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Synthesis and spectroscopic studies of chiral CdSe quantum dots

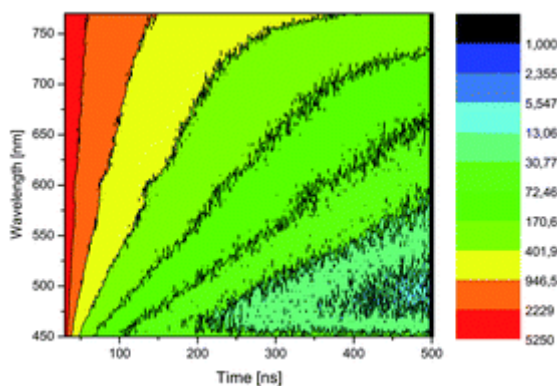
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Using microwave irradiation, water soluble, optically active, penicillamine (Pen) capped CdSe nanocrystals with broad spectral distribution (430–780 nm) of photoluminescence have been produced and studied by a range of instrumental techniques including absorption, circular dichroism and both steady state and time resolved photoluminescence spectroscopy. The photoluminescence of these nanocrystals is attributed to emission from surface defect states. The decay of the excited state in the nanosecond region, which can be analysed as a triple exponential, depends strongly on the emission wavelength selected, but only weakly on the excitation wavelength.

Graphical Abstract:



Introduction

Chirality is a common occurrence in the natural world and chiral compounds are very important in chemistry, biology, pharmacology and medicine. It has also been envisaged that chirality could play an important role in nanotechnology.^{1,2} The majority of existing research in this field has been focused on chiral organic, metallorganic and biological molecules and their supramolecular structures,³ while research in the area of chiral inorganic nanoparticles is still in the very early stage of its development. For example, there has been some work involving chiral optically active metallic gold^{4,5} and silver^{6,7} nanoparticles, as well as carbon nanotubes.^{8,9} However, there are currently only a few recent papers dealing with chiral light emitting semiconducting nanocrystals (quantum dots).^{10–14}

In general over the last decade much attention has been directed towards II–VI type CdS, CdTe and CdSe quantum dots (QDs).^{15–19} It is the ability to fine-tune their optical properties by chemical control of their size and shape (i.e. their degree of quantum confinement) which makes quantum dots particularly interesting. This level of optical control combined with QDs' resistance to photobleaching and their high level of solubility in practically any solvent (depending on the stabiliser used) make these nanomaterials potentially suited for roles as divergent as light emitting diodes,²⁰ biological sensors²¹ and photovoltaic devices.^{22–24} Thiol group containing amino acids have proved to be excellent stabilisers, with L-cysteine becoming one of the popular surface capping molecules for CdX (X ¼ S, Se, and Te) nanoparticles.^{18,25–31} In addition this use of stereospecific chiral stabilising molecules opened another avenue of interest in the area of quantum dot research, as chirality is a key factor in biological and biochemical interactions. Due to their unique photophysical properties, we believe that chiral QDs have a range of potential applications in photonics and biochemistry.^{13,32,33} The main aim of our work is to develop novel chiral CdSe based QDs by using chiral stabilisers and to investigate the properties of these materials. Here we

report the synthesis and detailed spectroscopic studies of new penicillamine stabilised CdSe QDs, which have been prepared using the dextrorotatory (D-) and levorotatory (L-) enantiomers, as well as the racemate (rac-) of the amino acid.

Results

Preparation of CdSe quantum dots was carried out using a method similar to that previously reported for penicillamine (Pen)-stabilised CdS,¹⁰ itself a variation of a method reported by Ni et al.³⁴ substituting Na_2SeSO_3 for CH_3CSNH_2 as the X2 source.^{35,36} Na_2SeSO_3 was prepared by the method reported by Bhuse et al. and used immediately.³⁷ As the penicillamine stabilising ligand is chiral it was used in both its enantiomeric forms, as well as the racemate. In order to obtain nanocrystals with a combination of high luminescence and strong optical activity the synthesis was initially optimised using a 2^2 factorial study, using quantum yield coupled with circular dichroism activity as the response.³⁸ A molar ratio of 1 : 1 : 1 Cd : Se : Pen was found to yield the most suitable particles.

