# Preparation of a novel CdS nanocluster material from a thiophenolate-capped CdS cluster by chemical removal of $SPh^-$ ligands

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Oxidation of the surface-capping $SPh^-$ ligands of the CdS cluster $[S_4Cd_{10}(SPh)_{16}]^{4-}$ in solution has been explored as a route to the synthesis of larger, well defined nanocrystals of CdS. Iodine was found to oxidise and remove the $SPh^-$ ligands and effect the growth of a CdS cluster with a sharp UV–VIS absorption peak at 371 nm. Electrospray mass spectra indicate that the first step in the transformation involves the loss of the four $[Cd(SPh)_4]$ units at the cluster corners. Characterisation by FTIR and UV–VIS spectroscopy and X-ray powder diffraction showed that the material consists of iodide-capped clusters of approximately 15 Å diameter. The isolated material redissolved in DMF where its emission spectrum showed a strong broad band at 510 nm.

Current research into semiconductor quantum dots is focused on their strongly size-dependent optical and electronic properties.[1] One of the key problems in their study is the development of methods that permit uniform clusters to be prepared. This is essential in order to distinguish properties which are truly inherent to the nanometre size from those associated with the variation in sample quality such as polydispersity in size and shape, and surface electronic defects due to uneven surface derivatization and poor crystallinity. Significant progress has been made in the controlled synthesis of group II–VI semiconductor crystallites.[2] One widely employed method is the use of kinetic trapping ligands, such as thiols, which cap the particle surface by direct coordination to surface atoms.[3–11] The process typically involves precipitation of the semiconductor material in the presence of the capping species,[3–7] or growth of larger clusters from molecular precursors which already incorporate the capping ligands.[8,9] One such precursor is the thiophenolate-capped CdS cluster ion $[S_4Cd_{10}(SPh)_{16}]^{4-}$ shown in Fig. 1.[10] Controlled aggregation of such clusters would seem to provide a route to well defined products. The addition of $S^{2-}$ to a solution of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ in dimethylformamide (DMF) has been reported to give a material with a sharp absorption maximum at 351 nm, which is blue-shifted from the bulk maximum, and evidence of a very small and well defined CdS cluster with quantum confinement.[8] The authors proposed the 55 atom cluster $[Cd_{20}S_{13}(SPh)_{22}]^{8-}$ as the structure. A further example is the fully characterised 15 Å CdS cluster $[S_{14}Cd_{32}(SPh)_{36}]\cdot 4DMF$ which was obtained from heat treatment of $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$.[9] The exact mechanisms of both these transformation processes are not known, but in each case they involve the removal of $SPh^-$ capping groups from the surface of the $[S_4Cd_{10}(SPh)_{16}]^{4-}$cluster. Here we report the results of a study on $[S_4Cd_{10}(SPh)_{16}]^{4-}$ where chemical removal of the $SPh^-$ caps by oxidation with iodine has been employed in an attempt to aggregate this precursor into larger cluster species.

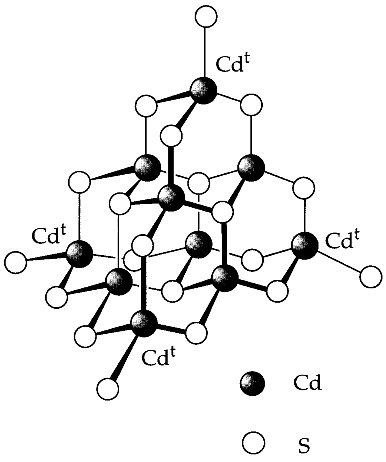

**Fig. 1** The structure of the $Cd_{10}S_{20}$ skeleton of $[S_4Cd_{10}(SPh)_{16}]^{4-}$. The four terminal $Cd^t$ atoms of the $[Cd^t(SPh)_4]$ units at the cluster corners are removed in the reaction with iodine.

