Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Stabilizing the Cubic Perovskite Phase of $CsPbI_3$ Nanocrystals by Using an Alkyl Phosphinic Acid

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Contents

Materials

Cesium carbonate (Cs_2CO_3, 99.995% trace metal basis), lead(II) iodide (PbI_2, 99.999% trace metal basis), 1-octadecene (ODE, 90%, technical grade), oleylamine (OLA, 70%, technical grade), oleic acid (OA, 90%, technical grade), tert-butanol (99.5%, anhydrous), and toluene (99.5%, analytical reagent) were purchased from Sigma-Aldrich. Bis(2,4,4-trimethylpentyl)phosphinic acid (TMPPA, 85%) was purchased from Cytec. All reagents were used without further purification.

Synthesis

Synthesis of Cs-oleate

The reaction was carried out using a standard Schlenk line. Cs_2CO_3 (0.1 g, 307 μmol) was suspended in a solution of ODE (5 ml) and OA (0.5 ml) in a 100 mL three-neck flask, and heated to 120 °C under vacuum with stirring. The reaction solution was degassed for 1 h at the target temperature. The suspension was then heated to 150 °C under N_2, with the temperature then maintained until all Cs_2CO_3 had fully dissolved. The solution was then kept at 100 °C before use.

Synthesis of Cs-TMPPA

The synthesis of Cs-TMPPA followed the same procedure as that used for the synthesis of Cs-oleate, except TMPPA (0.5 ml) was used instead of OA.

Synthesis of $CsPbI_3$ using OA ($CsPbI_3$-OA)

The reaction was carried out using a standard Schlenk line. PbI_2 (87 mg, 188 μmol) was suspended in a solution of ODE (5 ml), OA (0.5 ml), and OLA (0.5 ml) in a 100 mL 3-neck flask, and heated to 120 °C under vacuum with stirring, with the temperature maintained for 1 h. After dissolution of the PbI_2, the temperature of the reaction solution was increased to 140 °C under N_2. Then, 0.4 mL of the preheated Cs-oleate solution was injected into the reaction solution, and after 5 s the flask was submersed in a water bath to quench the reaction.

Synthesis of $CsPbI_3$ using TMPPA ($CsPbI_3$-TMPPA)

The synthesis of $CsPbI_3$-TMPPA followed the same procedure as that used for the synthesis of $CsPbI_3$-OA, except TMPPA (0.5 ml) was used to replace the OA, and 0.4 ml of the preheated Cs-TMPPA solution was injected. Synthesis at a hot injection temperature of 100 °C was also performed.

Purification

As-prepared crude solutions of $CsPbI_3$-OA and $CsPbI_3$-TMPPA in ODE were mixed with a tert-butanol anti-solvent, and then centrifuged for 30 min in a Beckman Coulter Allegra^{TM} X-22R Centrifuge. Larger anti-solvent ratios and higher centrifuge rotation speeds resulted in more NCs precipitating from solution. The supernatant was then discarded and the NCs were re-dispersed in toluene for storage and characterization.

Characterization

UV-vis Spectroscopy

UV-vis absorbance spectra for suspensions of NCs in toluene were collected using a Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer.

Photoluminescence (PL)

Photoluminescence spectra for suspensions of NCs in toluene were collected using a Horiba Fluoromax-4 spectrofluorometer.

Powder X-ray Diffraction (PXRD)

Samples were prepared for PXRD measurements by depositing suspensions of NCs in toluene on a glass substrate and heating the substrate to evaporate the toluene. XRD patterns were acquired on a Bruker D8 Advance diffractometer using a Cu source (Kα = 1.54 Å) at 40 kV, 40 mA, and a LynxEye detector.

Transmission Electron Microscopy (TEM)

TEM and HRTEM images were obtained on a FEI Tecnai G^2 T20 transmission electron microscope equipped with a LaB_6 electron source operated at 200 kV. Images were acquired by either a Gatan Orius SC200D CCD camera and a Gatan Orius SC600 CCD camera.

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H, ^{13}C, and ^{31}P NMR measurements were performed on a Bruker Bio Spin Av400H with a 9.4 T magnet and a 5 mm inverse 1H-X BBI autotuning broadband probe at a ^{1}H frequency of 400.13 MHz. All samples were measured in d_8-toluene unless noted. Diffusion coefficients as measured by diffusion-ordered spectroscopy (DOSY) given to two significant figures.

Supporting Figures and Tables

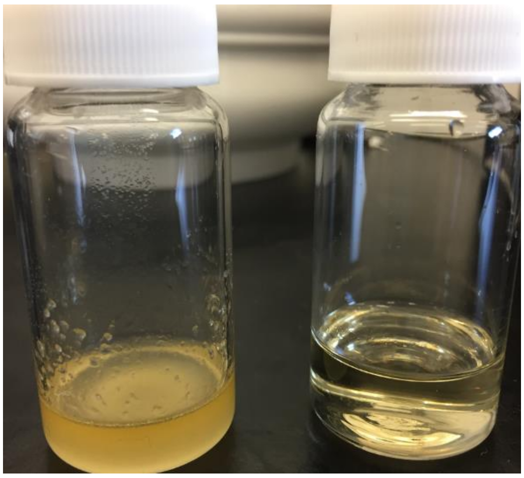


Fig. S1 Photo of the Cs-oleate (left) and Cs-TMPPA solutions (right) at 25 °C.

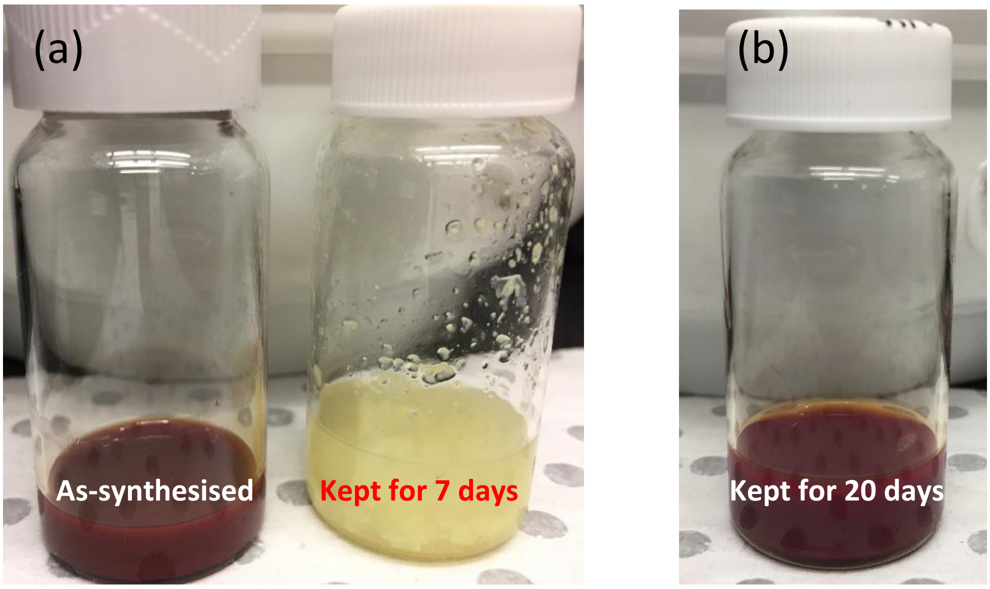


Fig. S2 (a) A crude solution of $CsPbI_3$-OA, as synthesised (left) and kept under ambient conditions for 7 days (right); (b) A crude solution of $CsPbI_3$-TMPPA kept under ambient conditions for 20 days.

