

Supplementary Information

Adamantyl Ligand induced one-dimensional CsPbBr₃ perovskite nanocrystals formation: mechanism and anisotropic photoluminescence

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1. Methods

Materials

All chemicals, CsBr, PbBr₂, PbI₂, PbCl₂, oleylamine, oleic acid, 1-adamantanemethylamine, neopentylamine (PNAm), CO₂ (99.99%), solvents were purchased from commercial suppliers (Sinopharm chemical reagent co., Meryer, Energy-Chemical, Teichemicals, Sigma-Aldrich, Huaerwen) and used without further purification.

Characterization

The SEM images were recorded by field-emission scanning electron microscope (JEOL JSM-7610FPlus) at an acceleration voltage of 5 kV. High-resolution TEM (HRTEM) images were obtained by Titan G2 60-300 with an image corrector high-resolution transmission electron microscopy system operating at 300 kV. Atomic force microscopy data was obtained through SPM-9700. PL lifetime and PL anisotropy were measured by steady-state transient modular fluorescence spectrometer (QuantaMaster 8000). Fourier transform infrared (FT-IR) spectra were measured on an INVENIO-R spectrometer using the KBr pellet as the background. UV-Vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. The PL spectra were measured by a RF-6000. The samples were tested by X-ray diffraction (XRD) using Empyrean from Panaco in the Netherlands. ¹H NMR spectra was recorded on Bruker Avance III 400 MHz with tetramethylsilane as an internal standard. The PLQY was measured by using quinine 0.5 M H₂SO₄ aqueous solution as a standard. The photographs were recorded by a Mi 11 Pro mobile phone.

Synthesis

AD-CsPbBr₃ NRs: The AD-CsPbBr₃ NRs was synthesized as the following procedures. CsBr (85.00mg, 0.40 mmol), PbBr₂ (0.40 mmol, 147.00 mg), OA (1.00 mL), and ADAm (0.14 mL) were ultrasonically dissolved in *N,N*-dimethylformamide

(DMF, 10.00 mL) at room temperature to prepare the precursor solution. With vigorous stirring, the precursor solution (1.00 mL) was quickly injected in a toluene solution (10.00 mL) placed in an ice bath. The solution immediately turns to transparent yellow-green, indicating the formation of perovskite nanocrystals. After stirring at this condition for 1 hour, the solution was centrifuged at a speed of 10000 rpm for 7 min, and the precipitation, **AD-CsPbBr₃** NRs, as a yellow solid was collected and dried in vacuum. The **AD-CsPbBr₃** nanowires and nanobelts were synthesized by the same methods only collected by centrifugation at different reaction times. Other perovskite nanocrystals used in this work were synthesized by the same methods by using different ligands or different ligands ratios.

Halide ions exchange reactions: Firstly, the halide ion precursor solution was prepared by refluxing a toluene solution (10.00 mL) containing PbX₂ (X = I or Cl, 0.36 mmol), OA (0.10 mL), and ADAm (0.10 mL) at 40°C for iodized salt and 120°C for chloride salt for 2 hours until the completely dissolution of the salts. The X⁻ ion exchange was operated by adding the corresponding precursor solution in the **AD-CsPbBr₃** toluene solution with measured stoichiometric ratio.

DFT calculations

All the calculations were carried out within the Vienna Ab initio Simulation Package (VASP) in which the projector-augmented-wave (PAW) pseudopotential is adopted for the core-electron interactions. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted for exchange-correlation functional in structural optimization⁵. The energy and force convergence criterion of structure optimization were set to be 10⁻⁵ eV and 0.001 eV/Å, respectively. The kinetic energy cutoff of 500 eV was adopted. To avoid the interactions between neighboring images, a vacuum space of ~15 Å between neighboring images was used. The details of the calculations are described in the Supplementary Information.

2. Characterization

Table S1. EDS diffraction analysis of element Composition of the **AD-CsPbBr₃** NRs

