Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Anisotropic and Hyperbranched InP Nanocrystals *via* Chemical Transformation of *in situ* Produced In_2O_3

Shuai Chen[a], Andreas Riedinger[a]*

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

*Corresponding author: riedinger@mpip-mainz.mpg.de

Experimental section

Chemicals and Materials:

All reagents were purchased and used without further purification. 1-octadecene (technical grade 90 %, ODE), indium acetate, indium chloride, indium oxide, indium bromide, indium iodide, hexadecaneamine (HDA) and triphenyl phosphite (TPOP) were purchased from Acros chemicals.

Methods:

Synthesis of indium phosphide at a different temperature: In a typical synthesis, 0.5 mmol of $InCl_3$, 0.5 mmol $In(ac)_3$ were mixed with 5 mmol of HDA, 1.5 mL of TPOP, and 15 mL of ODE. The obtained mixture was heated under argon flow to 150 °C in 15 min and maintained at this temperature for 60 min to dissolve the metal precursor and to ensure the removal of traces of low-boiling-point impurities. Afterwards, the solution was heated to 230 °C, 235 °C, 255 °C, 300 °C, 320 °C and kept at that temperature for 30 min. Then, the mixture was allowed to cool naturally to room temperature. Finally, NPs were thoroughly purified by multiple precipitations and redispersion steps, using 2-propanol for precipitation and hexane for redispersion.

Synthesis of indium phosphide with hot injection of TPOP: In a typical synthesis, 0.5 mmol of $InCl_3$, 0.5 mmol of $In(ac)_3$ were mixed with 5 mmol of HDA, and 15 mL of ODE. The obtained mixture was heated under argon flow to 150 °C in 15 min and maintained at this temperature for 60 min. Then during the second step to heated 300°C for 30 min, we added 1.5 mL of TPOP to the reaction at 270 °C. Then, the mixture was allowed to cool naturally to room temperature. Finally, NPs were thoroughly purified by multiple precipitations and redispersion steps, using 2-propanol for precipitation and hexane for redispersion.

Tracking the reaction process during the synthesis of indium phosphide: In a 100 mL three-necked flask, $InCl_3$ (0.5 mmol), $In(ac)_3$ (0.5 mmol), HDA (5 mmol) and TPOP (1.5 mL) were mixed in 1-octadecene (ODE) (15 mL). The mixture was heated up to 150 °C in 15 min under an inert atmosphere (argon) and kept at 150 °C for 15 min. Then the solution was heated up to 300 °C within 15 min. At 230 °C, 240 °C, 250 °C, 260 °C, 280 °C, and 300 °C, we took out the sample to measure PXRD and TEM.

Tracking the intermediate states during the heating process with and without TPOP added: In a 100 mL three-necked flask, $InCl_3$ (0.5 mmol), $In(ac)_3$ (0.5 mmol), and HDA (5 mmol) were mixed in 1-octadecene (ODE) (15 mL). Then the temperature was increased to 150 °C and 270 °C. We collected aliquots at both temperatures for analyses. When the temperature reached 270 °C, we added TPOP to this reaction and collected the final sample. We measured PXRD and TEM of all samples (Fig. S8).

Tracking the transition from In_2O_3 to form InP: In a 100 mL three-necked flask, $InCl_3$ (0.5 mmol), $In(ac)_3$ (0.5 mmol), and HDA (5 mmol) were mixed in 1-octadecene (ODE) (15 mL). Then the temperature was increased to 150 °C and 270 °C. At 270 °C, we collected an aliquot before we added TPOP to the reaction mixture. 5 min, 10 min, 13 min, 15 min, 18 min, 25 min, and 33 min after TPOP addition we collected aliquots and measures their PXRD patterns to track the transition.

Co-decomposition experiments of chloride ion sources with commercial In_2O_3: In a 100 mL three-necked flask, NH_4Cl (1.5 mmol), ammonium acetate (1.5 mmol), In_2O_3 (0.5 mmol), HDA (5 mmol) and TPOP (1.5 mL) were mixed in 1-octadecene (ODE) (15 mL). The mixture was heated up to 150 °C for 60 min. Later, the solution was heated up to 300 °C within 15 min and kept at this temperature for 30 min. Finally, NPs were thoroughly purified by multiple precipitations and redispersion steps, using 2-propanol for precipitation and hexane for

redispersion.

