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## ARTICLE

## Cl-capped CdSe nanocrystals via in-situ generation of chloride anions

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Halides cap and stabilize colloidal semiconductor nanocrystal (NCs) surfaces allowing for NCs surface interactions that may improve the performance of NC thin film devices such as photo-detectors and/or solar cells. Current ways to introduce halide anions as ligands on the surface of NCs produced by the hot injection method are based on post-synthetic treatments. In this work we explore the possibility to introduce Cl in the NC ligand shell in-situ during the NCs synthesis. With this aim, the effect of 1,2-dichloroethane (DCE) in the synthesis of CdSe rod-like NCs produced under different Cd/Se precursor molar ratios has been studied. We report on a double role of DCE depending on the Cd/Se precursor molar ratio (either under cadmium or selenium precursor excess). According to mass spectrometry (ESI-TOF) and nuclear magnetic resonance (<sup>1</sup>H-NMR), under Se precursor (Se dissolved in trioctylphosphine, TOP) excess conditions at 265°C ethane-1,2-diylbis(trioctylphosphonium)dichloride is released as by-product of the reaction between DCE and TOP. According to XPS studies chlorine gets incorporated into the CdSe ligand shell, promoting re-shaping of rod-like NCs into pyramidal-like ones. In contrast, under Cd precursor excess (CdO), DCE reacts with the Cd complex releasing chlorine-containing non-active species which do not trigger NCs re-shaping. The amount of incorporated chlorine in the ligand shell can thus be controlled by properly tuning the Cd/Se precursor molar ratio.

### Introduction

Colloidal semiconductor nanocrystals (NCs) show tunable and photostable luminescence properties along with broadband absorption and narrow emission, which makes them suitable for optoelectronic and photovoltaic applications.<sup>1,2</sup> For these purposes, high control over the synthetic procedure to obtain monodisperse, robust and highly emissive semiconductor NCs is required. The development of the hot-injection method<sup>3</sup> provides high control over size, shape, shape distribution and NCs surface composition for semiconductor materials such as CdSe,<sup>4,5</sup> PbSe<sup>6,7</sup> or PbS.<sup>8,9</sup> This method also allows fine control over the NCs growth, which is achieved by the use of long-alkyl chain surfactants acting both as metal complexing agents and ligands. These ligands form an insulating layer between NCs, restricting the charge transport between them and, as a consequence, devices containing such NCs (solar cells and photodetectors) may show low conversion efficiencies.<sup>10,11</sup> A less insulating ligand shell is obtained by the exchange of these long alkyl chain molecules for shorter ones, including thiols<sup>12,13</sup> or amines<sup>14,15,16</sup> in post-reaction treatments. The use of halides to perform ligand exchange reactions has recently been proposed.<sup>11,17,18,19</sup> Halide anions can be considered as the

shortest X-type (ionic) ligands, facilitating charge transport among NCs. The passivation role of halide anions in PbS systems has been reported<sup>11</sup> and other reports have evidenced the passivation effect of chlorine in CdSe NCs, highlighting the possibility of using halogenated molecules to efficiently displace both L (coordinative) and/or X type ligands.<sup>18,19</sup> Post-reaction treatments with chlorine-containing solutions seem to provide some benefits to certain colloidal NCs, such as more robust optical properties due to better passivation.<sup>20</sup> Furthermore, better performances of NCs-based solar cells have been achieved upon chlorine-based treatments of the NCs followed by thermal annealings.<sup>2</sup>

On the other hand, chloride anions are known to form complexes of Cd chalcogenides and thus, nucleation and growth kinetics can be manipulated by the use of halides.<sup>21</sup> Halides can be also used as etching agents, altering the initial shape of NCs.<sup>22,23,24</sup> The re-shaping of CdSe rod-like into pyramidal-like NCs is another example in which the presence of chlorine in the ligand shell also shows some benefits to promote interactions with graphitic surfaces, allowing for the fabrication of graphene-like-semiconductor NCs composites.<sup>25,26,27</sup>

In this work we have performed a systematic study on the size, shape and surface chlorine content of CdSe NCs synthesized from different Cd to Se precursor molar ratios in the presence of a chlorinated co-solvent (1,2-dichloroethane, DCE). Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) have been used as means to correlate the morphology and surface composition. Under Se precursor excess conditions, initial rod-like NCs modify their shape influenced by chloride anions, which result from the reaction between TOP and DCE at the synthesis temperature (265°C). These anions get incorporated in the NCs ligand shell and trigger the above mentioned re-shaping from rods to pyramids. The reaction between TOP and DCE has been evidenced by nuclear magnetic resonance (<sup>1</sup>H NMR) experiments and mass spectrometry (ESI-TOF). Density functional theory (DFT) calculations support the feasibility of the mechanism.