## Experimental

### Synthesis

The cluster $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$ was prepared by the previously described method.[12] To a solution of this compound (0.50 g, 0.152 mmol) in acetonitrile (50 ml) at room temperature was added slowly elemental iodine (0.31 g, 1.21 mmol, 16 mol equiv.) in acetonitrile (16 ml). The iodine solution decolourised instantly on contact with the $[S_4Cd_{10}(SPh)_{16}]^{4-}$ solution. The reaction mixture remained clear and colourless after all the iodine was added. After 30 min a strong and sharp UV absorption peak with a maximum at 371 nm was observed. To monitor the above reaction, UV–VIS spectra and electrospray mass spectra were recorded of reaction mixtures with $I_2/[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$ mole ratios of 2, 4, 6 and 8. A 15 min delay was allowed after each of the four additions of iodine to the cluster solution before the spectra were recorded.

When left overnight the iodine-oxidised cluster solution precipitated some off-white fibrous precipitate. From a near-saturated solution of the precursor, ageing resulted in the formation of a transient gel. Isolation of the material by slow evaporation of the original solution resulted in some cases in aggregation to a bulk-like CdS material. Isolation was therefore carried out in one of the following ways. The iodine-oxidised cluster solution was spray-dried at room temperature and atmospheric pressure onto a glass plate. This caused drying within seconds, and the material was scraped off and washed with methanol, leaving a pale yellow powder (elemental analysis: C, 7.71; H, 1.09; N, 1.63; I, 35.24%). The following empirical formula was calculated based on the assumption that the elements analysed for are present as $SPh^-$ and $I^-$ capping ligands and $Me_4N^+$ counter-ions: $S_{2.7}Cd_{3.5}I_{2.5}(SPh)_{0.3}(Me_4N)$. The material obtained by this method was sparingly soluble in DMF. Alternatively, a solution of thiophenol (PhSH, 0.27 g, 2.43 mmol) and triethylamine ($Et_3N$, 0.24 g, 2.43 mmol) in acetonitrile was added with stirring (after observation of the absorption peak at 371 nm) to recap the surface of the new clusters with $SPh^-$ ligands. This resulted in clouding of the original solution. An off-white solid was then collected by evaporation of the solvent followed by washing with methanol and acetonitrile (elemental analysis: C, 29.71; H, 2.76; N, 1.27; I, 3.24%). The material obtained by this method was soluble in DMF and sparingly soluble in acetonitrile.

The complexes $[Cd_4(SPh)_{10}][Me_4N]_2$ and $[Cd_4(SPh)_6I_4][Me_4N]_2$ were prepared by the previously described methods.[12,13]

### Characterisation

FTIR spectra were obtained at 4 $cm^{-1}$ resolution with a Digilab FTS-60 spectrometer employing an FTS-60V vacuum optical bench with a mercury lamp IR source, a 6.25 µm Mylar film beam splitter and a pyroelectric triglycine sulfate (TGS) detector. The isolated materials were dried under vacuum and pressed into discs in powdered polyethylene. UV–VIS spectra were obtained with the Shimadzu UV-2101Pc model using a 10 mm quartz pathlength cell. Electrospray mass spectra were obtained with a VG Platform II mass spectrometer using an acetonitrile mobile phase. Samples of the reaction mixtures of $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$ and iodine were diluted in acetonitrile to a solution typically of approximate concentration 0.1 mmol $l^{-1}$. The diluted solution was injected into the spectrometer *via* a Rheodyne injector fitted with a 10 µl sample loop. A Thermo Separation Products SpectraSystem P1000 LC pump delivered the solution to the mass spectrometer source (60 °C) at a flow rate of 0.01 ml $min^{-1}$, and nitrogen was employed both as the drying and the nebulising gas. A low cone voltage of 5 V was used which gave minimal fragmentation of the 'parent' cluster ions. Confirmation of the species detected was aided by comparison of the observed and predicted isotope distribution patterns. Theoretical isotope distribution patterns were calculated using the ISOTOPE computer program.[14] X-Ray powder diffraction data were obtained with a Philips 1050 goniometer with a graphite monochromator and a proportional detector. The power generator was operated at 40 kV and 20 mA. Photoluminescence spectra were measured on a Hitachi F-2000 fluorescence spectrophotometer equipped with a 150 W xenon arc lamp light source and monochromators for both excitation and emission (grating 900 lines $mm^{-1}$). The sample was placed in a 10 mm quartz cell and the spectrum was collected at room temperature with 240 nm $min^{-1}$ scan speed.

