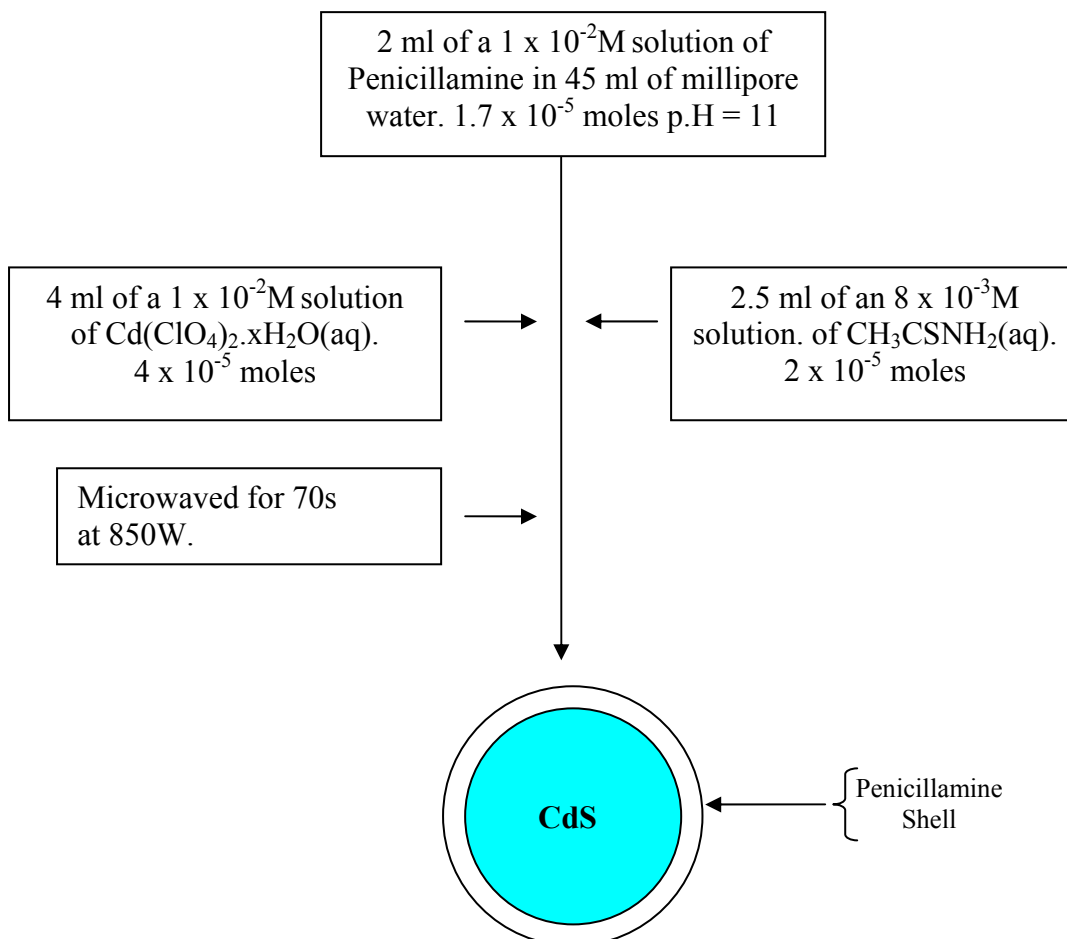


Electronic supporting Information

CdS Particle Preparation



Scheme 1: Preparatory scheme detailing CdS production. Particles were allowed to mature in the dark for at least one day before use.

