

Title: Structural investigations into colour-tuneable fluorescent InZnP-based quantum dots from zinc carboxylate and aminophosphine precursors

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Supporting Information

1. Materials and methods

Materials

For the InZnP nanoparticle synthesis: indium (III) chloride (InCl_3 , 98%), hexadecylamine (HDA, 90%), $\text{P}(\text{NMe}_2)_3$ (97%), zinc stearate (technical grade), and zinc diethyldithiocarbamate (ZDEC, 97%) were purchased from Sigma-Aldrich and used as received. Cadmium diethyldithiocarbamate (CDEC) was synthesised using a method by Trindade *et al.* (1). Hexane ($\geq 95\%$), methanol (99.8%), chloroform ($\geq 99\%$), ethanol ($\geq 99.5\%$), toluene (99.9%), butan-1-ol ($\geq 99.4\%$), and acetone ($\geq 99.9\%$) were purchased from Sigma-Aldrich. For analysis, Nile red (98%), fluorescein 27 (95%), sodium hydroxide (NaOH , $\geq 97.0\%$), and butylamine (99.5%) were purchased from Sigma-Aldrich.

Solvent preparation: 1-octadecene (1-ODE, $\geq 95.0\%$) was purchased from Sigma-Aldrich and was subsequently degassed using standard methods (2). Stock solutions of 0.1 M ZDEC, 0.1 M CDEC, and 1.0 M $\text{P}(\text{NMe}_2)_3$ in degassed 1-ODE were prepared and stored under nitrogen atmosphere for up to one month.

Methods

1.1 Synthesis of InZnP quantum dots

Zn:In molar ratio	Moles Zn ($\times 10^{-4}$)	Mass Zn stearate (g)
0.0 : 1	0.0	0.000
0.5 : 1	1.7	0.107
1.0 : 1	3.4	0.215
1.5 : 1	5.1	0.322
2.0 : 1	6.8	0.430
2.5 : 1	8.5	0.537
3.0 : 1	10.2	0.645

Table 1 Moles and masses of zinc stearate added during the synthesis of InZnP QDs, with 0.075g (3.4×10^{-4} mol) InCl_3 added in each instance.

Alloyed InZnP QDs were synthesised with varying Zn:In ratios in an air-free Schlenk line using a method based on that by Song *et al.* (3). During a typical reaction, InCl_3 (0.075 g, 3.4×10^{-4} mol), zinc stearate (see Table 1), and HDA (1.5 g, 4.1×10^{-3} mol) were added to a 100 ml three-necked flask with 20 ml 1-ODE. The reaction was further degassed at 120°C under vacuum and continuous stirring for 90 minutes, then cooled to room temperature under nitrogen. N_2 was subsequently maintained throughout the synthesis. 2 ml of pre-prepared

1 M $\text{P}(\text{NMe}_2)_3$ in 1-ODE was injected at room temperature, and the reaction heated rapidly to 220°C. The solution transitioned from colourless to coloured, with low-Zn syntheses turning red and high-zinc syntheses turning yellow. Aliquots were removed during heating and for up to eleven minutes after reaching 220°C. The aliquots were obtained with an airtight, flushed syringe, transferred to air-free vials, and stored in a glove box. After 10 minutes, the reaction was cooled in a water bath to 25°C. In some syntheses, a black solid was observed at the bottom of the reaction vessel which was identified by X-ray diffraction (XRD) as a mixture of indium metal and bulk cubic InP. When a 2:1 Zn:In ratio was used, the resultant InZnP QDs are written here as $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{P}$ and named species **1**. Subscripts in brackets indicate the relative molar concentrations of In and Zn added during the synthesis of InZnP.

1.2 Surface deposition of ZnS or CdS

ZDEC and CDEC are single-source precursors for ZnS and CdS, respectively (4; 5). Stock solutions of 0.1 M single-source precursor in dried 1-ODE were prepared in advance and stored under N_2 . Before use, the precursor suspension was stirred vigorously under N_2 for 5 minutes to ensure uniform dispersion. 0.3 ml of precursor solution was injected into 20 ml crude InZnP reaction solution without prior purification or cleaning. The reaction was heated rapidly to 300°C, forming a clear yellow-orange solution. After 30 minutes, the vessel was cooled to room temperature under N_2 . The reaction between **1** and ZDEC or CDEC resulted in $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PZnS}$ (**2**) and $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PCdS}$ (**3**), respectively.

1.3 Purification and extraction

All nanoparticles were cleaned using the same co-solvent procedure. One part hexane and one part methanol were added to two parts crude reaction solution. The mixture was shaken for 30 seconds and centrifuged at 3000 RPM for three minutes. The nanoparticle-containing upper hexane fraction was extracted and unreacted stearate descended into the methanol layer. The nanoparticle fraction was cleaned a further four times using the same procedure. An excess of ethanol was added to precipitate the QDs, and the turbid solution centrifuged at 4000 RPM. The product was re-suspended in hexane and precipitated with ethanol a further 3 times. For “air-free” samples, the above procedure was performed in a glove box; otherwise, it was under ambient conditions. The product nanoparticles were stored in toluene.

1.4 Post-synthesis processing

Ligand exchange to butylamine was performed to prevent charging during X-ray photoelectron spectroscopy (XPS) (6). Solutions of nanoparticles in 0.4 ml toluene were degassed for 15 minutes. 0.4 ml butylamine was injected to the solution in a glove box. After 24 hours the nanoparticles were precipitated with methanol, centrifuged at 4000 RPM for 3 minutes, and redissolved in hexane. They were then precipitated and centrifuged again, and dissolved in chloroform.

1.5 Absorption and photoluminescence emission spectroscopy

All spectra were measured in 1 cm path-length quartz cuvettes. UV-vis absorption spectroscopy was performed with a Hitachi U-4100 UV-vis-NIR spectrophotometer. PL

spectra of cleaned, air-exposed samples were taken with a Horiba FluoroMax4 and an OceanOptics QE Pro modular spectrometer with excitation of a 365 nm ThorLabs laser diode and a 415 nm bandpass filter. Crude, air-free samples were prepared in a glove box under N₂ atmosphere.

1.6 Raman spectroscopy

Colloidal InZnP quantum dots in toluene were drop-cast on a stainless steel substrate and the toluene evaporated under air. Raman characterisation of the air-dried suspension was undertaken on a Renishaw RM-100 coupled to 515 nm laser excitation wavelength acquired as a 2D map of 121 static spectral acquisitions, covering an area of 20 μm square with 1 μm step size, at incident laser power 1.9 mW for 30 seconds. The spectral acquisitions were summed to improve the signal-to-noise ratio (SNR), followed by a polynomial fit to remove the background that typically underlies Raman spectra of InZnP quantum dots, when using visible wavelengths, to which the material is opaque. The excitation wavelength of 515 nm falls within the optical absorption window for these nanocrystalline materials.

1.7 Quantum yield measurements

Fluorescence QY, Φ , was calculated with two standard methods. First, through comparison to reference dyes using a method by Grabolle *et al.* (7) with Nile red and fluorescein 27 as the dyes. Second, in an integrating sphere using a method by de Mello *et al.* (8).

