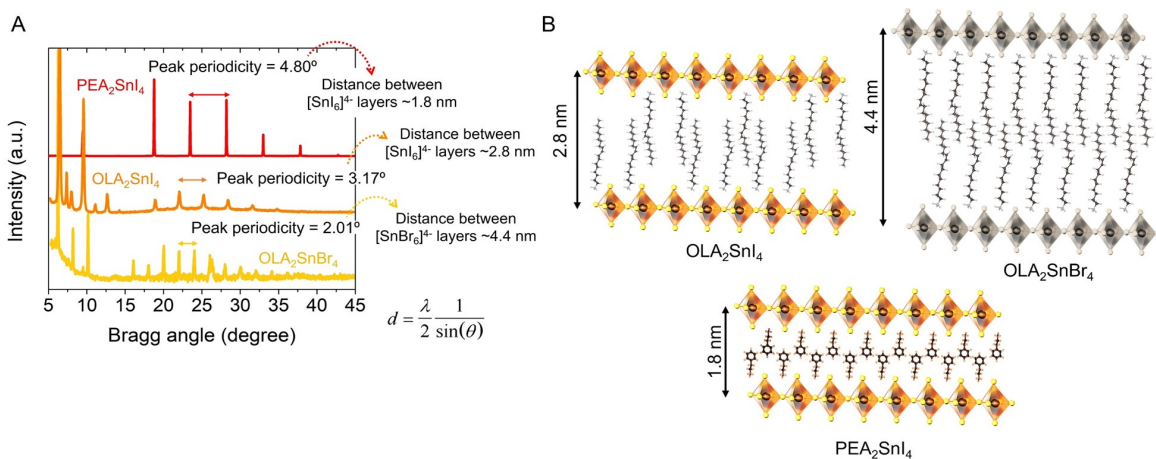


Figure S3. Determination of the periodic (d) spacing for OLA₂SnBr₄, OLA₂SnI₄, and PEA₂SnI₄ microcrystals. First, the peak periodicity was estimated from the (A) XRD patterns of each sample to be 2.01, 3.17 and 4.80 °, respectively. Through the Bragg equation, d (defined as the distance between [SnX₆]⁴⁻ octahedra layers, separated by the corresponding alkylammonium cation as shown in panel (B)) was estimated to be 4.4 and 2.8 and 1.8 nm, respectively.

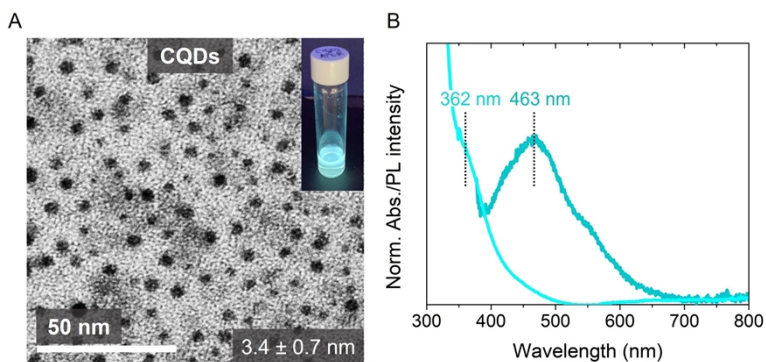


Figure S4. (A) TEM image and (B) absorption/PL emission spectra ($\lambda_{exc} = 350$ nm) of blue-emitting CQDs.

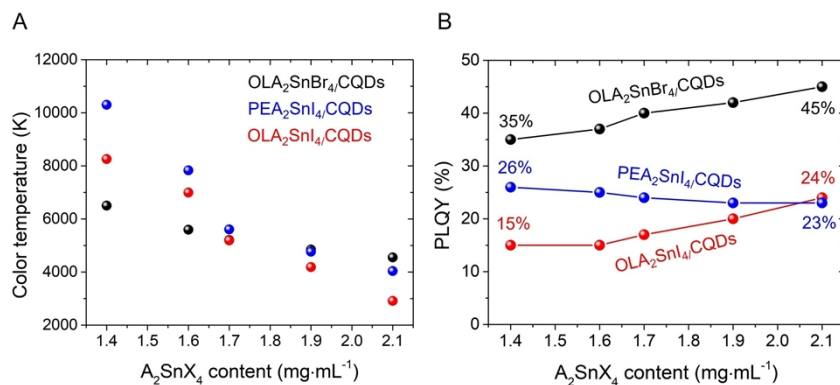


Figure S5. (A) Color temperature and (B) PLQY of the white-light emitting $A_2SnX_4/CQDs$ inks by varying the perovskite content.