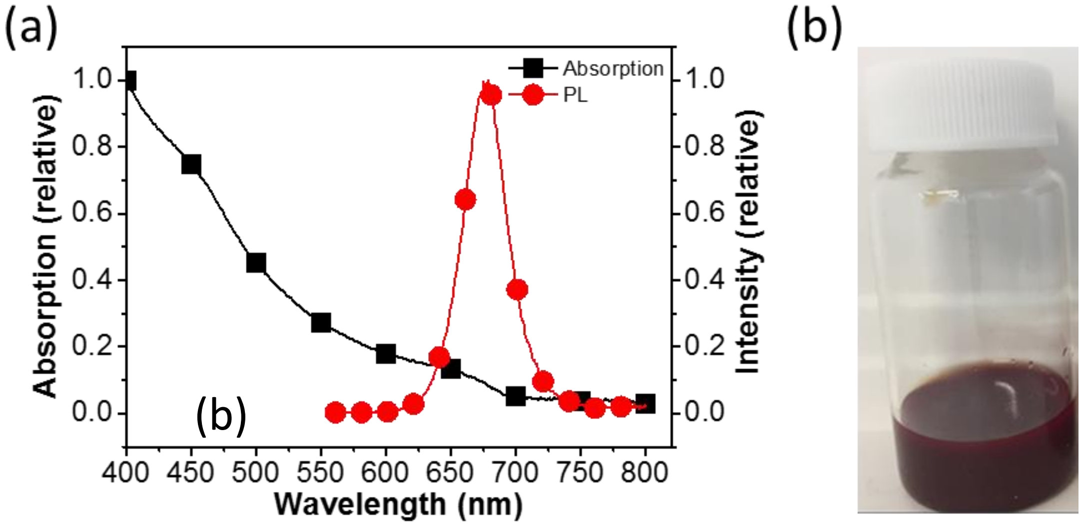
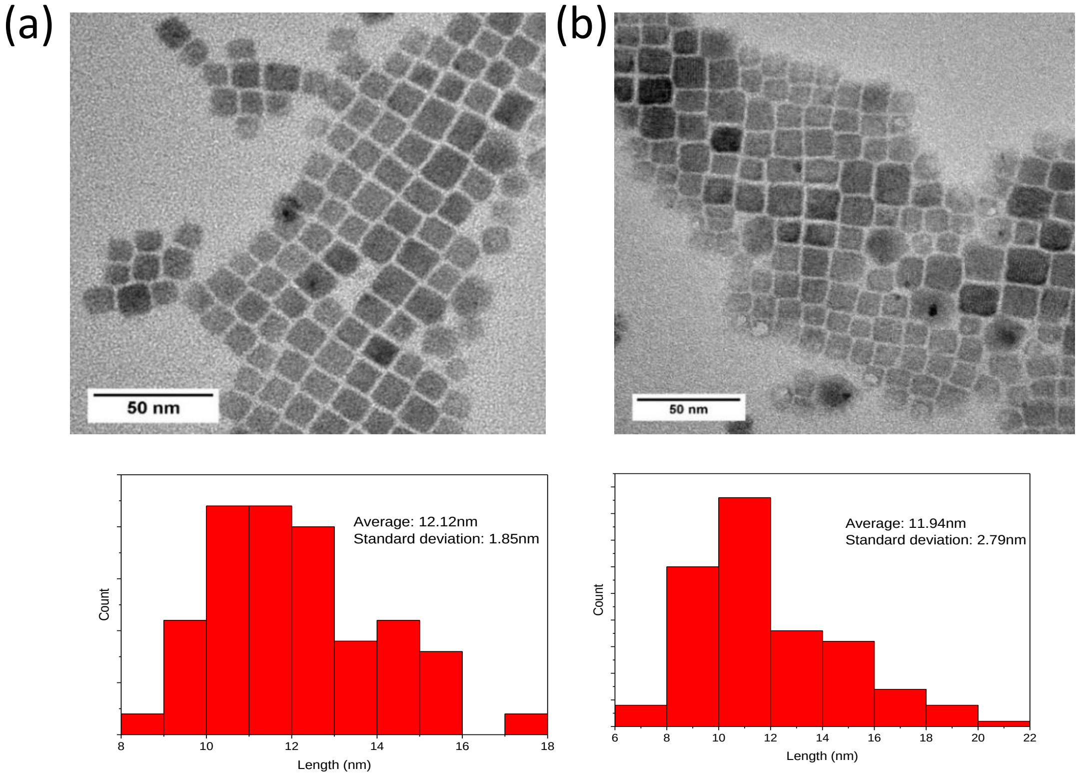


Fig. S3 (a) UV-Vis absorption and Photoluminescence spectrum and (b) a photo of CsPbI$_3$-TMPPA synthesised at 100 °C and kept for 7 days.



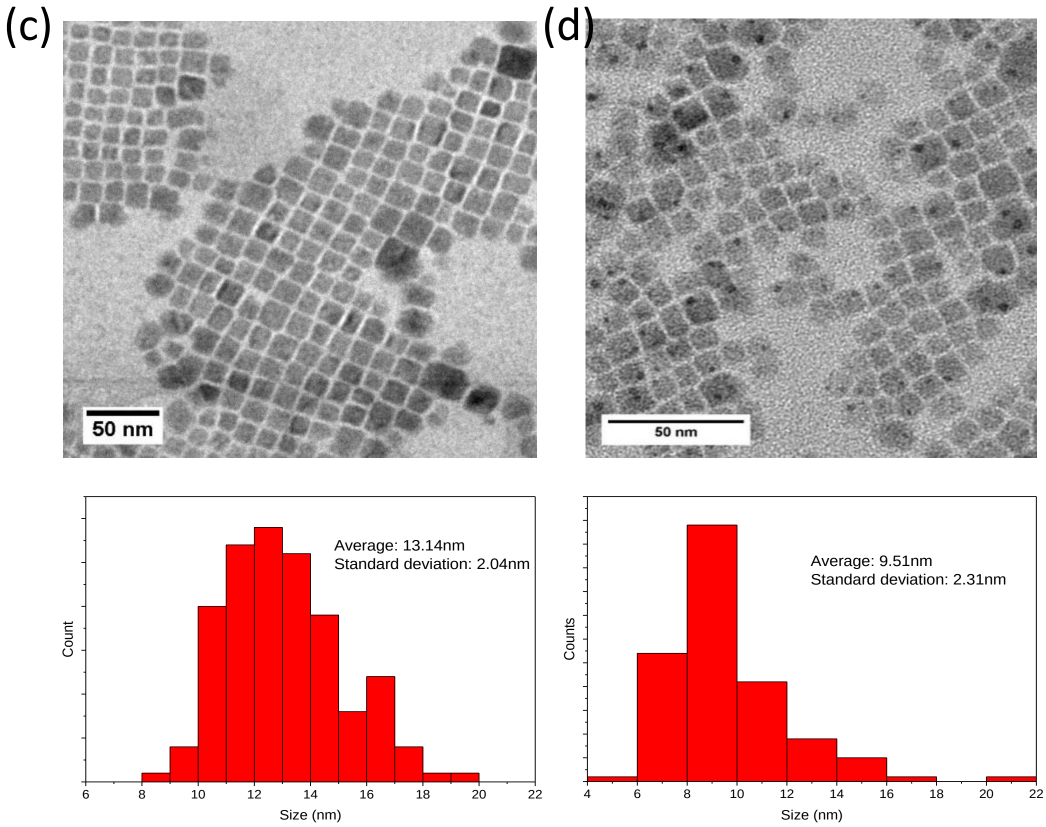


Fig. S4 TEM images and size distributions of (a) $CsPbI_3$-TMPPA, 1:3 solvent/anti-solvent (v/v), 8000 rpm, (b) $CsPbI_3$-TMPPA, 1:3 solvent/anti-solvent (v/v), 10000 rpm, (c) $CsPbI_3$-TMPPA, 2:1 solvent/anti-solvent (v/v), 10000 rpm, (d) $CsPbI_3$-OA, 1:3 solvent/anti-solvent (v/v), 10000 rpm.

