

Non-template Synthesis of CH₃NH₃PbBr₃ Perovskite Nanoparticles

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MATERIAL AND METHODS

Materials

All commercial materials were used as received: aqueous dispersion of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP Al 4083 (Heraeus); Aluminum oxide nanoparticles, <50 nm particle size (DLS), 20 wt. % in isopropanol (Aldrich); SPPO13 (2,7-bis(diphenylphosphoryl)-9,9'-spirobi[fluorene], Luminescence Technology Corp.) and pTPD (Poly[*N,N'*-bis(4-butylphenyl)-*N,N'*-bis(phenyl)-benzidine], American Dye Source Inc.). All the reagents used in the synthesis of the perovskites and the alkyl ammonium bromides were purchased from Aldrich and used as received. The organic solvents were of spectroscopic grade (Scharlab).

The precursors, methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$) and octylammonium bromide ($\text{CH}_3(\text{CH}_2)_7\text{NH}_3\text{Br}$), were synthesized by reaction of the corresponding amine in water/HBr, accordingly to the previously reported procedure.¹ In the case of octadecylammonium bromide ($\text{CH}_3(\text{CH}_2)_{17}\text{NH}_3\text{Br}$), it was prepared by using a similar methodology but the amine was previously dissolved in acetonitrile at 60°C and then HBr was added. In all cases, the precipitate was washed several times with diethyl ether, dried under vacuum and used without further purification.

Synthesis of P_{ODA1} . A solution of oleic acid (85 mg, 0.3 mmol) in 2 ml of octadecene was stirred and heated at 80 °C and then, octadecylammonium bromide (17.5 mg, 0.05 mmol) was added. Subsequent addition of methylammonium bromide (5.5 mg, 0.05 mmol dissolved in 100 μl of DMF) and lead(II) bromide (36.7 mg, 0.1 mmol dissolved in 100 μl of DMF) produced a yellow dispersion from which the nanoparticles were immediately precipitated by addition of acetone followed by centrifugation (7000 rpm, 10 min). Finally, the nanoparticles were dispersed in toluene.

Synthesis of P_{ODA2} . The same procedure than for P_{ODA1} was followed, except that the quantity of octadecylammonium bromide and methylammonium bromide was 21 mg (0.06 mmol) and 4.4 mg (0.04 mmol), respectively.

Synthesis of P_{ODA3} . The same procedure than for P_{ODA1} was followed, except that the quantity of octadecylammonium bromide and methylammonium bromide was 24.5 mg (0.07 mmol) and 3.3 mg (0.03 mmol), respectively.

Synthesis of P_{OA2} . A solution of oleic acid (85 mg, 0.3 mmol) in 2 ml of octadecene was stirred and heated at 80 °C and then, octylammonium bromide (12.6 mg, 0.06 mmol) was added. Subsequent addition of methylammonium bromide (4.4 mg, 0.04 mmol dissolved in 100 μl of DMF) and lead(II) bromide (36.7 mg, 0.1 mmol dissolved in 100 μl of DMF) produced a yellow dispersion from which the nanoparticles were immediately precipitated by addition of acetone followed by centrifugation (7000 rpm, 10 min). Finally, the nanoparticles were dispersed in

toluene.

Film preparation. Quartz substrates were extensively cleaned using detergent, de-mineralized water, and isopropyl alcohol, respectively, followed by 90 min UV-ozone treatment and 10 min of oxygen plasma cleaning in order to enhance good thin film formation. A colloidal solution of $\text{P}_{\text{OA}2}$ perovskite in toluene was spin-coated on top of the quartz substrates with 1000 rpm during 30 sec resulting in film thickness of ca. 20-30 nm.

Characterization Methods

UV-visible spectra of the samples were recorded using a quartz cuvettes spectrometer in a UV-visible spectrophotometer Agilent 8453E.

Steady-state fluorescence spectra were measured on a Amnisco Browman series 2 Luminescence spectrometer, equipped with a lamp power supply and working at room temperature. The AB2 software (v. 5.5) was used to register the data. All the data were acquired using 1cm×1cm path length quartz cuvettes, using an excitation wavelength of 350 nm.

Transmission electron microscopy TEM, high resolution TEM (HRTEM), selected area electron diffraction, and energy dispersive X-ray spectroscopy EDS in nanoprobe mode was carried out by using a Field Emission Gun (FEG) TECNAI G² F20 microscope operated at 200 kV. TEM samples were prepared from a toluene dispersion of the NPs, and a few drops of the resulting suspension were deposited onto a carbon film supported on a copper grid, which was subsequently dried.

The electroluminescent devices were made as follows. Indium tin oxide ITO-coated glass plates were patterned by conventional photolithography (Naranjo Substrates). The substrates were cleaned ultrasonically in water-soap, water and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 min. Next layers were prepared as follows:

Type 1: A layer of Al_2O_3 nanoparticles was coated by spin-coating on ITO at 2000 rpm from a dispersion of 1:2 isopropanol:ethanol v/v. After that, the sample was sintered at 300°C during 2 hours. The perovskite layer was coated using a two-step process: a) A solution of 50 mg/mL in DMF of PbBr_2 was spin-coated at 1500 rpm on the Al_2O_3 nanoparticle layer b) the substrate was dipped in a methyl ammonium bromide solution (10 mg/mL in 2-propanol). The SPPO13 layer was prepared from a solution of 10 mg/mL in anisole at 1000 rpm for 60s.

Type 2: An 80 nm layer of PEDOT:PSS was spin-coated on the ITO-glass substrate. After that, a chlorobenzene solution of 7 mg/mL was used to coat the pTPD layer at 2000 rpm during 30 s. The layer was annealed at 180°C for 30 minutes and after that, the samples were washed 3 times with chlorobenzene at 2000 rpm. The perovskite layer was prepared from POA2 nanoparticles in toluene (4 mg/mL).

Finally, all the devices were transferred into an inert atmosphere glove-box, where the barium/silver electrode was thermally evaporated using a shadow mask. The size of the device was 6.5 mm².