The effects of other halides (Br/ I): In a 100 mL three-necked flask, $InBr_3$ or InI_3 (0.5 mmol), $In(ac)_3$ (0.5 mmol), HDA (5 mmol) and TPOP (1.5 mL) were mixed in 1-octadecene (ODE) (15 mL). The mixture was heated up to 150 °C and kept at 150 °C for 60 min. Afterwards the solution was heated up to 300 °C within 15 min and kept at this temperature for 30 min. Finally, NPs were thoroughly purified by multiple precipitations and redispersion steps, using 2-propanol for precipitation and hexane for redispersion.

The effects of acetic acid: In a 100 mL three-necked flask, $InCl_3$ (0.5 mmol), $In(ac)_3$ (0.5 mmol), HDA (5 mmol) and TPOP (1.5 mL) were mixed in 1-octadecene (ODE) (15 mL). Later we added different amounts of acetic acid (10 µL, 20 µL, 30 µL, 40 µL) in different reactions. The mixture was heated up to 150 °C and kept at 150 °C for 60 min. Afterwards the solution was heated up to 300 °C within 15 min and kept at this temperature for 30min. Finally, NPs were thoroughly purified by multiple precipitations and redispersion steps, using 2-propanol for precipitation and hexane for redispersion.

Characterization:

Transmission Electron Microscopy. TEM samples were prepared by drop-casting the hexane dispersion onto a carbon coated copper grid. Routine TEM imaging was done using JEOL1400 TEM with an acceleration voltage of 120 kV.

X-ray Diffraction. Purified powder was used to perform XRD. Powder XRD patterns were collected on a Rigaku SmartLab Diffractometer, operated with wavelength Cu Kα radiation source (1.540593 Å) with increment steps of 0.01° and at 0.3°/min.

Supporting Data:

