Investigating the effect of ligand exchange on CuInS2 Quantum Dots

Introduction

Quantum Dots (QDs) are semiconductor nanocrystals made up of central metal atoms and molecules called ligands that attach to them by donating an electron to form a bond. They have captured much interest since their discovery in the 1980's because of their tuneable band gap. The ligands constantly detach and reattach so adding a large concentration of new ligands in solution can change them. ⟦CuInS⟧ _2 (CID) QDs are optically stable, small and relatively non-toxic. By exchanging long ligands for shorter ones, we aim to form a superlattice with a periodic structure and improve the conductivity.

Method

We synthesised the QDs by mixing indium acetate with copper iodide and adding dodecane thiol (DDT) as a passivator. We heated the solution to 210oC which changed its colour from yellow to deep red because of nucleation and crystal growth. The solution decomposes at high temperatures making it a source of sulphur. We attached a condenser to the equipment and used a nitrogen tap to lower the oxygen concentration. We let the solution cool to 60oC then added octadecene (ODE) to increase the volume (ODE doesn't react with the solution).

We cleaned the sample. We equally split it into 4 tubes and added 35ml of methanol, acetone, chloroform (in 1:2:1 ratio) to each. After centrifugation, the QDs stuck to the tube wall and we were able to pour the solution away. We did this 3 times, each iteration removing 90% of waste.

We used a spectrometer to measure absorption as a function of wavelength and did photoluminescence (PL) spectroscopy. We used the PL peak to calculate the size of the QD using:

$d=68.952-0.2136\lambda_{PL}+(1.717x10)\,\hat{}\,(-4)\,(\lambda_{PL})\,\hat{}\,2$

nd used this to calculate the concentration using Beer's Law:

$\epsilon(E_1) = 830d\,\hat{}\,3.7$

$A(\lambda) = \varepsilon(\lambda)\, C\, L$

where A is the absorption at PL peak wavelength, C is the concentration and ε is the molar extinction coefficient at the first excitation peak.

The PL and absorption peaks are shon in figures 1 and 2 respectively.

Using this concentration, we calculated the number of moles of MPA required for a QD to MPA ratio of 1:1000, from which we could find the mass and therefore the volume. We mixed 2ml of the QDs, 2ml of the ODE and 0.386ml for the 1:1000 ratio. We then heated the sample to 130 degrees and kept it there for 15 minutes to allow the ligand exchange to happen. After this we let the sample return to room temperature and then cleaned it using centrifugation. We repeated this using dimethylformamide (DMF) instead of ODE to see which would work better.

To test to see if the exchange had been successful we did NMR spectroscopy using chloroform as the solvent.

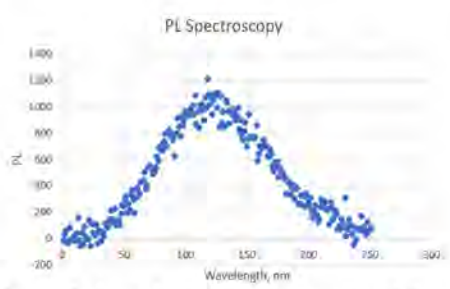

Figure 1: A graph of PL against wavelength from PL spectroscopy

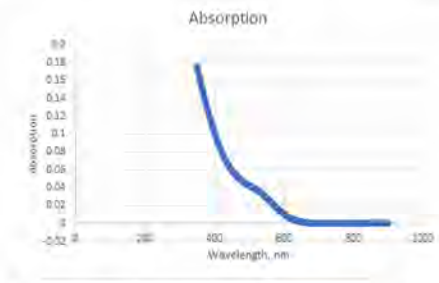

Figure 2: A graph of absorption against wavelength

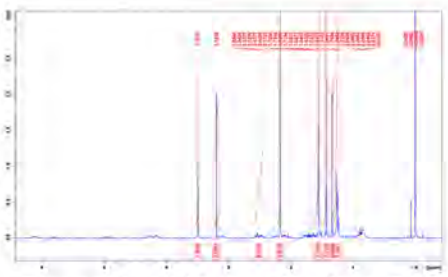

Figure 3: NMR graph when ODE was the solvent

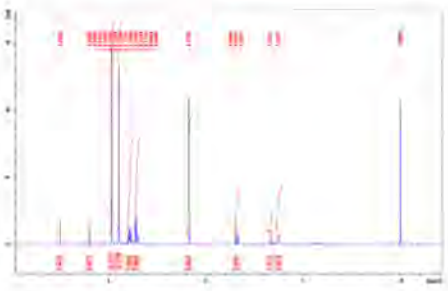

Figure 4: NMR graph with DMF as the solvent

Results and discussion

Figure 3 and 4 show the NMR data collected when ODE was used and when DMF was used respectively. Figure 2 shows a quartet and a triplet peak at around 2.8 ppm. If MPA had fully bound to the surface the quartet shoud have changed to a triplet but that isn't the case with our data. This suggests that perhaps some of the MPA has bound to the the QD surface but there is still some in solution. To improve this, next time *would allow the sample to stay at 130 degrees for longer too allow more time for the exchange to happen.*

In figure 1 we don't have the peaks at around 2.8 ppm which tells us the exchange has been unsuccessful. This is because MPA has a low solubility in ODE. After we completed the exchange, photoluminescence was non-existant because of damage done to the surface of the QD. To prevent this we should have made a ZnS shell around the QD to protect it from damage.

To make the exchange more successful I could have added iodide/bromide which may have improved the exchange.

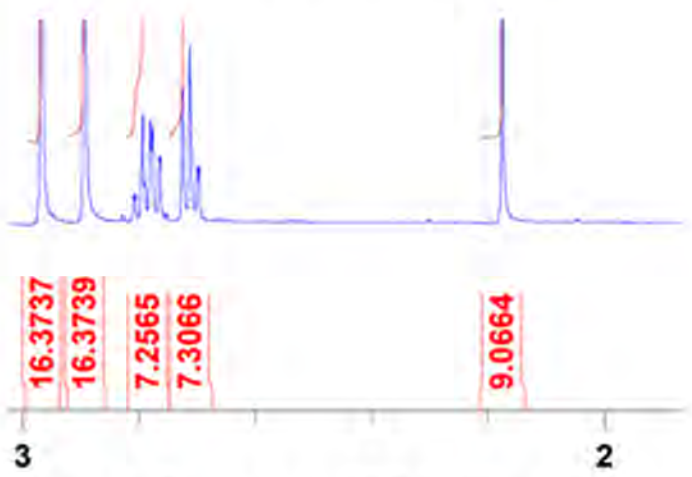

Figure 5: Zoom in on DMF NMR graph

Conclusion

This project has been a fantastic opportunity for me to learn a topic I was unfamiliar with beforehand from an expet in the field. I have developed a keen interest in QDs and I will continue to research them in the future and potentially as part of my third year project. Unfortunately we were unable to test the conductivity or deposit the QDs onto a surface. The NMR data sugests that some MPA bound tp the surface but there was some still in solution when DMF was the solvent so I believe if we alowed the sample to stay at 130 degrees for longer than 15 minutes,it would have been more successful

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Lincoln Academy of Learning and Teaching

UROS funded

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