element	Atomic fraction /%	error /%
Cs	21.02	3.01
Pb	21.07	3.10
Br	57.92	6.45

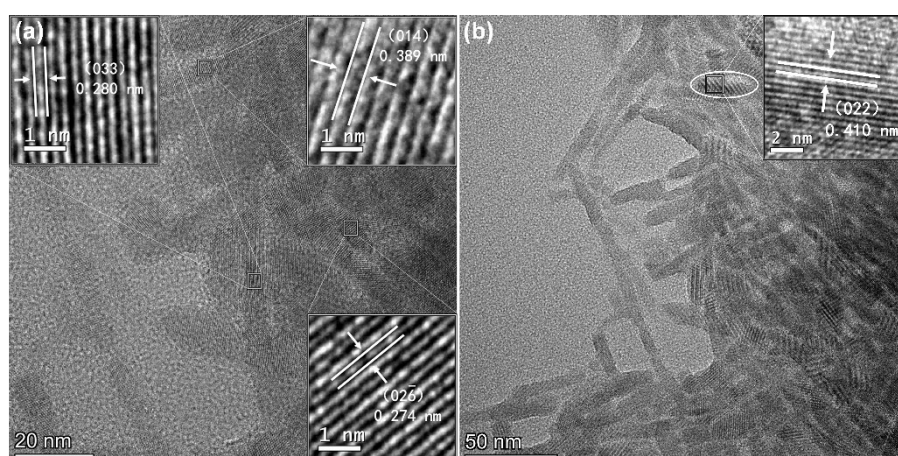


Figure S1. Lattice spacing in TEM images of **AD-CsPbBr₃** NRs

3. Halide ion exchanges

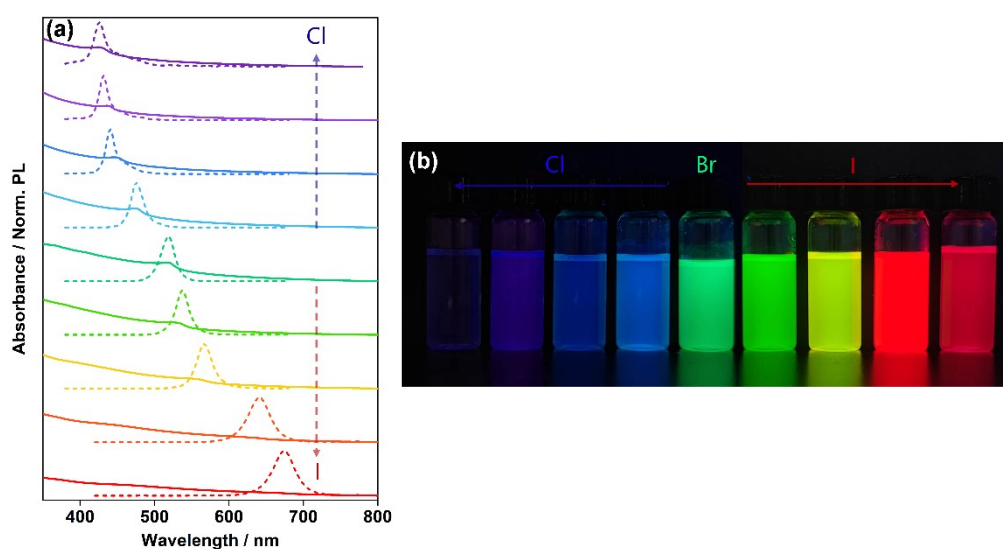


Figure S2. UV absorption spectra and PL spectra of the **AD-CsPbBr₃** NCs after exchanging with different concentrations of Cl^- or I^- precursor, (b) the corresponding photographs.

Table S2. The fitting lifetimes of the CsPbX₃ NCs

Entry	τ_1 / ns	B_1 / %	τ_2 / ns	B_2 / %	τ_{av} / ns
CsPbCl ₃	1.07	95.64	13.19	4.36	5.49
CsPbBr ₃	8.95	90.54	63.68	9.46	32.29
CsPbI ₃	33.63	77.33	197.73	22.67	137.48

