

Ligand Induced chirality in In₂S₃ nanoparticles

Electronic Supplementary Information

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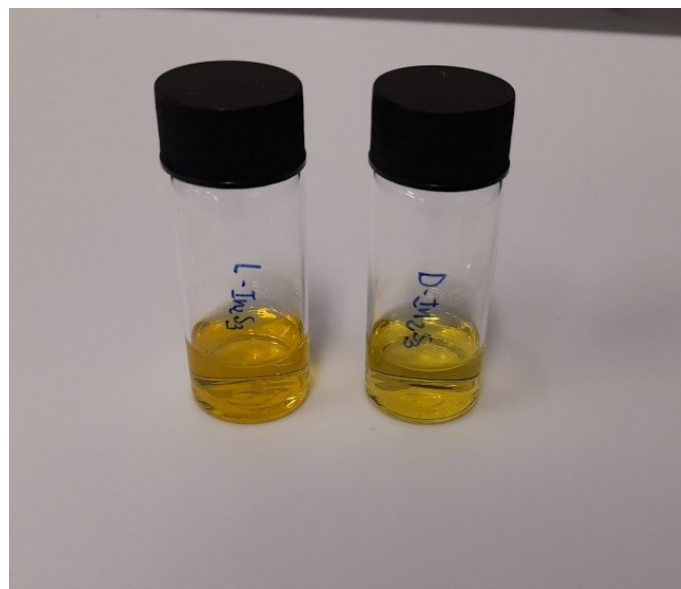


Figure S1: picture of L-In₂S₃ and D-In₂S₃ colloidal solutions in water at pH 9.0 in the presence of 48.0 mM of L or D-cysteine.

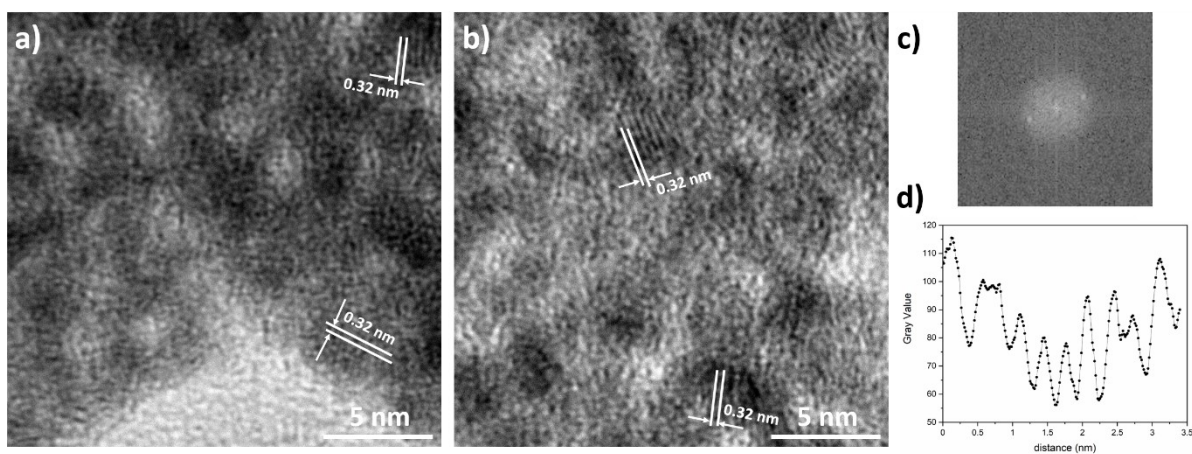


Figure S2: HR-TEM analysis of L-In₂S₃ (a) and D-In₂S₃ (b) NPs. FFT (c) and line profile (d) analysis of D-In₂S₃ NPs reported in figure (b).

