Supporting Information

Inorganically Coated Colloidal Quantum Dots in Polar Solvents by Microemulsion-Assisted Method

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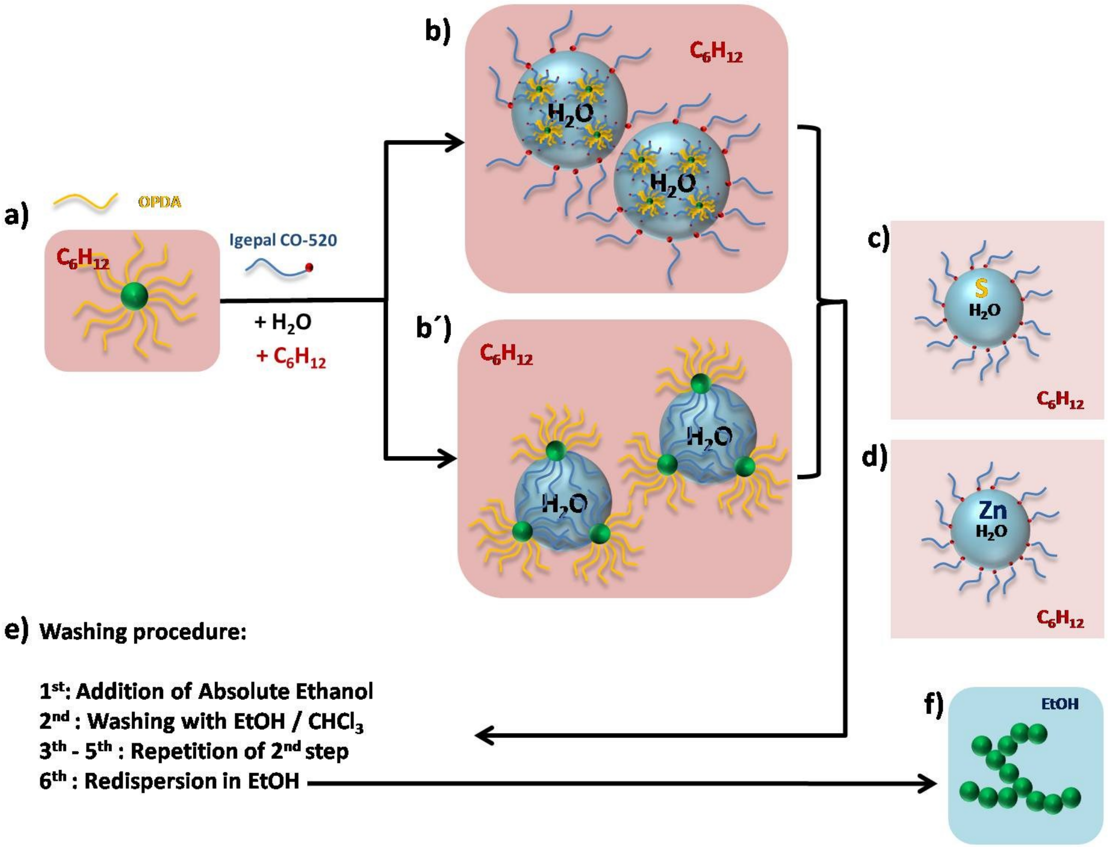
Figure S1: Sketch of the followed experimental procedure and suggested mechanisms for the NC transferring to the water micelle



e) Washing procedure:

1st: Addition of Absolute Ethanol
2nd : Washing with EtOH / $CHCl_3$
3th - 5th : Repetition of 2nd step
6th : Redispersion in EtOH

Figure S1. Sketch of the methodology that combines SILAR with water-in-oil microemulsions. CdSe NCs produced by hot injection (a) are included in a microemulsion (b and b´), where different S (c) and Zn precursors (d) are added as microemulsions and after washing procedure (e) the NCs are redispersed in Ethanol (f).

In figure S1 a sketch of the experimental procedure is represented. The initial ODPA-capped CdSe NCs dissolved in cyclohexane (a) were transferred to the microemulsion by addition of Igepal CO-520, water and cyclohexane. Despite of the fact that we do not have experimental evidences about how the hydrophobic NCs are transferred to the microemulsion, there are two main scenarios which can be considered: A ligand exchange process or the NCs insertion in the water phase thanks to the tail-to-tail intercalation of the NCs capping layer and the surfactant. In this latter case, the polar head of Igepal creates a water layer surrounding the NCs and providing the NCs transfer to the water drops.