The thickness of the films was determined with an Ambios XP-1 profilometer. Thin film photoluminescence spectra and quantum yields were measured with a Hamamatsu C9920-02 Absolute PL Quantum Yield Measurement System. It consists of an excitation light source (a xenon lamp linked to a monochromator), an integration sphere and a multi-channel spectrometer. Current density and luminance versus voltage sweeps were measured by using a Keithley 2400 source meter and a photodiode coupled to the Keithley 6485 pico-amperometer calibrated using a Minolta LS100 luminance meter. Electroluminescence spectra were recorded with an Avantes fiber-optics photo-spectrometer. The devices were not encapsulated and were characterized inside the glovebox.

Stability tests of toluene colloidal solutions of P_{OA}2 under light illumination

Test 1. A toluene colloidal solution of P_{OA}2 was irradiated for up to 60 min, using 10 x 10 mm quartz cuvette placed in a Luzchem photoreactor equipped with eight UV-A lamps (316-400 nm, maximum at 351 nm). The room-temperature fluorescence of the sample ($\lambda_{\text{exc}} = 350$ nm, $\lambda_{\text{em}} = 528$ nm) was recorded every 3 min.

Test 2. A toluene colloidal solution of P_{OA}2 was illuminated for up to 160 min, using 10 x 10 mm quartz cuvette placed in the sample-holder of a PTI- LPS-220B spectrometer equipped with a Xenon lamp (75 W). The Felix 32 analysis software was used to register the data.

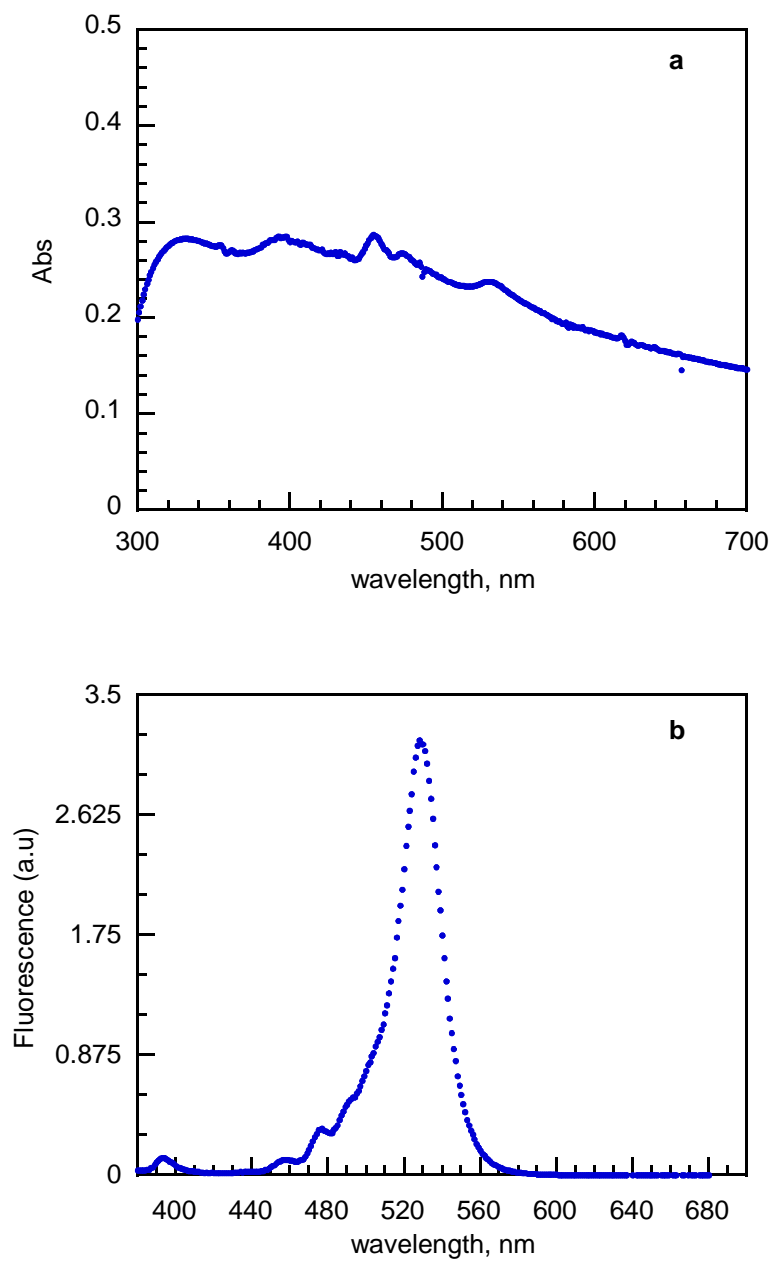


Figure S1. Absorption (a) and room-temperature emission (b) spectra of **P_{ODA1}** in toluene ($\lambda_{\text{exc}} = 350 \text{ nm}$; $\lambda_{\text{em}} = 393, 457 \text{ nm}, 475 \text{ nm}, 529 \text{ nm}$; FWHM = 26 nm)