4. Morphology regulation

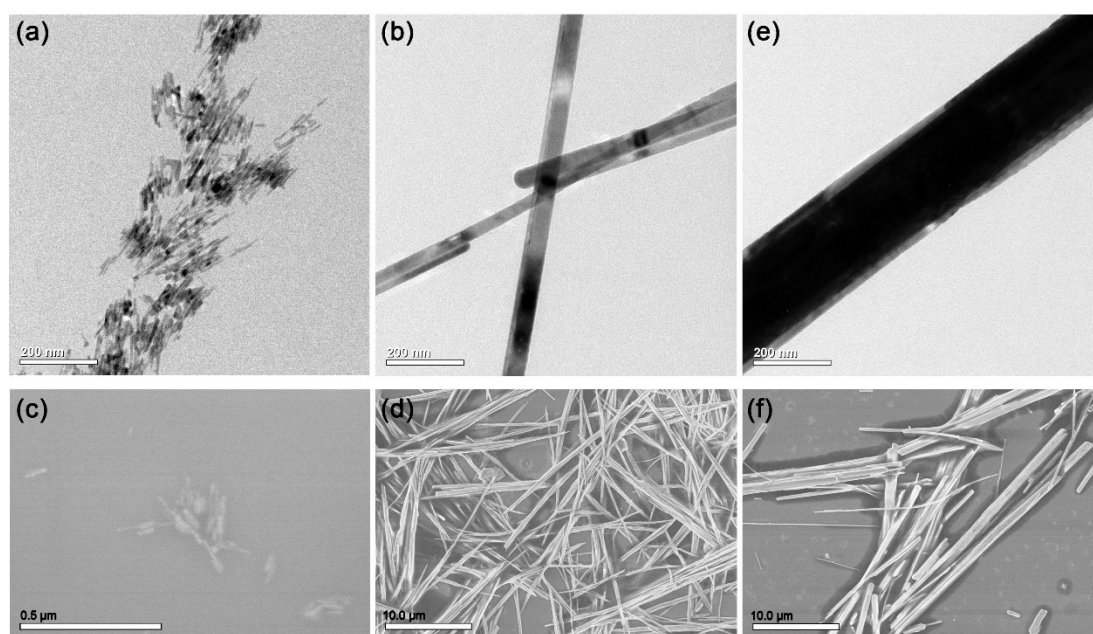


Figure S3. TEM images of (a) AD-CsPbBr₃ NRs, (b) nanowires, (c) nanobelts, SEM images of (d) AD-CsPbBr₃ NRs, (e) nanowires, (f) nanobelts

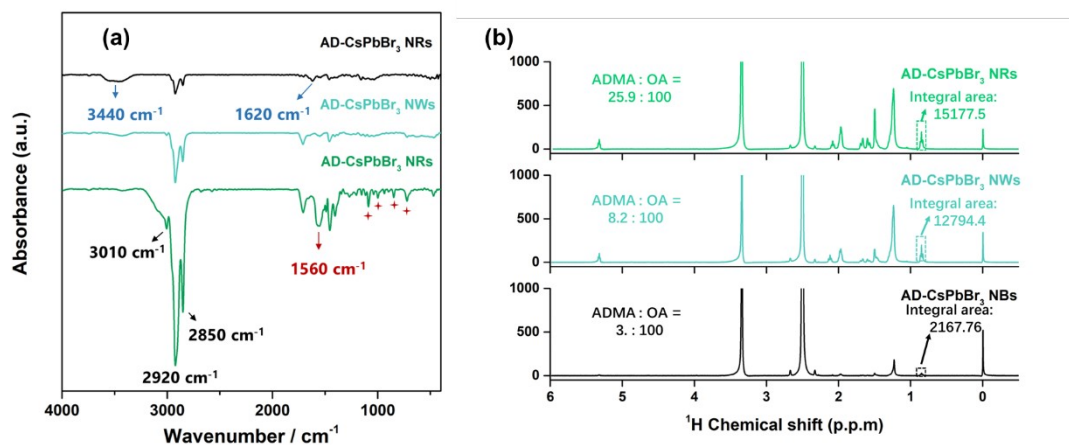


Figure S4. (a) IR spectra of the AD-CsPbBr₃ NRs, nanowires, and nanobelts. (b) ¹H NMR of the AD-CsPbBr₃ NRs, nanowires, and nanobelts dissolved in DMSO-D₆