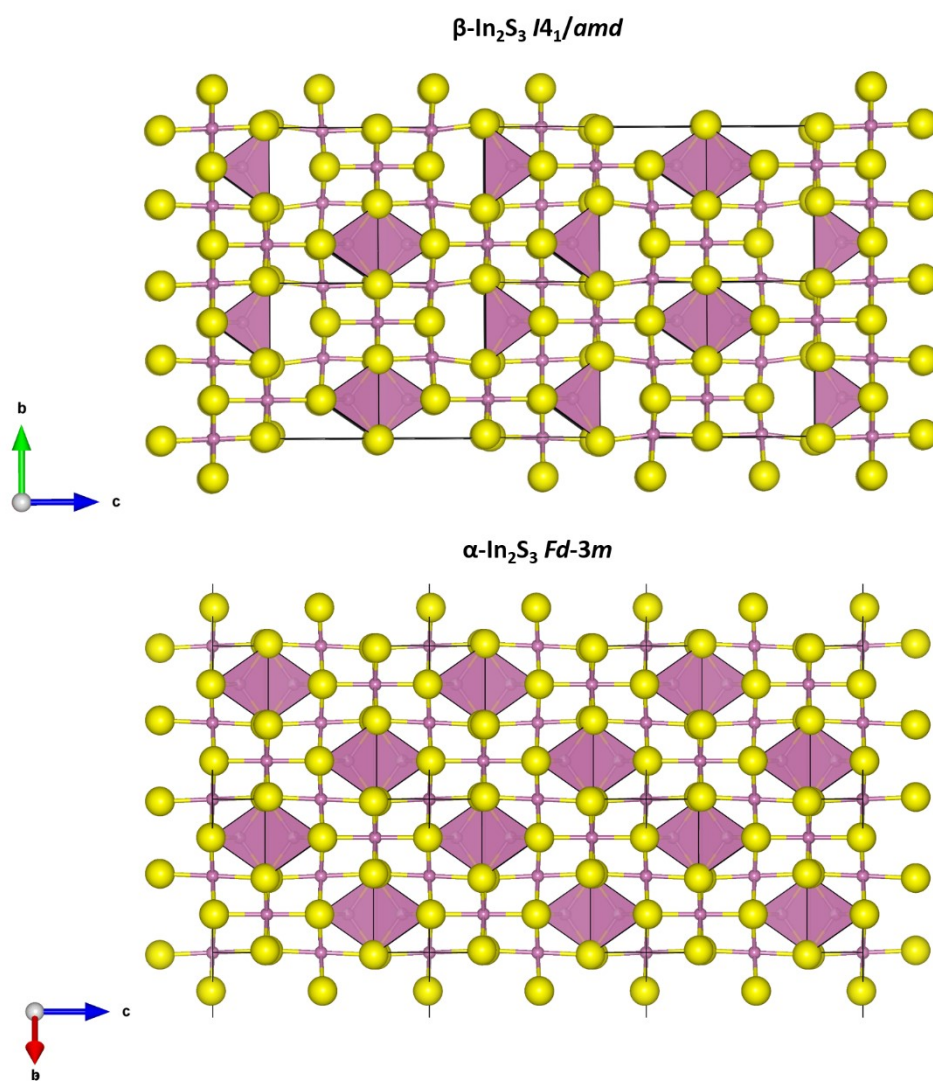


Figure S3: representation of the crystallographic structure of $\beta\text{-In}_2\text{S}_3$ (top) ICSD 133317 and $\alpha\text{-In}_2\text{S}_3$ (bottom) ICSD 133338.¹

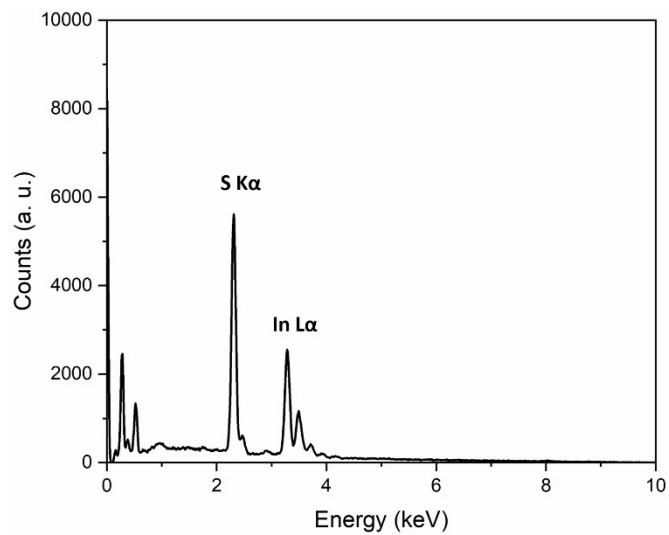


Figure S4: EDS spectra of L-In₂S₃ nanoparticles.