Table S1 Summary of the size of NCs with different washing parameters

Group number	Solvent/Anti-solvent	Rotation speed (rpm)	Average size (nm)	Standard deviation (nm)
a	1:3	8000	12.1	1.8
b	1:3	10000	11.9	2.8
c	2:1	10000	13.1	2.0
d ($CsPbI_3$-OA)	1:3	10000	9.5	2.3

NC size variation during washing

The effect of different washing parameters (solvent/anti-solvent ratio, centrifuge rotation speed) on the isolated NC size is presented in Fig. S3a-d and Table S1. Increasing the polarity of the solution by introducing greater amounts of anti-solvent or using higher rotation speeds to generate larger centrifugal forces resulted in the precipitation smaller NCs. Measurements of $CsPbI_3$-TMPPA samples indicated that a greater amount of anti-solvent (S3b compared to S3c) or a larger rotation speed (S3b compared to S3a) yielded smaller average particle sizes and larger size distributions. Using the same washing parameters (S3b compared to S3d) gave $CsPbI_3$-OA NCs with a 2 nm smaller average size.

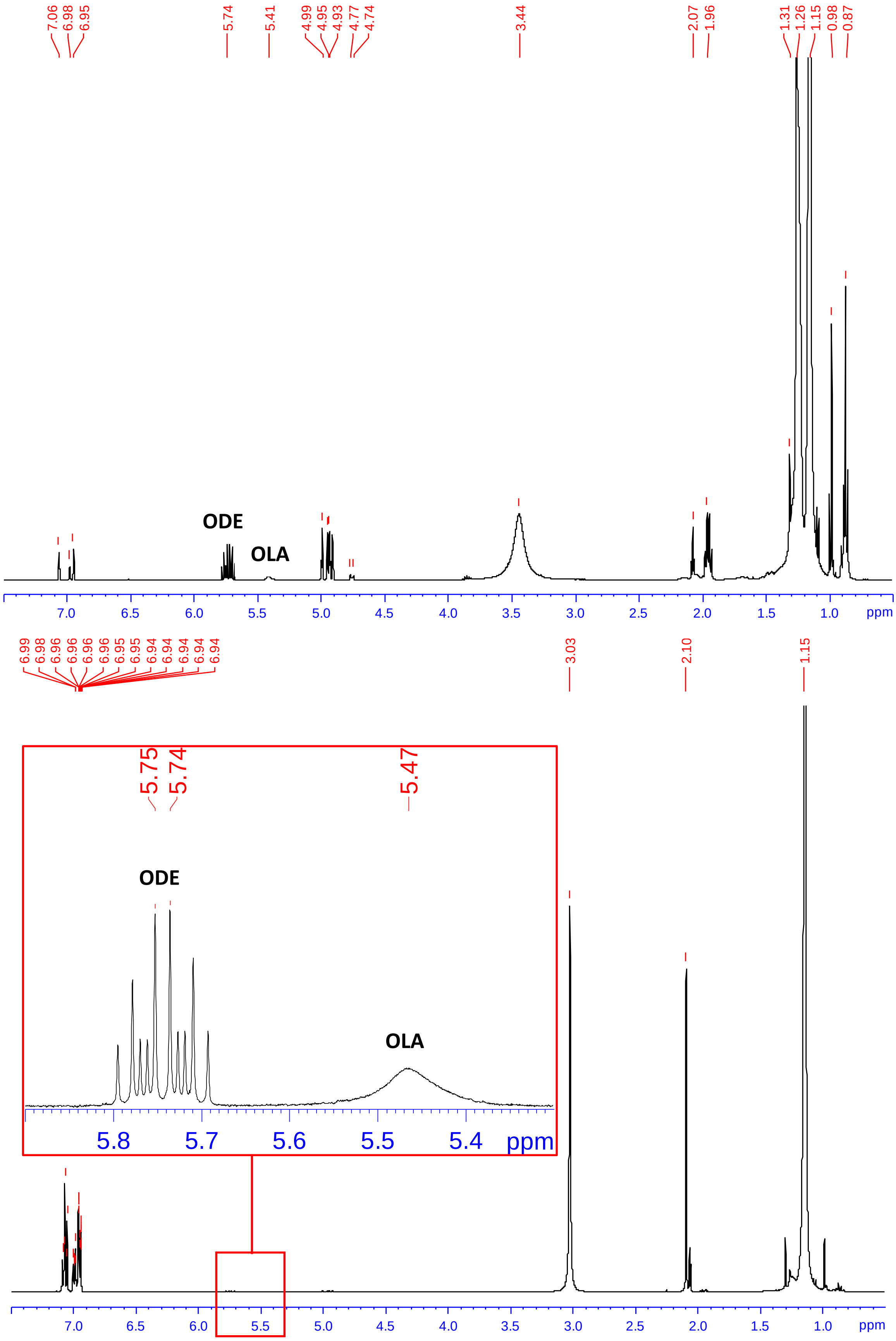


Fig. S5 ^{1}H NMR spectrum of a concentrated solution of CsPbI$_3$-TMPPA NCs washed once (top) and washed twice (bottom).