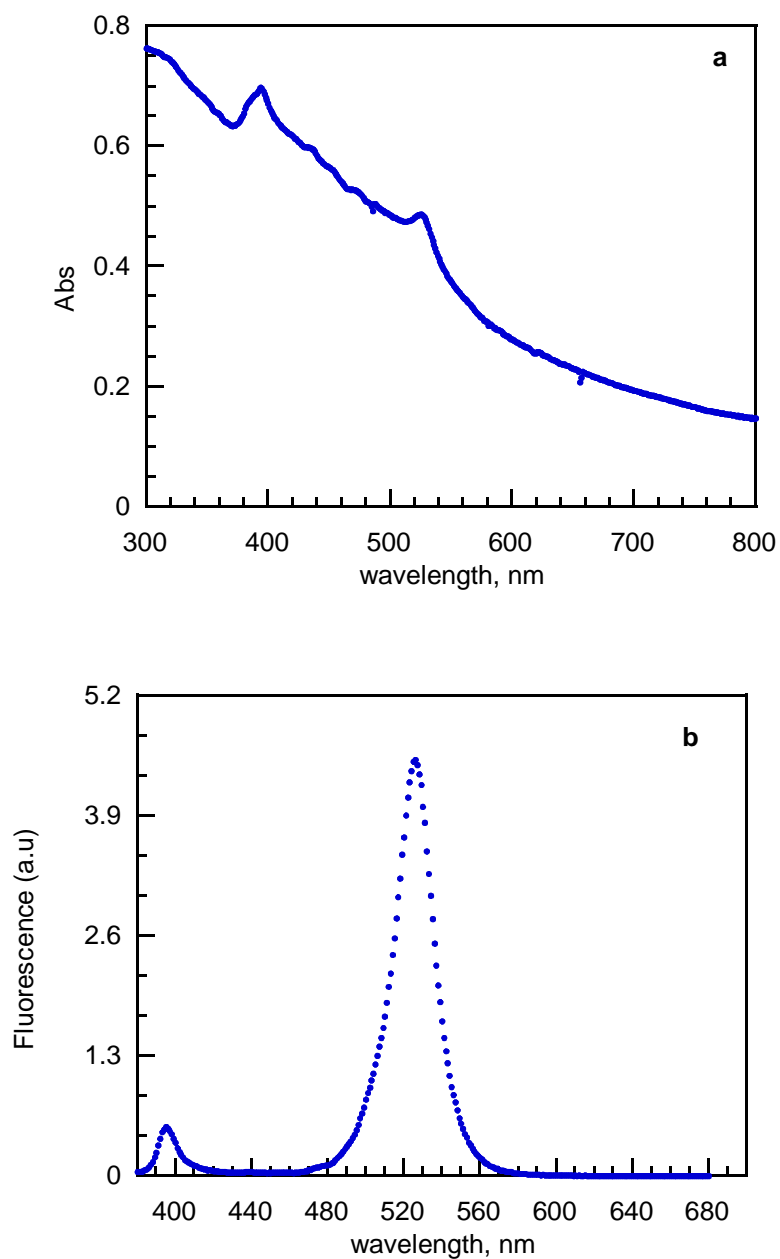


Figure S2. Absorption (a) and room-temperature emission spectra (b) of **P_{ODA2}** in toluene ($\lambda_{\text{exc}} = 350$ nm; $\lambda_{\text{em}} = 395$ and 526 nm; FWHM = 24 nm)

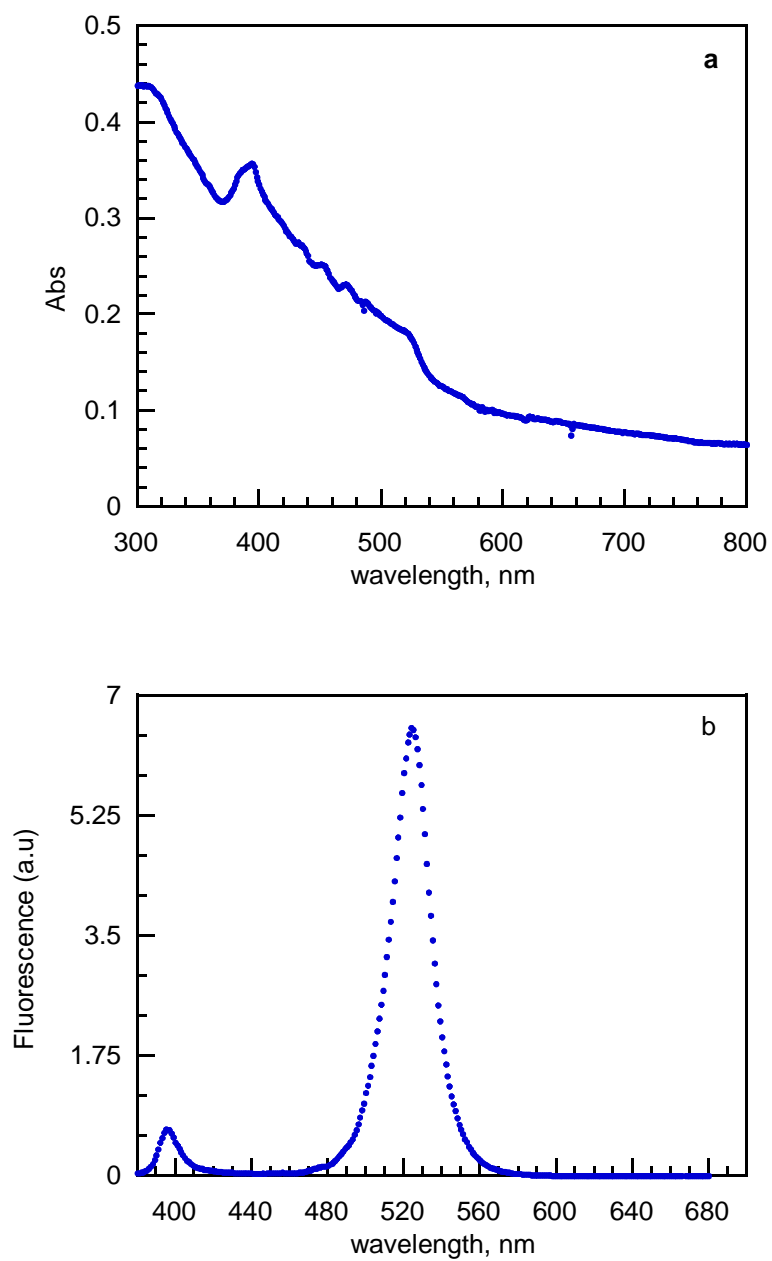


Figure S3. Absorption (a) and room-temperature emission (b) spectra of **P_{ODA3}** in toluene ($\lambda_{\text{exc}} = 350$ nm; $\lambda_{\text{em}} = 395$ and 524 nm; FWHM = 23 nm)