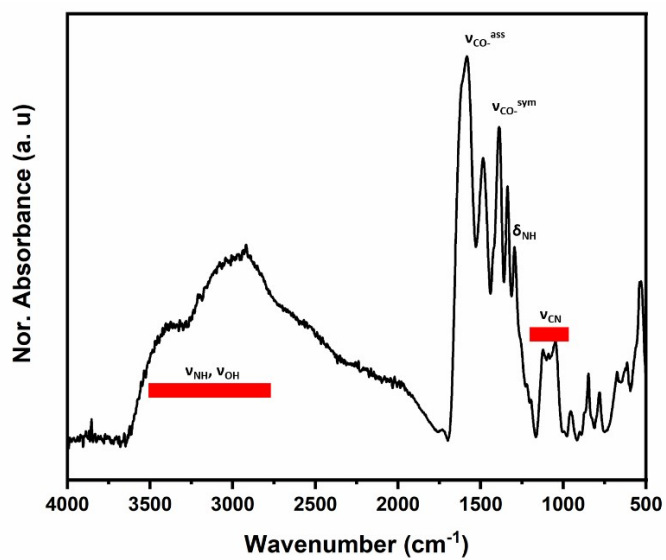


Figure S5: FTIR spectra of L-In₂S₃ NPs.

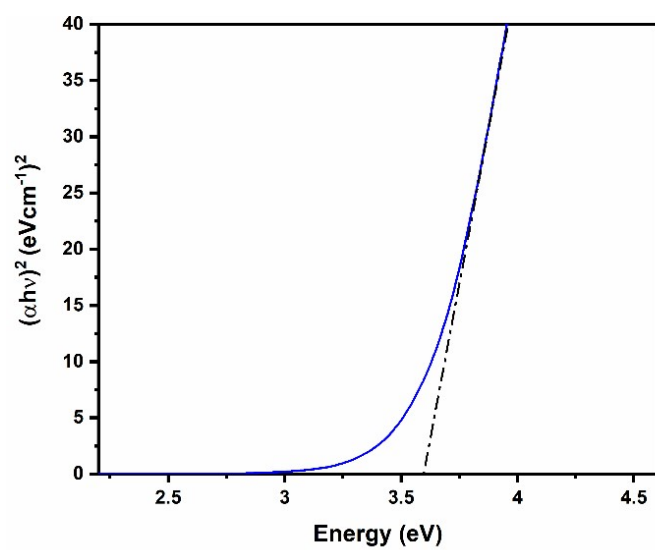


Figure S6: determination of the optical band gap of L-In₂S₃ NPs according to the $(\alpha h\nu)^2$ vs energy plot.

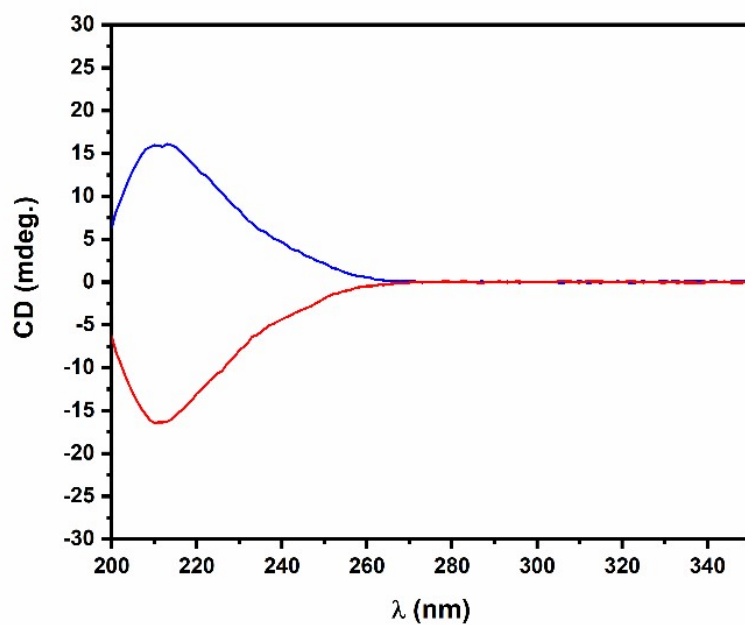


Figure S7: CD spectra of L (blue) and D (red) cysteine solutions at pH = 9.0.