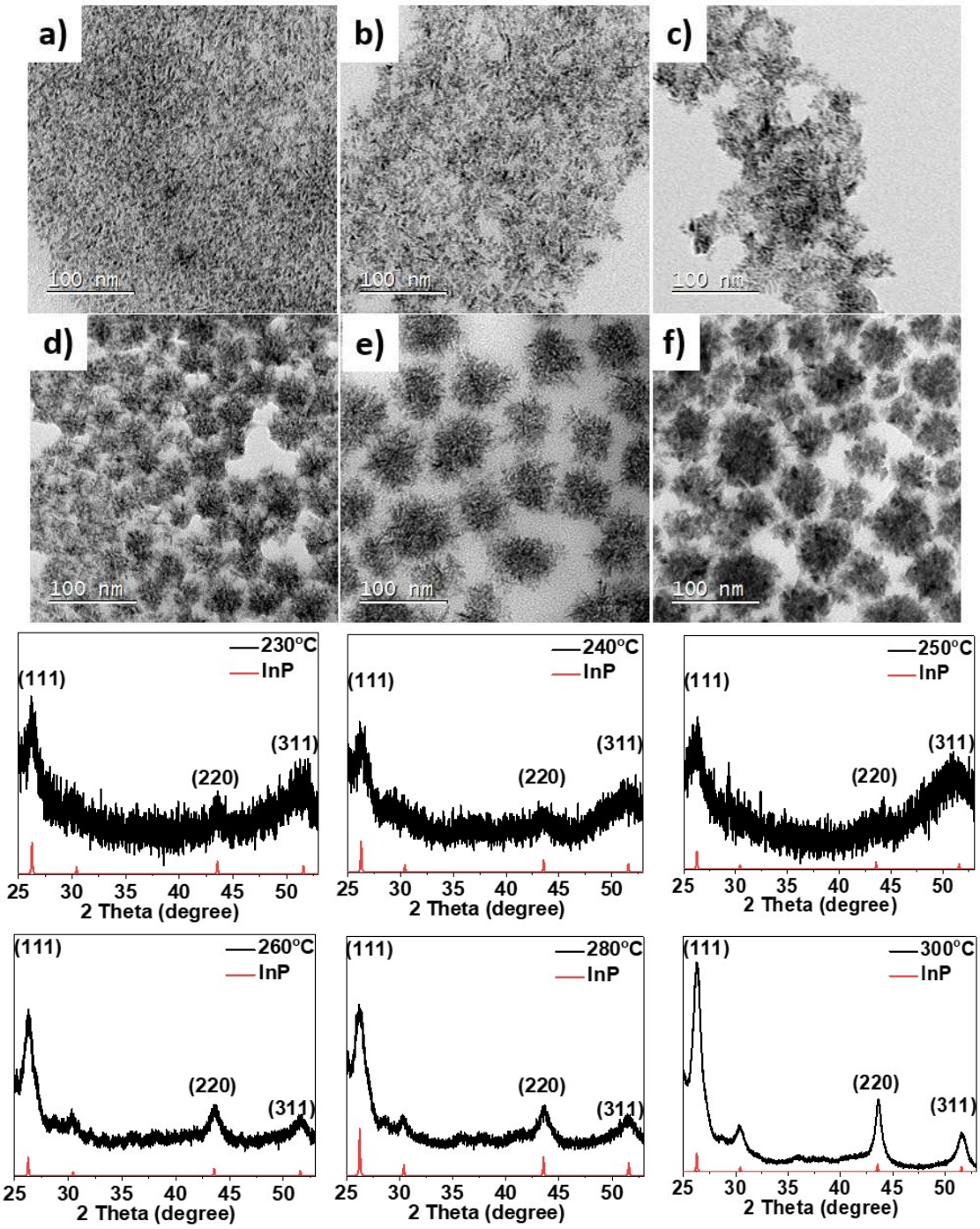

Fig. S1. TEM images and PXRD of InP NCs synthesized at different temperature. (a) 230 °C; (b) 240 °C; (c) 250 °C; (d) 260 °C; (e) 280 °C; (f) 300 °C.

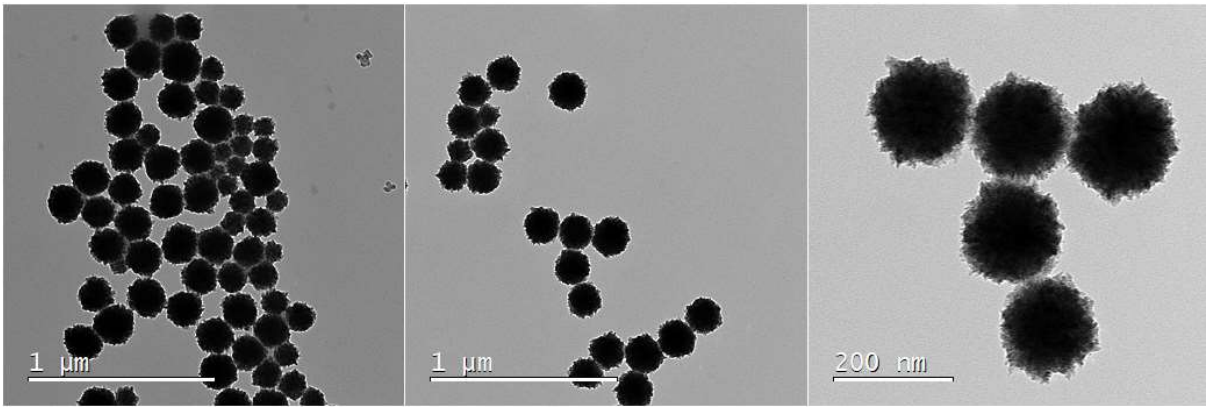

Fig. S2. TEM of InP with 1 mL TPOP added.

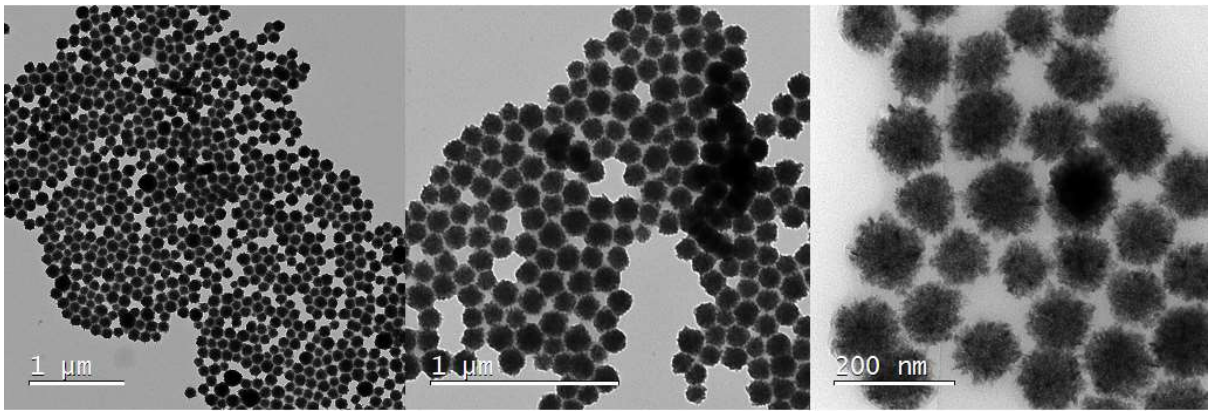

Fig. S3. TEM of InP with 1.5 mL TPOP added.