We suggest either a partial anchoring of the ligand to the NC surface providing solubility in polar media (route b) or the intercalation of the aliphatic chains of the original hydrophobic ligands with the alkyl chains of the surfactant, allowing the NCs transfer to the water drops (route b`). The S and Zn precursor were added as microemulsions prepared maintaining the ratio water/igepal/cyclohexane constant.

We firstly added the calculated amount of S microemulsion and stirred the samples for 48 hours (c). Later, the calculated amount of Zn microemulsion was added and the mixture stirred again for 48 hours (d). After this time, the washing procedure was performed (e).
To break the microemulsion absolute ethanol was added doubling at least the microemulsion volume. This mixture was sonicated and centrifuged (9000 RPM, 20 minutes) producing the NCs precipitation. This precipitate was redispersed in 5 ml of ethanol and further 5 ml of chloroform were added. This mixture was sonicated and centrifuged again (9000 RPM, 30 minutes). This last step was repeated three times more to ensure the NCs washing. Finally, the washed NCs were redispersed in polar solvents (f).

Figure S2: Low-Resolution Transmission Electron Microscopy (TEM) images of treated NCs

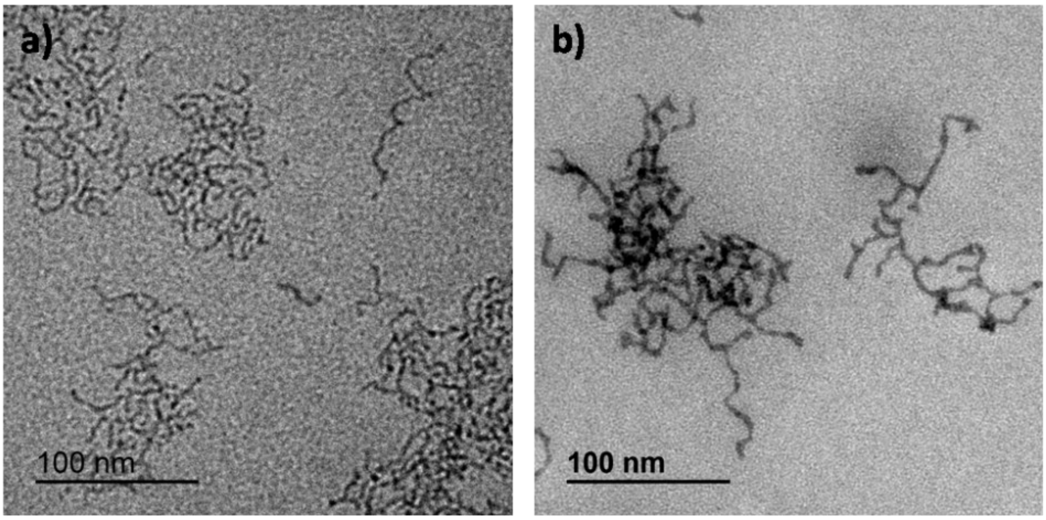


Figure S2. TEM images NCs treated with TA+ZnAc (a) and TC+ZnAc (b).

Figure S3: High-Resolution Transmission Electron Microscopy (HRTEM) images of treated NCs