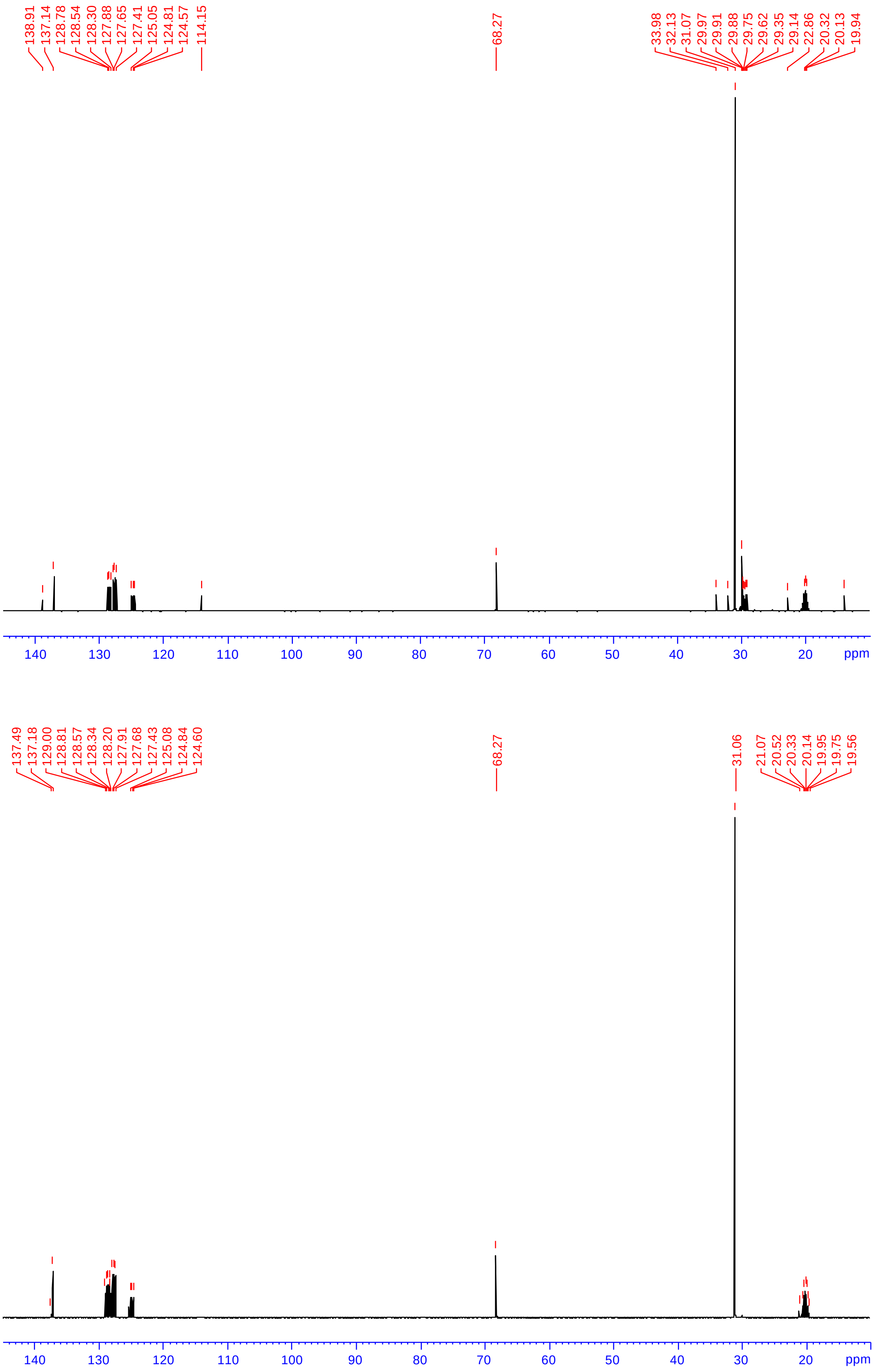


Fig. S6 ^{13}C NMR spectrum of a concentrated solution of $CsPbI_3$-TMPPA NCs washed once (top) and washed twice (bottom).

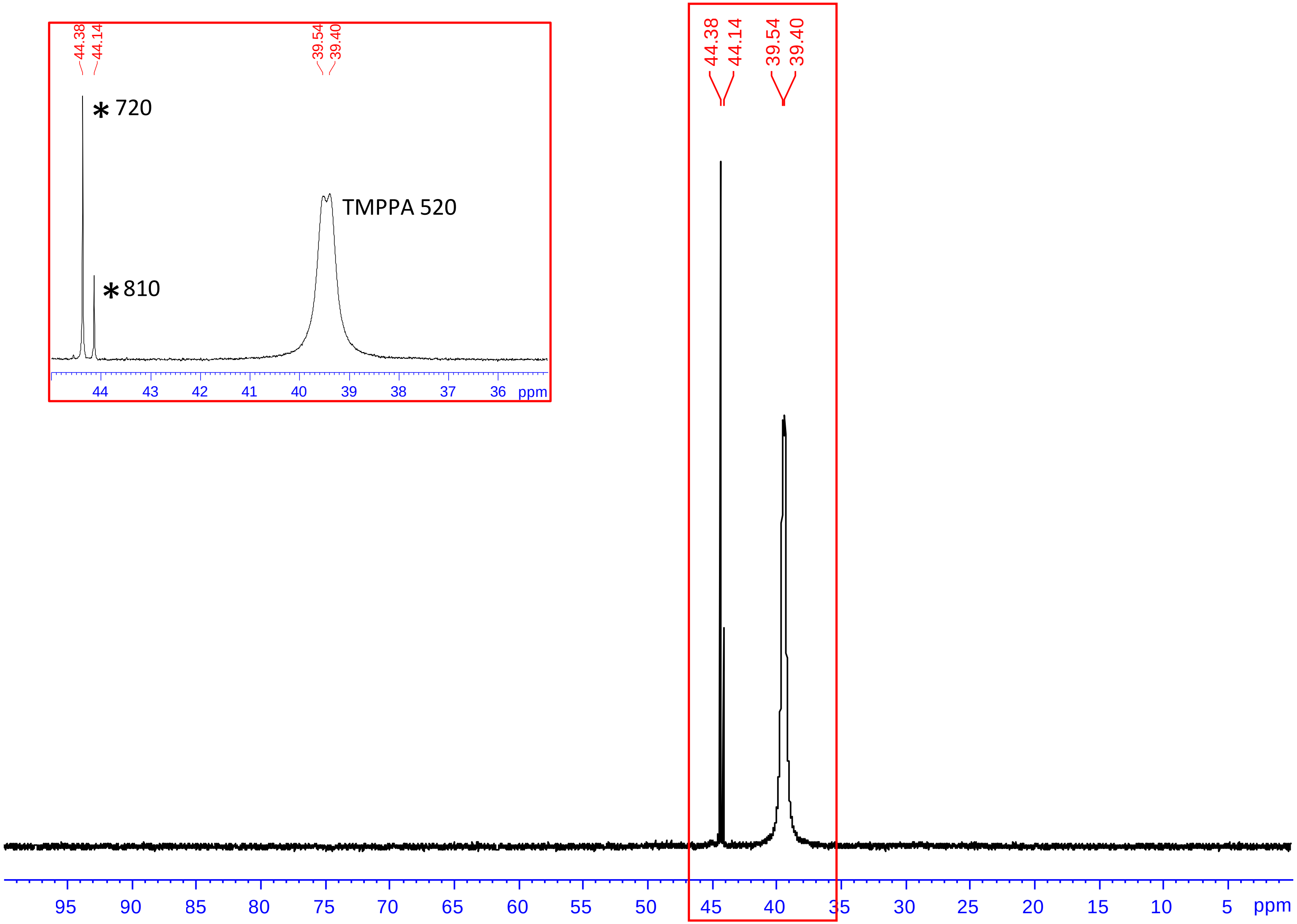


Fig. S7 ^{31}P NMR spectrum of a concentrated solution of CsPbI$_3$-TMPPA NCs (washed once). Asterisks (*) denote organophosphorus impurities. Annotated diffusion coefficients as measured by DOSY given in μm^2 / s.