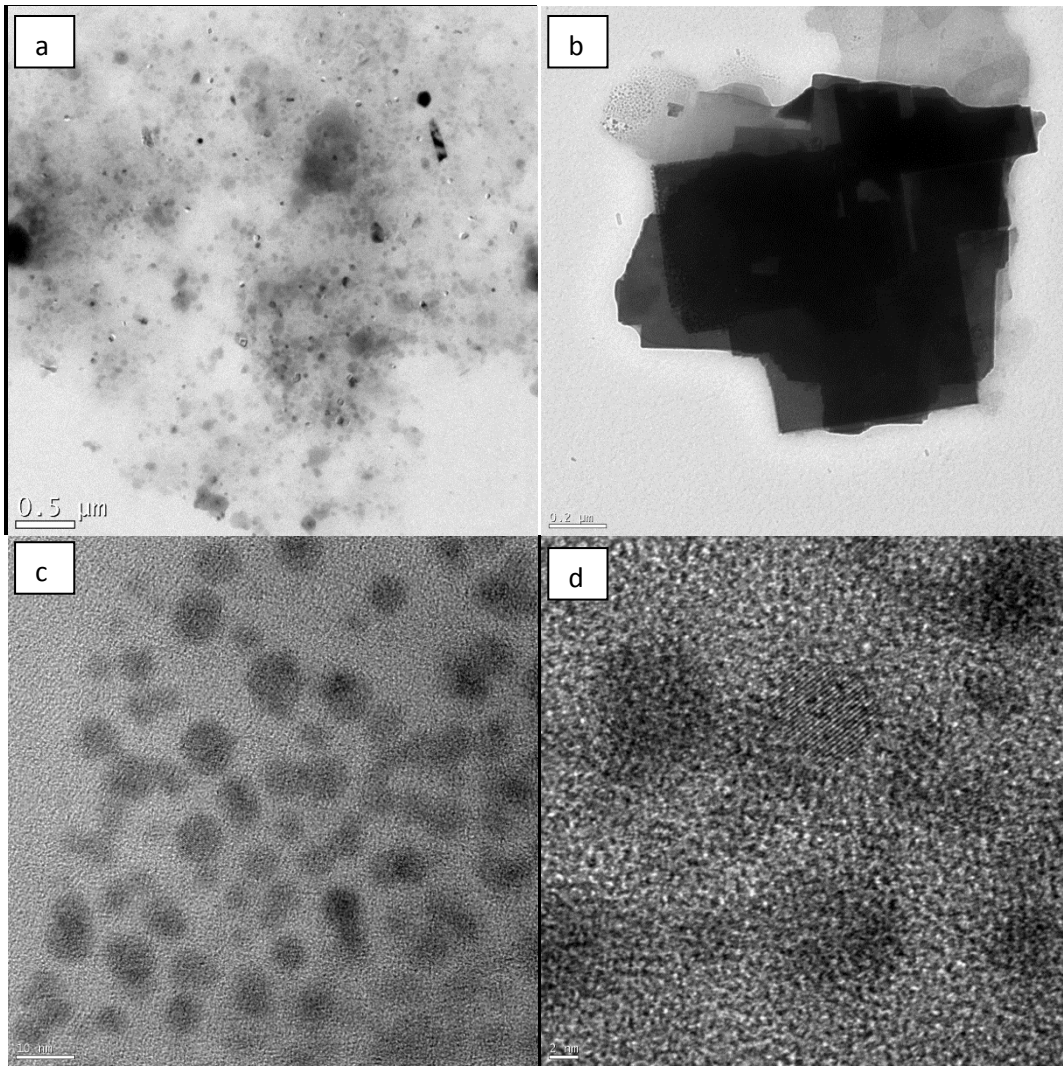


Figure S4. TEM images of P_{ODA1}, scale bar: 0.5 μm (a), 0.2 μm (b), 10 nm (c) and 2 nm (d).