Ligands and ligands' concentration effects on the morphologies

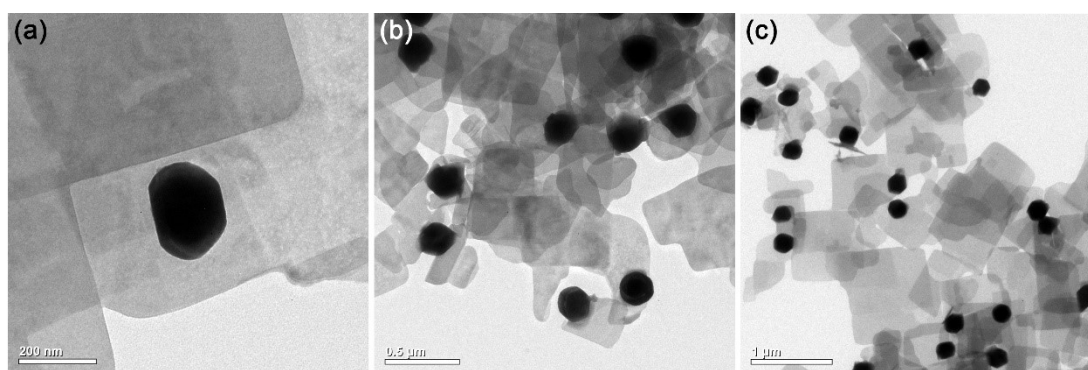


Figure S5. TEM images of the perovskite NCs synthesized with CHAm

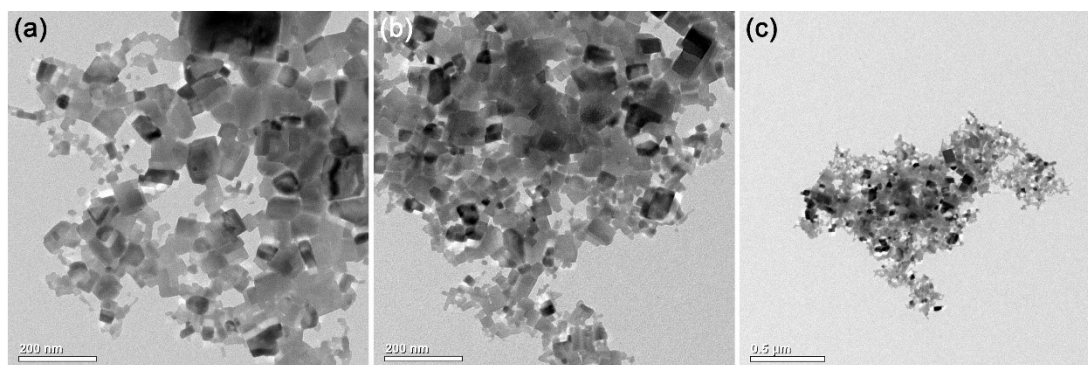


Figure S6. TEM images of the perovskite NCs synthesized with PNAm

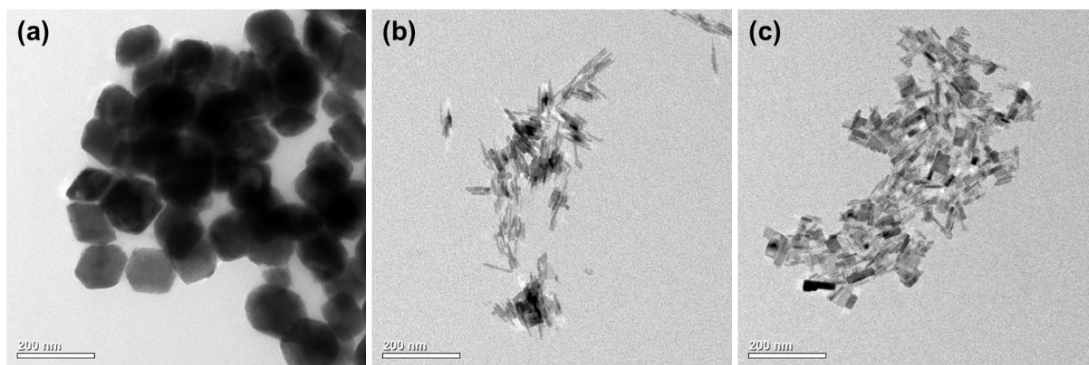


Figure S7. TEM images of the perovskite NCs synthesized with different amounts of ADAm (a) 0.16 mmol/mL, (b) 0.08 mmol/mL, and (c) 0.04 mmol/mL

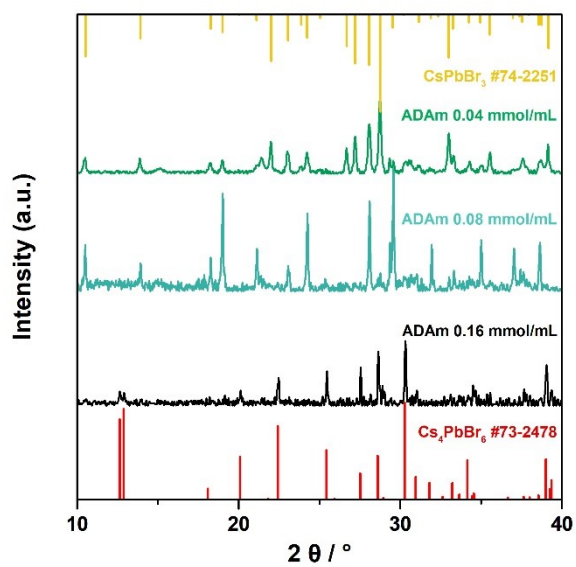


Figure S8. XRD patterns of the perovskite NCs synthesized with different amounts of ADAm