## Results and Discussion

The $[S_4Cd_{10}(SPh)_{16}]^{4-}$ cluster consists of a supertetrahedral fragment of the cubic (sphalerite) CdS lattice terminated by twelve bridging and four terminal thiophenolate ligands (Fig. 1).[12] The $S_4Cd_6$ core unit has a diameter of *ca.* 7 Å. Previously it has been shown that the terminal ligands can be substituted by a halide by the reaction of stoichiometric amounts of either benzoyl chloride (PhCOCl), elemental bromine or iodine.[15] The substitution with, for example, iodide involves the reduction of iodine ($I_2$) to iodide ($I^-$) by the oxidation of thiophenolate ($SPh^-$) to diphenyldisulfide (PhSSPh):

$$[S_4Cd_{10}(SPh)_{16}]^{4-} + 2\ I_2 \rightarrow [S_4Cd_{10}(SPh)_{12}I_4]^{4-} + 2\ PhSSPh \qquad (1)$$

Further reaction with iodine was expected to cause oxidation of the bridging $SPh^-$ caps. Aggregation of cluster cores would then be enhanced owing to substitution of the bulky $SPh^-$ ligands with the much smaller and less strongly binding $I^-$ ligands. The change in the UV–VIS spectrum of the $[S_4Cd_{10}(SPh)_{16}]^{4-}$ cluster solution on stepwise titration with iodine is shown in Fig. 2. The absorption maximum for size-quantized semiconductor particles, corresponding to the excitation energy, is known to shift to shorter wavelengths with decreasing particle size owing to an increase in the HOMO–LUMO bandgap.[16] Bulk CdS has an absorption threshold at *ca.* 516 nm.[17] The starting cluster $[S_4Cd_{10}(SPh)_{16}]^{4-}$ has no absorption above 320 nm [Fig. 2(a)].[17] It is known that the lowest optical absorption of either bulk CdS or CdS clusters corresponds mainly to the transfer of an electron from a tetrahedral sulfur (HOMO or valence band) to cadmium atoms (LUMO or conduction band).[8] Thus, any aggregation of clusters leading to CdS species with tetrahedral sulfides was therefore expected to give a red shift of the absorption. For the reaction of 2 and 4 mol equiv. of $I_2$ with $[S_4Cd_{10}(SPh)_{16}]^{4-}$ a slight blue shift in the strong UV absorption edge at about 300 nm was observed. Assuming that substitution of $SPh^-$ with $I^-$ is occurring in analogy with reaction (1), these mixtures would contain the cluster species $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ and $[S_4Cd_{10}(SPh)_8I_8]^{4-}$, respectively. The UV spectra for these two solutions were very similar and only that of $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ is shown in Fig. 2(b). To aid the interpretation of the shift to shorter wavelengths we recorded the UV spectra of the complexes $[Cd_4(SPh)_{10}][Me_4N]_2$ and $[Cd_4(SPh)_6I_4][Me_4N]_2$, and of a mixture of $[Cd_4(SPh)_{10}][Me_4N]_2 + 5I_2$ [Fig. 2(e)–(g)]. The structure of $[Cd_4(SPh)_{10}]^{2-}$ consists of four fused $Cd(SPh)_4$ tetrahedra with six bridging and four terminal thiophenolate ligands. The structure also represents one of the four fused adamantanoid cages that comprise the $[S_4Cd_{10}(SPh)_{16}]^{4-}$ cluster. In $[Cd_4(SPh)_6I_4]^{2-}$ the terminal ligands have been replaced by iodide. The cadmium-containing species in the