1.8 Electron microscopy

QDs in toluene were cleaned a further 3 to 5 times using the method described previously, diluted in toluene and drop-cast onto 3 nm ultra-thin holey carbon TEM grids from Agar Scientific. TEM images were taken on a JEOL JEM-2100 with a Gatan Orius CCD camera or a FEI Tecnai T20, both operating at 80 kV. Energy-dispersive X-ray spectra (EDS) were obtained with an Oxford Instruments 80 mm thin-window EDS detector (XEDX system) incorporated into the JEOL JEM-2100. STEM images were obtained with a FEI Titan G2 ChemiSTEM with accelerating voltage 200 kV and beam current 800 pA. EDS spectrum images were collected with the Titan's (SuperX) 4 SDD with total collection angle of 0.7 sr. The total image collection time was between 3 and 30 minutes. Energy-dispersive X-ray spectra (EDS) were obtained with an Oxford Instruments 80 mm thin-window EDS detector with a 0.28 sr collection angle (XEDX system) incorporated into a JEOL JEM-2100. Elemental quantification was performed using a standardless Cliff Lorimer analysis. Particle sizes were measured using ImageJ and the line measure function, the best estimate was used as to the boundaries of the nanoparticles for the measurements. The large error bars on the diameters in d incorporate both the broad size distribution and the uncertainty in the measurement.

1.9 X-ray diffraction

Powder X-ray diffraction (XRD) was performed on a STOE STADI-P transmission diffractometer in thin-foil mode with a molybdenum X-ray source at 0.7093 Å, 50 kV, and 30 mA. X-rays were monochromated with a germanium-111 crystal to give K_{α1} only. Samples were mounted on

cellulose triacetate foils supplied by STOE. XRD reference patterns were from the Crystallography Open Database (COD) (9; 10; 11) and the International Centre for Diffraction Data (ICDD). QualX2.0 (12) and Eva (Bruker, U.S.) were used for phase ID analysis.

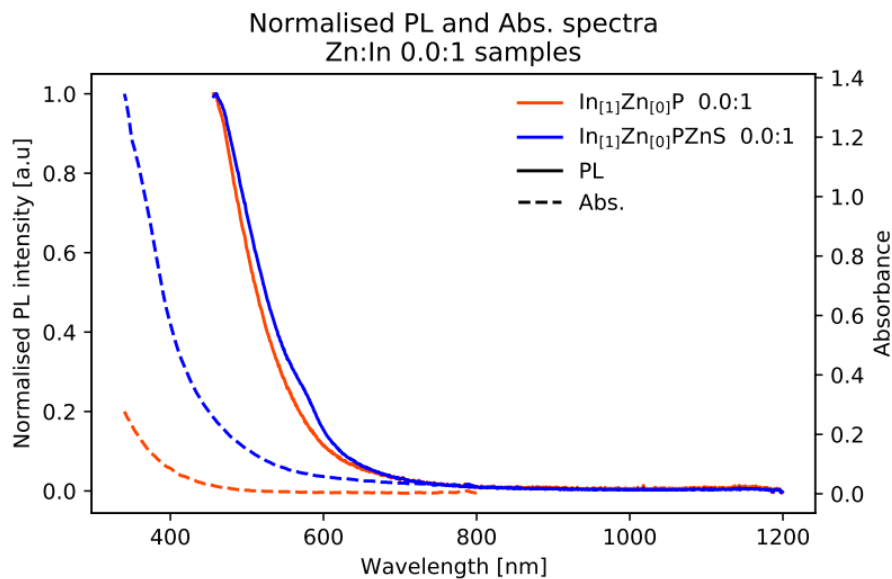
1.10 X-ray photoelectron spectroscopy

XPS of samples in atmospheric conditions was performed on a Kratos Axis Ultra with excitation from focussed monochromatic Al $K_{\alpha 1}$ (1486.6 eV) X-rays and using an electron flood gun for charge neutralisation. Peaks were recorded with a pass energy of 40 eV. Depth-profiling SR-excited XPS was performed on the I311 beamline ($43 < h\nu < 1500$ eV) equipped with a SCIENTA SES200 hemispherical analyser at MAX-lab, Lund, Sweden. XP spectra were recorded at room temperature in normal emission geometry using horizontal linear polarised light. Spectra were fitted using CasaXPS software and additional analysis, including correction for photon flux, was with Igor Pro software (WaveMetrics Inc., US). Depth profiling was obtained through varying the photoelectron kinetic energy (KE) of each core level measured from 135 to 800 eV in six steps. The exception was the spectra for Zn 2p: due to energy limitations of the beam line, the Zn 2p spectra could only be acquired at photoelectron KEs of 135–335 eV in four steps. The peak areas were corrected for photoionisation cross-section at each photon energy and the relative atomic concentrations calculated. All binding energies were calibrated to hydrocarbon C 1s at 284.8 eV. Colloidal QD samples were ligand-exchanged to butylamine using the method described above and deposited via drop casting onto gold-coated silicon. To ensure air-free characterisation, samples were processed and stored in a glove box and entered through the fast entry lock of the UHV chamber within 5 to 30 minutes of deposition. The inelastic mean free path (IMFP) was obtained using the NIST Electron IMFP database software v1.2 and the relationship between the sampling KE and sampling depth subsequently obtained using a model by Shard *et al.* (13).

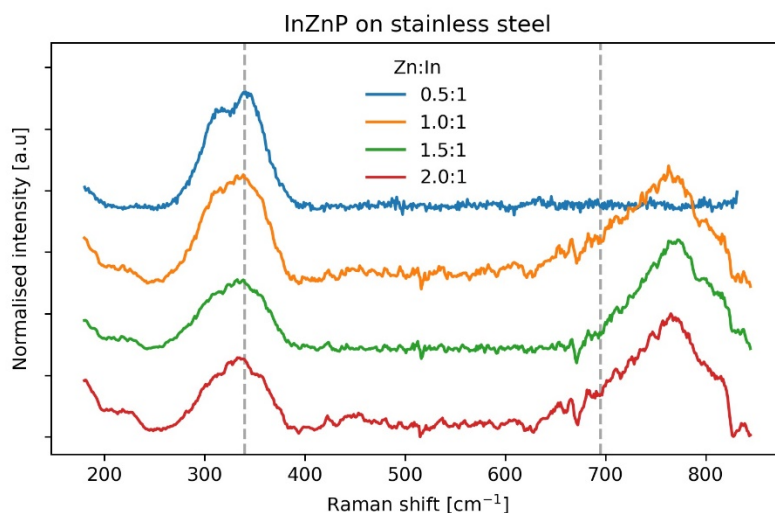
2. Further experimental results

2.1 PL and absorption spectroscopy for Zn:In 0.0:1 samples.

Extra PL and absorption spectra for the samples synthesised without zinc stearate (titled “0.0:1” or $\text{In}_{[1]}\text{Zn}_{[0.0]}\text{P}$ in the main text) are included below.



