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Chiral highly luminescent CdS quantum dots†

Mícheál P. Moloney,[ab] Yurii K. Gun'ko*[ab] and John M. Kelly[a]

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Strongly white-emitting (λ_{max} = 495 ± 10 nm) D- and L- penicillamine capped CdS nanoparticles, which show strong circular dichroism in the range 200–390 nm, have been prepared.

Because of quantum confinement effects due to their nanometer size, fluorescent semiconductor nanocrystals or quantum dots (QDs) have remarkable optical, physical and chemical properties, which differ markedly from the bulk material.[1–9] The ability to tune their optical properties, combined with the ease of surface modification has led to QD's proposed application in *inter alia* light emitting devices, fluorescent sensors and bioassays.[2–4,10–12]

Chirality is one of the most important factors of molecular recognition and therefore development of chiral luminescent nanosized probes would provide very useful tools for both chemistry and biology. Although there have been some recent publications on the preparation of chiral gold[13,14] and silver[15,16] nanoparticles, similar systems based on QDs have not yet been reported. In this communication we describe the synthesis and characterisation of green-white or blue-white emitting, optically-active, water-soluble chiral CdS QDs, which we believe should have a broad range of potential applications.

These chiral CdS QDs (Fig. 1) have been prepared using microwave induced heating with the racemic (*Rac*), D- and L- enantiomeric forms of penicillamine (Pen) being used as the stabilizers.‡ A 2^3 factorial study[17] was employed to optimise the particle synthesis and consequently their optical properties (see ESI†). It was found that a molar ratio of 2 : 1 : 1 cadmium to thioacetamide to penicillamine gave QDs with the highest luminescent intensity while also retaining a sharp band edge maximum. All three types of CdS particles (D-, L-, and *Rac* penicillamine) have absorption bands with maxima in the range 335–345 nm (Fig. 2). These bands are assigned to the first excitonic (1_{sh}–1_{se}) transition.[18] The maximum wavelength of the *Rac* particles is the shortest, consistent with these particles being smaller, which has been confirmed by dynamic light scattering. Particle diameters were measured as 2.1 ± 0.3 nm, 2.2 ± 0.3 nm and 1.4 ± 0.2 nm for D-, L- and *Rac*- CdS samples respectively (see ESI† for histogram). The smaller size of the *Rac* sample size may possibly be due to the complementary nature of the D- and L- acids allowing for closer packing of the stabilizer on the surface of the *Rac*-CdS.

The emission spectra of all the QDs show broad bands between 370 and 710 nm with the maximum wavelength in the range 485–505 nm (Fig. 2), so that under UV light the D- and L- Pen stabilized particles give bright green-white emission, while the *Rac*-Pen stabilised ones give off bright blue-white photoluminescence. The emission spectra of each particle type was found to be independent of excitation wavelength, consistent with uniform particle distribution. The quantum yield, measured against Coumarin 153, of all QDs was 20 ± 4%. Although the quantum yield is quite high compared to those reported for other CdS nanoparticles in aqueous solution,[19,20] it is lower than that of the exciton emission found for CdS QDs in organic solvents.[21–26] It is also noticeable that samples with less well defined band edges have higher quantum yields. It is most probable that this emission is due to defects or trapped states on the surfaces of the crystals.

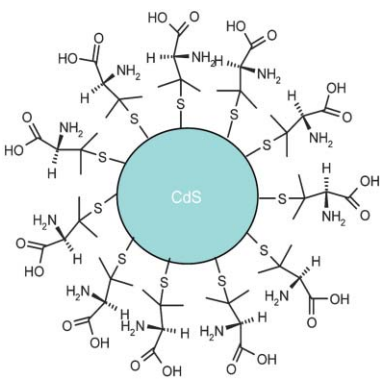

Fig. 1 Schematic presentation of the D-penicillamine stabilized CdS nanoparticle.

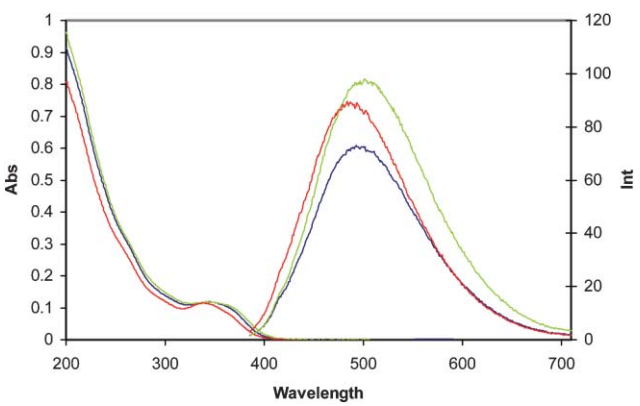

Fig. 2 Optical spectra (UV-vis absorption – left and emission – right) of CdS nanocrystals stabilized with D-Pen (Blue), L-Pen (Green), and *Rac*-Pen (Red). Excitation wavelength for all emission spectra is 365 nm.