Ligand exchange and Chiral Memory: In order to investigate the contribution of a chiral memory effect, a phase transfer ligand exchange using achiral 1-dodecanthiol was developed (**Figure S8a**) following a previous works on chiral memory in excitonic CdTe quantum dots from Nakashima and coworkers.² In this process, L or D-In₂S₃ NPs colloidal solution in water were precipitated with the addition of few microliters of HCl 1.0 M to reduce the pH around 6.0. The NPs pellet was collected by centrifugation and washed five times with water. Then, the NPs are dispersed in water at pH 12 with the addition of NaOH 1.0 M. The aqueous colloidal solution (1.0 ml) is mixed with 2.0 ml of 1-dodecanthiol 30 mM solution in ethanol (2.0 ml), causing the NPs precipitation. Then, the NPs are extracted using cyclohexane (2.0 ml) and gently shaking the mixture to favourite the extraction. The samples were left undisturbed for half an hour to allow the phase separation, then, the organic layer was removed. The NPs were precipitated with the addition of ethanol and collected by centrifugation, the particles were cleaned three times before being dispersed in cyclohexane and stored at 4 °C for further characterisations. The UV-Vis absorption spectra (**Figure S8b**) confirms that the nanoparticles core is unaffected by the ligand exchange process. The FTIR analysis (**Figure S9a**) shows the absence of all the peaks related to cysteine, instead, the expected peaks for 1-dodecanthiol are observed. In particular, a sharp peak related to the aliphatic ν_{CH_3} is observed at 2975 cm⁻¹, followed by a broader peak at 2890 cm⁻¹ that is related to ν_{CH_2} . The broad band observed between 1500 and 1280 cm⁻¹ is related to the overlap of CH₃ and CH₂ bending modes and two bands at 1090 and 1045 cm⁻¹ are related to $\nu_{\text{C-C}}$.³ This observation confirms the successful of the ligand exchange process.^{2,4}

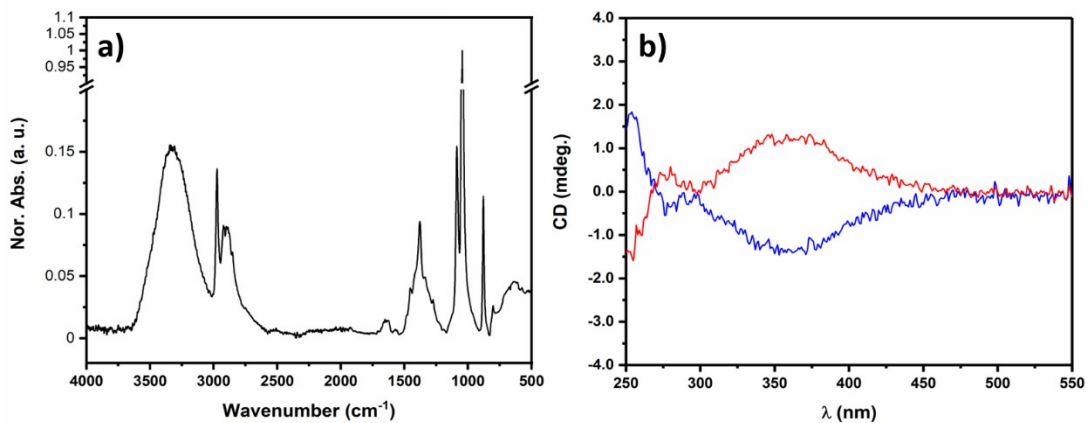


Figure S9: a) CD spectra of L (blue) and D (red) In_2S_3 NPs after ligand exchange with 1-dodecanthiol. b) FTIR analysis of L- In_2S_3 NPs after ligand exchange with 1-dodecanthiol.

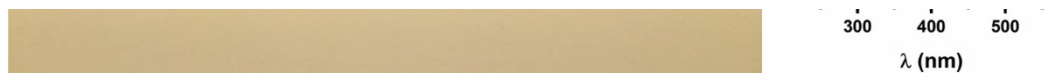


Figure S8: a) L and D- In_2S_3 NPs colloidal solutions without (left) and with (right) 1-dodecanthiol. B) UV-Vis absorption spectra of In_2S_3 NPs before (red) and after (black) the ligand exchange process.

The CD spectra of L and S In_2S_3 NPs colloidal solutions after ligand exchange with 1-dodecanthiol is reported in **Figure S9b**. The CD signal of L- In_2S_3 in cyclohexane shows two negative peaks centred at 360 and 275 nm which are consistent with the peaks observed for the NPs in water, the minor shift can be associated with the variation of the particle interface and dielectric constant of the solvent. The opposite spectra can be observed for D- In_2S_3 NPs after ligand exchange. Interesting a different trend is observed at shorter wavelengths, the spectra of the NPs after ligand exchange is characterised by an inversion point at around 265 nm which can be due to the reduction of peaks related to ligand to metal electronic transitions which fall in the UV range.⁵