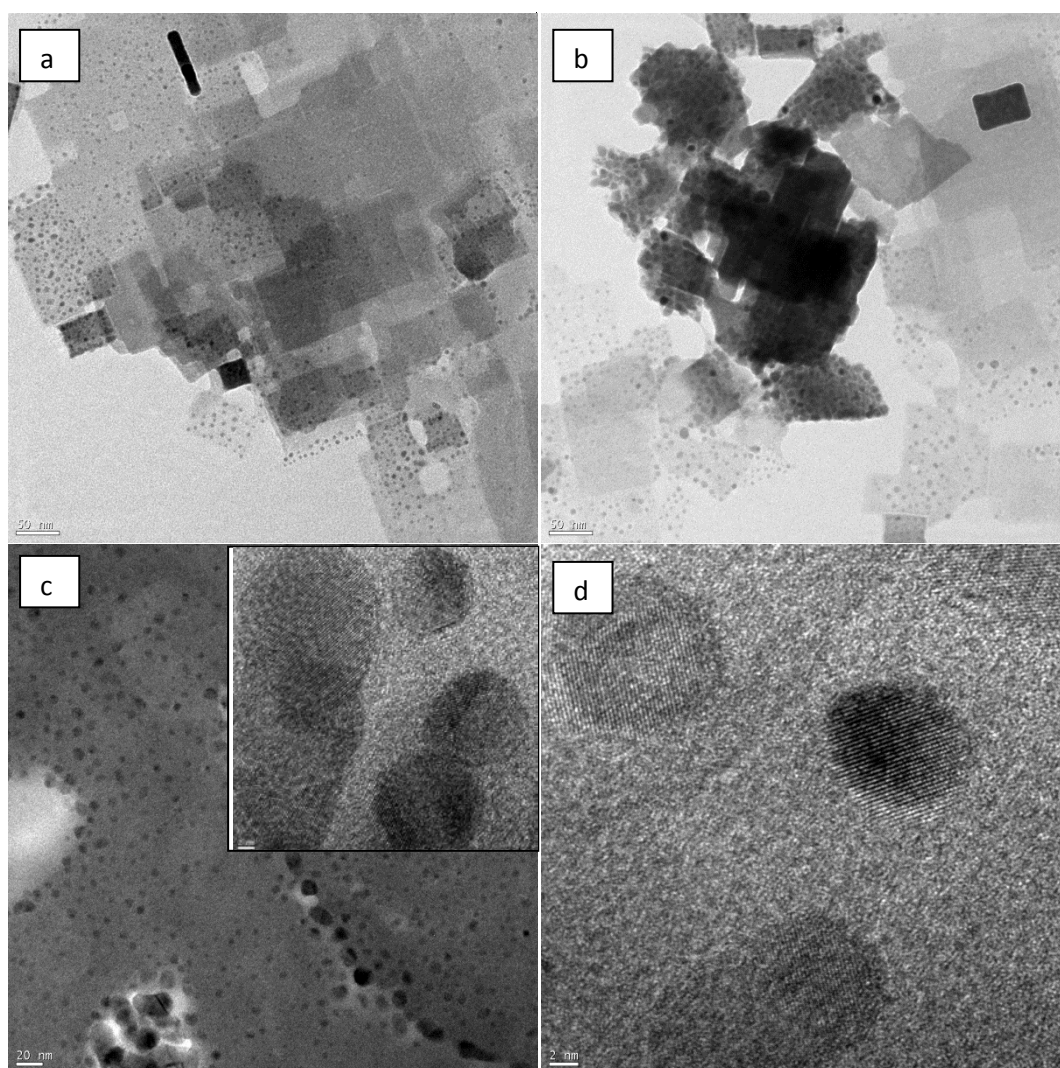


Figure S5. TEM images of P_{ODA2} , scale bar: 50 nm (a), 50 nm (b), 20 nm (c) and 2 nm (d).

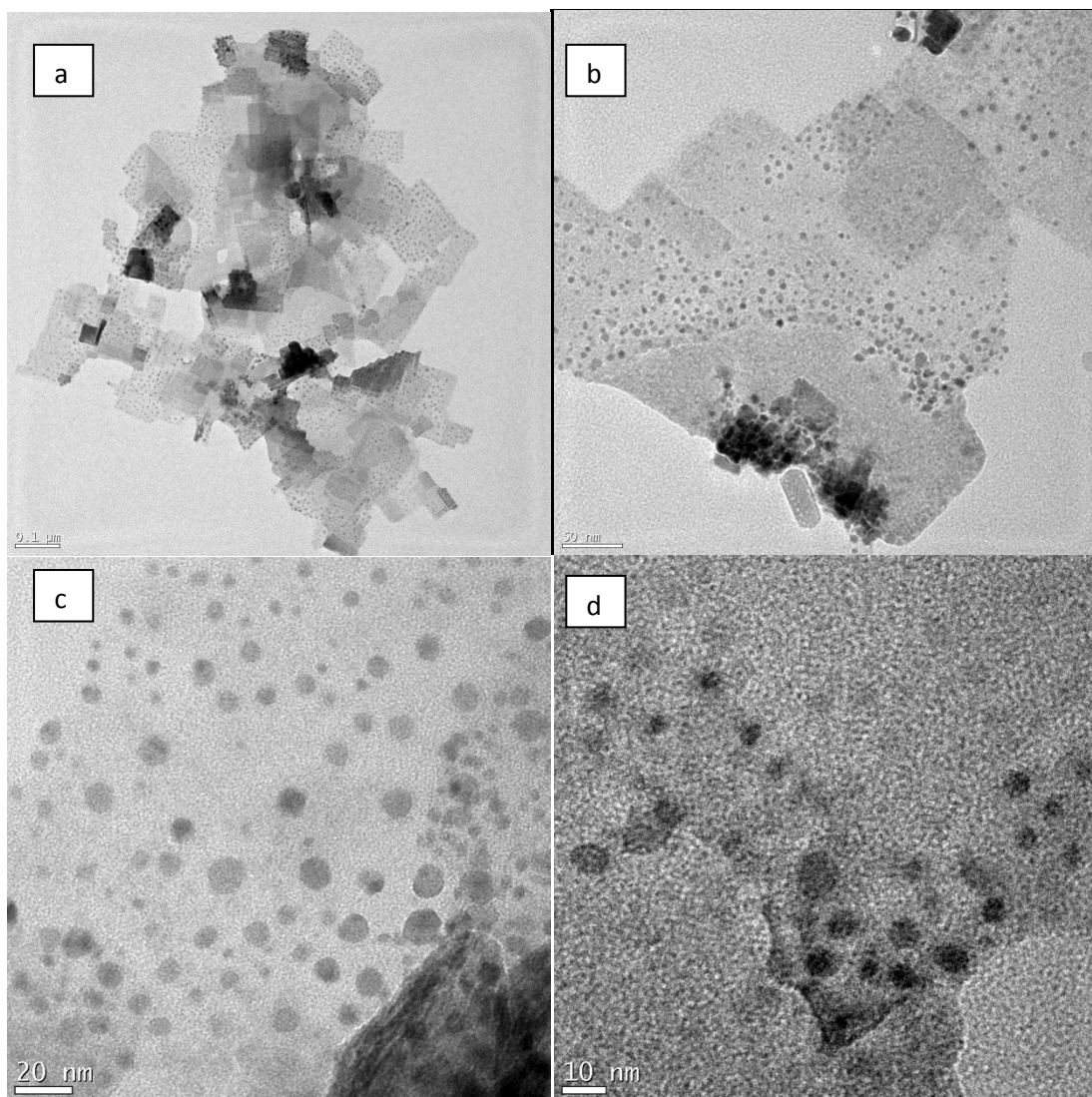


Figure S6. TEM images of P_{ODA3} , scale bar: 0.1 μm (a), 50nm (b), 20 nm (c) and 10 nm (d).

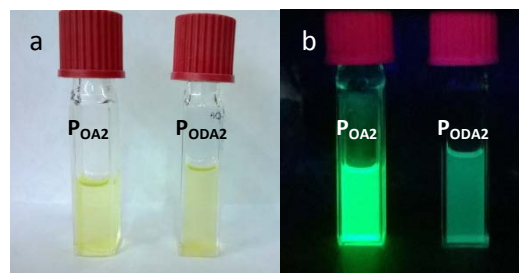


Figure S7. Photographs of P_{OA2} and P_{ODA2} in toluene under lab light (a) and UV-light (b).