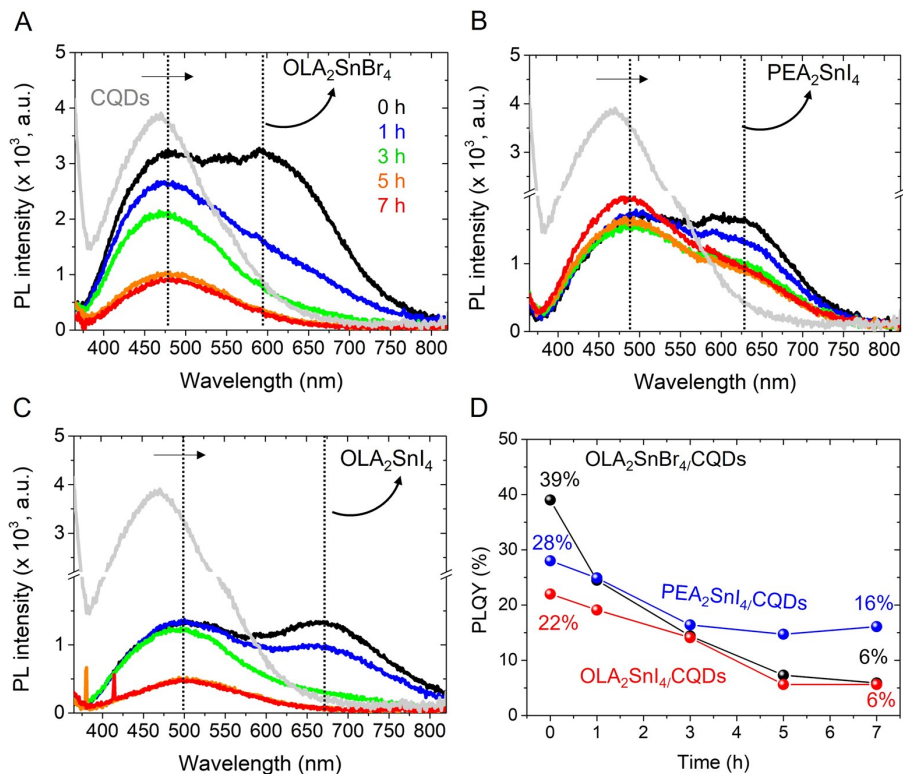
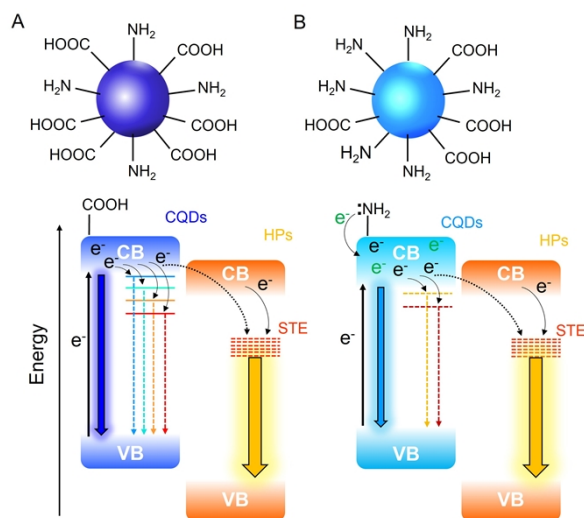


Figure S6. PL spectra of the prepared NW-emitting inks composed by (A) $OLA_2SnBr_4/CQDs$, (B) $PEA_2SnI_4/CQDs$ and (C) $OLA_2SnI_4/CQDs$ systems by varying aging time. (C) PLQY of NW-light emitting $A_2SnX_4/CQDs$ systems in function of the aging time.



Scheme 1. PL mechanism of CQDs under high density of (A) surface -COOH (through the formation of surface states) and (B) -NH₂ functional groups (filling of surface states to narrow the energy gap between valence and conduction bands), promoting charge transfer to STE states into the A₂SnX₄ perovskites.