The absorption spectra for each of the CdSe penicillamine samples are presented in Fig. 1(a). Local maxima of the absorption bands corresponding to the lowest-energy allowed exciton transition ($1S_{3/2}(h)-1S_{1/2}(e)$) for D-, L-, and rac-Pen stabilised CdSe QDs were observed at around 420 nm. Circular dichroism (CD) studies were carried out on all three samples and showed that D- and L-penicillamine stabilised particles possess corresponding mirror images of circular dichroism bands, while the particles prepared with a racemic (rac) mixture showed no CD response (Fig. 1(b)). It should be noted that the CD signal observed is quite different from that of the original free D- and L-penicillamine which shows, as expected, a near symmetrical image only in the far UV with the strongest dichroism signal at 234 ± 2 nm.¹⁰

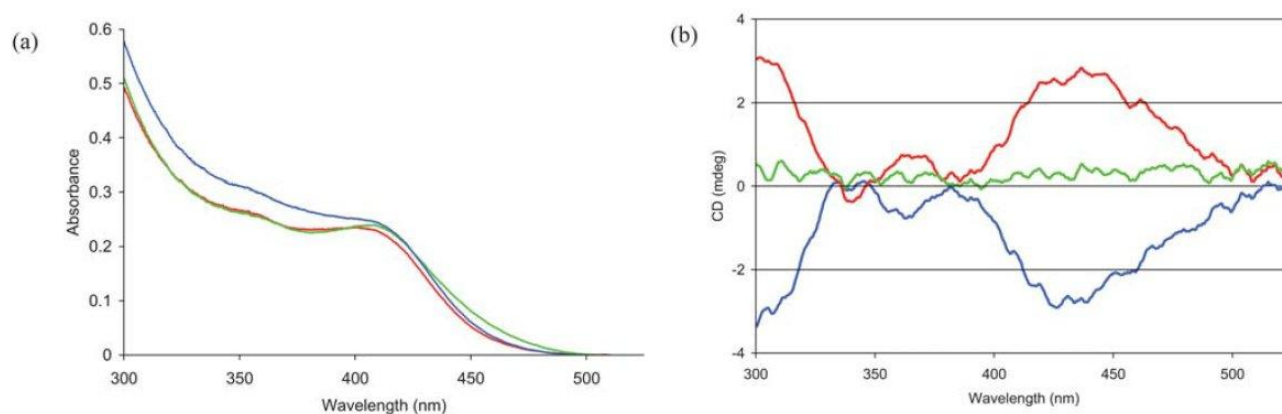


Fig. 1 (a) UV-Vis absorption spectra of D- (blue), L- (red), rac-Pen (green) stabilised CdSe nanoparticles and (b) CD spectra of D- (blue), L- (red) and rac-Pen (green) stabilised CdSe QDs. The spectra were smoothed using 11 points Savitzky–Golay method.

The emission spectra for all three types of dots were initially recorded using 420 nm as the excitation wavelength. The spectral distributions of photoluminescence (PL) in each case are very broad covering the region between 430 and 780 nm with maximum at 545 nm, 543 nm, and 553 nm, for D-, L- and rac-Pen stabilised CdSe QDs respectively, so that in all cases there is a very significant shift between the first absorption (or excitation) and emission band maxima (see Fig. 2). The PL quantum yields, measured against coumarin 153, are similar for all three samples (Table 1) and close to those already reported in the literature for water soluble CdSe particles.³⁹ All these facts are consistent with the emission originating from defect centres rather than being exciton-based. To probe the nature of this room temperature luminescence in more detail we have carried out a thorough steady state and time-resolved study as a function of both excitation and emission wavelengths.