Preparation of Penicillamine stabilized CdS nanocrystals

2 ml of a basic aqueous 1 x 10⁻²M solution of Penicillamine, (2 x 10⁻⁵ moles of D-, L- or Rac), was added to 45 ml of Millipore water in a 60 ml conical flask. The pH was adjusted to 11 by the dropwise addition of 1M NaOH. 4 ml of a 1 x 10⁻²M Cd(ClO₄)₂.xH₂O(aq) and 2.5ml of an 8 x 10⁻³M of CH₃CSNH₂(aq) were then added and the solution was stirred well. The resulting homogeneous solution was then transferred to a clean dry 200ml beaker and placed into a conventional microwave and irradiated for 70s at 850W. The resulting clear, colourless, solution was then returned to the conical flask and stored in the dark for at least one day. The resulting colloid

was then examined using uv-vis and luminescent spectroscopy. The colloid was found to absorb in the uv, (~340nm), and emit in the visible, (~500nm). The volume of the colloid was then reduced to ~5ml using the rotary evaporator and propan-2-ol was added to precipitate out the particles. The particles were collected by centrifugation. The particles were washed several times with a propan-2-ol, water mixture, (9:1), and finally redispersed in millipore water. Once re-dispersed in water the colloids were concentrated using the rotary evaporator until all remaining propan-2-ol was removed.

Statistical Analysis

To ensure maximum luminescence the above process was optimised using a 2^3 factorial study. This process involved the examination of the luminescent intensity as the concentrations of all three reactants were methodically varied. This study showed that the most luminescent dots were produced when the cadmium concentration was in excess to both the thioacetamide and the penicillamine, but an excess of cadmium over thioacetamide seemed to be the most important of the two (Table 1).

	1	2	3	4	5	6	7	8
Cd:S:Pen	1:1:1	1:1:2	1:2:1	1:2:2	2:1:1	2:2:1	2:1:2	2:2:2
Int	264	221	27	16	657	80	366	481

Table 1: 2^3 factorial study of D-Penicillamine capped CdS. $1 = 2 \times 10^{-5}$ moles.

As particles with a Cd^{2+} to S^{2-} ratio of 1:2 gave the weakest luminescence these batches were discounted and all further studies involved particles with a ratio of 2:1 cadmium to thioacetamide.

With this in mind a second factorial study, this time 2^2 was then carried out, (the relative concentration of thioacetamide was left at 1). The Cadmium and Penicillamine concentrations were increased step by step, Figure 1. This study showed that as the concentration of cadmium was increased in relation to the penicillamine the luminescence also increased. However a balance must be struck

between luminescent strength and particle stability as any further reduction in the penicillamine concentration would lead to reduced particle stability.

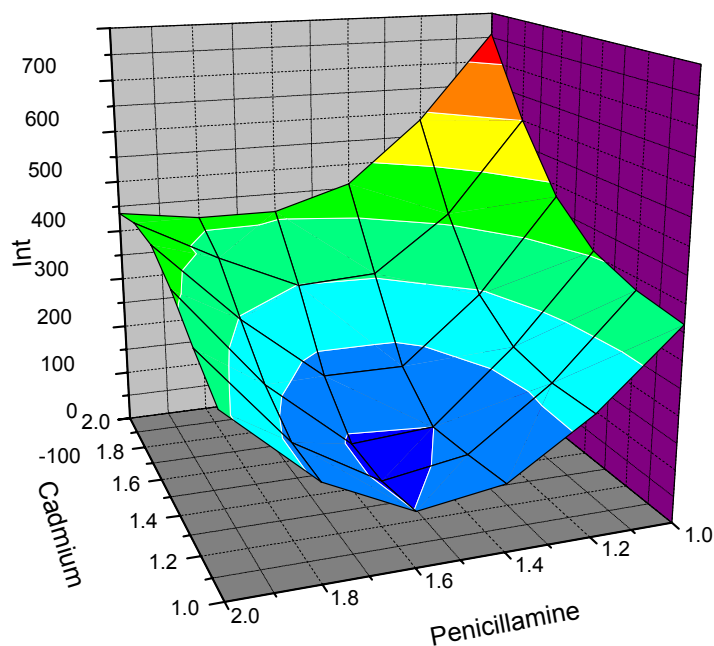


Figure 1: Examination of the response, (Luminescent Intensity), as the Cd and penicillamine concentrations are increased. The ratio of 1:1:1 corresponds to equal concentrations of 2×10^{-5} moles. Thioacetamide equals 1 through the experiment.