[a]*School of Chemistry, Trinity College Dublin, Dublin 2, Ireland*
[b]*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland.*
E-mail: igounko@tcd.ie; Fax: +353-1-671 2826; Tel: +353-1-608 3543
† Electronic supplementary information (ESI) available: preparation scheme, statistical analysis, TEM images, CD, UV-vis, PL and CPL spectra. See DOI: 10.1039/b704636g

The relatively high quantum yield of these penicillamine capped QDs can be attributed to a combination of factors. Firstly it is known that penicillamine is a strongly coordinating ligand, and we believe that penicillamine molecules chelate cadmium ions on the surface of the nanocrystals providing better surface passivation and consequently higher luminescence efficiency. Secondly the reaction conditions were engineered for slow particle nucleation and growth.[27]

Circular dichroism (CD) studies of the particles gave particularly striking results. D- and L - penicillamine stabilized particles produced corresponding mirror image CD scans (Fig. 3) while the particles prepared with a Rac mixture showed only a weak signal. The CD observed is quite different from that of the free D- and L- penicillamine which show, as expected, a near symmetrical image with maxima/minima at 234 $\pm$ 2 nm (see ESI† and Fig. 4A). However, the CD spectra of D- and L- penicillamine stabilized CdS QDs are more complex, with maxima/minima at 207 $\pm$ 3, 252 $\pm$ 2, 293 $\pm$ 3, 320 $\pm$ 2 and 345 $\pm$ 2 nm (Fig. 3), wavelengths much longer than those where the penicillamine ligands themselves absorb.

The opposite preference for left or right polarized light in the region of the CdS exciton bands is particularly intriguing. The presence of optical activity may be due to chirality induced in the quantum dots upon reaction, in a manner similar to that previously proposed for metallic nanoparticles.[13–15] In order to understand the formation mechanism of these chiral QDs, CD measurements were carried out at all stages of the particles preparation (Fig. 4). Both L- and D- samples demonstrated similar behaviour but showed bands of opposite chirality. The CD data is consistent with the initial formation of a cadmium penicillamine complex, (band *ca.* 210 nm). Addition of thioacetamide results in the appearance of signals at *ca.* 290 and 320 nm in the CD spectra. These signals are probably those of small CdS clusters in which penicillamine is coordinated in a fashion similar to that proposed for other similar CdS systems.[28,29] Subsequent microwave irradiation causes the nucleation centres to grow, forming CdS nanocrystals. This results in a red shift in the CdS band edge and shifts the corresponding CD signals to the range between 320 and 370 nm respectively. We believe that the chirality of the nanocrystals is a direct consequence of the chirality of the

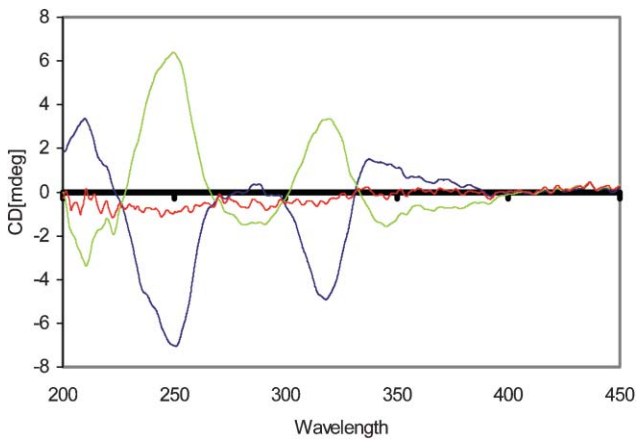

Fig. 3 CD scans of the D- (Blue), L- (Green) and *Rac*-Pen (Red) stabilized CdS QDs (θ deg = δA/32.98). The spectra have been recorded using Jasco J-810 spectropolarimeter.