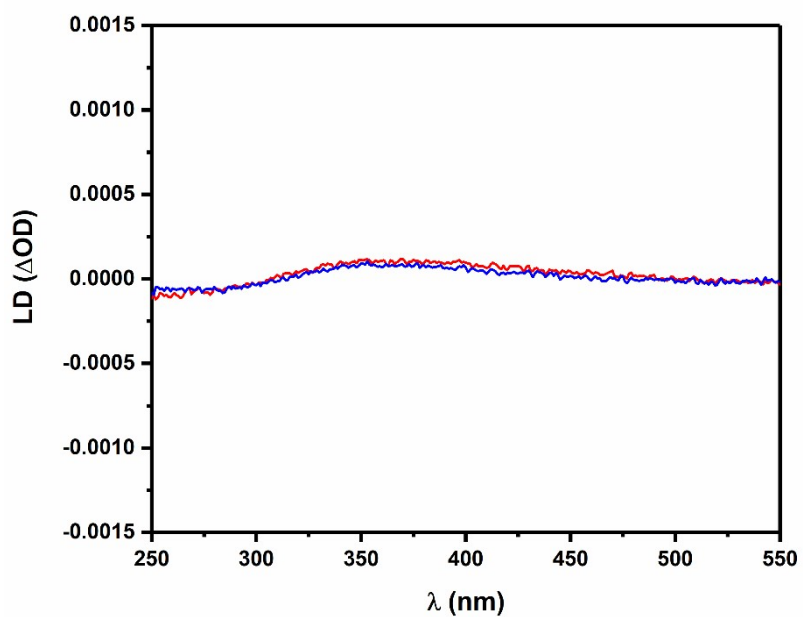


Figure S10: LD spectra of L (blue) and D (red) In_2S_3 NPs colloidal solutions.

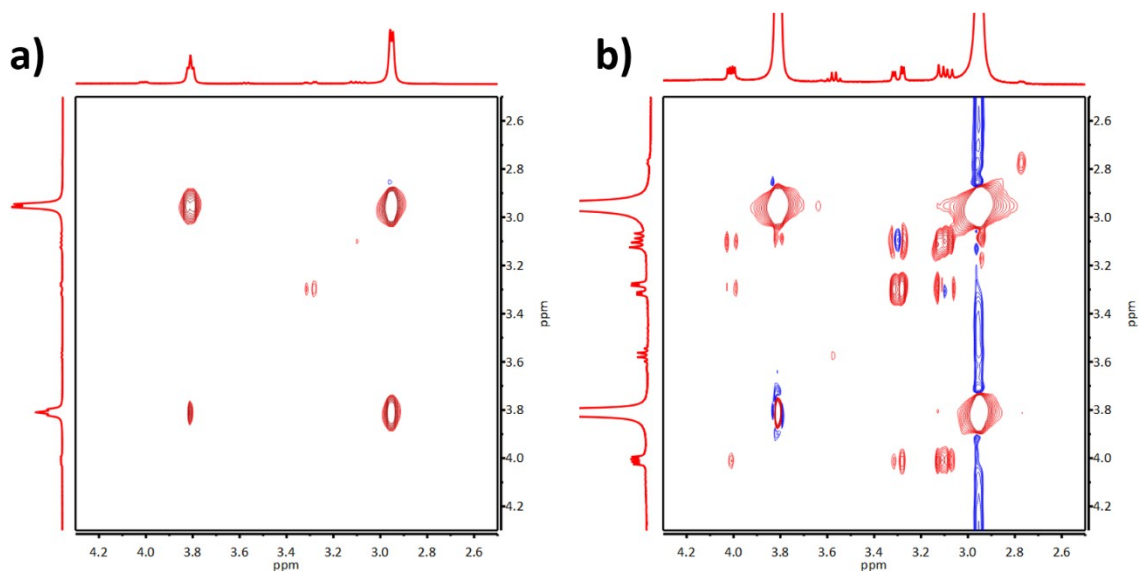


Figure S11: left) COSY spectra of L- In_2S_3 NPs and right) detail of the COSY spectra highlighting the peaks of lower intensity related to the cysteine disulfide dimer spin system.