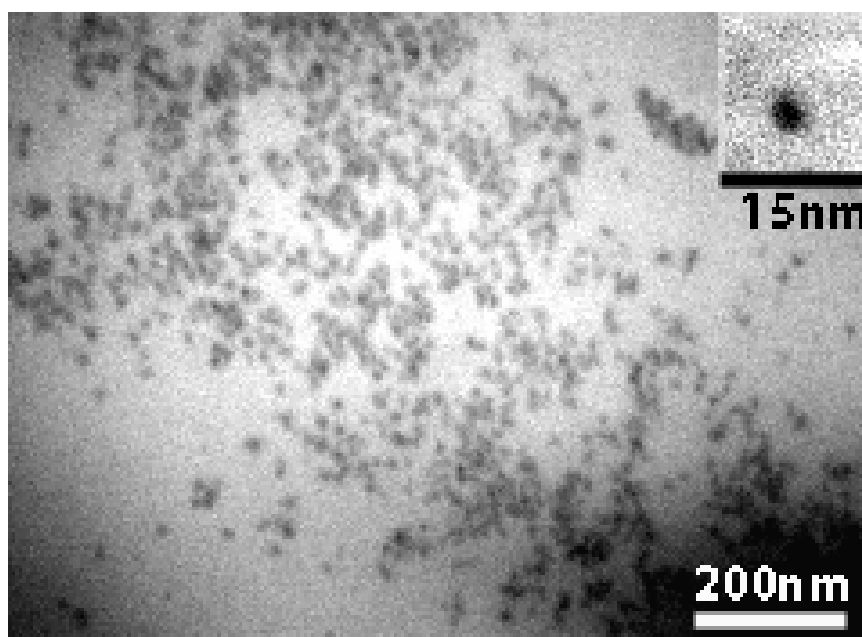


Figure 2: TEM image of *D*-penicillamine stabilized CdS. Note the clumping effect, this is attributed to H bonding between the penicillamine carboxyl groups present on the surface of the nanocrystals.