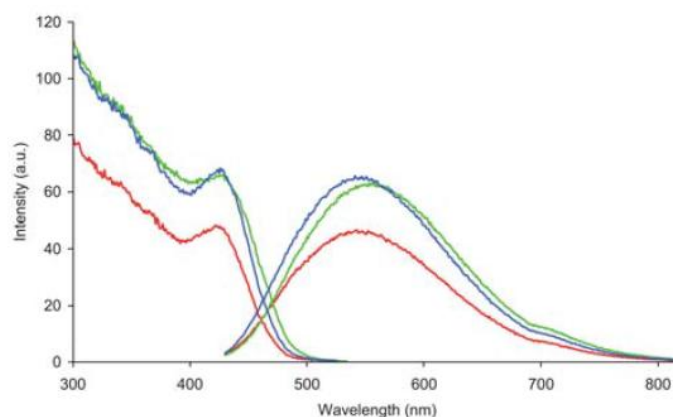


Fig. 2 Excitation and emission spectra of D- (blue), L- (red), rac-Pen (green) stabilised CdSe nanoparticles. Excitation wavelength for emission spectra is 420 nm. Excitation spectra were recorded at detection wavelength corresponding to the emission maximum.

The emission lifetimes of the three CdSe QD types were also examined using time correlated single photon counting (TCSPC) methods. In all cases the decay was non-exponential and triple exponential analysis was required to obtain satisfactory χ^2 values (generally between 0.9 and 1.1). It is possible that these decays are due to a distribution of lifetimes but this was not investigated in this work. Table 1 gives the resulting lifetime values obtained for the D-, L- and rac-Pen stabilised CdSe particles measured at the maximum of their respective emission bands using a 370 nm ‘‘Nanoled’’ as the excitation source.

Sample	QY (%)	B_1 (%)	τ_1 /ns	B_2 (%)	τ_2 /ns	B_3 (%)	τ_3 /ns
D-	6 ± 1	9	8 ± 1	39	41 ± 4	52	145 ± 3
L-	5 ± 1	8	9 ± 1	32	45 ± 5	61	162 ± 3
rac-	6 ± 1	7	10 ± 1	34	51 ± 5	59	161 ± 3

Table 1 Quantum yields and tri-exponential fitting parameters (lifetimes and relative contributions) for the fluorescence decays measured at the maximum of the PL bands using a 370 nm ‘‘Nanoled’’

Whereas the CD spectra of the three samples clearly show different chiral signals, the basic optical responses (PL and time-resolved PL) are all similar as expected, since the recorded PL data represents unpolarised emission. Therefore we subsequently focused our attention on the photoluminescence of enantiomeric L-Pen capped quantum dots. Firstly the photoluminescence decay curves of L-Pen capped CdSe were measured as a function of the emission wavelength in the spectral range from 450 nm to 770 nm (in 5 nm steps). In this experiment the acquisition was limited to 5000 counts at each particular wavelength, resulting in a map of normalized emission decay curves. Fig. 3(a) shows a contour plot constructed from such a map for L-Pen capped CdSe in aerated aqueous solution.