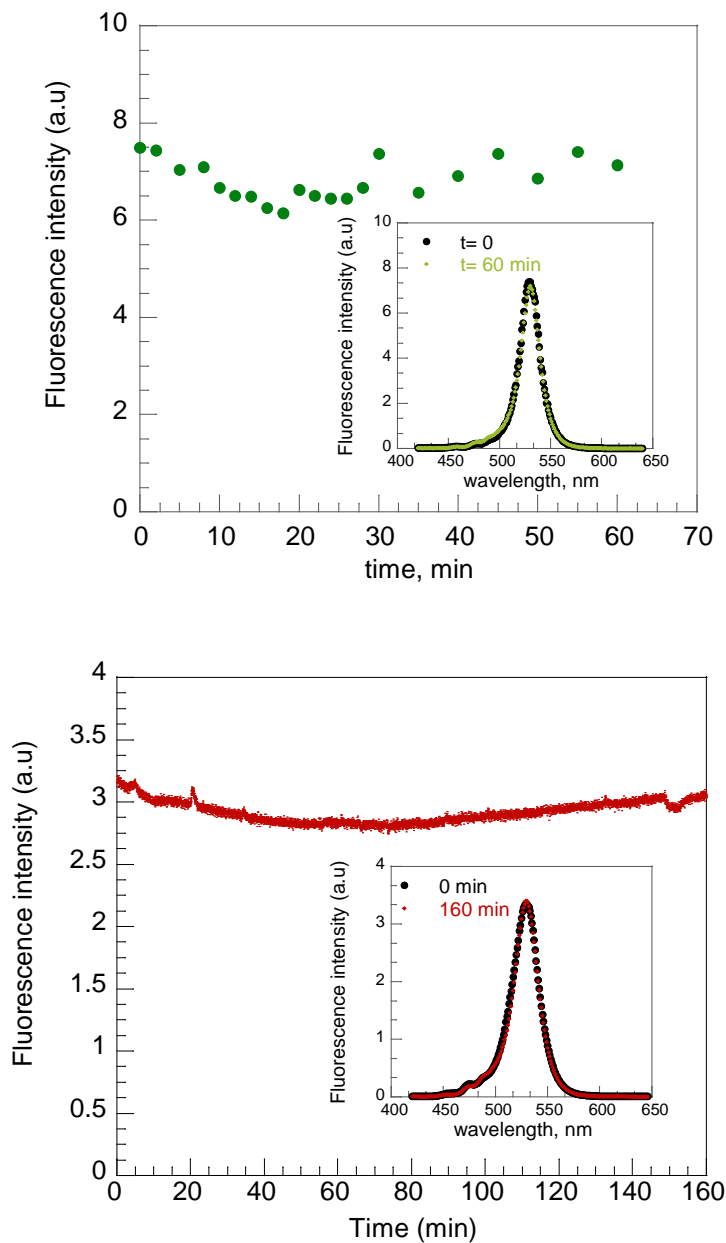


Figure S8. Room-temperature fluorescence intensity of P_{OA2} in toluene ($\lambda_{em}=528$ nm) as a function of the illumination time. Top: the sample was irradiated by using eight UVA lamps (intensity $5.3 \text{ mW}\cdot\text{cm}^{-2}$); inset: fluorescence spectra of the sample ($\lambda_{exc}=350$ nm; $\lambda_{em}=528$ nm) before and after 60 minutes irradiation. Bottom: the sample was continuously irradiated by using a fluorimeter excitation lamp ($\lambda_{exc}=350$ nm); inset: fluorescence spectra of the sample ($\lambda_{exc}=350$ nm; $\lambda_{em}=528$ nm) before and after 160 minutes of illumination.

Dispersibility of P_{OA2} in organic solvents

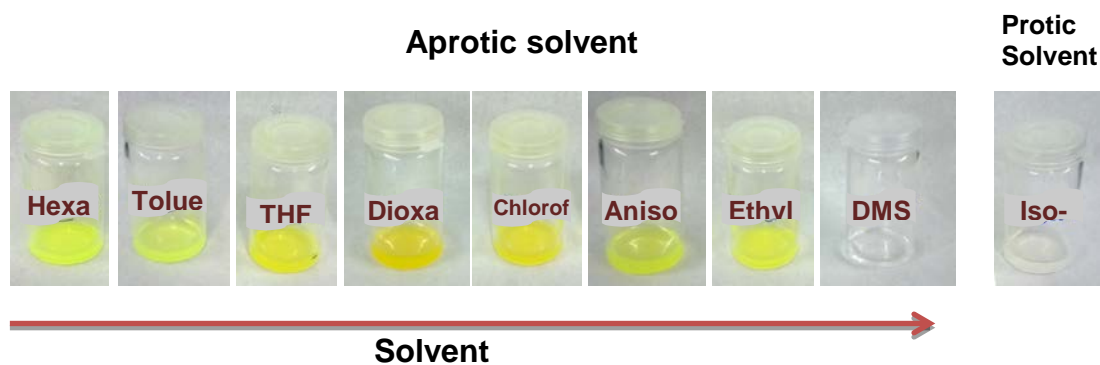


Figure S9. Photographs of the solutions obtained after solid P_{OA2} (2 mg) was dispersed in different organic solvents (1 mL); methanol led to the same result to isopropanol (this photograph has not been included).