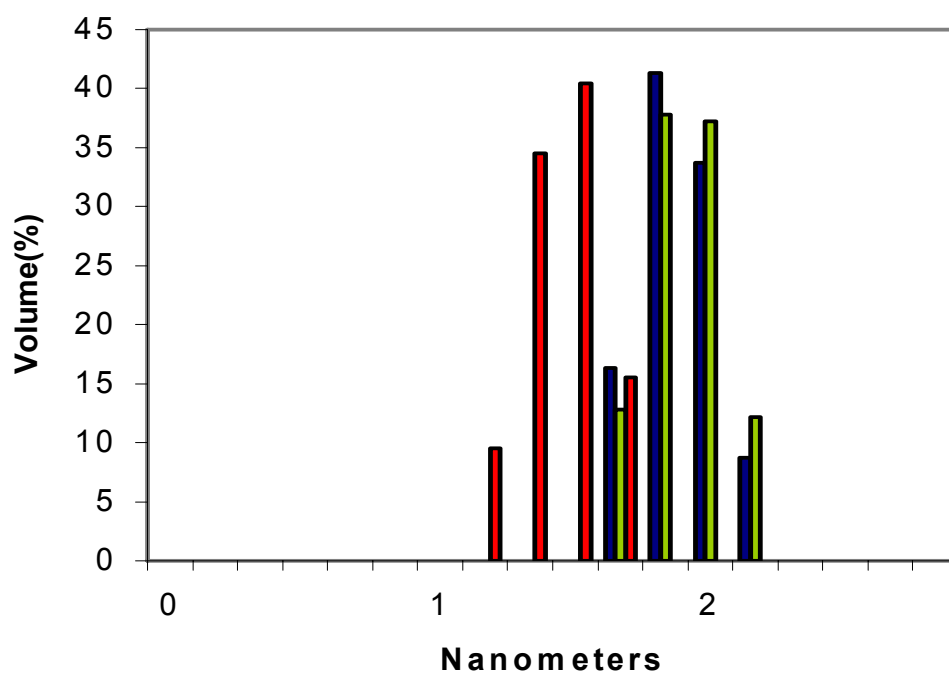


Figure 3: Size distributions, (scatter and histogram), by volume of washed *D*-CdS, (blue), *L*-CdS, (lime), and *R*-CdS, (red). Particle sizes were measured as 2.1 ± 0.3 nm, 2.2 ± 0.3 nm, and 1.4 ± 0.2 nm for *D*-, *L*- and *R*- CdS QDs respectively (PDI = 1). The measurements have been performed using Zetasizer Nano-ZS from Malvern Instruments.

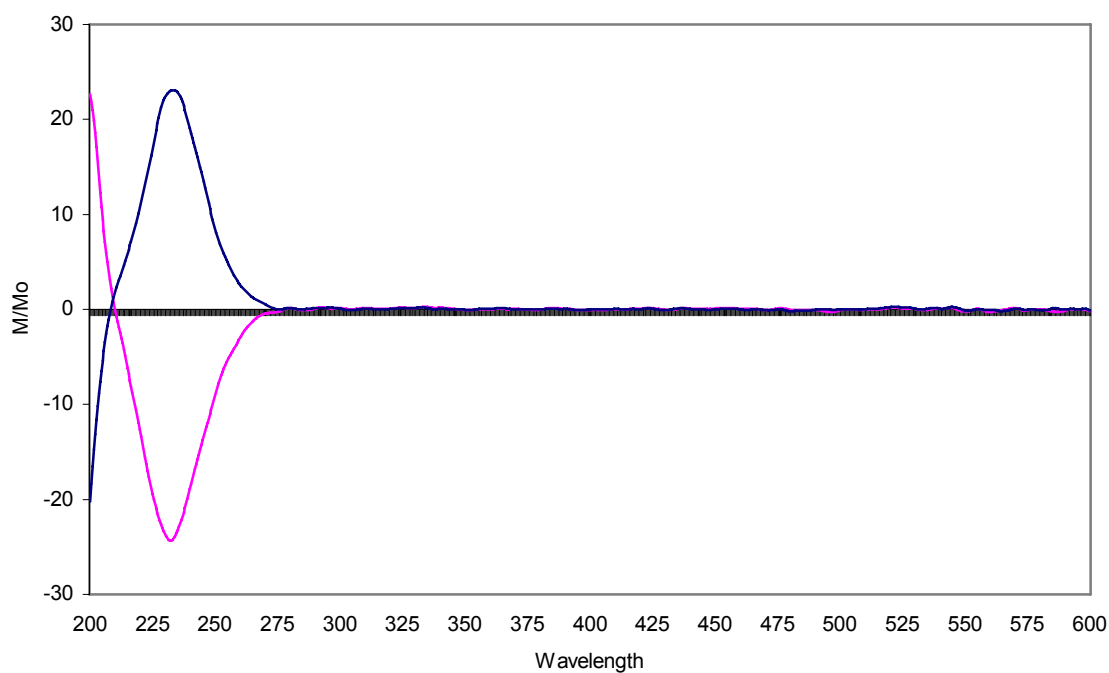


Figure 4: CD scan of initial free *D*- (pink) and *L*- (blue) penicillamine. Note the absence of any signal above 230 nm. The spectra have been recorded using Jasco J-810 Spectropolarimeter.