The incorporation of halogen anions as ligands during the NCs synthesis represents a versatility procedure, which may have advantages in solution processed optoelectronics.

## Experimental Section

**Materials.** Cadmium oxide (CdO, 99.998%) and octadecylphosphonic acid (ODPA, 97%) were purchased from Alfa Aesar and trioctylphosphine oxide (TOPO, 98%) from Merck. Aldrich supplied trioctylphosphine (TOP, 90%), toluene (99.5%) and methanol (99.8%). 1,2-dichloroethane (DCE, 99.5%) was purchased from Panreac. All these chemical reagents and solvents were used without further purification. XPS experiments were performed on NCs covering Highly Oriented Pyrolytic Graphite substrates (HOPG) ZYB quality, with a thickness of 2 mm purchased from NT-MDT.

**In-situ Chlorine incorporation in CdSe NC ligand shell. Synthesis from different Cd/Se precursor molar ratios.** CdSe NCs synthesis was performed following a variation of the method previously reported.<sup>28</sup> NCs obtained from a Cd/Se precursor molar ratio of 0.5 were prepared by stirring and heating (under nitrogen) 0.025 g ( $2 \cdot 10^{-4}$  mol) of CdO (cadmium precursor) and 0.20 g ( $6 \cdot 10^{-4}$  mol) of ODPA, using 2.9 g ( $8 \cdot 10^{-3}$  mol) of TOPO as reaction media. The solution turned clear at around 250°C, evidencing the Cd(ODPA)<sub>2</sub> complex formation. Afterwards the temperature was decreased to 80°C and 4 μL ( $5 \cdot 10^{-5}$  mol) of DCE were injected with a Hamilton glass microsyringe 701SN with an 11 cm needle to assure reaching the level of the solution. After the addition of the chlorinated source, the temperature was increased to 265°C, and 0.43 mL of Se dissolved in TOP (selenium precursor) (1M) ( $4 \cdot 10^{-4}$  mol) were injected for nucleation. For the growth regime, the temperature was kept at 255°C for 21h. After this time, the reaction was quenched by decreasing the temperature to 70°C and adding 3 mL of toluene. The preparation of NCs from different Cd/Se precursor molar ratios was carried out analogously but with different relative Cd, Se and chlorine precursor concentrations. In order to facilitate the Cd(ODPA)<sub>2</sub> complex formation, the ODPA/CdO molar ratio was fixed to 3 in all cases. Detailed information about the corresponding amounts can be found in Table S1 (see Supporting Information). As previously mentioned, CdSe NCs with chlorine on their surface are prone to decorate graphitic surfaces.<sup>25-27</sup> Thus, the CdSe synthetic reactions were carried out in the presence HOPG substrates (1 cm<sup>2</sup>) included in the pot.<sup>27</sup> This methodology guarantees the coverage of one single layer of NCs on the surface, which turns out to be essential to prevent charging effects during XPS measurements. Once the reaction was finished, CdSe NCs attached to the HOPG substrates were purified by washing the substrates in toluene baths. NCs not attached to the HOPG substrates were purified by

centrifugation/redispersion processes, using toluene as solvent and methanol as non-solvent. Finally, the purified NCs were redispersed in toluene and maintained in dark at 4°C. CdSe NCs were synthesized from Cd/Se precursor molar ratios of 4, 2, 1, 0.5 and 0.25 in the presence of DCE. Blank experiments were also carried out in the absence of DCE to discard the effect of the different Cd/Se molar ratio on the re-shaping of the NCs (images in Figure S2 in the Supporting Information).