2.2 Raman spectroscopy

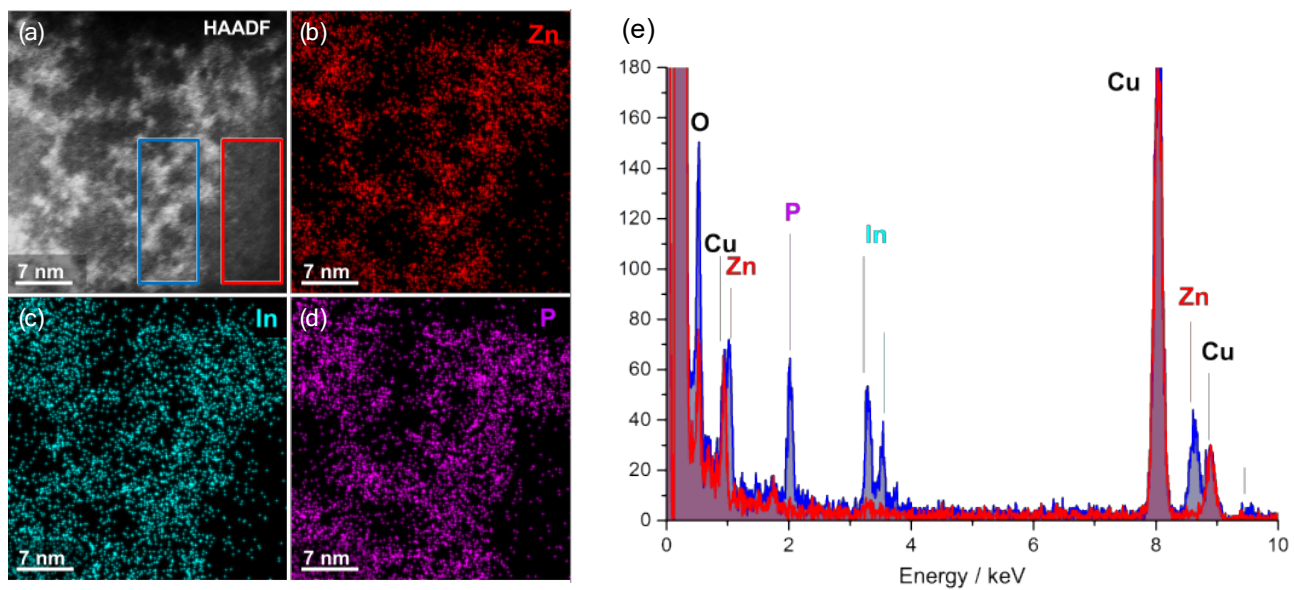


Raman spectra for $\text{In}_{[x]}\text{Zn}_{[y]}\text{P}$ samples with Zn:In ratios from 0.5:1 to 2.0:1.

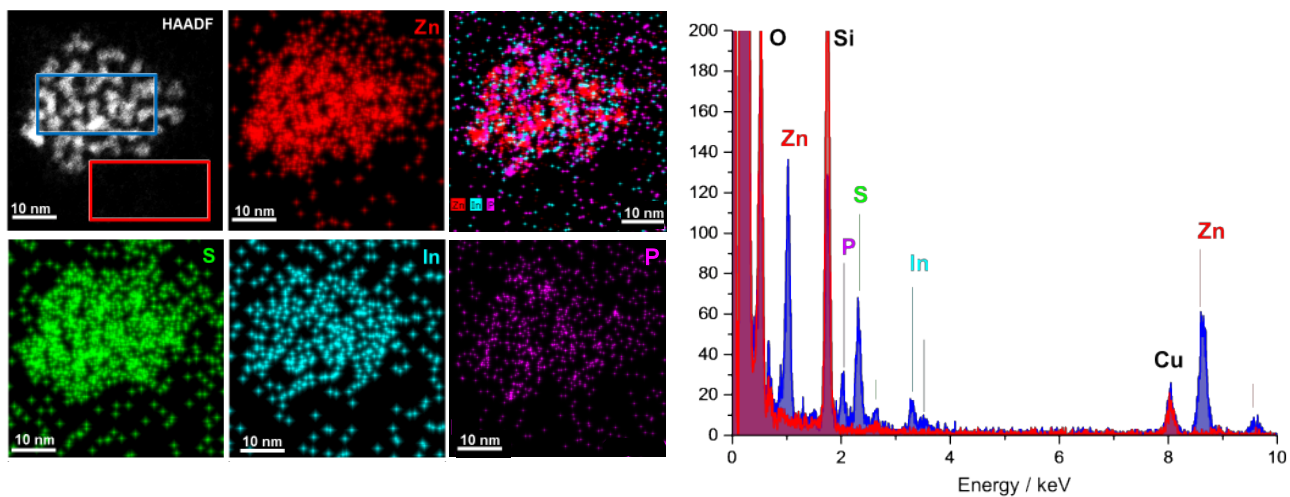
2.3 EDAX maps

In each image below, the EDS for a region containing nanoparticles is plotted in blue on the right; the analysis region is marked by a blue box in the corresponding HAADF image. A background region is marked by a red box and the EDX spectrum is plotted in red on the right. Cu is an artefact due to stray scattering from the nearby TEM support grid.

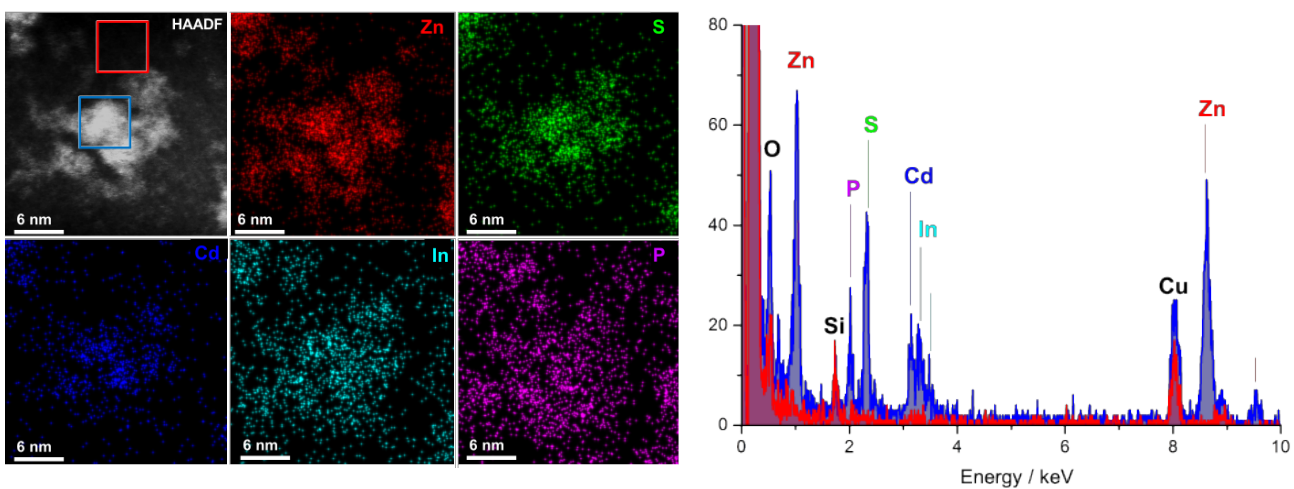
2.3.1 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{P}$ (1)



2.3.2 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PZnS}$ (2)