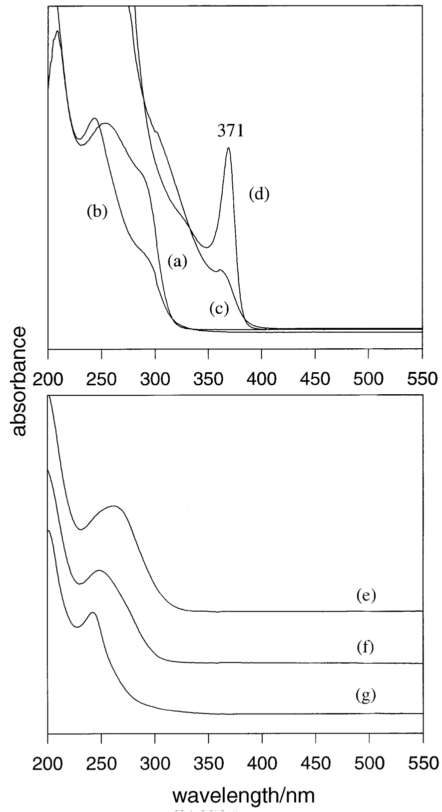

**Fig. 2** UV–VIS absorption spectra of (a) a solution of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ in acetonitrile and 15 min after reaction with (b) 4 mol equiv. of $I_2$, (c) 6 mol equiv. of $I_2$ and (d) 8 mol equiv. of $I_2$. Below: UV absorption spectra of (e) $[Cd_4(SPh)_{10}][Me_4N]_2$, (f) $[Cd_4(SPh)_6I_4][Me_4N]_2$ and (g) of a mixture of $[Cd_4(SPh)_{10}][Me_4N]_2$ + 5 $I_2$, in acetonitrile.

mixture of $[Cd_4(SPh)_{10}]^{2-}+5I_2$ has been shown by electrospray mass spectrometry to be predominantly $[CdI_3]^-$ ions (see text below). Compared with the spectrum of $[Cd_4(SPh)_{10}]^{2-}$ [Fig. 2(e)] the spectrum of $[Cd_4(SPh)_6I_4]^{2-}$ [Fig. 2(f)] shows a blue shift in the absorption peak from 264 nm to 250 nm. This shift can be attributed to a band due to Cd–I charge transfer which is observed at 242 nm in the spectrum of $[CdI_3]^-$, Fig. 2(g). The blue shift in the absorption of $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ is therefore consistent with absorption due to Cd–I charge transfer at 242 nm associated with the terminal $I^-$ ligands. Reaction of 6 mol equiv. of $I_2$, which corresponds to the removal of 12 of the 16 $SPh^-$ ligands on the cluster surface, is seen to result in a red shifted peak occurring at 360 nm [Fig. 2(c)].

Based on the fact that the position of the Cd–I charge transfer band in Fig. 2(b), (f), (g) did not appear to be very dependent on the Cd coordination environment and occurred well below 300 nm, we attribute this red shift to the occurrence of aggregation of clusters which are no longer sufficiently capped to remain separate. On complete removal of the $SPh^-$ caps from the cluster surface by the reaction of 8 mol equiv. of $I_2$ a strong and sharp peak developed at 371 nm [Fig. 2(d)]. This further red shift from 360 nm to 371 nm is consistent with the expectation that loss of the remaining $SPh^-$ caps would result in more unsaturated cadmium atoms with a tendency to coordinate to sulfides both inter- and intra-molecularly. This is likely to give an increase in the number of tetracoordinated Cd and S atoms, and thus, the formation of larger CdS species. The excitation peak at 371 nm is sharp and this is indicative of a uniform material consisting of small CdS clusters.[8,9] A correlation between crystallite size and absorption maxima for CdS particles has been given in the literature,[16] and using this the particle diameter was estimated to be *ca.* 15 Å.