### Chlorine incorporation to CdSe NCs ligand shell in two steps.

**Synthesis from CdSe rods.** Previously prepared and purified CdSe rods were used in all the cases as starting samples. They have been synthesized analogously to the one-step CdSe NCs in the absence of DCE. CdSe rods were purified by centrifugation/re-dispersion in toluene and methanol and kept in the dark at 4°C. The resulted CdSe rods show an average diameter of  $4.3 \pm 0.5$  nm, a length of  $11.8 \pm 1.3$  nm and an absorption maximum of 623 nm. To perform the chlorine incorporation reactions, 2 mL of the CdSe rods (optical density 1.12) were loaded with 2.9 g of TOPO under nitrogen atmosphere into a three-necked reaction flask and heated until 120°C. The mixture was stirred under vacuum at this temperature to completely eliminate the toluene. To add the required amount of DCE, the temperature was dropped until 80°C. Then, the mixture was heated until the TOP injection temperature (265°C) was reached. Aliquots were taken at 2h, 4h, 5.3h and 21 h to follow the re-shaping of the NCs with reaction time. Three reaction temperatures were studied namely, 80°C, 150°C and 265°C.

**Experiments for the chloride generation study.** To prevent oxidation of TOP, the direct mixing of DCE and TOP as well as the reaction at 265°C and the samples preparation for NMR and mass spectrometry experiments were carried out under nitrogen. In a three-necked flask coupled to a Schlenk line an equimolar mixture of DCE and TOP was stirred at room temperature for some minutes. Afterwards, a first aliquot was taken as a representative sample of the direct mixing of DCE and TOP at room temperature. A second aliquot was taken after keeping the temperature at 265°C for 21 hours. NMR samples were prepared using deuterated chloroform (CDCl<sub>3</sub>) as solvent. The NMR tubes, containing the precise concentration of CDCl<sub>3</sub> were purged and filled under nitrogen. <sup>1</sup>H NMR spectra were recorded on a Bruker AMS-300 MHz. <sup>1</sup>H NMR spectra were acquired with sufficient relaxation delay to allow complete relaxation between pulses. The samples for mass spectrometry were prepared analogously, using chloroform as mobile phase. Mass spectra data were acquired in an ESI-TOF (6224, Agilent) mass spectrometer equipped with a 1200 Agilent HPLC. The data were acquired in a mass range of m/z 110-3200.

**Characterization.** Absorption measurements were carried out in a Varian Spectrophotometer Cary 50. Photoluminescence spectra were recorded in a spectrofluorometer Horiba Jobin Yvon Fluoromax-4. Transmission electron microscopy (TEM) images were obtained in a JEOL 1010 microscope, operating with an acceleration voltage of 100 keV. Size distribution data were obtained by measuring the NCs sizes from TEM images. At least one hundred NCs were measured in each sample. XPS measurements have been performed using a monochromated Al-Kα source (hν = 1486 eV) and a PHOIBOS 150 electron energy analyzer. Spectra for Cd 3d, Se 3d, and P 2p were recorded using pass energy of 10 eV, whereas spectra for Cl 2p were recorded with 20 eV. Using these pass energies we obtained a FWHM for the Cd 3d<sup>5/2</sup> line of 1 eV and 1.3 eV, respectively. The binding energies were referenced to Cd 3d<sup>5/2</sup> at 405.2 eV. Charge neutralization was deemed to be unnecessary, since no movement of the Cd 3d<sup>5/2</sup> line with time has been detected. In order to evaluate the

feasibility of the reaction between TOP and DCE, DFT calculations had been performed using the ORCA software.<sup>29</sup> The simulations were performed using the hybrid functional B3LYP with the Ahlrichs TZV basis set.<sup>30</sup>

## Results and discussion

Pyramidal shaped CdSe NCs synthesized in the presence of the chlorinated precursor DCE can be interpreted as a fingerprint of the chlorine incorporation into the ligand shell.<sup>27</sup> To survey the correlation between Cd, Se and Cl precursors in the chlorine incorporation to the NC ligand shell, we developed a series of experiments in which the Cd/Se precursor molar ratios were varied from 4 (Cd precursor excess, CdO) to 0.25 (Se precursor excess, Se@TOP), as stated in Table S1 (see Supporting Information). Representative TEM images of CdSe samples obtained for Cd/Se precursor molar ratios of 2, 1 and 0.5 are depicted in Figure 1 along with size histograms both for the diameter and the length of the NCs.