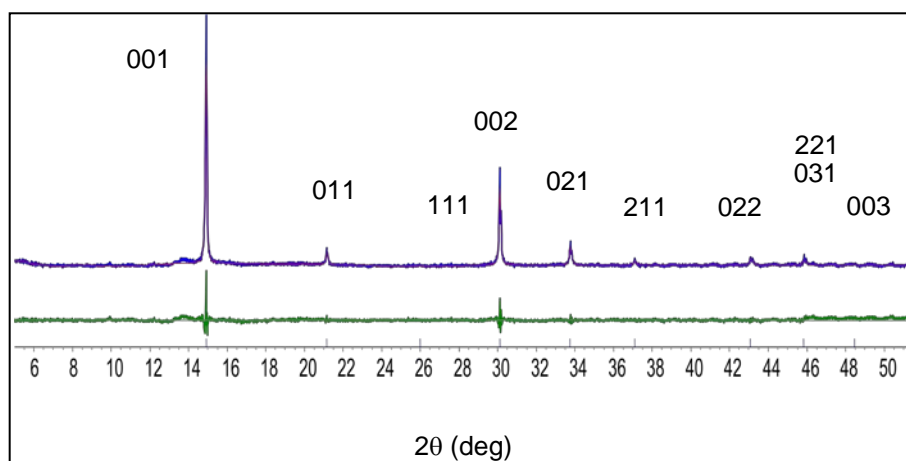


Figure S10. Observed (*blue*) and calculated (*red*) profiles and difference plot $[(I_{obs} - I_{calcd})]$ (*green*) of the X-ray powder diffraction Pawley refinement for P_{OA2} ($\lambda = \text{Cu } K_{\alpha}$, 2θ range 5.0–50.0 °); tick marks indicate peak positions for P_{OA2} (see Table S1).

Table S1: XRD parameters of P_{OA2} ($\lambda = \text{Cu } K_{\alpha}$)

hkl	d (Å)	2-theta (°)
001	5.93482	14.91526
011	4.19655	21.15379
111	3.42647	25.98318
002	2.96741	30.09099
021	2.65413	33.74296
211	2.42288	37.07516
022	2.09828	43.07498
221	1.97827	45.83172
003	1.97827	45.83172
031	1.87676	48.46513

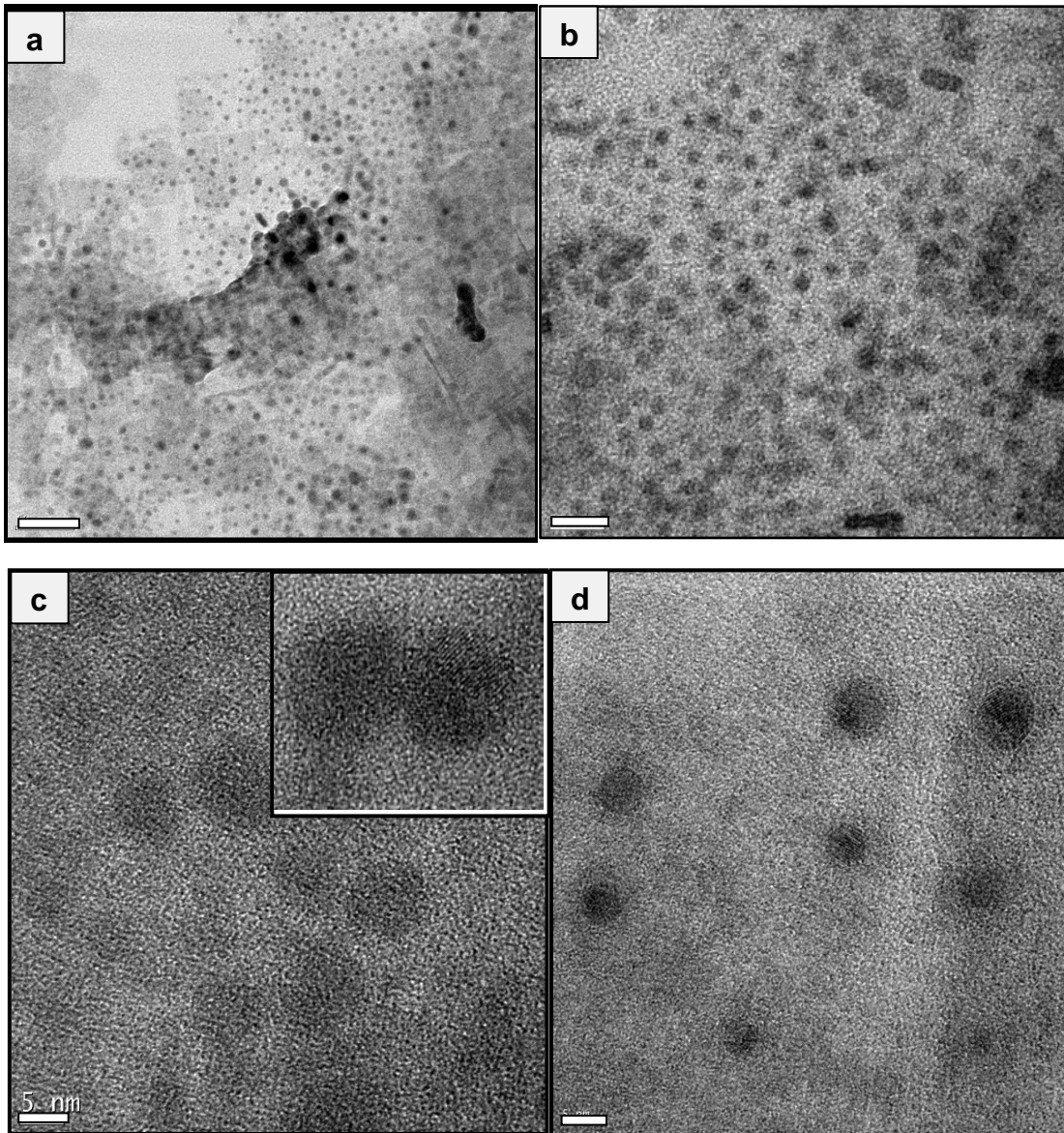


Figure S11. TEM images of P_{OA2} ; scale bar: 50 nm (a), 20 nm (b) and 5 nm (c, d). Inset in c: zoom of two NPs.