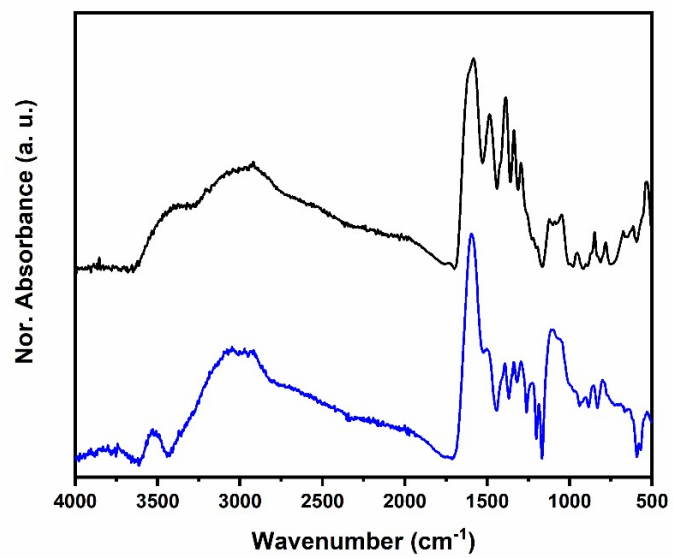


Figure S12: FTIR analysis of L-In₂S₃ NPs before (black) and after (blue) ligand removal treatment.

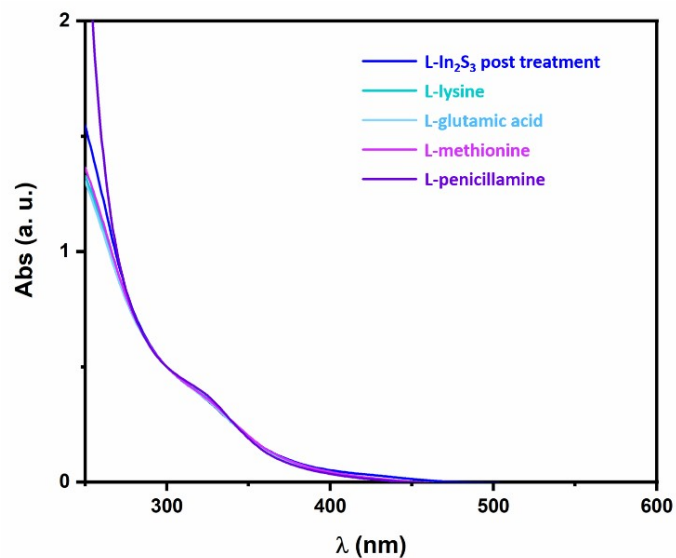


Figure S13: UV-Vis absorption spectra of L-In₂S₃ NPs after ligand removal treatment and in the presence of 48.0 mM of the second ligand.

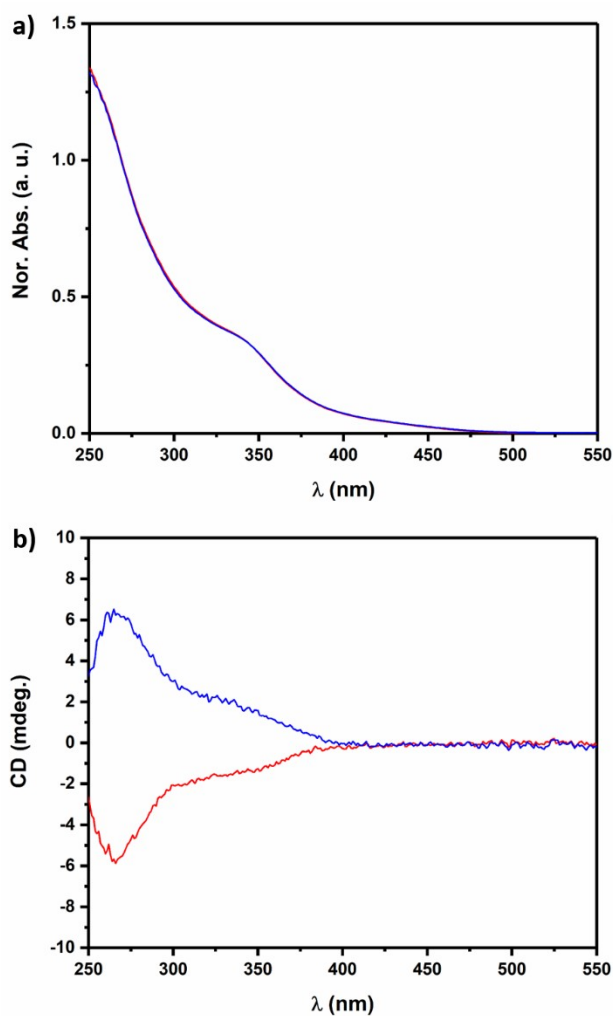


Figure S14: UV-Vis absorption a) and CD b) spectra of In₂S₃ NPs stabilised by L (blue) and D (red) penicillamine.

References.

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