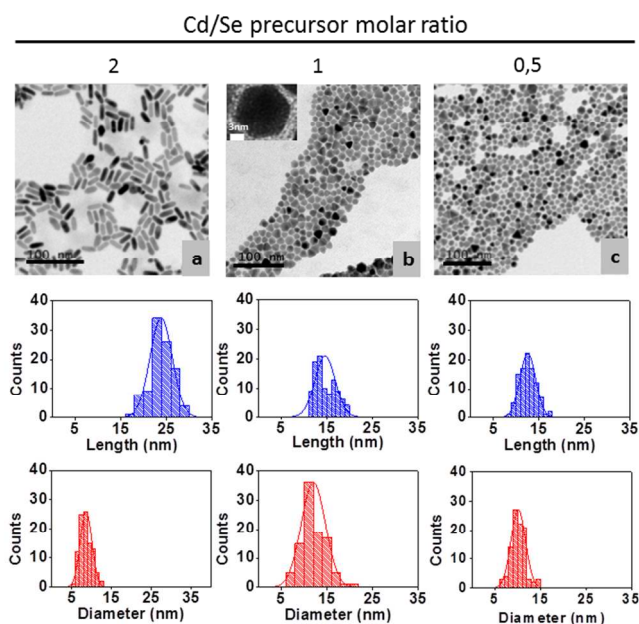


Figure 1: TEM images of CdSe NCs obtained after 21 hours of reaction from Cd/Se precursor molar ratios of 2, 1 and 0.5 in the presence of DCE. The inset in b shows a pyramidal NC in the [001] direction. The histograms correspond to the length (blue) and diameters (red) of the NCs.

When the NCs synthesis is carried out in the absence of DCE, the shape of the NCs is rod-like regardless the Cd/Se precursor molar ratio (see TEM images of the control experiments in Figure S2, Supporting Information). As it can be observed in the TEM images in Figure 1, for stoichiometric Cd/Se conditions or under Se precursor excess the addition of DCE during CdSe synthesis leads to a re-shaping from rods into pyramids. However, under Cd precursor excess the addition of DCE does not trigger the re-shaping. Thus, the incorporation of chlorine might be driven by a chlorine-containing specie (different from the precursor, DCE) which must be generated in-situ under certain reaction conditions, in which the Cd/Se precursor molar ratio might play a crucial role. In order to quantify the effect of DCE in the shape evolution, the size of rod-like and pyramidal NCs has been measured for the samples

shown in Figure 1. As clearly seen in the histograms, the morphological anisotropy observed for samples obtained under Cd precursor excess conditions (Figure 1 a) turns into a more isotropic shape for samples with stoichiometric Cd/Se ratios or Se precursor excess (Figure 1 b, c). Aspect ratios around 3 are observed for rods and close to 1 for pyramids. The width of the size distribution of the NCs does not exceed 10% of the mean radius for Cd/Se precursor molar ratios ranging from 2 to 0.5. The synthesis with molar ratios out of this range yields either bigger NCs and/or highly polydispersed ones (i.e. NCs obtained from Cd/Se precursor molar ratios of 4 and 0.25, images not shown). We attribute such polydispersity to the large difference between Cd and Se precursor concentrations, which might enable a high monomer saturation regime during nucleation and first growth stages, promoting further severe Ostwald ripening.<sup>28</sup> However, the Cl incorporation can be controlled so as to obtain smaller and highly monodisperse NCs, as it will be demonstrated below.

In order to obtain quantitative surface composition information and to investigate the integration of Cl in the ligand shell XPS analyses have been performed. Since the 2p P and 2p Cl XPS peaks are related exclusively to the NCs ligand shell,<sup>27</sup> we calculated the normalized areas Cl/Cd and P/Cd, between elements comprising the ligand shell (Cl or P) and a component of the NC core (Cd). Figure 2 shows the XPS Cl/Cd and P/Cd normalized areas plotted as a function of the Cd/Se precursor molar ratio in the synthesis. The numeric data concerning the normalized areas studied for each sample are gathered in Table S3, where the Se/Cd and the Cl/P normalized areas have also been included (Supporting Information). It is worth noting that these ratios do not correspond to quantitative concentration values of elements present in the samples but qualitative amounts of different elements composing the shell relative to a given amount of Cd.