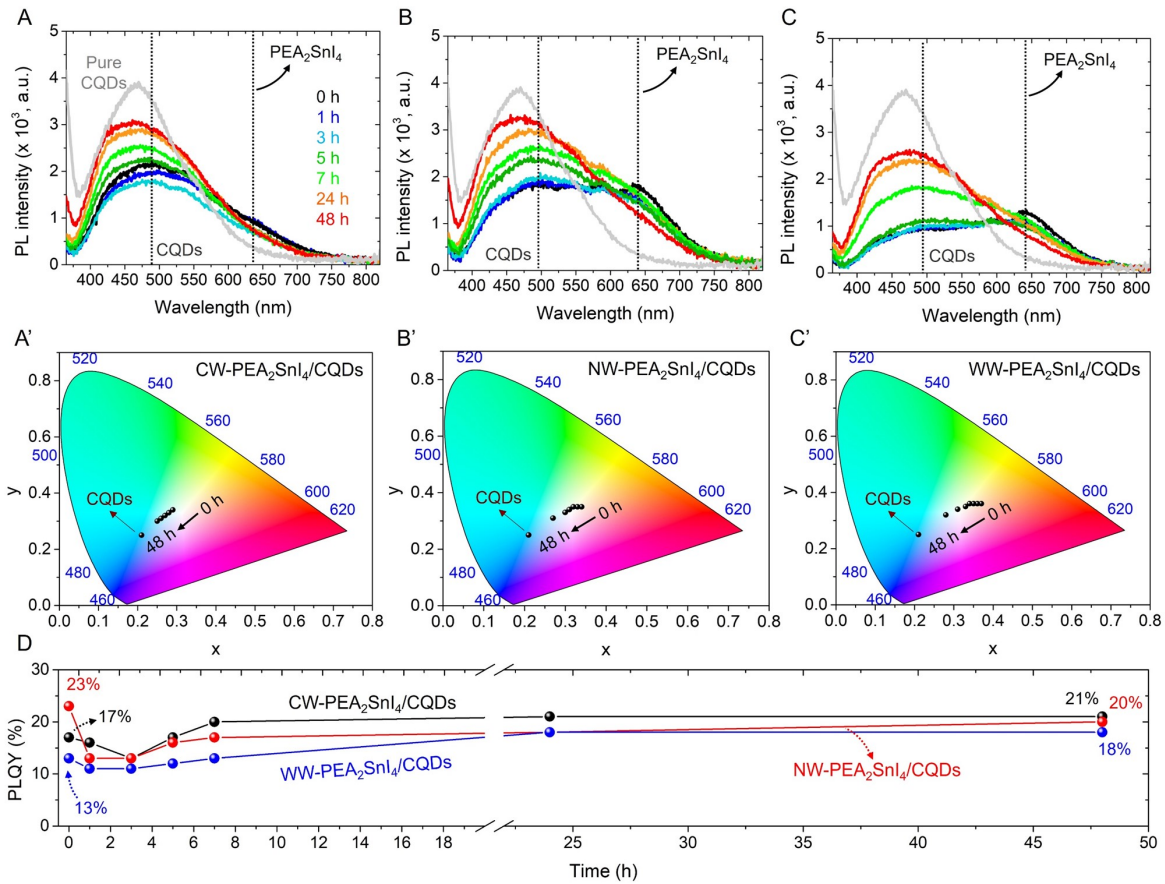


Figure S7. (A, B, C) PL spectra, (A', B', C') chromaticity diagram and (D) PLQY of the prepared (A, A') CW-, (B, B') NW- and (C, C') WW-light emitting PEA₂SnI₄/CQDs mixtures by varying aging time. Perovskite content was 1.4, 1.7 and 2.1 mgmL⁻¹ into the 6 mgmL⁻¹ CQDs solution, respectively.

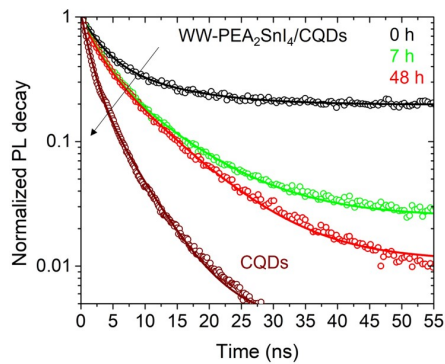


Figure S8. Time-resolved PL decay measurements of WW-light emitting PEA₂SnI₄/CQDs inks by varying aging time: 0 h (black curve), 7 h (green curve) and 48 h (red curve). PL decay of native CQDs (dark red curve) was also obtained for comparative purposes. Solid lines correspond to the fitting of PL

decays through a bi-exponential equation: $y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2}$.