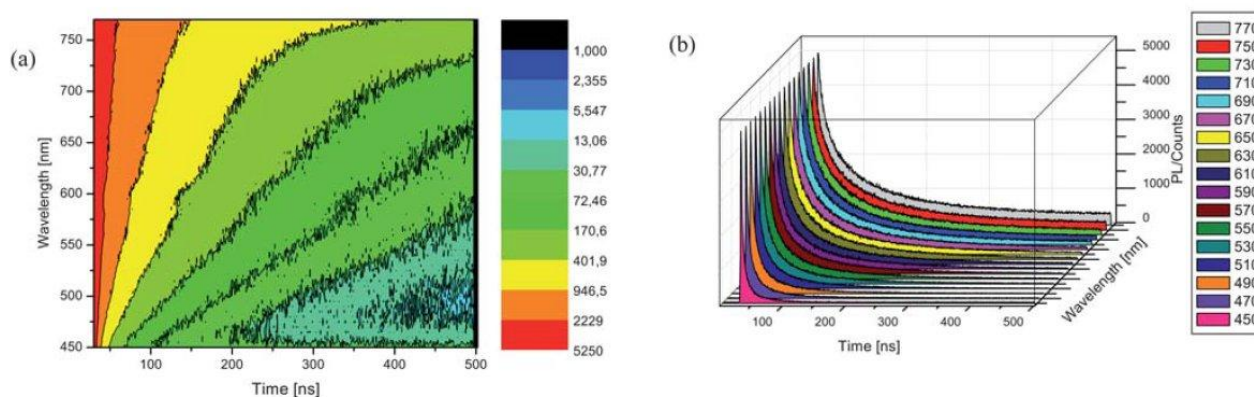


Fig. 3 (a) Contour plot constructed from the normalized emission decay curves of CdSe L-Pen measured at different wavelengths with 5 nm intervals (PL intensity scale is logarithmic) and (b) a plot of chosen decay curves excited with 295 nm ‘‘Nanoled’’.

The corresponding decay curves at chosen wavelengths (20 nm steps) are presented in Fig. 3(b). As an example, the results of triexponential analysis of the decay curves at 450 nm, 576 nm and 705 nm are presented in Table 2. It may be noted that at longer detection wavelengths both the proportion and lifetime of the longer lived species are increased, implying that the defects emitting at lower energy are more stable. As such longer-lived states might possibly be affected by oxygen, the PL lifetimes for L-Pen stabilised CdSe at these selected wavelengths were also determined for an argon purged sample (Table 2).

Aerated/nm	B_1 (%)	τ_1 /ns	B_2 (%)	τ_2 /ns	B_3 (%)	τ_3 /ns	Degassed/nm	B_1 (%)	τ_1 /ns	B_2 (%)	τ_2 /ns	B_3 (%)	τ_3 /ns
450	32	1.7 ± 0.3	42	9 ± 2	26	46 ± 4	450	30	2.0 ± 0.2	45	11 ± 2	25	45 ± 3
560	7	9 ± 1	32	44 ± 4	61	158 ± 4	560	8	9 ± 1	32	42 ± 3	60	161 ± 3
705	3	10 ± 2	21	52 ± 3	76	184 ± 5	705	4	9 ± 2	22	49 ± 3	74	187 ± 3

Table 2 The fitting parameters (lifetimes and relative contributions) obtained from a tri-exponential fit to PL decay data for aerated and argon degassed L-Pen capped CdSe measured at different emission wavelengths and excited with a 295 nm ‘‘Nanoled’’

These results show that there is no significant difference in lifetime values for aerated and argon purged samples indicating that quenching of excited states by oxygen has a negligible effect. The strong variation of the decay times with detection wavelength implies that emission spectra should shift to longer wavelengths with time and for this reason we have determined the time-resolved emission spectra (TRES) by slicing the emission TCSPC decay curves and setting an identical acquisition time for each wavelength measurement. The TRES for CdSe L-Pen capped quantum dots (at different times between 0 and 430 ns) are presented in Fig. 4 and reveal, as expected, that there is a shift of the emission band maximum from ca. 560 nm to 600 nm over this time range.