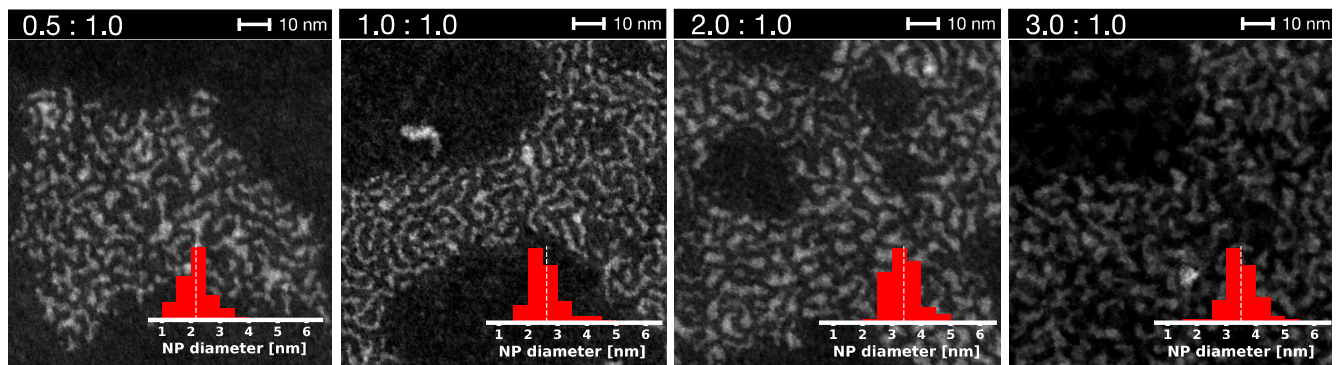


2.3.3 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PCdS}$ (3)

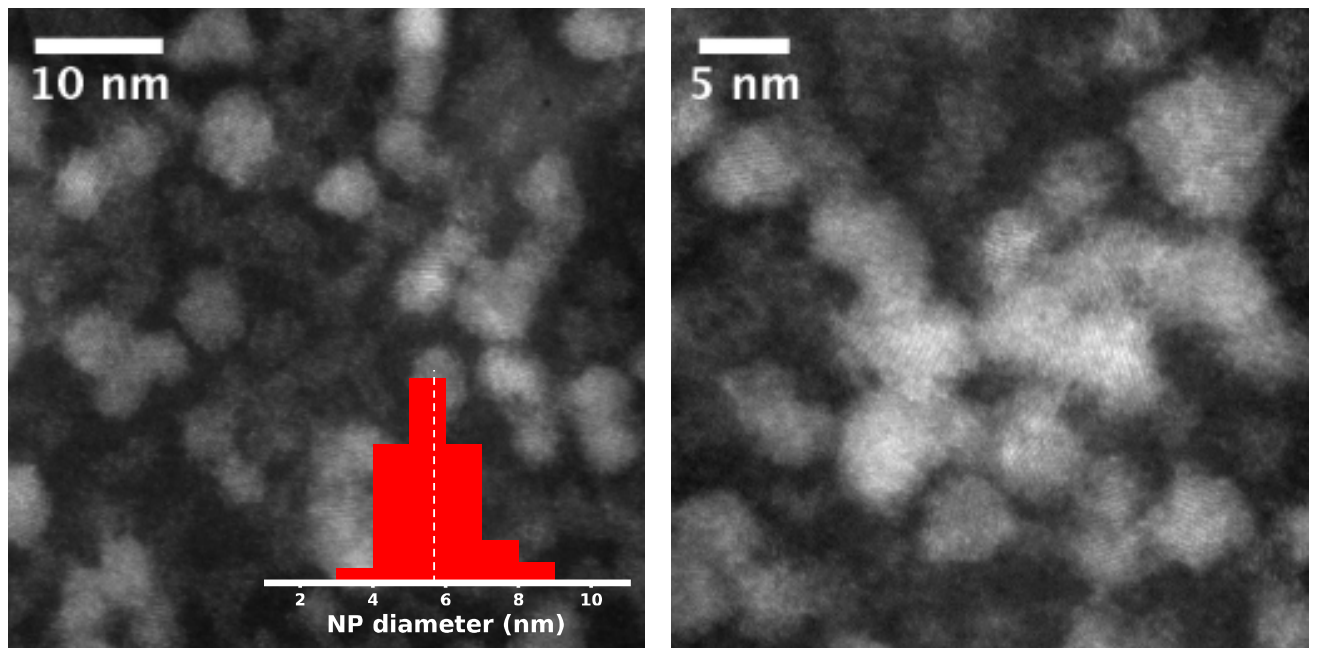


2.4 STEM images

2.4.1 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{P}$



2.4.2 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PCdS}$



2.5 Synchrotron radiation-excited X-ray photo electron spectroscopy

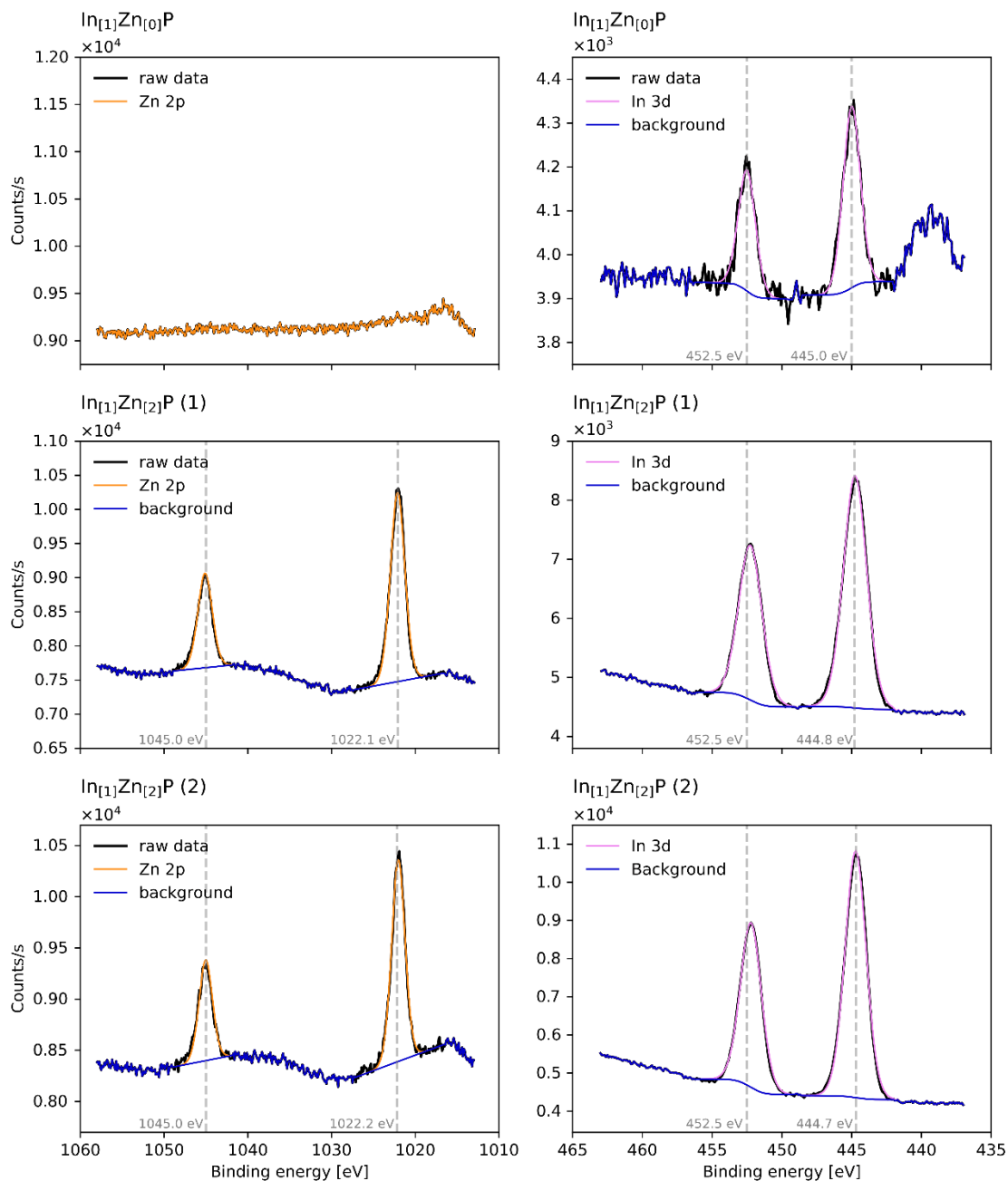
2.5.1 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{P}$ (1)