Table S1. Determination of time resolved PL decay fitting parameters of the WW-light emitting PEA₂SnI₄/CQDs ink, by varying the aging time (0, 7 and 48 h) shown in Figure S5, through the use of a

bi-exponential equation: $y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2}$.³ The corresponding PL decay fitting parameters of native CQDs were also obtained for comparative purposes.

Aging time (h)	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	τ _{avg} (ns)
0	0.52	7.24	0.48	25.06	15.80
7	0.59	6.84	0.41	24.27	13.98
48	0.62	6.33	0.38	22.96	12.65
CQDs	0.77	3.35	0.33	12.84	6.82

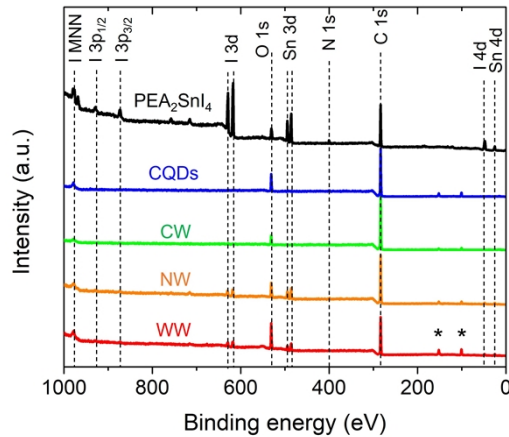


Figure S9. XPS survey spectra of the native PEA₂SnI₄ HPs, CQDs and the corresponding CW-, NW- and WW-light emitting PEA₂SnI₄/CQDs inks. Asterisks (*) correspond to the presence of Si impurities from the material synthesis.

Table S2. Chemical atomic composition of native PEA₂SnI₄ HPs, CQDs and the corresponding CW-, NW- and WW-light emitting PEA₂SnI₄/CQDs inks.

Sample	Atomic concentrations (%)										Estimated fractions				
	C- (C,H)	C-N	C-O	COOH	C=O	(C=O)- N@, Sn-O	COOH	I ⁻	I ₂	Sn ²⁺	C-NH ₂ , (C=O)- N*	C- NH ₃ ⁺	O/ (I+O)	Sn-O/ (Sn+S-O)	I ₂ / (Sn+I ₂)
Sn-HPs	64.71	8.94	2.08	-	6.15	4.27@	-	4.31	2.32	3.76	3.05*	0.41	0.61	-	0.62

CQDs	78.90	5.66	1.30	2.28	10.51	-	0.29	-	-	-	1.05	-	-	-	-
CW	81.64	7.20	1.15	2.27	6.05	0.29	0.09	0.03	0.03	0.05	1.20	-	0.99	0.85	0.38
NW	76.57	6.47	1.15	1.74	9.04	1.31	0.27	0.24	0.65	1.38	1.17	-	0.92	0.49	0.32
WW	71.44	4.74	1.05	1.35	17.34	1.11	0.35	0.37	0.53	0.94	0.80	-	0.95	0.54	0.36

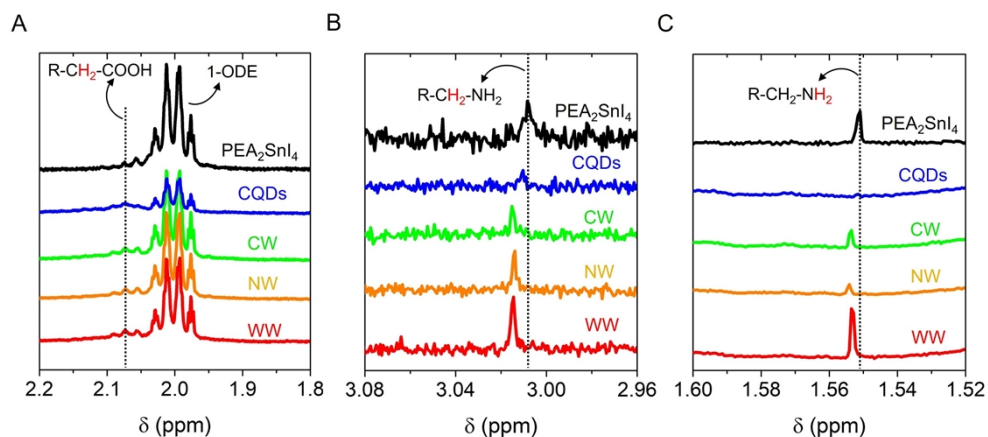


Figure S10. ^1H (400 MHz, toluene- d_8 , 298 K) NMR spectra of native PEA_2SnI_4 HPs, CQDs and the CW-, NW- and WW-light emitting $\text{PEA}_2\text{SnI}_4/\text{CQDs}$ inks. Panel (A) shows the spectra section where the signal ascribed to CH_2 - near to COOH moiety appears, while panels (B) and (C) depict the NMR signals assigned to CH_2 - bonded to NH_2 and proton coming from the amine functional group, respectively.