The material was isolated in solid form either by rapid removal of the solvent by spray-drying, or by recapping with $SPh^-$. The far-IR spectra of the two solids are compared to those of the starting material $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$ and bulk wurtzite CdS in Fig. 3. Previously we have assigned the peak at 288 $cm^{-1}$ in the spectrum of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ to the $\nu(Cd-S)$ stretching frequencies of the internal Cd—S bonds of the cluster core.[18] The $\nu(Cd-S)$ stretching frequencies of the bridging and terminal $SPh^-$ ligands both occur in the region 150–175 $cm^{-1}$. The band at 417 $cm^{-1}$ is due to the $\nu(C-S)$ stretching mode of thiophenolate and the 477 $cm^{-1}$ band originates from a thiophenolate $\delta(SPh)$ bending mode. The position of the $\nu(Cd-S)$ core band maximum for CdS clusters has been observed to progressively shift (accompanied by band broadening) to the CdS bulk value of 241 $cm^{-1}$ for the transverse optical (TO) mode with increasing core size up to *ca.* 40 Å.[18] The spectrum of the spray-dried product [Fig. 3(c)] shows a $\nu(Cd-S)$ core band centred around 260 $cm^{-1}$. This band is stronger and broader than the $\nu(Cd-S)$ band at 288 $cm^{-1}$ in $[S_4Cd_{10}(SPh)_{16}]^{4-}$ which is consistent with a larger CdS core in the new cluster material. The thiophenolate bands in the region 400–500 $cm^{-1}$ are very weak, and this is in accord with the low $SPh^-$ content in the empirical formula $S_{2.7}Cd_{3.5}I_{2.5}(SPh)_{0.3}(Me_4N)$ calculated from the elemental analysis data. A new band appears at 140 $cm^{-1}$ and this position matches that of the $\nu(Cd-I)$ stretching frequency found for the terminal $I^-$ ligands of $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ and $[Cd_4(SPh)_6I_4]^{2-}$.[18] There is additional intensity at a slightly lower frequency, 120 $cm^{-1}$, and a possible assignment for this band is a $\nu(Cd-I)$ stretching mode of bridging iodide ions. This would be expected to occur at a lower frequency compared with the terminal stretches. The observation of these bands therefore suggests that the cluster surface is capped by $I^-$ ligands, and this is also consistent with the I analysis of 35.24 mass% or 25 mol%. The presence of $Me_4N^+$ counter-ions as indicated by the N analysis suggests that the cluster material is partly ionic.

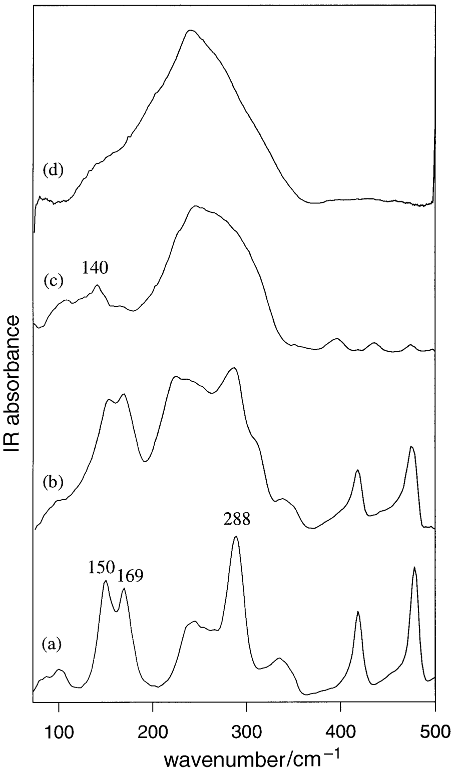

**Fig. 3** Low-frequency FTIR spectra of (a) $[S_4Cd_{10}(SPh)_{16}]^{4-}$, (b) the new iodine-oxidised cluster material recapped with $SPh^-$, (c) the new cluster material isolated by spray drying from the original solution and (d) bulk (wurtzite) CdS. The $\nu(Cd-S)$ stretching frequencies of the internal (Cd—S) bonds in $[S_4Cd_{10}(SPh)_{16}]^{4-}$ occur at 288 $cm^{-1}$. The new spray-dried cluster material shows a broad and strong $\nu(Cd-S)$ core band centred at *ca.* 260 $cm^{-1}$. The corresponding peak position in bulk CdS is 241 $cm^{-1}$.