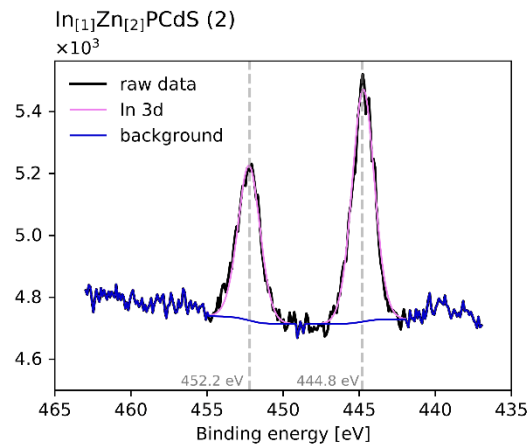
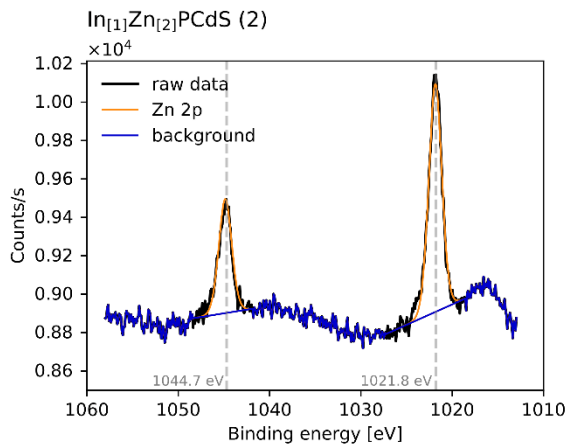
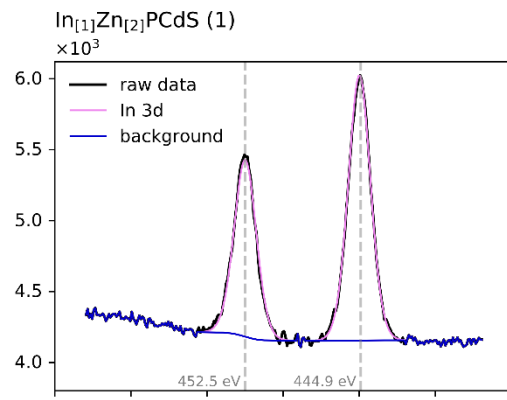
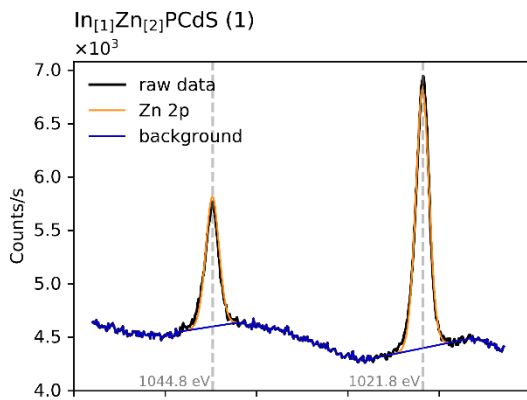
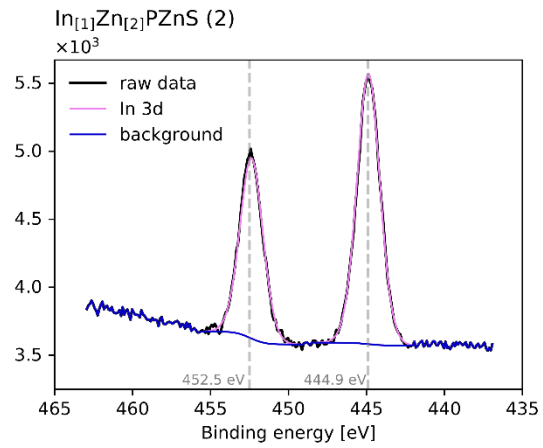
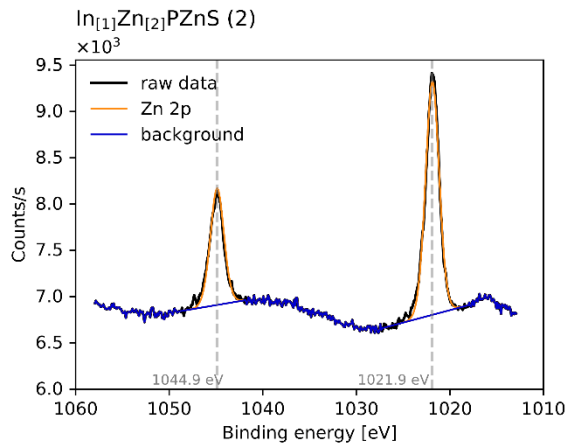
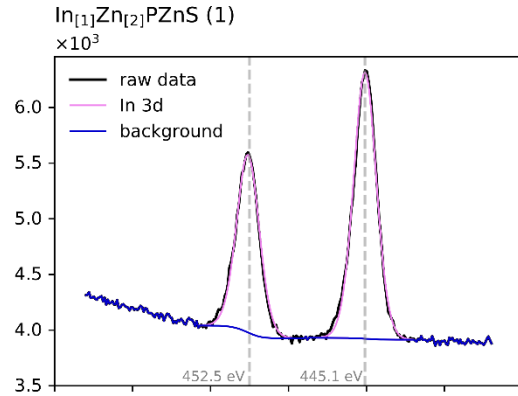
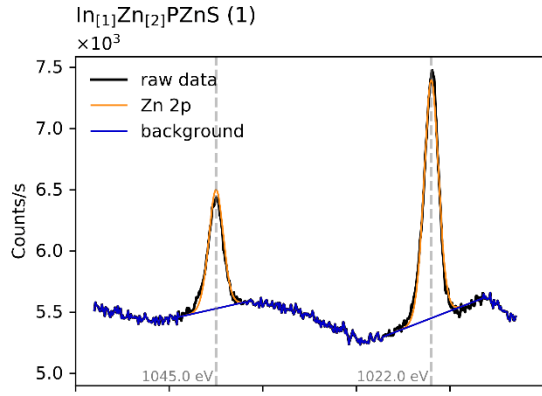
2.5.2 $\text{In}_{[1]}\text{Zn}_{[2.0]}\text{PCdS}$ (3)