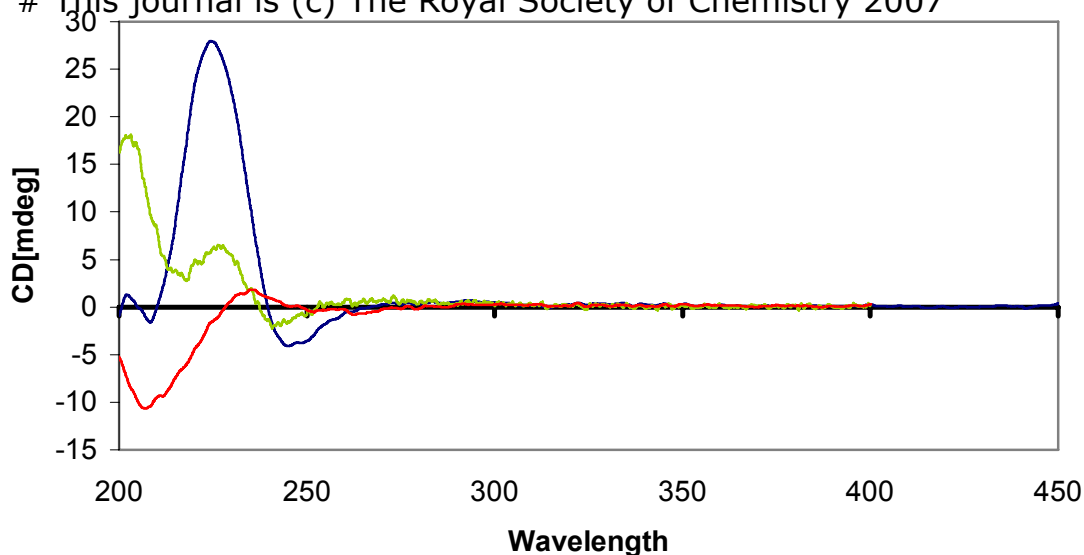


Figure 5: Control CD scans of *D*-penicillamine - $\text{Cd}(\text{ClO}_4)_2$ solution (lime line), *D*-penicillamine - thioacetamide solution (red line), and *D*-Pen CdS co-precipitation supernatant (blue line). Note the absence of any signal beyond 260 nm. All samples were treated by microwave radiation and left to mature for three days. Both the *D*-Pen- $\text{Cd}(\text{ClO}_4)_2$ and the *D*-Pen- thioacetamide samples were prepared and treated analogously to normal *D*-Pen CdS, but without the addition of thioacetamide or $\text{Cd}(\text{ClO}_4)_2$ solutions respectively.