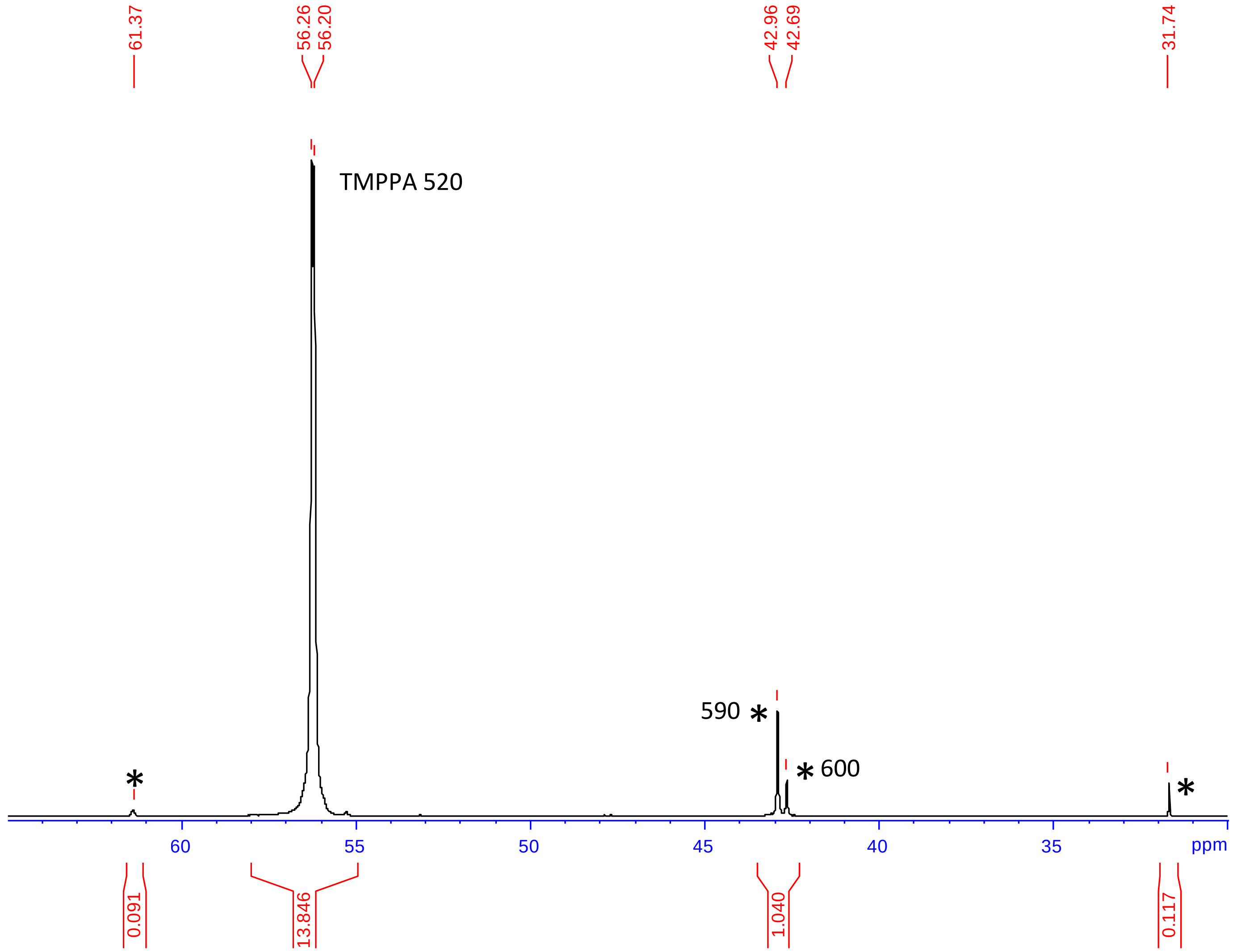


Fig. S8 ^{31}P NMR spectrum of neat TMPPA. Asterisks (*) denote organophosphorus impurities. Annotated diffusion coefficients as measured by DOSY given in μm^2 / s.

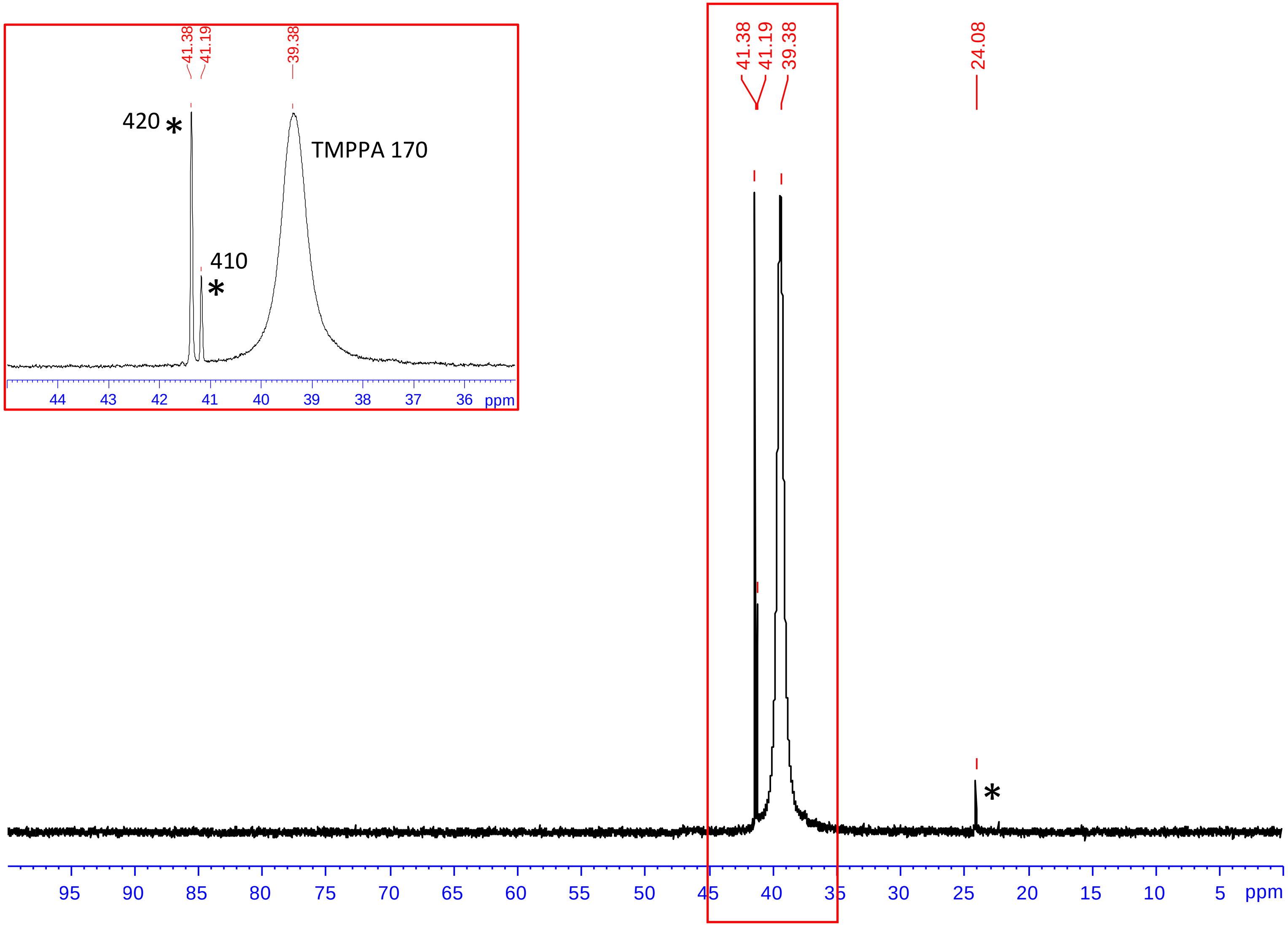


Fig. S9 ^{31}P NMR spectrum of TMPPA with an excess of OLA present in solution. Asterisks (*) denote organophosphorus impurities. Annotated diffusion coefficients as measured by DOSY given in μm^2 / s.