The recapped cluster material also shows an intense $\nu(Cd-S)$ band at 260 $cm^{-1}$. In this case, however, an additional strong shoulder at 288 $cm^{-1}$ is present. This is the same as the wavenumber of a band in the spectrum of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ assigned to the $\nu(Cd-S)$ stretching frequencies of the Cd—S bonds of the core, and indicates that the material contains some CdS core units similar to that in $[S_4Cd_{10}(SPh)_{16}]^{4-}$. This mixture of bands is surprising as the $[S_4Cd_{10}(SPh)_{16}]^{4-}$ cluster is soluble in acetonitrile and would have been removed during the extensive washing employed. This fact discounts the possibility that the material consists of a mixture of CdS particles and $[S_4Cd_{10}(SPh)_{16}]^{4-}$clusters. Instead, it suggests that cluster species with the same core structure as in $[S_4Cd_{10}(SPh)_{16}]^{4-}$ are connected to the main cluster material. The absence of the shoulder peak at 288 $cm^{-1}$ in the spectrum of the spray-dried product shows that these connected cluster cores are caused by the addition of $SPh^-$. The amount of $SPh^-$ added to cap the new cluster material was equivalent to or greater than the amount required to completely regenerate $[S_4Cd_{10}(SPh)_{16}]^{4-}$. However, the only change in the absorption spectrum with the addition of $SPh^-$ was a 1 nm red-shift of the 371 nm peak, indicating little effect on the size and structure of the core of the new clusters. The occurrence of the 288 $cm^{-1}$ band in the IR spectrum, however, shows that some of the new material partially reverts to species which have the core structure of $[S_4Cd_{10}(SPh)_{16}]^{4-}$.

In Fig. 4 the X-ray powder diffraction pattern of the spray-dried product is compared with the patterns of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ and bulk (wurtzite) CdS. The new cluster material shows two peaks at $2\theta=(26\pm2)^\circ$ and $2\theta=(45\pm4)^\circ$ which match the positions of the crystalline CdS peaks in the bulk. The pattern for $[S_4Cd_{10}(SPh)_{16}]^{4-}$ is significantly different from both, which can be interpreted in terms of the small

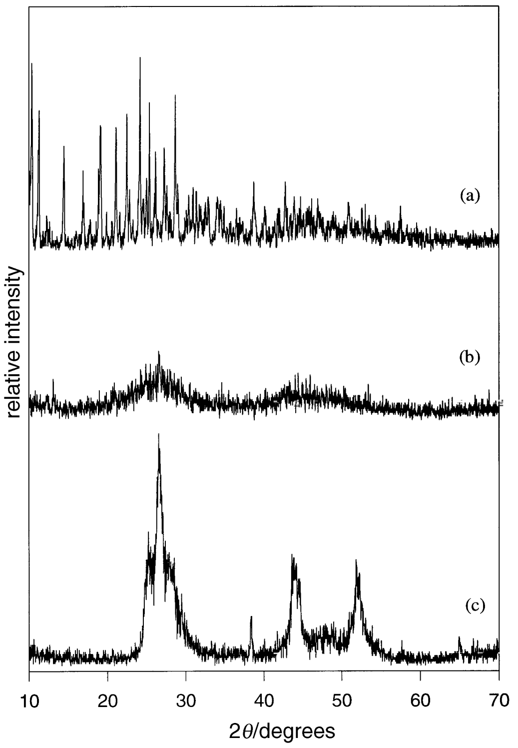

**Fig. 4** X-Ray powder diffraction patterns for (a) $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$, (b) the spray-dried cluster material and (c) bulk (wurtzite) CdS

cluster size and the fact that its CdS core structure only has tricoordinate sulfurs as opposed to tetrahedral coordination in bulk CdS. The observation of crystalline-like CdS peaks in our new cluster material is consistent with the tetracoordinated sulfurs in this cluster as shown in the far-IR spectrum. The large bandwidths and lower intensities compared to bulk CdS are supporting evidence of very small clusters. The bandwidths agree well with the patterns reported by Herron *et al.*[4] for thiophenolate-capped CdS clusters of less than 15 Å diameter and with that of a 12 Å diameter CdSe cluster reported by Murray *et al.*[3] The presence of species with the core unit of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ in the thiophenolate-recapped material was also observed in the X-ray powder diffraction pattern (not shown). The spectrum showed features of both spectrum (a) and (b) in Fig. 4.

The sharp UV–VIS peak at 371 nm is indicative of a well defined molecular CdS cluster core. The optical properties can therefore be assumed to be intrinsic of one cluster species, without ambiguities from size dispersion. On photoexcitation the material emits green light at about 510 nm (Fig. 5). The excitation spectrum shows absorption bands at 350 nm and 376 nm. There was no difference in these spectra for the original cluster solution in acetonitrile and for the solid redissolved in DMF. This indicates that the core structure of the new clusters remains intact in the solids and in DMF. The optical properties compare well with those of the $[S_{14}Cd_{32}(SPh)_{36}]\cdot 4DMF$ cluster with a CdS core of *ca.* 12 Å diameter.[9] A sharp absorption peak was observed at 358 nm for this cluster, and the excitation spectrum in tetrahydrofuran (THF) showed sharp absorptions at 313 nm and 366 nm. A broad emission band was centred at *ca.* 500 nm.