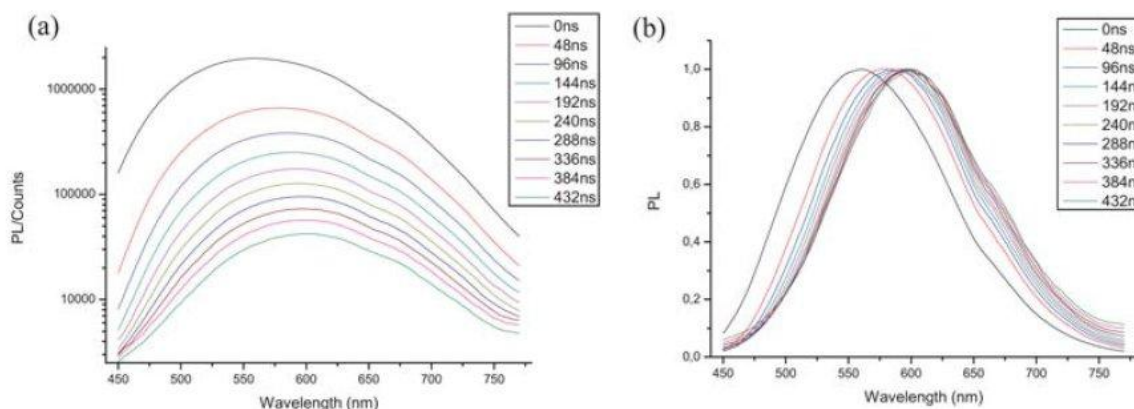


Fig. 4 Time resolved emission spectra of CdSe L-Pen obtained by PL kinetic traces slicing (using a moving time window (ca. 48 ns)) at delays given in the legend. (a) Cumulative log counts measured at constant acquisition time and (b) normalized to unity. The full width half maximum for these curves is decreasing from 580 (top curve) to 500 meV (bottom curve).

Given the strong dependence of the measured lifetimes of the excited states on the detection wavelength it was of interest to see whether the excitation wavelength had a similar strong effect. As will be discussed below, a strong excitation wavelength effect would be expected if the reason for the longer-lived nature of the long-wavelength emission was a major inhomogeneity of the sample. However, as may be seen in Table 3, the PL lifetimes at 450, 560 and 705 nm determined using different excitation sources 295 nm, 340 nm and 370 nm ‘‘Nanoleds’’ are closely similar in each case.

	B_1 (%)	τ_1 /ns	B_2 (%)	τ_2 /ns	B_3 (%)	τ_3 /ns
CdSe L-Pen@450 nm						
LED 295 nm	32	1.7 ± 0.3	42	9 ± 2	26	46 ± 4
LED 340 nm	31	1.4 ± 0.3	40	8 ± 2	29	40 ± 3
LED 370 nm	33	1.7 ± 0.3	40	10 ± 2	27	45 ± 4
CdSe L-Pen@560 nm						
LED 295 nm	7	9 ± 1	32	44 ± 4	61	158 ± 4
LED 340 nm	7	10 ± 2	30	44 ± 7	63	157 ± 5
LED 370 nm	8	9 ± 1	32	48 ± 5	61	162 ± 3
CdSe L-Pen@705 nm						
LED 295 nm	3	10 ± 2	21	52 ± 3	76	184 ± 5
LED 340 nm	2	8 ± 2	21	50 ± 4	77	189 ± 8
LED 370 nm	4	9 ± 2	25	52 ± 3	71	189 ± 5

Table 3 The fitting parameters (lifetimes and relative contributions) obtained as a result of a tri-exponential fit to PL decay data for L-Pen capped CdSe collected at 450, 560 and 705 nm from excitation at 295, 340 and 370 nm

Discussion

For the first time, it is shown that CdSe nanoparticles can be prepared which show strong circular dichroism in the visible and near UV spectral regions. These penicillamine-stabilised CdSe samples each show a maximum absorption in the region of 420 nm. This is consistent with the particles having a size of 4.2 nm (± 0.5 nm) and this has been confirmed by TEM analysis (Fig. 5). The CD spectra of the optically active samples prepared using the D- and L-enantiomers show a mirror-image relationship to each other. As expected the rac-stabilised particles give no CD signal (Fig. 1(b)). A key feature is that the CD signal originates already near 500 nm and is strongest in the region corresponding to the lowest-energy allowed exciton transition, close to the band edge of the nanoparticles. The general optical properties of these CdSe nanoparticles are similar to penicillamine stabilised CdS nanoparticles previously published by us,¹⁰ where theoretical DFT calculations showed that the chiral stabilising ligand binds to Cd and S on the particle surface in a chelating manner.¹¹ This distorts the crystal structure of the outer atoms, effectively creating a chiral shell around an achiral core. We propose that the same mechanism is in action here, yielding nanoparticles that have chiral defects on their surface, giving rise to the CD activity in the band edge region.