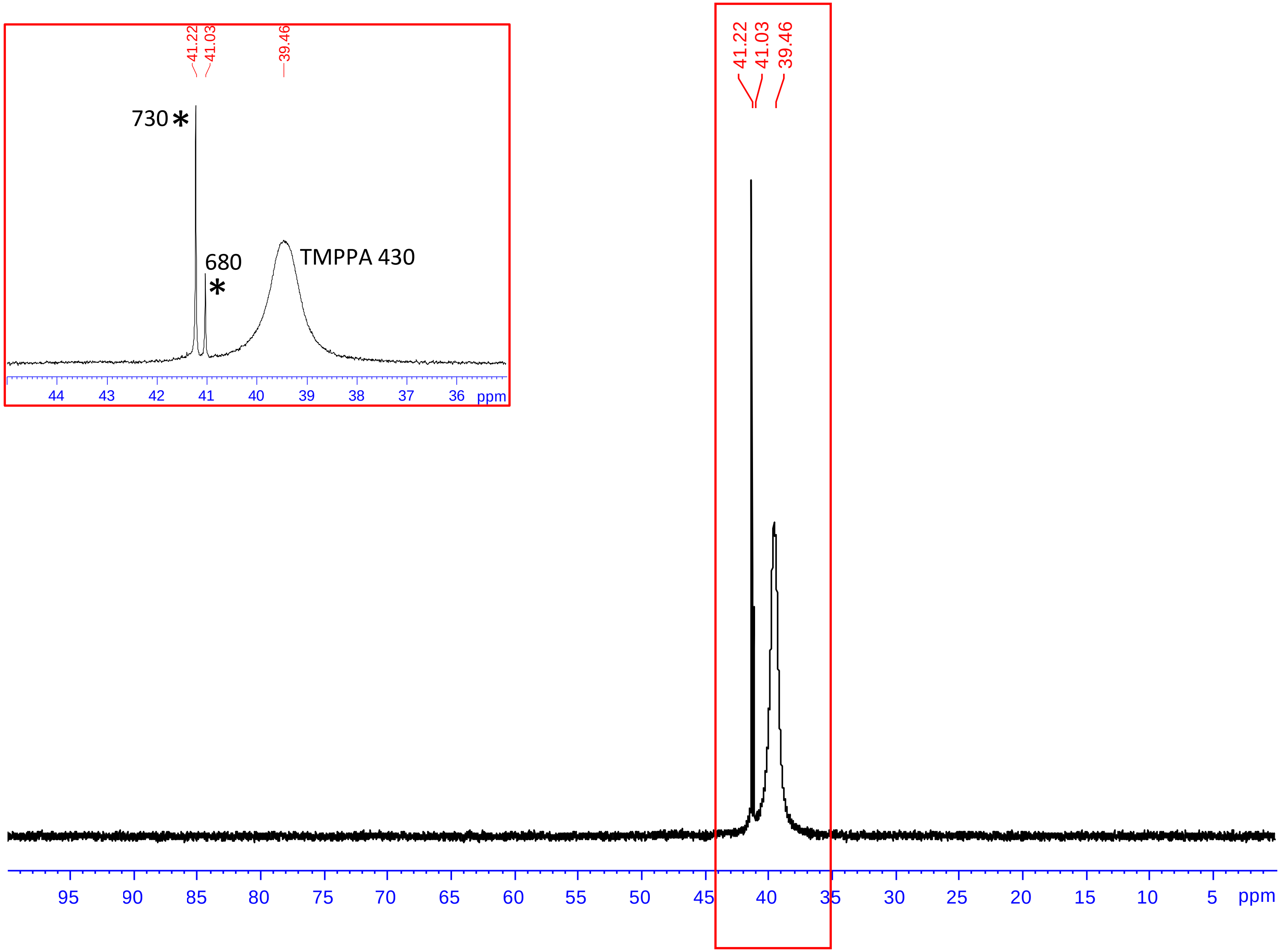


Fig. S10 ^{31}P NMR spectrum of a Pb-TMPPA/OLA precursor solution. Asterisks (*) denote organophosphorus impurities. Annotated diffusion coefficients as measured by DOSY given in μm^2 / s.

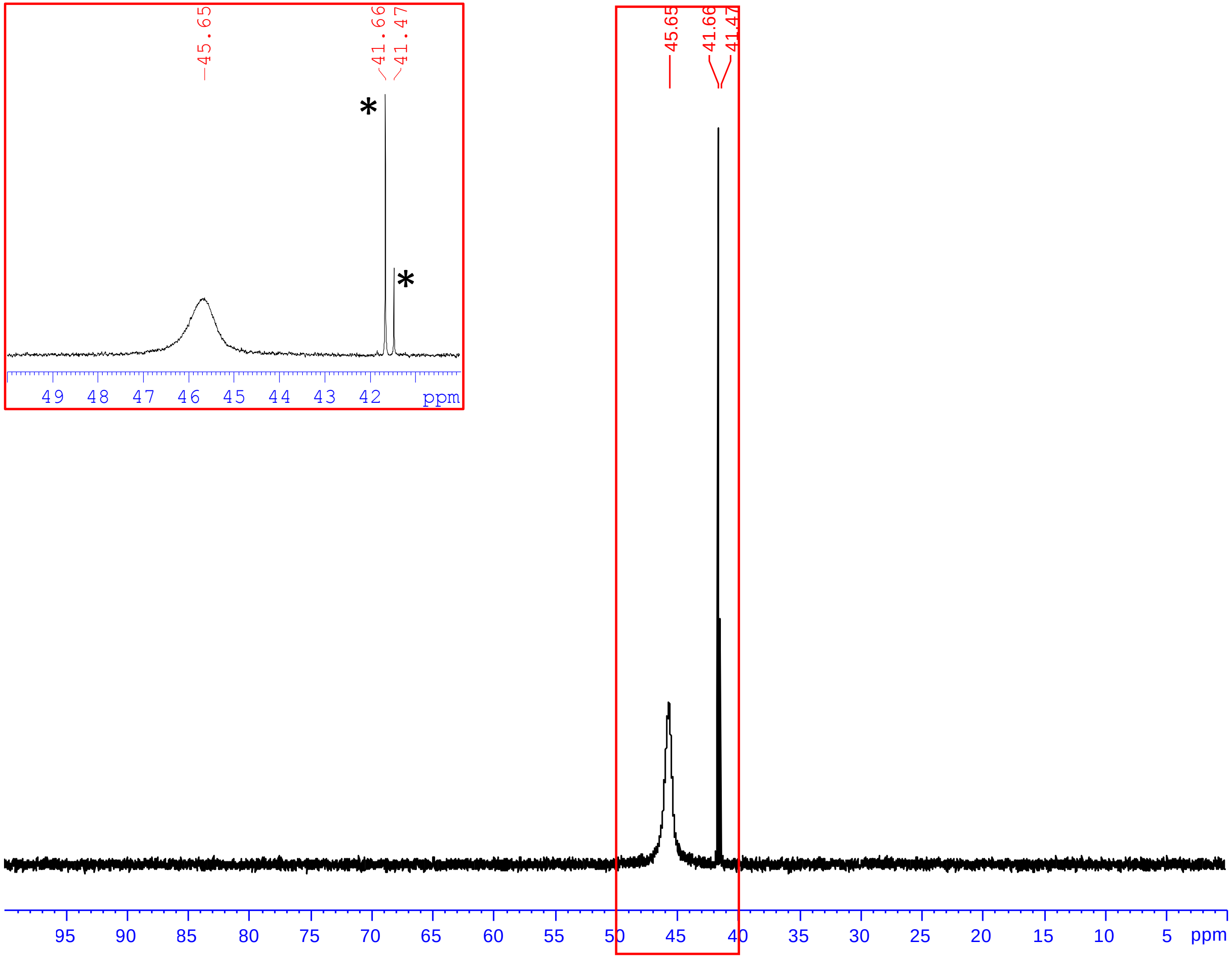


Fig. S11 ^{31}P NMR spectrum of a Pb-TMPPA solution synthesised by a reaction of PbO with TMPPA in diphenyl ether/d_8-toluene. Asterisks (*) denote organophosphorus impurities.