As it can be observed in Figure 2, the Cl/Cd and P/Cd XPS normalized areas show noticeable variations as a function of the Cd/Se precursor molar ratio. For low Cd/Se values (Cd/Se < 1), low P/Cd and high Cl/Cd values are observed. This trend is the opposite for high Cd/Se values (Cd/Se > 1). In a previous work we proposed that the ligand shell of rod-like CdSe NCs is composed of octadecylphosphonic acid (ODPA) related species (both double deprotonated octadecylphosphonic acid and its anhydrides) whereas the incorporation of chlorine as ligand entails the substitution of ODPA anhydrides and further reshaping of the initial rods.<sup>27</sup>

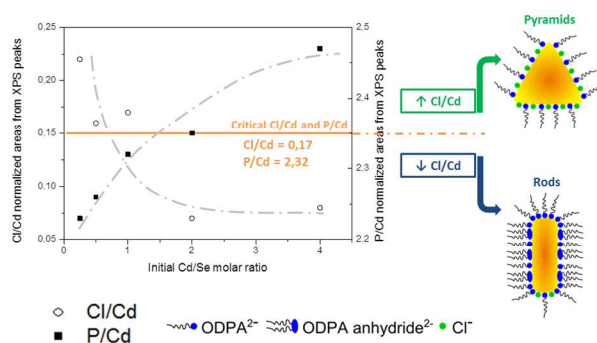


Figure 2: Cl/Cd (circles) and P/Cd (dark squares) normalized areas calculated from XPS data and plotted versus the Cd/Se precursor molar ratios. The horizontal continuous line indicates the minimum Cl value to promote the re-shaping of rod-like to pyramidal-like NCs. The discontinuous curved lines are only a guide for the eye. The experimental error associated to the relative peak areas is around 10%.

The fact that the Cl/Cd and P/Cd ratios follow opposite trends as a function of the Cd/Se precursor molar ratio supports this mechanism. Based on these results, we observe that the minimum NC chlorine content (as Cl/Cd) necessary to perform the re-shaping from rods to pyramids is around 0.17. The fact that as the Cd/Se precursor molar ratio decreases (1 to 0.25), the Cl/Cd ratio obtained from the XPS data increases (0.17 to 0.22) indicates a more effective Cl incorporation in the ligand shell under Se precursor excess conditions. A tentative ligand distribution has been represented in the schemes of Figure 2. Our results indicate that while an excess of Cd precursor does not favour the incorporation of Cl in the ligand shell, the excess of Se precursor does, pointing to different pathways of DCE during the reaction depending on the Cd/Se precursor molar ratio. CdSe NCs synthesized under initial Cd excess conditions are rod-shaped even with the addition of relatively large DCE amounts (see Table S1).

This can be rationalized assuming a reaction between the excess of the Cd complex ( $\text{Cd}(\text{ODPA})_2$ ) and the chlorinated precursor, releasing by-products such as  $\text{CdCl}_2$ , that may modify both nucleation and/or growth processes.<sup>21,22,24,31</sup> These chlorinated species however, do not trigger a shape modification of the NCs (see Figure 1). The reactivity between the Cd-ODPA complex and chlorine is furthermore proved by a series of experiments in which DCE/CdO molar ratios exceeding 1.3 lead to Cd precursor unable to react with Se@TOP. This result evidences the ability of DCE to displace ODPA ligands from the Cd complex, what may also lead to partial substitution of ODPA in the complex (i.e. Cl-Cd-ODPA). Therefore, in Cd precursor excess conditions, the Cd complex might mainly have evolved to  $\text{CdCl}_2$  (not triggering the re-shaping), although a small amount may form Cl-Cd-ODPA complexes. The NCs obtained from the latter complexes are expected to have both ODPA related species and a small amount of Cl in the ligand shell. This could be the case of the slight amount of chlorine content found in rod-like CdSe NCs synthesized from Cd/Se precursor molar ratios of 2 and 4 (See ligand distribution schemes in Figure 2 and numeric data in Table S3, Supporting Information).

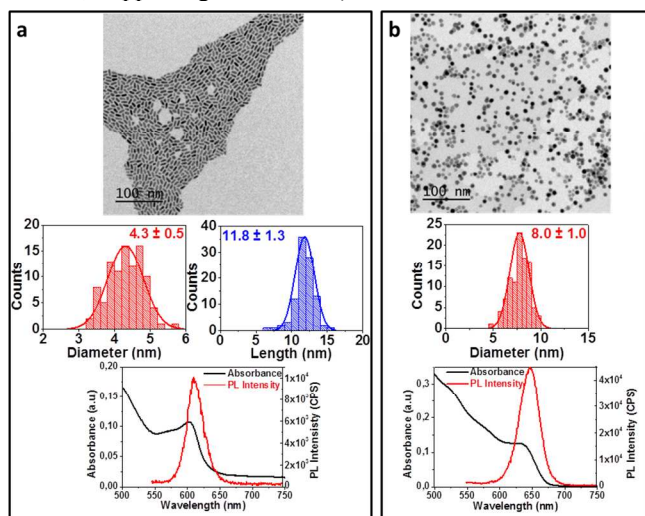


Figure 3: Chlorine incorporation in two steps: TEM images, size distribution data and optical measurements of the initial toluene dispersed rod-like CdSe NCs (a) and the pyramidal-like CdSe ones (b) resulted after 2h hours of reaction with a DCE/TOP molar ratio of 0.06 at 265°C.