2.6 Monochromatic X-ray photo electron spectroscopy

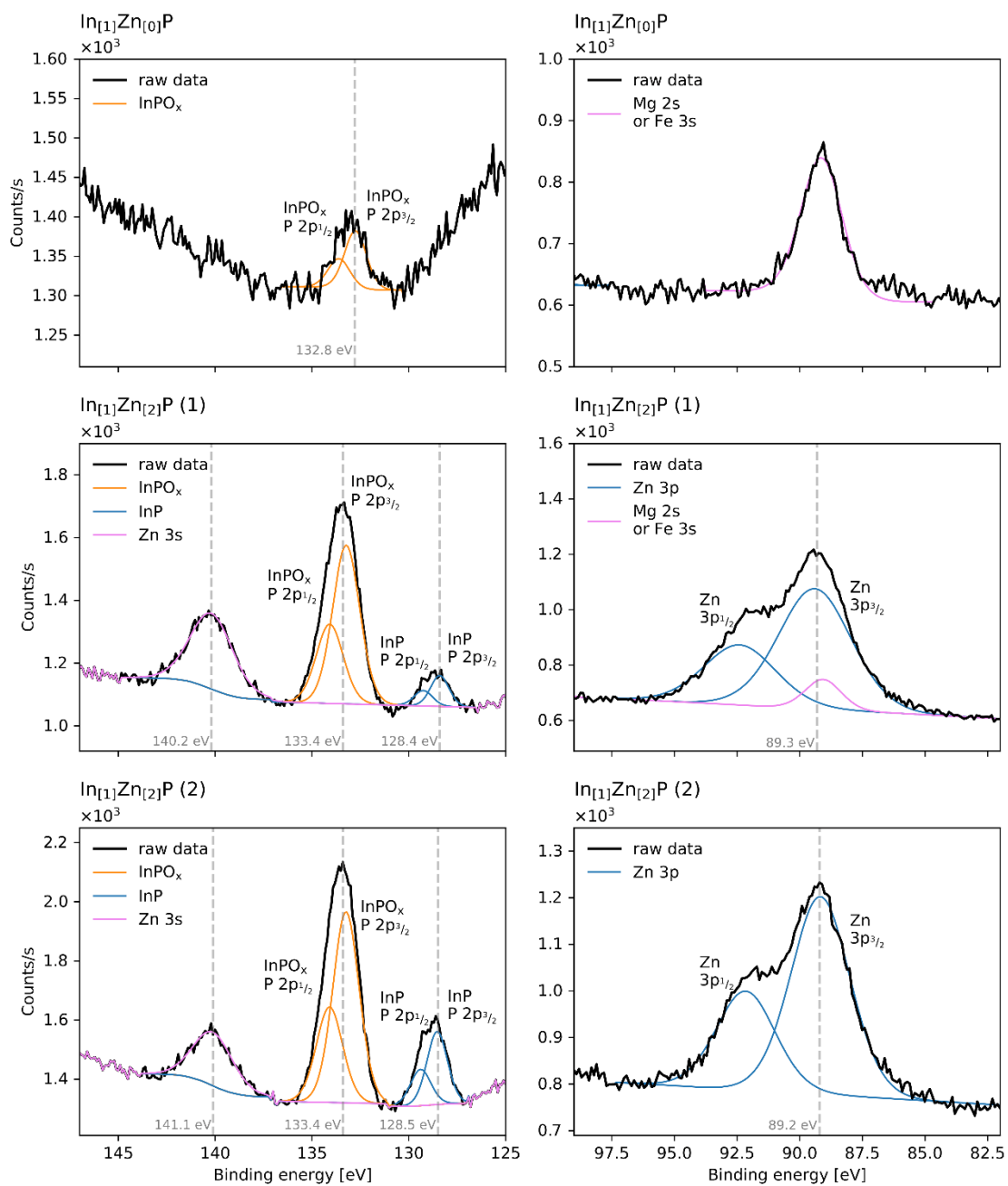
Two repeat samples for each material were analysed with XPS and the spectra plotted in the images below.

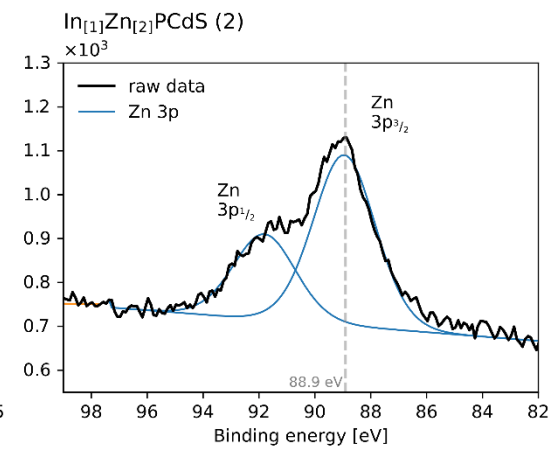
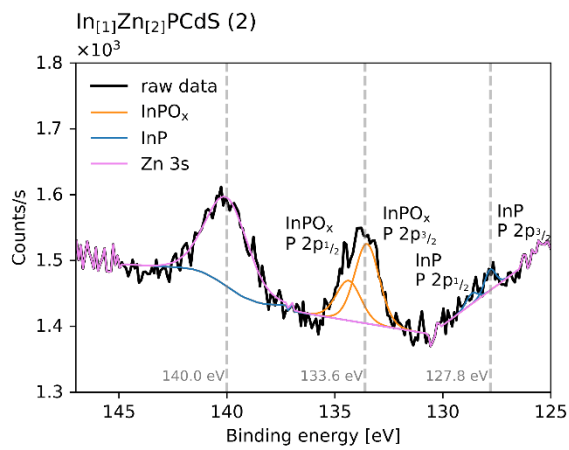
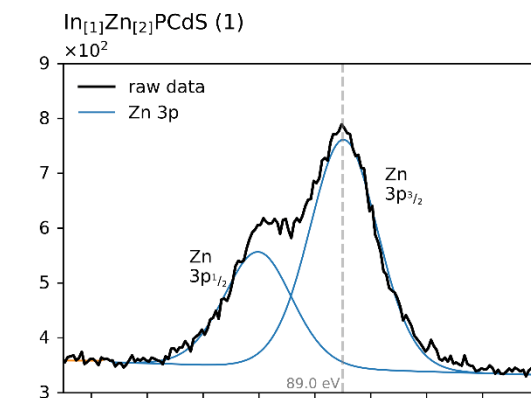
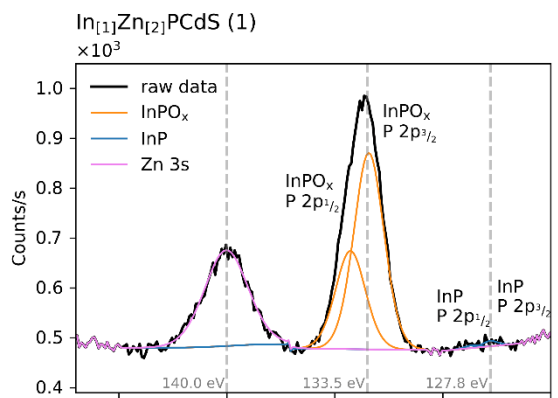
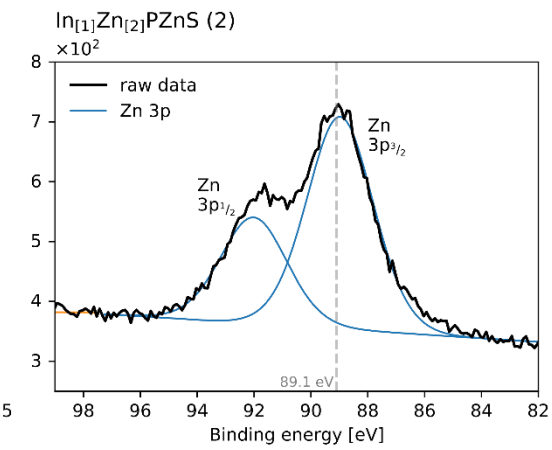
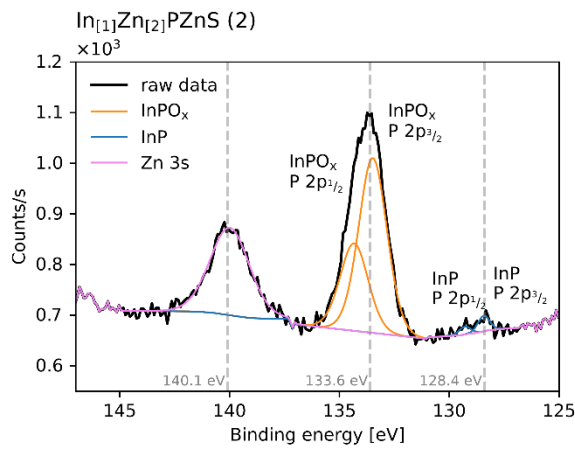
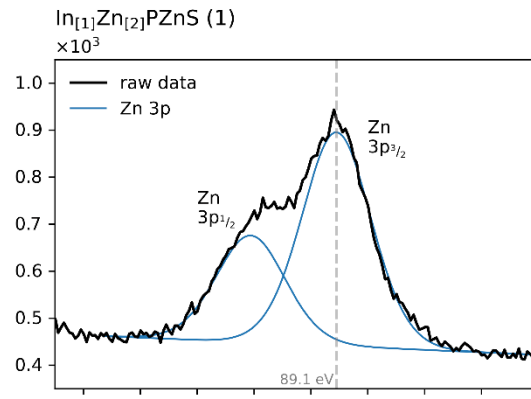
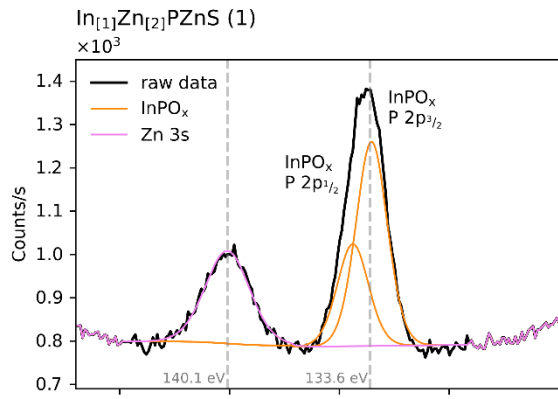
2.6.1 Zn 2p and In 3d spectra