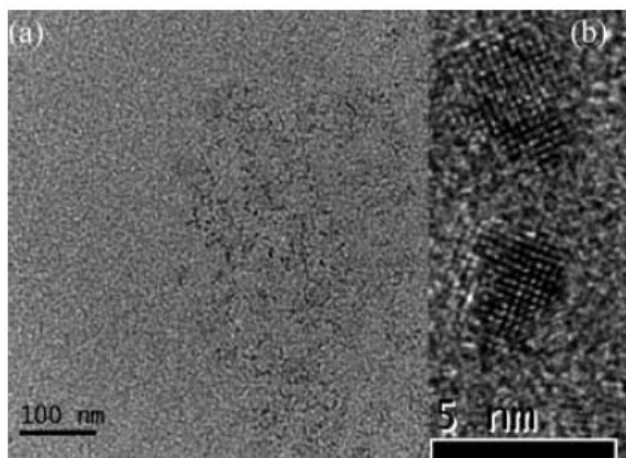


Fig. 5 (a) Transmission Electron Microscopy (TEM) and (b) High Resolution TEM of CdSe L-Pen capped QDs.

However, our CdSe particles are rather different from recently reported cysteine stabilised CdTe particles with atomic origin of chiral sites which are topologically similar to that in organic compounds.¹⁴ The CdSe nanoparticles all show photoluminescence, covering the region between 430 and 780 nm (Fig. 2). The lack of a significant emission band close to the absorption band-edge indicates that the exciton emission is quenched and we propose that the main contribution to the photoluminescence is due to defects or trapped states on the surfaces of the quantum dots. While in principle a broad emission could be caused by excitonic emission from a distribution of nanoparticles of varying size, we do not believe that this is the case here.

Generally, time resolved photoluminescence of quantum dots reveals various processes and the emission decay profile needs to be described using multiexponential distribution.⁴⁰ In the case of simple biexponential analysis it is assumed that each dot's emission lifetime is made up of two components^{41,42} and the shorter lifetime, τ_1 , is typically attributed to the intrinsic recombination of the initially populated core states.^{43–46} The origin of the longer component τ_2 , although long disputed, is now considered to be a result of the interference of surface states (i.e. the presence or absence of surface defects), with the recombination of the electron–hole pairs.^{47,48} However, in many cases higher order kinetics have been required to analyze decay traces.^{40,49} As bi-exponential analysis of emission decay curves gave unsatisfactory fits (due to unacceptable residuals and chisquared (χ^2) values) we used a tri-exponential decay model to determine the emission lifetimes of these particles (Table 1). As can be seen, the lifetime τ_1 , τ_2 and τ_3 values and the relative amplitude factors (B1, B2 and B3) are all quite similar for D-, Land rac-Pen CdSe. From the two plots Fig. 3(a) and (b), and Table 2, it is evident that both the lifetimes of the emitting excited states and the contribution of the long-lived component strongly depend on the emission wavelength i.e. the longer the emission wavelength the larger the lifetime values and the larger the contribution of the long-lived component. It may be noted, however, that these lifetimes do not depend on the excitation wavelength used, which is as expected if the particles are reasonably monodisperse. Although, as previously mentioned, the observed emission is mainly from defect states, there may be a very small excitonic contribution at the shortest wavelengths. Emission from either the band edge exciton (BEE) or the charged exciton (CE) could explain the observed Stark effect and multiexponential photoluminescence.⁵⁰ In addition, the presence of dark exciton states, which was suggested for other CdSe quantum dots, may also contribute to further complications in the emission decay profile as they may be involved in the energy transfer of dark excitons.⁵¹