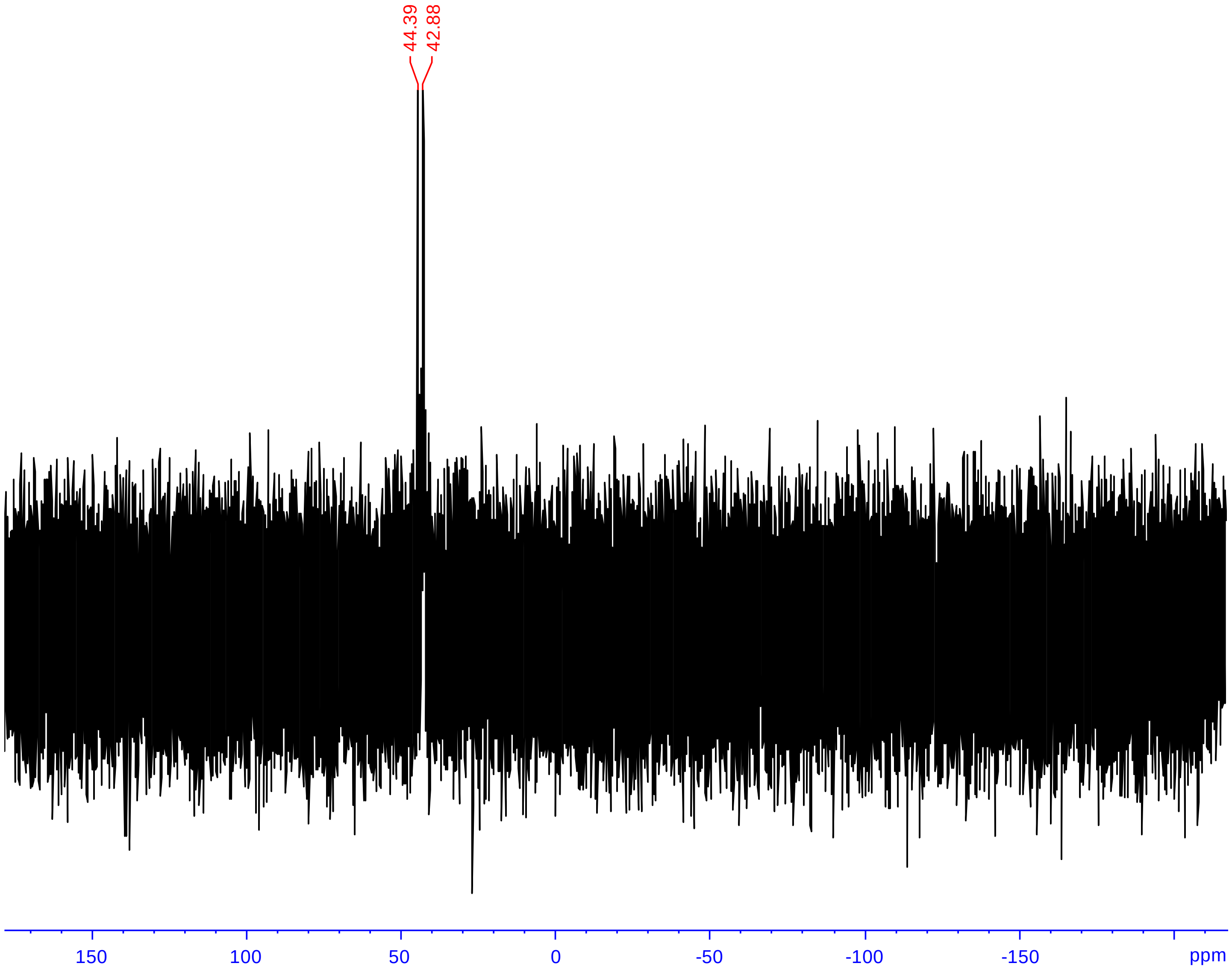


Fig. S12 ^{31}P NMR spectrum of a $CsPbI_3$-TMPPA solution washed twice to remove all TMPPA species. Note 5 hour scan duration.

^{31}P NMR DOSY measurements

The ^{31}P NMR spectrum of neat TMPPA contains minor peaks attributable to organophosphorous impurities (Figure S8). As the diffusion coefficient and peak position and shape of these species do not significantly change between the ^{31}P NMR spectra of neat TMPPA, isolated $CsPbI_3$ NCs, Pb-TMPPA, and Pb-TMMPA/OLA and TMPPA/OLA mixtures (Figures S7-S11), it can be assumed that they do not interact with the surface of the NCs, but rather are retained after isolation of the NCs, like residual ODE and tert-butanol.

Attempts to form a Pb-TMPPA solution using PbI_2 as a lead source failed, with the PbI_2 failing to dissolve, even at elevated temperatures. In order to form a Pb-TMPPA complex, PbO was reacted with TMPPA in diphenyl ether at elevated temperatures, giving a homogenous solution. The ^{31}P NMR signal for the TMPPA species in this control solution was present at 45 ppm, a shift of ~6 ppm in comparison to the TMPPA species in the NMR spectra of TMPPA/OLA and α-$CsPbI_3$ NCs (Fig. S11). A shift of this magnitude cannot be solely attributed to solvent effects, therefore it is ascribed to the formation of a Pb-TMPPA species in solution.

When PbI_2 was reacted with TMPPA in the presence of the OLA the signal for the TMPPA species was at the same position as that observed for the TMPPA/OLA control solution (Fig. S9-10), indicating that in the former TMPPA oleylammonium ion pairs form rather than a Pb-TMPPA complex. However, the dissolution of the PbI_2 precursor indicates that this ion pair must be interacting with the PbI_2 in some fashion which remains to be determined.

Interestingly, DOSY measurements of the control solution of TMPPA with excess OLA, which was used to confirm the formation of a TMPPA/oleylammonium ion pair, gave a lower diffusion coefficient for TMPPA of 170 μm^2 / s. This lower than expected diffusion coefficient is postulated to potentially be due to either the massive excess of OLA significantly altering the viscosity of the solution, or the additional amine leading to the formation of an amine-solvated TMPPA/oleylammonium ion pair in solution.[1] Determination of the cause of the significant decrease in the diffusion coefficient of TMPPA in the presence of excess OLA is outside the scope of this study.

OA, oleyammonium-oleate addition to $CsPbI_3$-TMPPA solution.

To verify the effect of adding OA or oleyammonium-oleate on α-$CsPbI_3$-TMPPA stability, 50 ul of OA or oleyammonium-oleate were added to 1 ml of an as-prepared $CsPbI_3$-TMPPA solution and compared with a neat $CsPbI_3$-TMPPA solution. The results in Fig. S13 show the addition of OA decreases the stability of the α phase, with δ-CsPbI3-TMPPA forming. Fig. S14 shows the rapid phase transformation after oleyammonium-oleate addition.

TMPPA addtion to $CsPbI_3$-OA solution.

To verify the effect of adding TMPPA on α-$CsPbI_3$-OA stability, 10ul of TMPPA were added to 1ml of an as-prepared $CsPbI_3$-OA solution and compared with a neat $CsPbI_3$-TMPPA solution. The results in Fig. S15-16 showed the addition of TMPPA prolonged the stability of the α-$CsPbI_3$-OA.