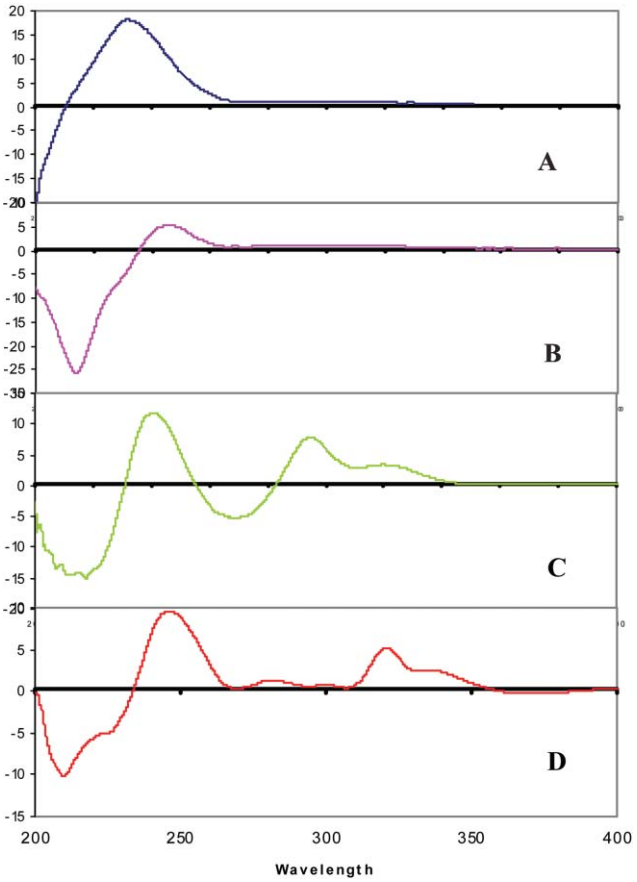

Fig. 4 CD monitoring of the formation of CdS nanoparticles stabilised with L- penicillamine at pH = 11: **A**, blue line – the free penicillamine stabiliser, **B**, magenta line– after addition of $Cd(ClO_4)_2$, **C**, green line – after addition of the thioacetamide, **D**, red line – after the microwave treatment. Note: the final CdS samples were not left for maturation and were not purified in these monitoring experiments. UV and PL data are available in the ESI†.

precursors. In agreement with this we have also demonstrated that these optically active samples cannot be prepared by reacting non-chiral citrate stabilised quantum dots with D-penicillamine. Additionally we have carried out control experiments to show that the observed CD effects are not a consequence of the effect of microwave irradiation on solutions of D-Pen and $Cd(ClO_4)_2$ nor of the reaction of thioacetamide and D-Pen. None of these control samples produced CD signals above 260 nm (see ESI†).

It was interesting to find out whether the chiral QD samples emit circularly polarised light. We therefore performed Circularly Polarised Luminescence spectroscopy (CPL)[30] studies of the chiral QDs. However, no optical activity in the light emitted by the chiral QDs was observed (see ESI†). This indicates that the luminescence from the defect trapped states on the surface of the particle does not result in circular polarised light.

In conclusion, we have prepared strongly emitting chiral D-Pen and L-Pen capped CdS QDs. Using CD spectroscopy we have shown that they are optically active and possess almost identical mirror images of one another in the range of 200–390 nm. We believe that these QDs could find important applications, including their use as fluorescent chemical and biochemical chirality sensors and molecular recognition nanodevices. In addition they might

have potential for some biomedical uses. For example, it is known that certain proteins and drugs only show activity to one enantiomer, (*e.g.* the transactivator protein of type-1 human immunodeficiency virus shows a preference for D- over L-penicillamine).[31] Further work on the chiral quantum dots will include a detailed investigation of the photophysical, photochemical and dichroic properties as well as their biochemical behavior.

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Notes and references

‡ *Preparation of penicllamine stabilized CdS nanocrystals*

2 ml of a basic aqueous 1×10^{-2} M solution of penicillamine, (2×10^{-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 1 M NaOH. 4 ml of a 1×10^{-2} M $Cd(ClO_4)_2.xH_2O$ and 2.5 ml of an 8×10^{-3} M of CH_3CSNH_2 were then added and the solution was stirred vigorously. The resulting homogeneous solution was then transferred to a clean dry 200 ml beaker and placed into a microwave oven and irradiated for 70 s at 850 W. The resulting clear, colourless, solution was then transferred to the conical flask and stored in the dark for at least one day. The volume of the colloid was then reduced to ~5 ml using the rotary evaporator and propan-2-ol was added to precipitate out the nanoparticles. The particles were collected by centrifugation. The particles were washed several times with a propan-2-ol – water mixture (9 : 1), and finally re-dispersed in millipore water. UV-vis, CD and fluorescence spectroscopy was carried out on the stable suspensions in water.

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