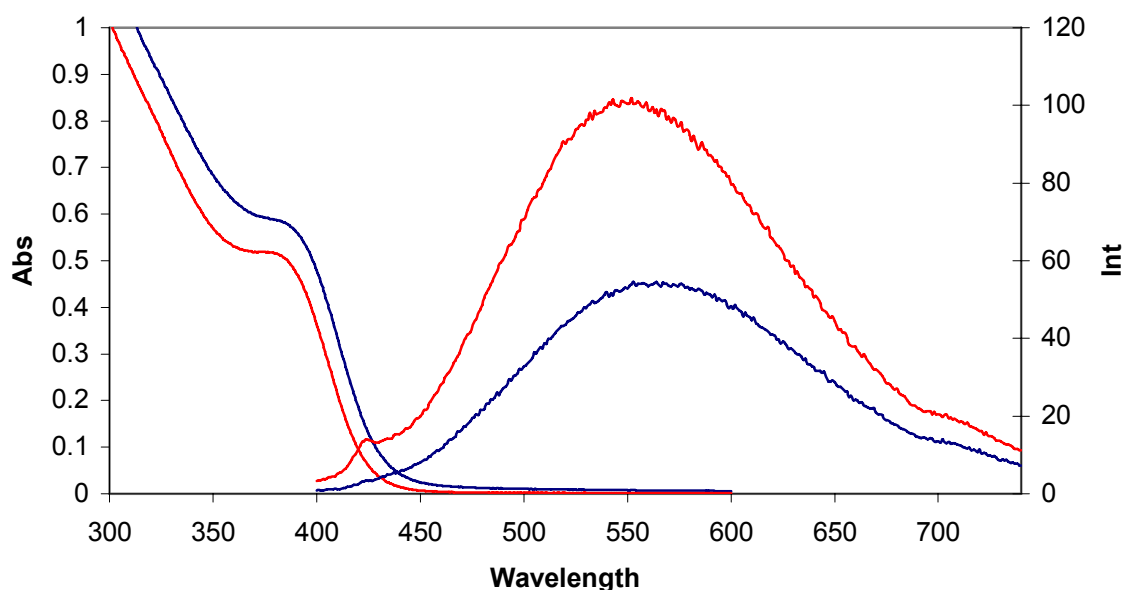


Figure 6: UV-vis and PL spectra of citrate stabilized CdS nanocrystals, (blue line), and after addition of *D*-Penicillamine solution (red line). Excitation wavelength was 380nm. Particles were prepared as described earlier using tri-sodium citrate in place of penicillamine. 4ml of a *D*-Pen solution ($1 \times 10^{-2} \text{M}$) was then added and the CdS colloid and was stirred vigorously. Ligand substitution can be seen by both the blue shift and removal of scattering in the UV signal, and the increase in the luminescence.

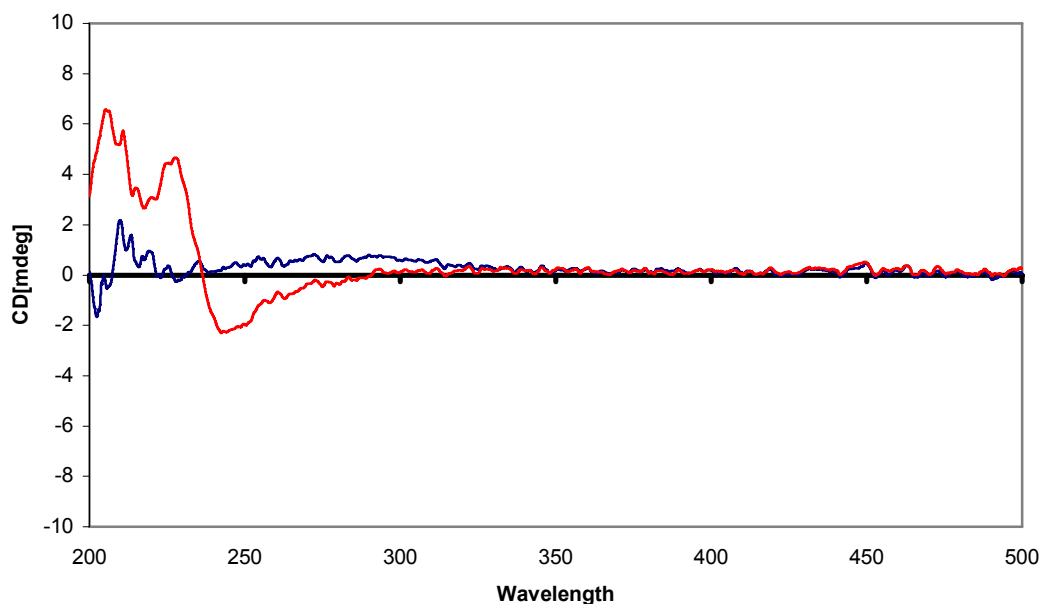


Figure 7: CD scans of citrate stabilized CdS nanocrystals (blue), and after addition of *D*-Penicillamine solution and microwave treatment (red line). Original citrate stabilized CdS particles are not optically active but some scattering is visible between 200 and 250 nm. Addition of *D*-Penicillamine to the particles and microwave treatment result in the appearance of some signals below 270 nm.