Our time-resolved emission spectral study shows that, while the emission maximum shifts significantly over time to longer wavelengths, the overall shape and full width half maximum of these spectra change only slightly (580 meV between 0 and 48 ns to 500 meV between 430 and 478 ns). In particular even after a relatively long time (hundreds of nanoseconds) the emission is still very broad. Such a red-shift (see normalized PL spectra in Fig. 4(b)) and lifetime dependence on emission wavelength are consistent with there being many competing emissive states with different lifetimes. If we accept a single particle scenario i.e. that the observed PL dynamic and lifetime distribution are characteristic of all, or at least the majority, of nanocrystals in solution, then the population of lower lying traps becomes more significant over time due to relaxation processes (between emitting defect states). The other possibility is that the broad emission originates from the superposition of photoluminescence signals from many nanocrystals with different types of traps (and hence defect excited states). It would be perhaps be rather naive to believe that all the nanoparticles have identical emitting traps and therefore at this stage of the research we propose that both scenarios may be appropriate. It is worth remembering that in the case of excitonic emission the PL lifetime dependence on wavelength is usually explained in terms of QD size distribution,⁴⁹ or by the energy transfer of the dark exciton.⁵¹ However, in penicillamine stabilized CdSe, emission originates from surface traps and size distribution should not play an important role unless different types of traps are selectively associated with different sizes of nanoparticles. For example, the number of dislocations (which might produce extra states in the bandgap) may be greater for larger nanocrystals.⁵² Analysis of these nanoparticles though by TEM has shown them to have a very narrow size distribution of 4.3 ± 0.5 nm (Fig. 5). Thus, we finally assign the photoluminescence as arising from superposition of PL signals from different nanoparticles, all of which can have multiple and not necessarily the same emitting defect states. In order to address this question directly it will be necessary to carry out single particle fluorescence experiments.

Experimental

General procedures

$\text{Cd}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x \approx 6$), Na_2SO_3 (99%), Se (99.99%) and the stabilizers D-penicillamine (99%) and L-penicillamine (99%) were supplied by Aldrich. Millipore water was deoxygenated by boiling for one hour and then cooling to room temperature under argon.

UV-Vis absorption spectra were recorded at room temperature using a SHIMADZU UV2401 PC UV-Vis scanning spectrometer. Steady state photoluminescence spectra were recorded using Varian Cary Eclipse spectrofluorimeter working

in fluorescence mode. Fluorescence was detected at right angles to excitation. The photoluminescence lifetime and time resolved emission spectra measurements were performed using a time correlated single photon counting (TCSPC) spectrometer (Fluorolog 3 Horiba Jobin Yvon) and different semiconductor diode lasers (295 nm, 340 nm, and 370 nm “Nanoled”—HORIBA Jobin Yvon) with pulse duration shorter than 1 ns for excitation. Circular dichroism (CD) activity measurements were made on a JASCO J-810 CD/UV spectrometer. All samples were measured in a 1 cm quartz fluorescent cell with excitation and emission monochromator slits set to 5 nm unless otherwise stated.

Synthesis of CdSe QDs

The synthesis was initially optimised using a 2^2 factorial study, keeping the selenium concentration constant and varying the cadmium and penicillamine. From this, a molar ratio of 1 : 1 : 1 cadmium to selenium to penicillamine was found to be the most suitable. Thus, 2mL of an aqueous 1×10^{-2} M solution of D-, L- or rac-penicillamine were added to degassed Millipore water (40 mL) in a 100 mL flask, under a constant flow of Ar. The pH was adjusted to 11.5 by the dropwise addition of 1MNaOH. 1×10^{-2} Cd(ClO₄)₂·xH₂O (2 mL) and 1×10^{-2} M of Na₂SeSO₃ (2 mL) were then added and the solution was stirred vigorously. The resulting homogeneous solution was then transferred to a CEM Star System 6 microwave and irradiated for 40 seconds at 1500 W. The resulting clear, yellow, solution was then stored in the dark for at least one day. The volume of the colloid was then reduced to ~3mL 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 measurements were carried out on the stable suspensions in water.

Conclusions

In conclusion, for the first time, aqueous chiral CdSe quantum dots have been synthesised. The nanoparticles show a very broad distribution of photoluminescence and the above studies clearly show that the luminescence originates from emissive defect states. It is also apparent that there must be a range of states associated with each individual quantum dot, with the shift of the emission band to longer wavelengths at longer times after excitation suggesting traps of varying depth. If this is indeed the case then it is unlikely that the particles will show circularly polarised emission, but it is hoped to confirm this in future experiments. We also intend to carry out further photophysical measurements (and in particular transient absorption measurements) to better characterise the complex luminescence dynamics.

Acknowledgements

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