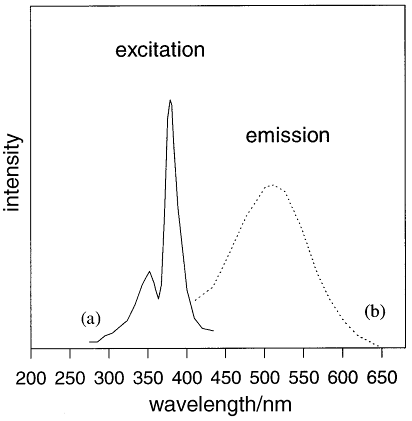

**Fig. 5** Photoluminescence spectra of the spray-dried cluster material in distilled DMF at room temperature: (a) excitation and (b) emission. The excitation wavelength for the emission spectrum was 320 nm. The monitoring wavelength for the excitation spectrum was 550 nm.

The exact nature and molecularity of the transformation is closely related to the role of iodine and the capping properties of $I^-$. Recently we have demonstrated that electrospray mass spectrometry (ESMS) is a powerful technique for the characterisation of thiometalate complexes and of thiolate-capped chalcogenide clusters,[19,20] including $[S_4Cd_{10}(SPh)_{16}]^{4-}$. This relatively new technique allows ions to be transferred from solution to the gas phase followed by conventional mass analysis. The electrospray ionisation process is soft and results in minimal fragmentation of the 'parent' cluster ions. Consequently, the observed species are likely to be representative of the actual species present in solution. Table 1 lists the species detected in the negative-ion electrospray mass spectrum (taken at a cone voltage of 5 V) of the reaction mixture corresponding to $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ [eqn. (1)]. The parent ion $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ is observed together with $[S_4Cd_{10}(SPh)_{12}I_3]^{3-}$, which is the more intense species formed from the parent ion by loss of $I^-$. The loss of $I^-$ from $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ is expected owing to the relative high charge density on the cluster. Loss of $I^-$ provides a route for loss of negative charge, the driving force for fragmentation. Peaks due to the fragment ions $[CdI_2(SPh)]^-$ and $[CdI_3]^-$ are weak and show that minimal fragmentation of the cluster is occurring at this low cone voltage. On further reaction with iodine, corresponding to the removal and substitution of 8 $SPh^-$ caps with 8 $I^-$ ligands, the peaks due to $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ and $[S_4Cd_{10}(SPh)_{12}I_3]^{3-}$ disappear. No new peaks are observed which can be assigned to $[S_4Cd_{10}(SPh)_8I_8]^{4-}$ or any other cluster species with $I^-$ ions substituted for $SPh^-$ in the bridging positions. This observation is consistent with electrospray mass spectra of the cadmium iodide complex $[Cd_4(SPh)_6I_4]^{2-}$ which shows no fragment ions which indicate that the $I^-$ ions are present as bridging ligands between cadmium atoms in these systems.[19] Bridging halide ligands are known to occur in the $[Cd_2X_6]^{2-}$

**Table 1** Anionic species observed in the ES mass spectra at a cone voltage of 5 V of $[S_4Cd_{10}(SPh)_{16}][Me_4N]_4$ after reaction with various amounts of iodine[a]

| | | mole ratio $I_2/[S_4Cd_{10}(SPh)_{16}]^{4-}$ | | | |
|---|---|---|---|---|---|
| | | 2 | 4 | 6 | 8 |
| ion | *m/z* | relative peak height (%) | | | |
| $I^-$ | 127 | 100 | 100 | 36 | 12 |
| $[CdI_2(SPh)]^-$ | 475 | 3 | 5 | 6 | 3 |
| $[CdI_3]^-$ | 493 | 5 | 38 | 100 | 100 |
| $[S_4Cd_{10}I_4(SPh)_{12}]^{4-}$ | 767 | 5 | — | — | — |
| $[S_4Cd_{10}I_3(SPh)_{12}]^{3-}$ | 981 | 37 | 1 | — | — |
| $[(Me_4N)S_4Cd_{10}I_4(SPh)_{12}]^{3-}$ | 1048 | 7 | 1 | — | — |
| $[(Me_4N)S_4Cd_{10}I_3(SPh)_{12}]^{2-}$ | 1508 | 6 | — | — | — |