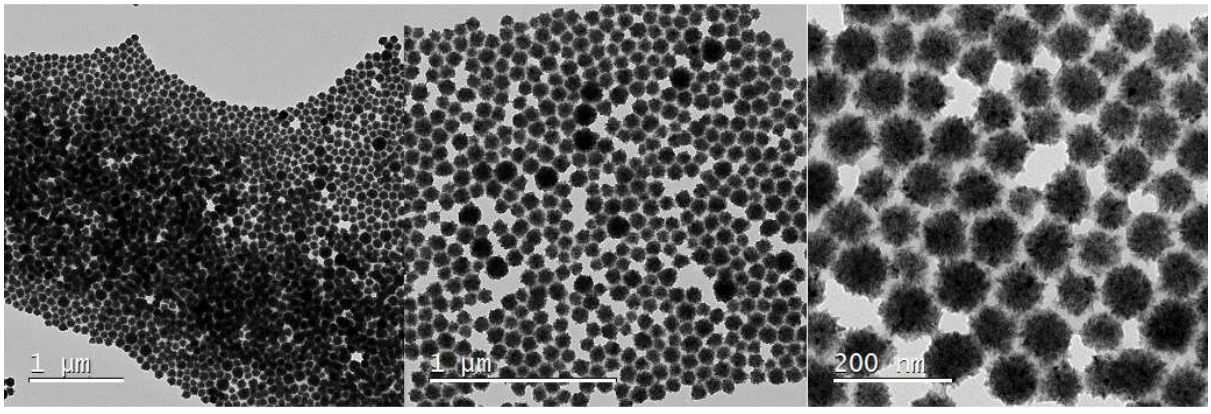

Fig. S4. TEM of InP with 2 mL TPOP added.

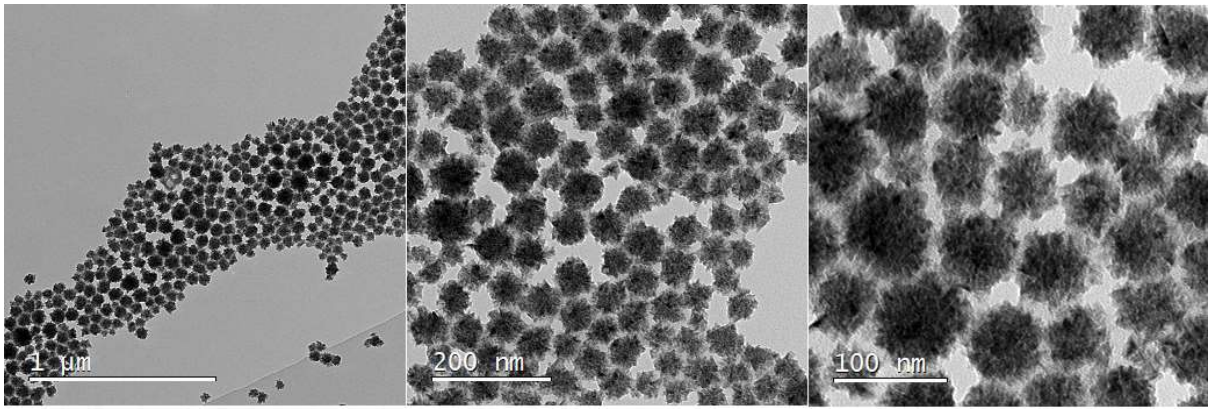

Fig. S5. TEM of InP with 2.5 mL TPOP added.