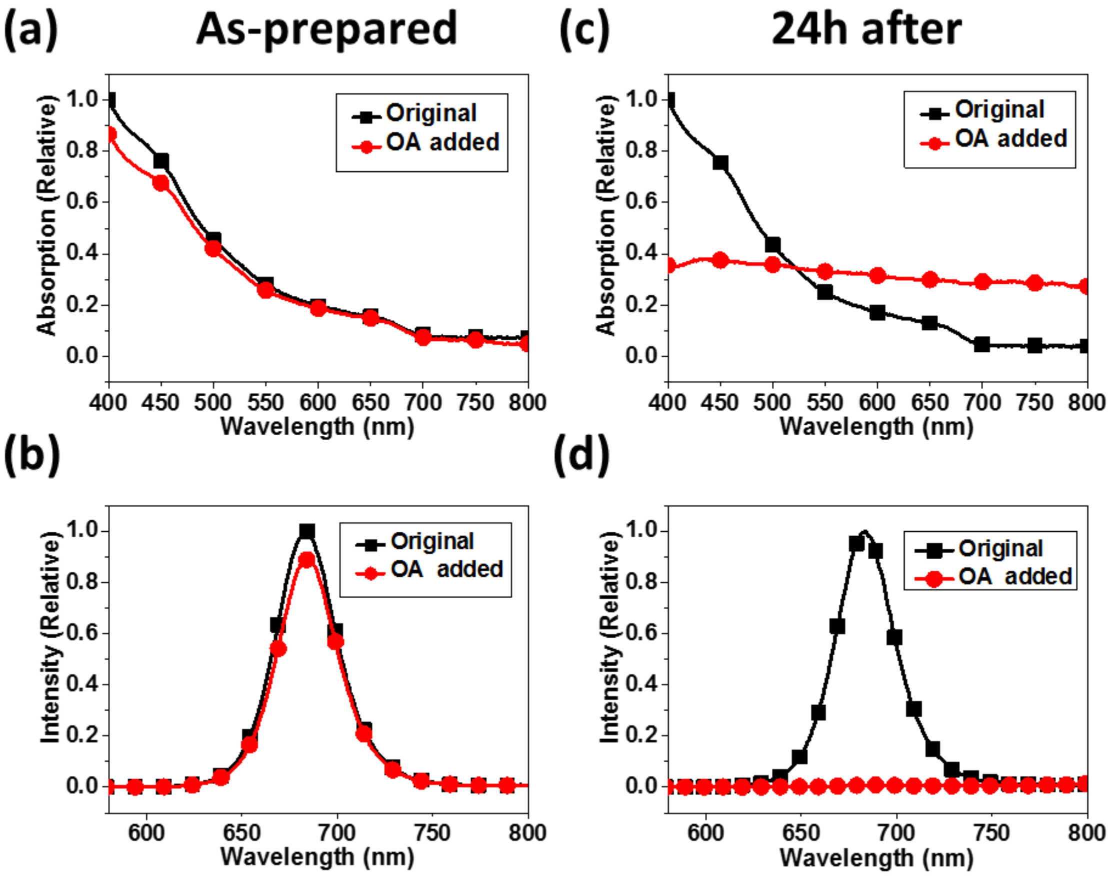


Fig. S13 (a) UV-Vis absorption and (b) PL spectra of as prepared $CsPbI_3$-TMPPA and OA-added $CsPbI_3$-TMPPA solutions. (c) UV-Vis absorption and (d) PL spectra of these samples after 24 h under ambient conditions.

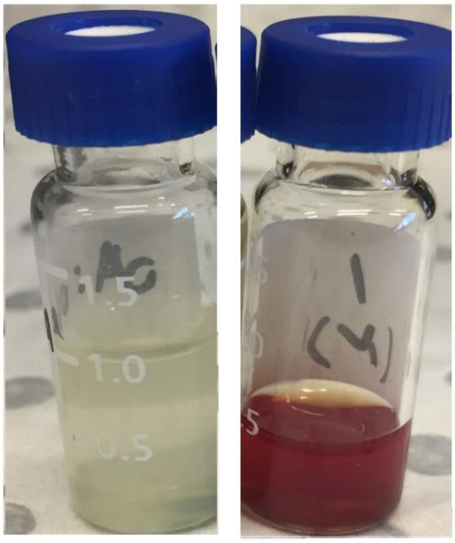


Fig. S14 $CsPbI_3$-TMPPA solution with oleylammonium-oleate added (left) and as-prepared $CsPbI_3$-TMPPA solution (right).

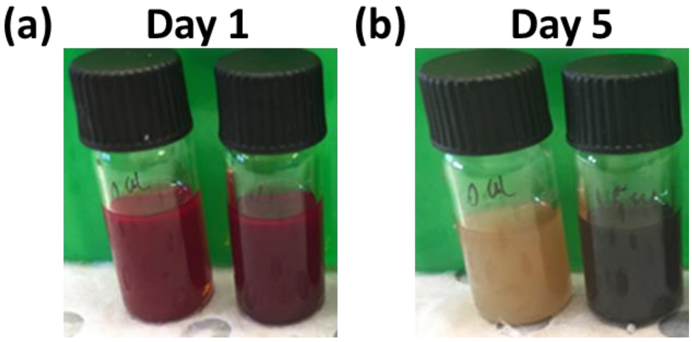


Fig. S15 Original $CsPbI_3$-OA solution (left) and TMPPA-added solution (right) on (a) Day 1 and (b) Day 5.

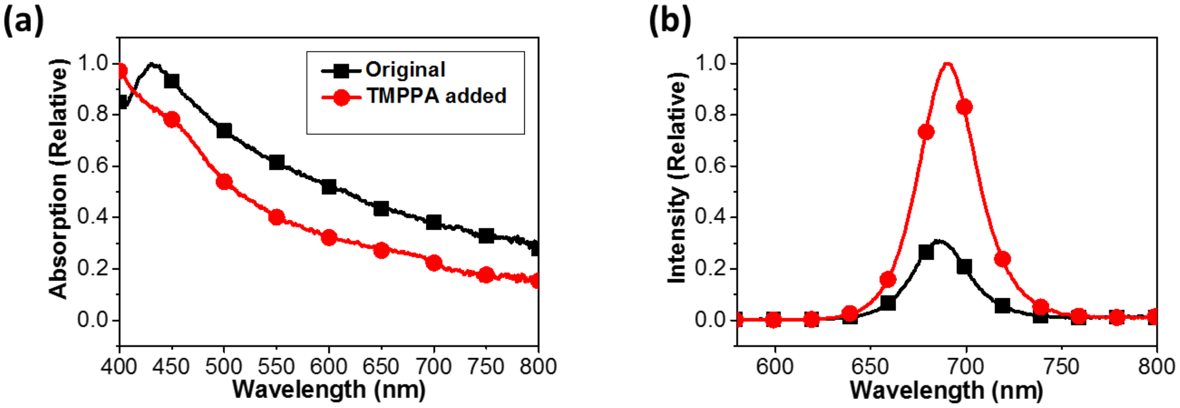


Fig. S16 (a) UV-Vis absorption and (b) PL spectra for original $CsPbI_3$-OA and TMPPA-added $CsPbI_3$-OA solutions after 3 days.

References

1. D. Cholico-Gonzalez, M. Avila-Rodriguez, G. Cote, A. Chagnes, *J. Mol. Liq.*, 2013, **187**, 165–170.