In contrast to Cd precursor excess conditions, the incorporation of Cl in the ligand shell under Se precursor excess is clearly

favoured. We performed a series of blank experiments to conclude that the reaction between TOP (or TOP@Se) and DCE is responsible for the incorporation of Cl on the NCs ligand shell, triggering the re-shaping of the NCs. As a result of this knowledge, controlled incorporation of chlorine in the ligand shell of CdSe NCs can be obtained at will, either in-situ or in a two-step process by post-treatments of previously synthesized NCs (see experimental section).

A representative sample is shown in Figure 3 where previously synthesized rod-like CdSe NCs have been used to carry out systematic experiments. This two-step synthesis was designed with the double aim of obtaining smaller and highly monodisperse chlorine-containing CdSe NCs and to confirm the possibility to perform the chlorine incorporation over previously synthesized CdSe NCs. Figure 3a corresponds to the initial 4.3 nm rod-like CdSe NCs used as starting material and Figure 3b depicts the TEM images of the CdSe NCs obtained after mixing the starting rod-like CdSe NCs with DCE and TOP (see Experimental Section). As evidenced by the images (Figure 3b), this procedure leads to quasi-monodispersed pyramidal shaped CdSe NCs after 2 hours of reaction. Longer reaction times did not produce observable differences in shape, size or size distribution (images not shown). However DCE/TOP molar ratios higher than 0.29 point to a severe etching effect (dissolution of NCs after 30 minutes of reaction), driven by a higher concentration of the generated chloride anions, which should be eventually responsible for the NCs dissolution. The absorption and emission properties of the initial rods and pyramids obtained by the two-step procedure are depicted in Figure 3. An expected red shift is observable for pyramids due to bigger sizes (see histogram). Furthermore, an increase in the photoluminescence (PL) intensity is apparent for pyramids compared to rods. Several works have reported on the PL increase upon passivation with chlorine.<sup>19, 20, 23</sup> In the here reported case, since the two-step method includes a new synthetic procedure in extra TOP and TOPO (known to contain phosphonic-acid impurities), the PL increase may also be related to a better passivation due to phosphonic impurities and not to the presence of chloride on the surface. Thus, the PL intensities of rods and pyramids are not directly comparable. This topic will be the focus of further research.

In order to follow the reaction and to understand the influence of this combination during the NCs synthesis, Nuclear Magnetic Resonance ( $^1\text{H}$  NMR) and Mass Spectrometry (ESI-TOF) have been employed to analyse the reactivity between TOP and DCE at RT and at the synthetic temperature condition, 265°C. Upon mixing DCE and TOP at RT no appreciable physical change was observed. However, during the cooling step from 265°C, a high increase of viscosity of the reaction mixture was evident below 80°C, suggesting the formation of new products. The  $^1\text{H}$  NMR spectra of the initial mixture DCE/TOP (top) and the resulted reaction product after treatment at 265°C (bottom) are shown in Figure 4a. The peaks observed in Figure 4a (top) are the ones characterizing the individual unreacted species. A sharp singlet peak is observed at around 3.7 ppm, which is assigned to the protons in the methylene groups of DCE. A series of multiplet peaks with different intensities can be observed in the range between 0.9 and 1.4 ppm, which are assigned to the protons in the alkyl chains. The peak at around 0.9 ppm is in agreement with the chemical shift of methyl groups, while the peak at around 1.3 is related to the protons in methylene groups corresponding to  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$  and  $\text{C}_7$ . The small shoulder at around 1.4 ppm has been assigned to the protons situated in  $\text{C}_1$  and  $\text{C}_2$  in TOP, since they

might be more deshielded by P. The smaller peaks between 1,5 and 1,7 ppm are in agreement with protons  $C_1$  and  $C_2$  in the alkyl chains in TOPO. Thus, we cannot discard a slight oxidation of TOP into TOPO during the reaction due to impurities in DCE or even during the analysis procedure. Besides that, all these peaks correspond to the individual species, DCE and TOP, discarding any reaction at room temperature. The comparison with the  $^1\text{H}$  NMR spectrum obtained at 265°C indicates that the main difference is the absence of the peak assigned to DCE. On the other hand, the series of peaks observed between 0.9 and 1.7 do not allow us to establish a clear identification of the reaction product beyond that it might have a similar structure than trioctylphosphines.