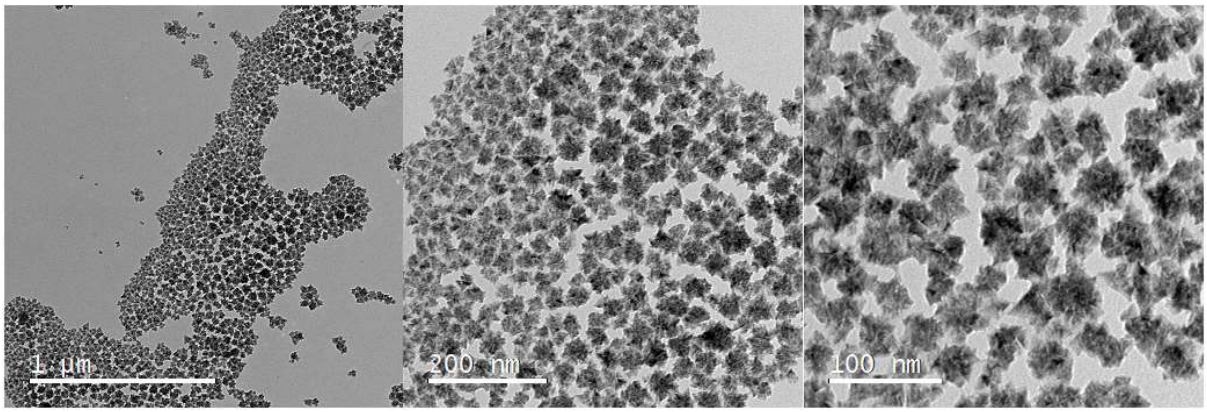

Fig. S6. TEM of InP with 3 mL TPOP added.

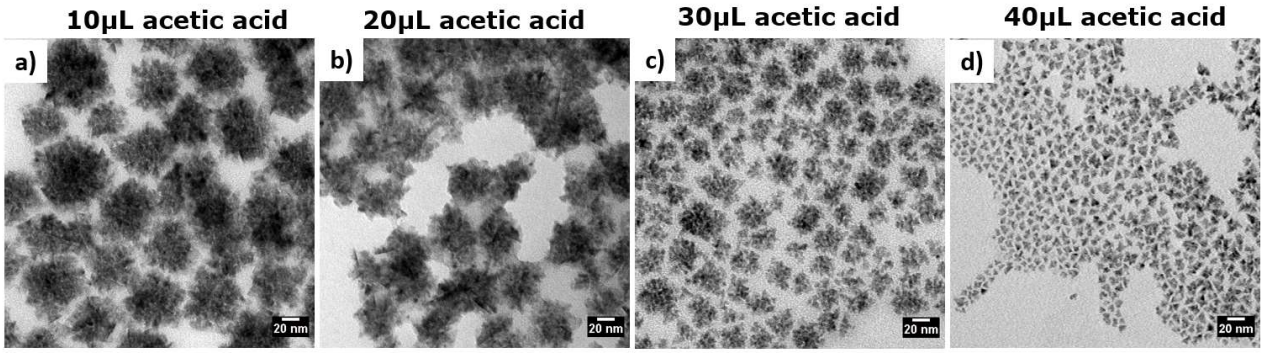

Fig. S7. TEM of InP with different amounts of acetic acid added.

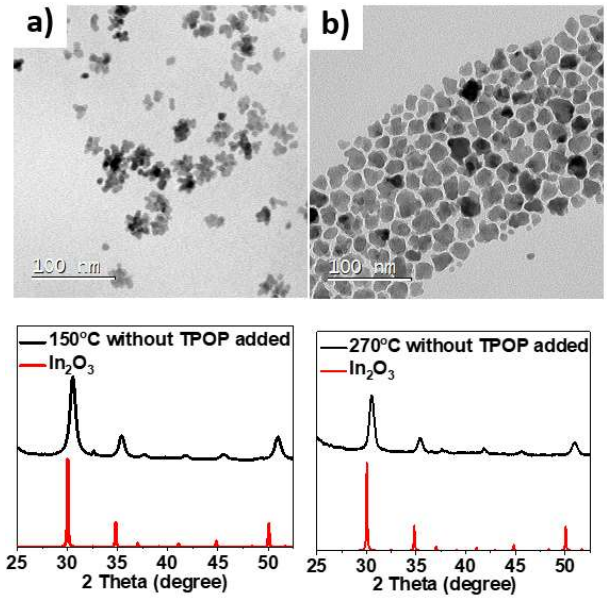

Fig. S8. TEM images and PXRD of the intermediate states before TPOP addition. (a) 150 °C without TPOP added; (b) 270 °C without TPOP added.