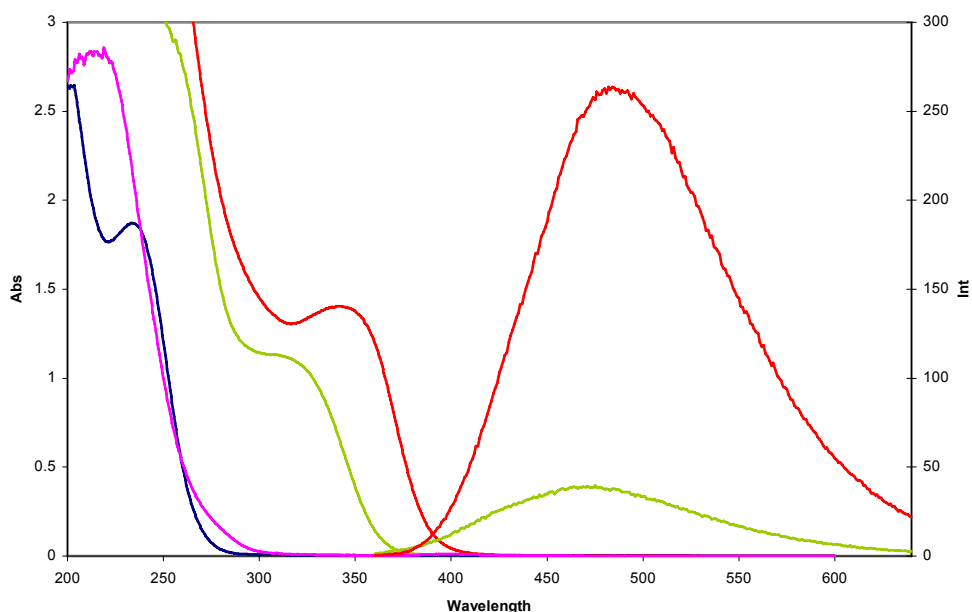


Figure 8: UV-Vis and PL monitoring of the formation of *L*-Pen CdS: free *L*-penicillamine stabiliser (blue line), after addition of $\text{Cd}(\text{ClO}_4)_2$ (magenta line), after addition of the thioacetamide (green line) and after the microwave treatment (red line). PL excitation wavelength is 340nm. These spectra correspond to one in figure 4 in the main text.

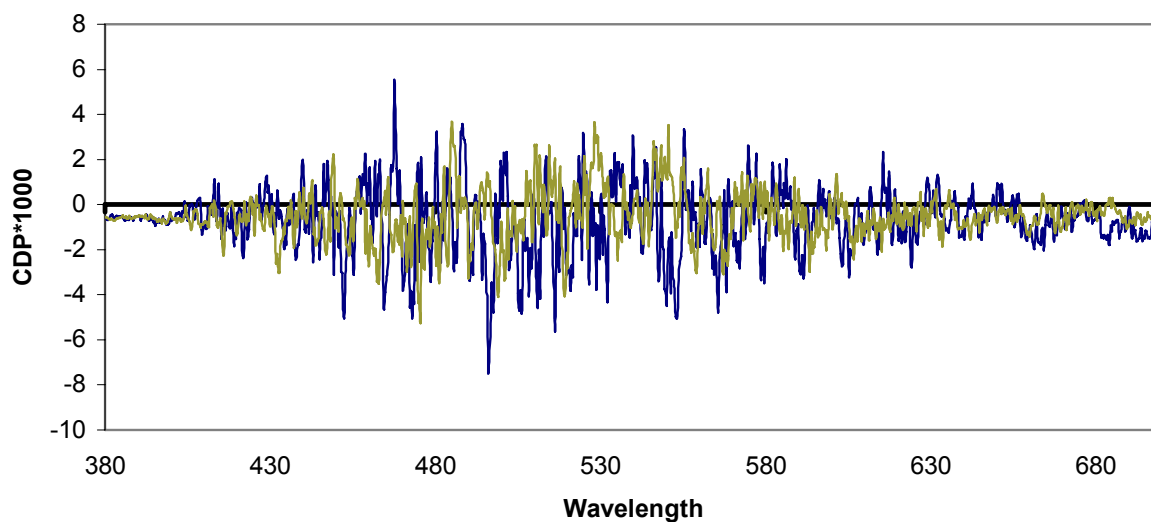


Figure 9: Circularly Polarised Luminescence (CPL) spectroscopy of *D*-CdS, (blue), and *L*-CdS, (lime). The intensity of the scan has been increased by a factor of 1000 to demonstrate the lack of any real structure, i.e. it is just amplified background noise.