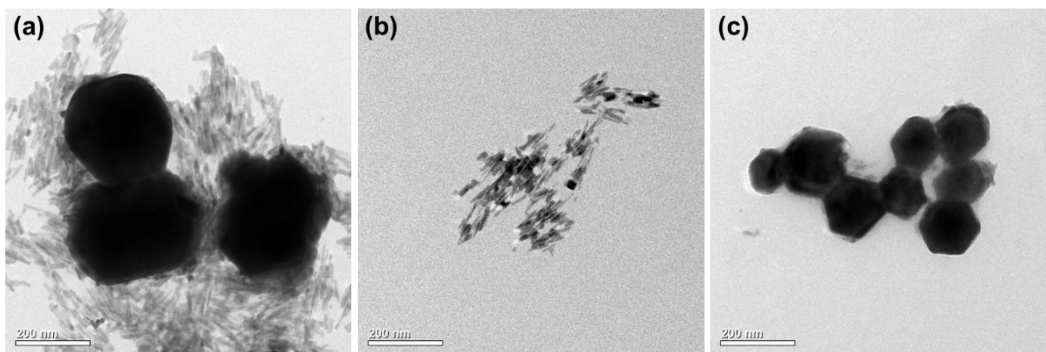


Figure S9. TEM images of the perovskite NCs synthesized with different amounts of OA (a) 0.64 mmol/mL, (b) 0.32 mmol/mL, and (c) 0.16 mmol/mL

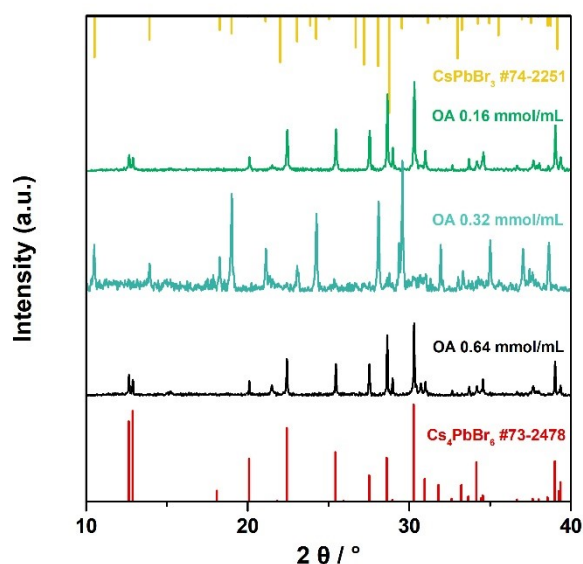


Figure S10. XRD patterns of the perovskite NCs synthesized with different amounts of OA

5. Calculations

All the calculations were carried out within the Vienna Ab initio Simulation Package (VASP) in which the projector-augmented-wave (PAW) pseudopotential is adopted for the core-electron interactions²⁻⁴. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was adopted for exchange-correlation functional in structural optimization⁵. The energy and force convergence criterion of structure optimization were set to be 10^{-5} eV and 0.001 eV/Å, respectively. The kinetic

energy cutoff of 500 eV was adopted. To avoid the interactions between neighboring images, a vacuum space of ~ 15 Å between neighboring images was used.

Surface Energy Calculations

To calculate the surface energy of δ -CsPbBr₃ nanorods, we employed a finite size plate technique. Specifically, we established a slab model based on the crystal structure of orthorhombic CsPbBr₃, as determined by the standard card. After analyzing the potential capping surfaces of CsPbBr₃ and their impact on the overall surface energy, we identified the (002) and (011) facets as suitable for calculating the surface energy. By comparing the surface energy of these two facets, we can determine the most probable capping surface for the nanorods. This approach will enable us to gain a better understanding of the surface properties of CsPbBr₃ and its potential applications. The formula for calculating the surface energy of the slab model is shown below:

$$E_{surface} = \frac{E_{slab} - nE_{bulk}}{A}$$

where E_{slab} represents the total energy of the surface slab model, E_{bulk} is the energy of a unit in the bulk phase, and A represents the surface area of the surface slab.

The parameters of (002) and (011) facets for the surface energy calculation are given in Table S3. From Table S3 the surface energy of (002) and (011) are $0.062 \text{ eV } \text{Å}^2^{-1}$ and $0.030 \text{ eV } \text{Å}^2^{-1}$. (002) has twice the surface energy than (011), the smaller the surface energy the more stable the nanocrystals can exist, so the CsPbBr₃ nanorods prefer to be finally terminated by (011), (01) and (200) facets.