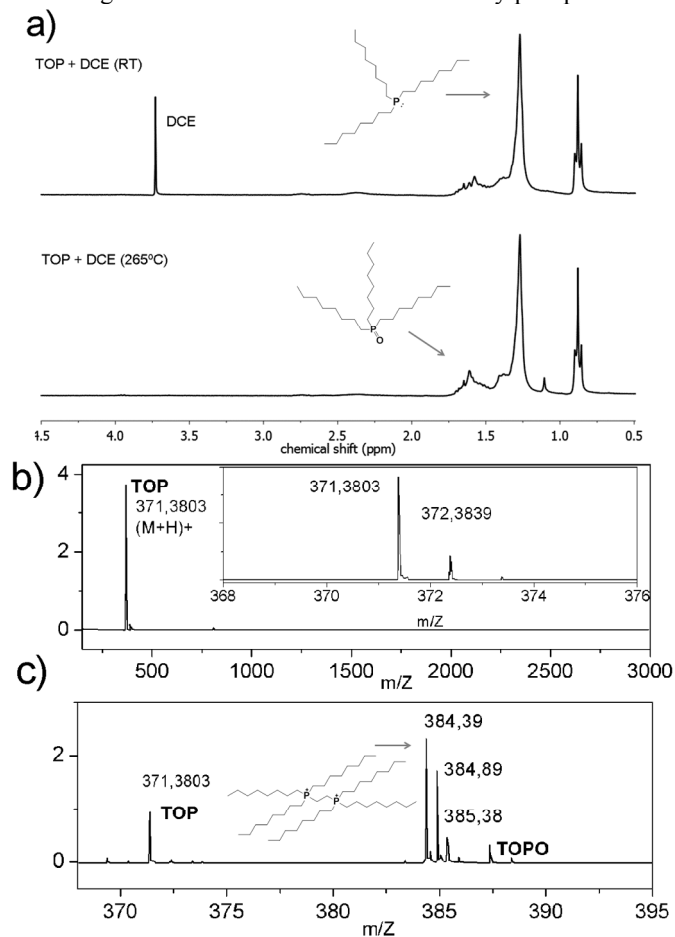
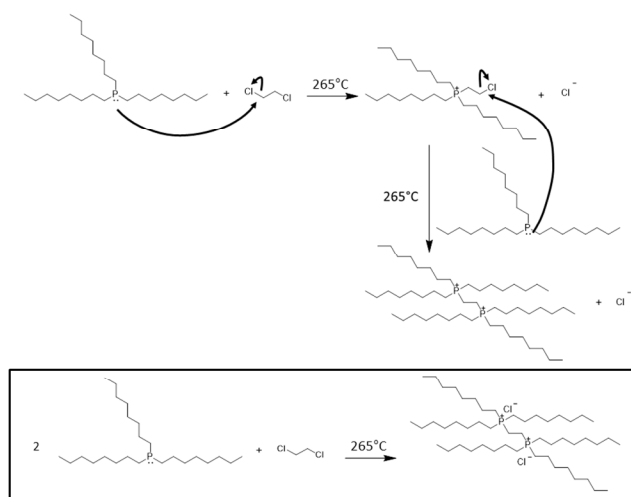


Figure 4: (a)  $^1\text{H}$  NMR spectra of the direct mixing (under nitrogen) of DCE and TOP (top) and the product obtained after reaction at 265°C (bottom). (b) ESI-TOF mass spectrum of TOP, demonstrating no relevant impurities. The inset shows a smaller spectral range where the  $(M+1)^+$  and its correspondent isotopes are observed. (c) ESI-TOF mass spectrum of the product obtained from the reaction between DCE and TOP at 265°C, ethane-1,2-diylbis(trioctylphosphonium)dichloride.

The chemical shift observed at 1.1 ppm could be attributed to protons situated close to chlorine and oxygen atoms.