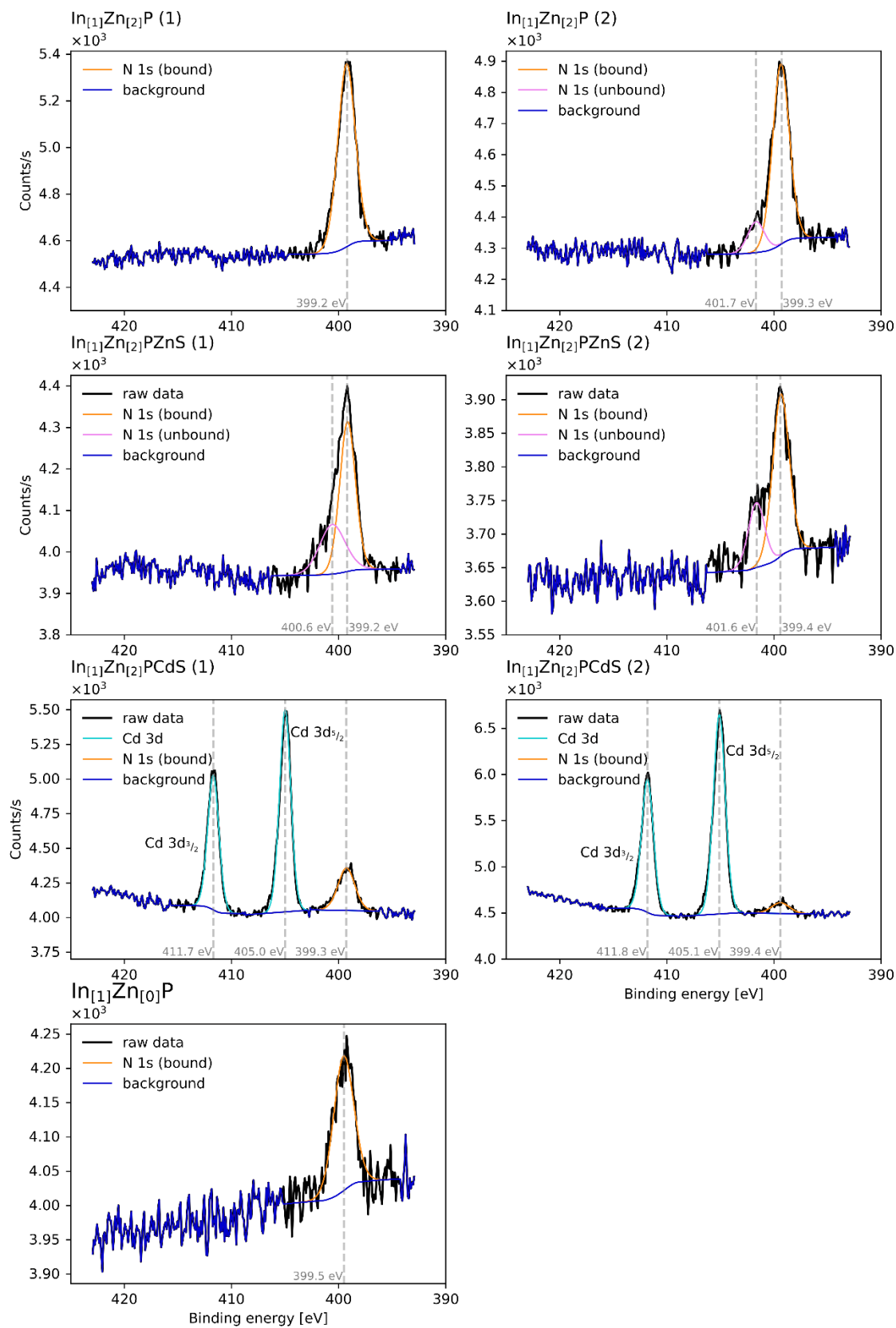


2.6.2 P 2p (InPO_x and InP), Zn 3s, and Zn 3p



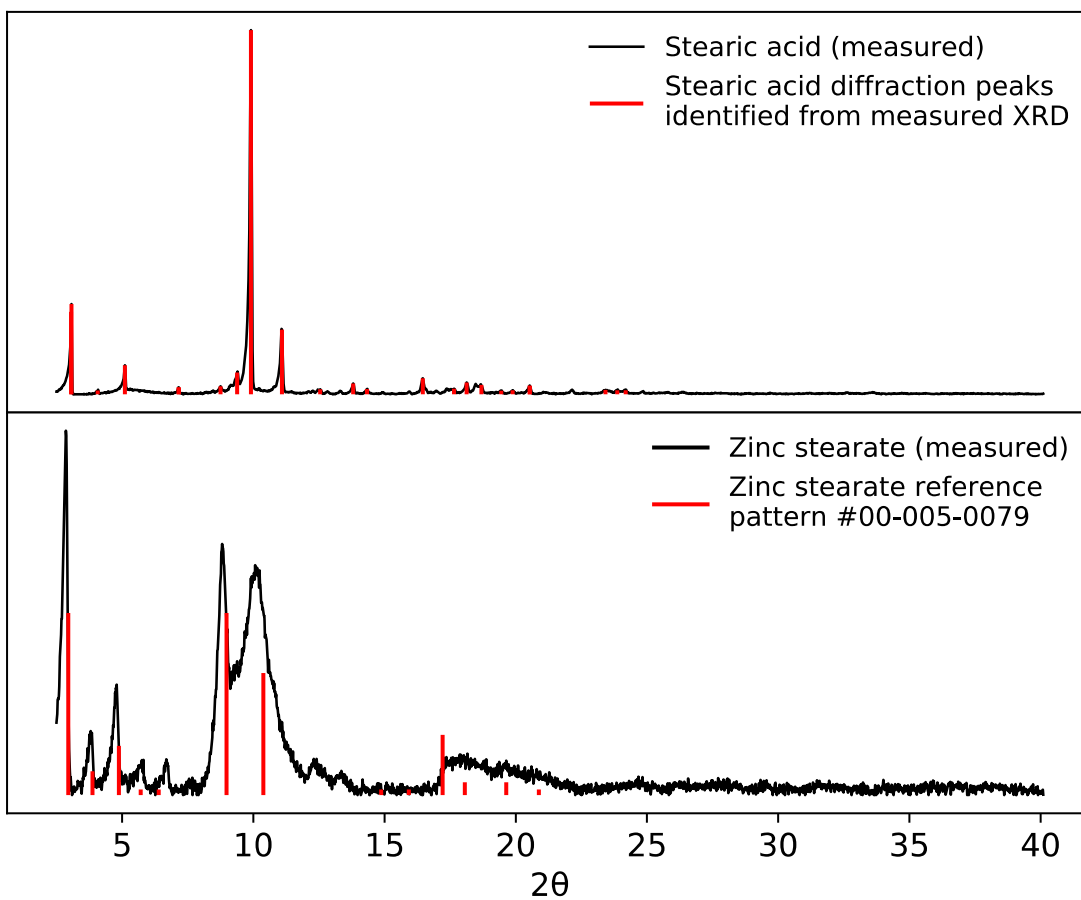


2.6.3 N1s (bound and unbound) and Cd 3d



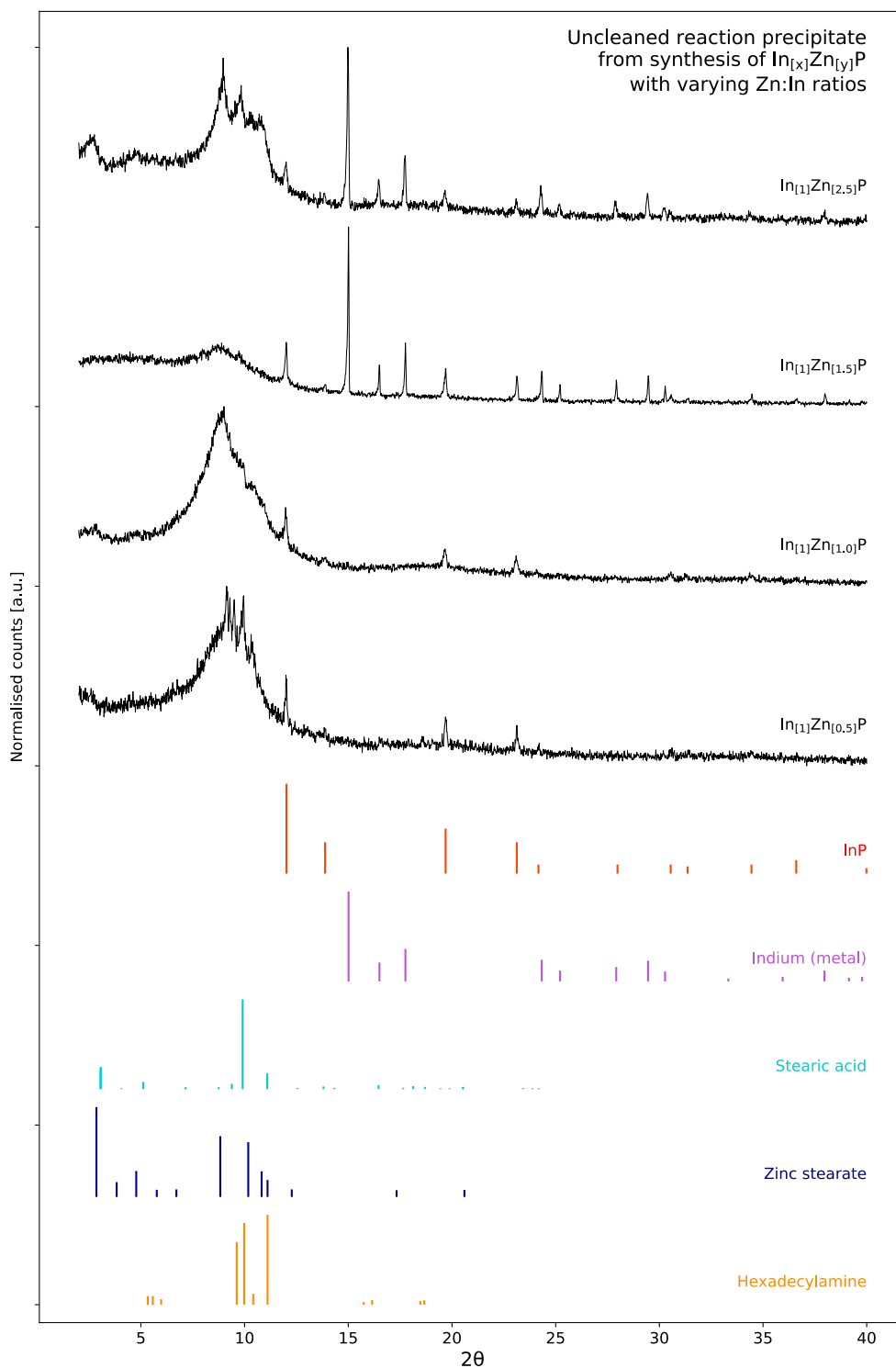
2.7 XRD

2.7.1 Measurement of stearic acid and zinc stearate samples to identify peaks associated with surface ligands.



2.7.2 XRD analysis of precipitate from reaction

Dark coloured precipitate formed during the synthesis of InZnP nanoparticles. XRD analysis (below) identified this precipitate as a mixture of In metal and crystalline bulk InP. The greater the Zn:In ratio of the reaction, the greater the amount of indium metal that formed in the precipitate, relative to the amount of InP that also precipitated. This could suggest that Zn was taking the place of In in the alloyed InZnP nanoparticles that remained in solution, resulting in greater precipitation of excess In.



3. Bibliography

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