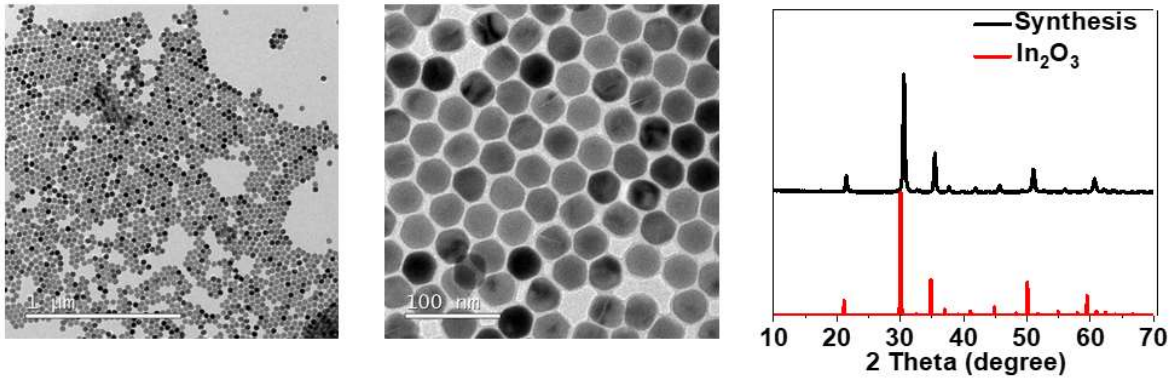

Fig. S9. Results of the co-decomposition experiments of ammonium chloride as chloride ion sources with commercial In_2O_3 nanoparticles.

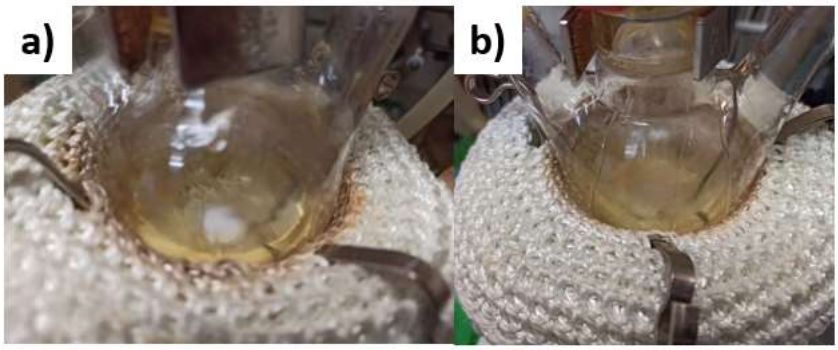

Fig. S10. Photographs of the reaction vessel for reactions carried out with only $InCl_3$ (a) or $In(ac)_3$ (b).

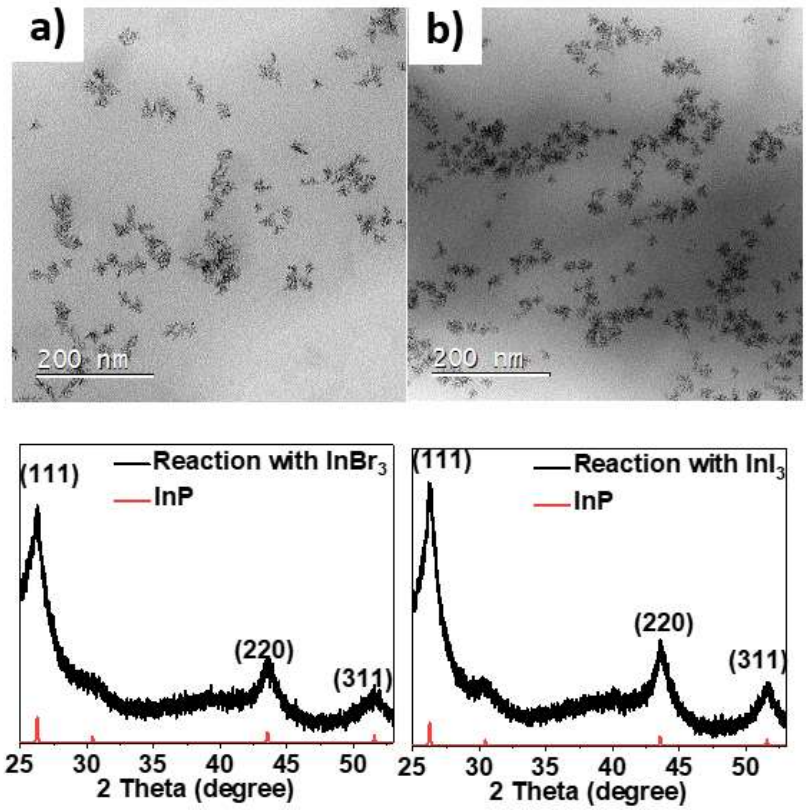

Fig. S11. Reaction products when $InBr_3$ (a) or InI_3 (b) was used instead of $InCl_3$.