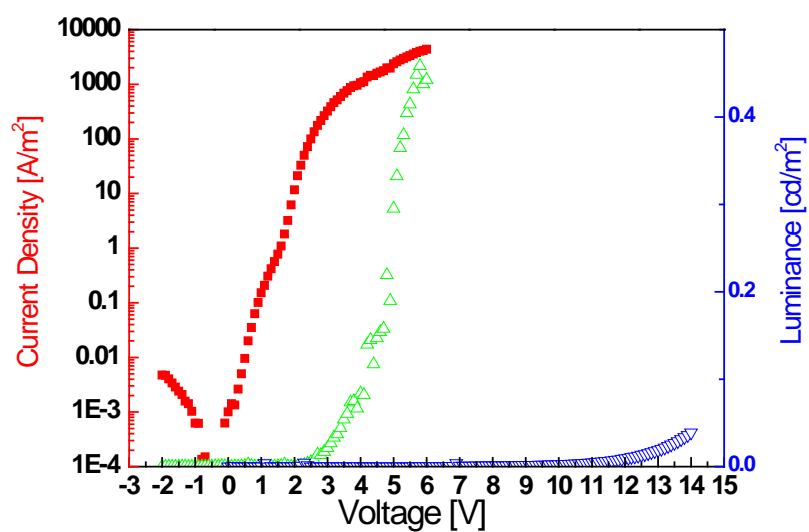


Figure S12. Current density (red solid squares) and room-temperature luminance (open symbols) versus applied voltage for device type I (ITO/ Al_2O_3 /n-Perovskite/SPPO13/Ba/Ag; blue down triangles) and type II (ITO/PEDOT:PSS/pTPD/ $\text{P}_{\text{O}A2}$ /Ba/Ag; green up triangles).

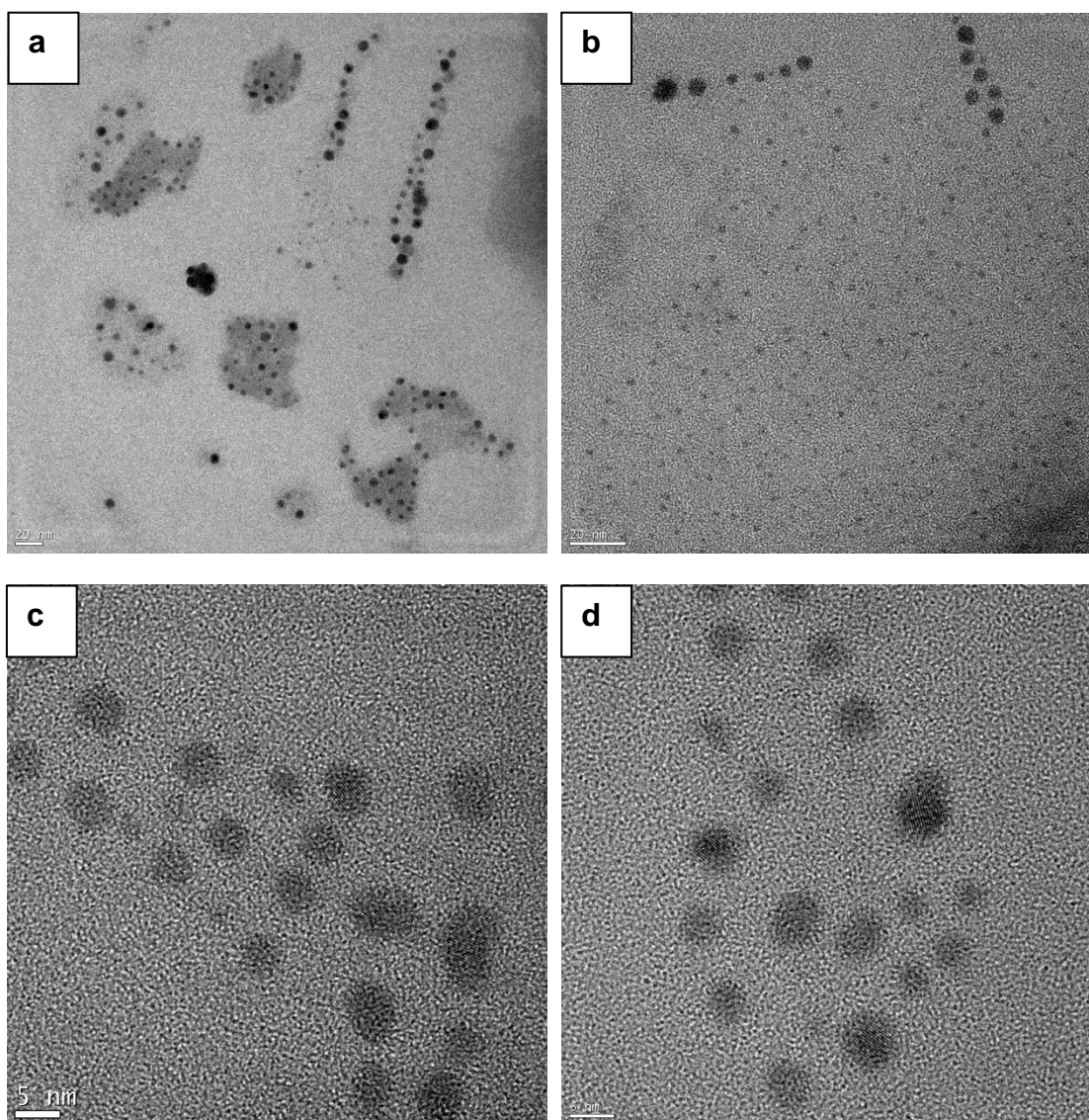


Figure S13. TEM images of ODA-capped $\text{CH}_3\text{NH}_3\text{PbI}_3$ nanoparticles synthesized by performing small variations on the strategy reported in the manuscript, scale bar: 20 nm (a, b) and 5 nm (c, d).

(1) Papavassiliou, G. C.; Pagona, G.; Karousis, N.; Mousdis, G. A.; Koutselas, I.; Vassilakopoulou, A. *Journal of Materials Chemistry* **2012**, *22*, 8271.