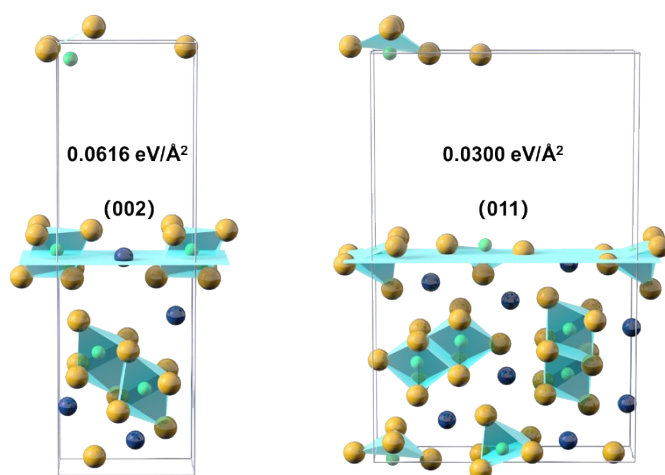


Figure S11. Comparison of surface energy between δ -CsPbBr₃ (002) crystal plane and (011) crystal plane

Table S3. δ -CsPbBr₃ surface energy related parameters

Facets	$E_{\text{bulk}}/\text{eV}$	$E_{\text{slab}}/\text{eV}$	$A/\text{\AA}^2$	$E_{\text{surface}}/\text{eV \AA}^{-2-1}$
(002)	-63.923	-61.169	44.683	0.062
(011)	-63.923	-125.209	89.265	0.030

Ligand Adsorption

In this study, we found that the presence of ADAM is crucial for the synthesis of CsPbBr₃ nanorods, as it directly affects their growth through its varying coordination ability on different surfaces. To gain insight into the binding of ADAM on the exposed surface of CsPbBr₃ nanocrystals, we examined its interaction with three crystal surfaces: (011), (01), and (200). Our investigation aimed to shed light on the underlying mechanisms of nanorod formation in the presence of ADAM.

The formula for calculating the binding energy of the ligand absorption is shown below:

$$E_{\text{abs}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{ADAM}}$$

where E_{total} , E_{surface} and E_{ADAM} are the total adsorption energy of the system, the energy of the slab model without adsorption and the energy of the ADAM, respectively. The

calculated parameters of the binding energy of ADAm at (01), (011) and (200) crystal planes are given in Table S4. Table S4 illustrates the minimum binding energy (-0.174 eV) between ADAm and the (011) surface. A lower binding energy generally indicates greater stability of surface adsorption, while a positive value implies instability. In contrast, the binding energies of ADAm with the (01) and (200) surfaces are 6.438 eV and -0.008 eV, respectively.

Table S4. Binding energy of ADAm ligand adsorption on the different exposed surfaces of δ -CsPbBr₃ nanostructure.

Facets	$E_{\text{total}}/\text{eV}$	$E_{\text{surface}}/\text{eV}$	$E_{\text{ADAm}}/\text{eV}$	E_{abs}/eV
(013)	-544.881	-372.862	-178.457	6.438
(011)	-554.411	-375.779	-178.457	-0.174
(200)	-553.251	-374.786	-178.457	-0.008

6. Photoluminescence

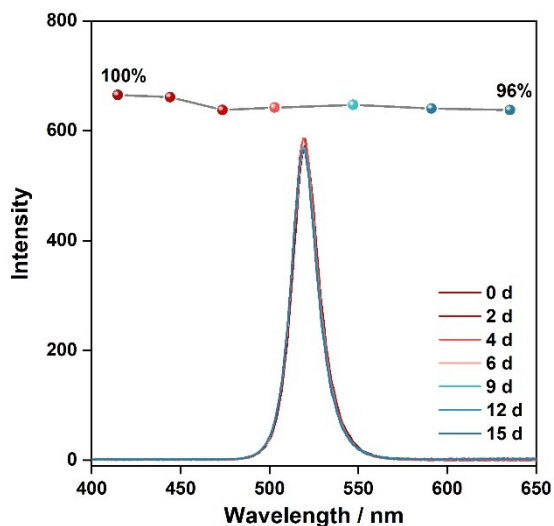


Figure S12. PL stability of AD-CsPbBr₃ NRs in n-hexane