In order to better investigate the reaction between TOP and DCE at high temperature, we have performed ESI-TOF mass spectrometry analysis of the reaction product. The ESI-TOF spectrum of TOP (Figure 4b) evidences the absence of significant impurities, indicating that the main reaction products should proceed from the reaction between TOP and/or TOPO and DCE. Figure 4c shows the ESI-TOF spectrum of the reaction product. The main peak dominating the spectrum is situated at  $m/z$  384.39. This peak can be unambiguously attributed to ethane-1,2-diylbis(trioctylphosphonium)dichloride. This assignment is also supported by the fact that the  $M+1$  and  $M+2$  peaks of ethane-1,2-diylbis(trioctylphosphonium)dichloride are separated by a difference of 0.5, according to a doubly charged product (a zoomed spectrum can be found in the supporting information, Figure S3). The intensity relations correspond to the abundance of the carbon isotopes. The peaks at 371.38 and 387.37 are assigned to TOP and TOPO, respectively, and correspond to the singly charged species which have peaks of  $M+1$  and  $M+2$  separated by a difference of 1. The presence of unreacted TOP and a slight amount of TOPO is also supported by  $^1\text{H}$  NMR. The peak in the ESI-TOF spectrum ( $m/z = 384.39$ , Figure 4c), together with the disappearance of the DCE peak after mixing with TOP at high temperature (Figure 4a) evidences the ethane-1,2-diylbis(trioctylphosphonium)dichloride generation. This reaction may occur through a substitutional mechanism, as depicted in Scheme 1. It is clear that the proposed reaction mechanism in Scheme 1 only occurs at relative high temperatures, since the simple mixing of TOP and DCE at RT do not produce any  $^1\text{H}$  NMR peaks different from the ones characterizing the individual species. In order to support the proposed mechanism of reaction between DCE and TOP we employed DFT simulations (B3LYP/TZV). For that, we calculated the enthalpy for the reaction shown in Scheme 1 by subtracting the calculated enthalpy of formation of the products from the ones of the initial reagents. Two molecules of TOP react with one of DCE to form ethane-1,2-diylbis(trioctylphosphonium)dichloride. This results in a reaction enthalpy of -0,88 eV indicating the feasibility of the mentioned reaction.



Scheme 1: Proposed mechanism for the chloride anions generation as by-products of the reaction between DCE and TOP at 265°C.

According to the literature chloride anion generation could be achieved either by chemical or photochemical routes. Anderson and Owen have reported the possibility of exchange carboxylate ligands with chloride ligands in CdSe NCs by mixing them with chlorotrimethylsilane in  $\text{Bu}_3\text{P}$  solution at RT.<sup>19</sup> In a recent paper by Lim et al.<sup>23</sup> the generation of chloride anions is suggested as the main driven force for the anisotropic etching of phosphonic capped CdSe NCs, which is in accordance with our results. However, they did not observe pyramidal shapes, which might be due to the short reaction time in their case. These two works reports on the generation of chloride anions at room temperature. However, as proved in Figure 4, only at high temperatures the rupture of DCE molecule is apparent. The role of other halogen-containing sources (i.e., bromine, iodine) on the shape evolution of the NCs has been also recently reported.<sup>32</sup>

## Conclusions

The addition of a chlorinated solvent (DCE) in the synthesis of CdSe NCs produces different NCs size and shapes depending on the Cd/Se precursors concentration. While NCs produced under Cd precursor excess conditions show rod-like shape and a comparatively low amount of Cl on their surface, NCs produced under Se precursor excess conditions modify their shape from rods to pyramids containing higher amounts of the halogen on their surface. This effect is produced by the presence of chloride anions, released in-situ upon reaction between TOP and DCE at 265°C. We propose that this reaction proceeds through the formation of ethane-1,2-diylbis(triethylphosphonium)dichloride as by-product. The chloride anions generation in-situ allows high versatility to incorporate halogen anions as ligands to a wide range of samples, which may have advantages in solution processed optoelectronics.

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## Notes and references

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Electronic Supplementary Information (ESI) available: Table S1 shows the molar amounts of precursor used to prepare CdSe NCs from different Cd/Se precursor molar ratios. Figure S2 shows TEM images of the control experiments. These consist on the synthesis of CdSe NCs from Cd/Se precursor molar ratios of 4, 2, 1, 0.5 and 0.25 in the absence of DCE. Table S3 shows the relative XPS peak areas of CdSe samples synthesized from different Cd/Se precursor molar ratios.. See DOI: 10.1039/b000000x/

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