[a] The observed *m/z* values are those of the most intense peak within the isotopic mass distribution for the species concerned. In all cases the observed isotopic mass distribution agreed well with the calculated pattern,[11] and the observed *m/z* agreed with that calculated for the most abundant species.

complexes.[21] Their absence from the species detected in the spectrum of $[Cd_4(SPh)_6I_4]^{2-}$ is therefore thought to be due to the presence of thiophenolate ions which are much stronger bridging ligands. While the $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ and $[S_4Cd_{10}(SPh)_{12}I_3]^{3-}$ cluster ions disappear from the spectrum the peak due to $[CdI_3]^-$ becomes more intense, and this ion becomes progressively more intense with the increase in the $I_2/[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ mole ratio to 6 and 8. This observation suggests that the four terminal cadmium atoms of the $CdI(SPh)_3$ cluster corners in $[S_4Cd_{10}(SPh)_{12}I_4]^{4-}$ are lost. This result is consistent with the substitution of the bridging $SPh^-$ ligands, which connect the terminal $Cd^t$ atoms to Cd atoms of the $S_4Cd_6$ core, with non-bridging $I^-$ ions (refer to the structure in Fig. 1). Removal of all the 16 $SPh^-$ caps on the cluster corresponds to the removal of all four cluster corners, leaving only the $S_4M_6$ core unit.

Assuming that all the four $Cd^t$ cadmium atoms are lost as $[CdI_3]^-$ , as indicated by the mass spectrum, one can write the complete oxidation reaction as:

$$[S_4Cd_{10}(SPh)_{16}]^{4-} + 8I_2 \rightarrow S_4Cd_6I_4 + 4[CdI_3]^- + 8PhSSPh \tag{2}$$

According to this equation each of the remaining $S_4Cd_6$ cluster cores may have four capping $I^-$ ligands and this may explain the fact that instant precipitation of macrocrystalline CdS does not occur at this stage. The ES mass spectra, however, taken in both negative and positive ion modes, do not show any peaks that can be attributed to this or any other $S_4Cd_6$ core species. The reason for this is most probably a low stability of the charged species. The subsequent aggregation of these species to larger uniform clusters which occur with ageing of the solution for 15–30 min, suggests that the aggregation process is controlled by iodide caps. The formation of a gel at high concentrations shows that the material can form a long-range network of chains of clusters. Thus, individual clusters are allowed to form cluster–cluster bonds, and a likely explanation for this is that the $I^-$ ligands offer limited steric protection.

## Conclusions

It has been shown that the oxidation and removal of the surface capping $SPh^-$ ligands of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ clusters in solution, aided by iodine, causes the controlled aggregation of cluster cores. The observation of a sharp UV–VIS absorption peak at 371 nm and the increased intensity and shift of the $\nu(Cd-S)$ frequency of the core in the direction of the value for bulk CdS reveal new electronic properties and Cd—S bonding with tetrahedral geometry. IR, X-ray and optical data imply that the aggregation process involves rehybridization of the $S_4Cd_6$ cores to form well defined nanoparticles of CdS of about 15 Å diameter. In the first step the terminal SPh ligands of $[S_4Cd_{10}(SPh)_{16}]^{4-}$ are substituted with iodide. Electrospray mass spectra indicate that the $I^-$ ions are poor bridging ligands between the Cd atoms, and that further substitution with iodide results in the cleavage of the four terminal Cd atoms of the $Cd(SPh)_4$ units of the cluster corners in the original cluster. The mechanism of aggregation of the remaining $S_4Cd_6$ cluster cores is not known, but capping iodide ions are expected to play a role in the controlled growth of uniform CdS crystallites.

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