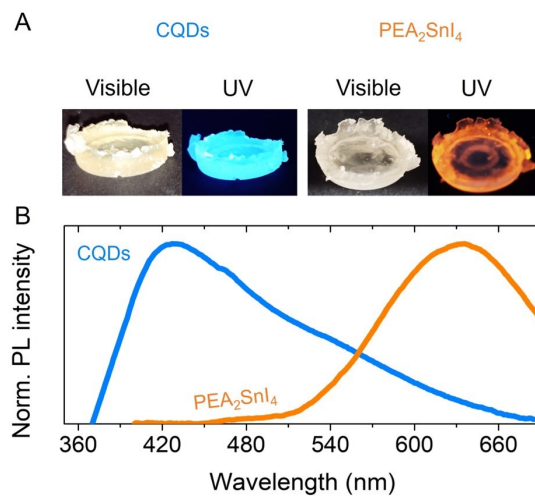


Figure S11. (A) Photographs (under visible and UV light) and (B) PL spectra of blue-emitting CQDs and orange-emitting PEA_2SnI_4 HPs acrylate polymeric composites.

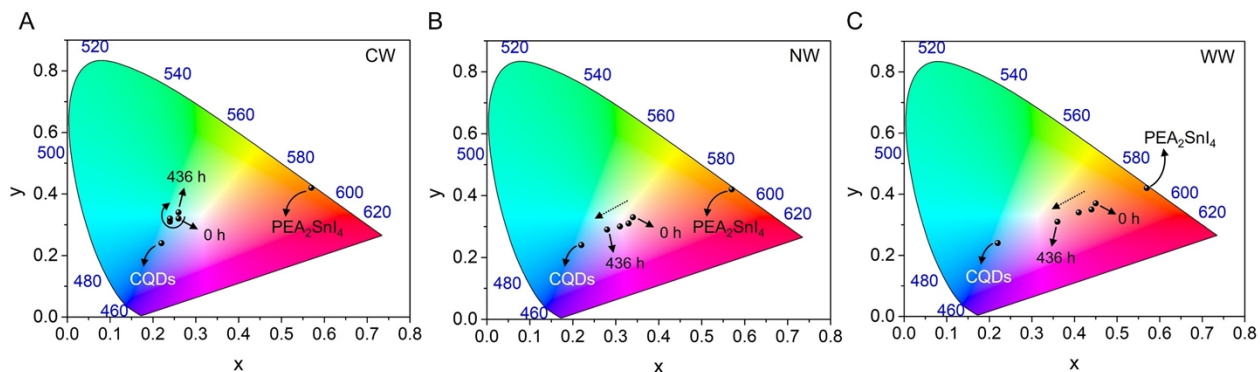


Figure S12. Chromaticity diagram estimated from PL spectra shown in Figure 5B-D of the prepared (A) CW-, (B) NW- and (C) WW-light emitting $\text{PEA}_2\text{SnI}_4/\text{CQDs}$ 3D composites by varying aging time under ambient air and RH $\sim 50\%$.

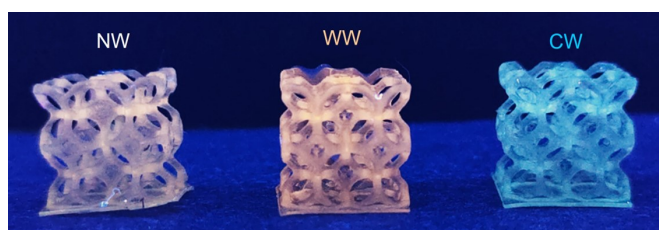


Figure S13. Small 3D printed networks fabricated from CW-, NW-, and WW-light emitting $\text{PEA}_2\text{SnI}_4/\text{CQDs}$ inks. Dimensions of 3D printed networks (length x width x height) were 1 x 1 x 1 cm.

References

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