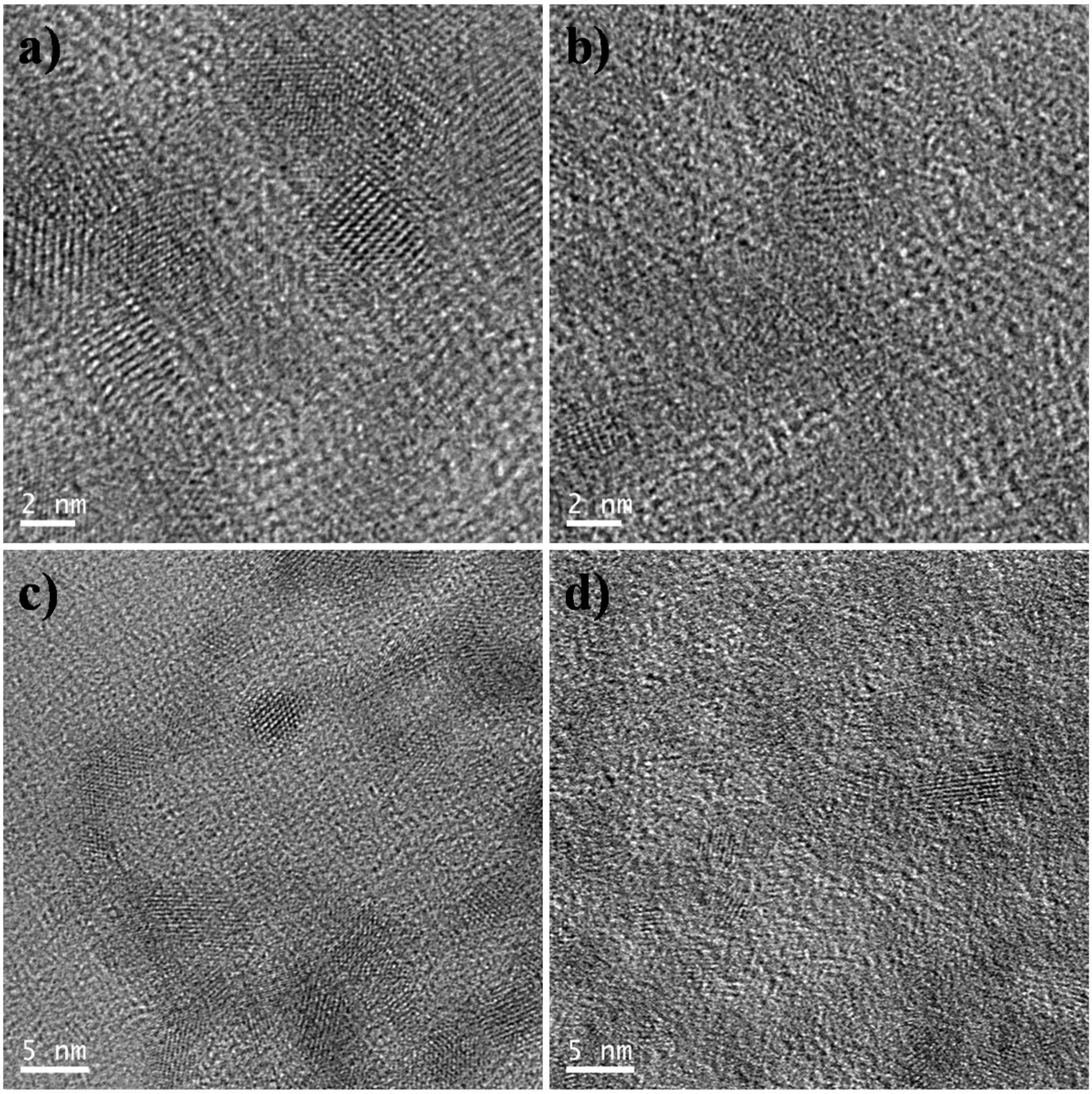


Figure S3. HRTEM images at magnifications of 1.5 million and 300 thousand of TA+ZnAc treated NCs (a and c) and TC+ZnAc treated NCs (b and d).

Figure S4: Small Angle X-ray Scattering results of samples in microemulsion.

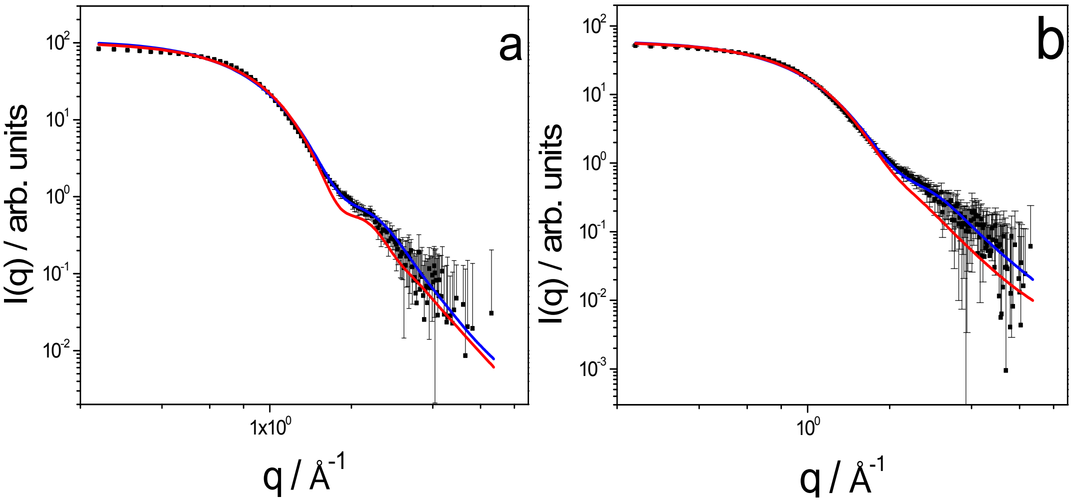


Figure S4. Experimental SAXS data (dotted line) and theoretical fits with two models: electronic density for spherical NCs (red full line) and core@shell (two different electronic densities) spherical NCs (blue full line) on samples (a) TA+ZnAc and (b) TC+ZnAc.

Table S1: fitted SAXS parameters for a homogeneous sphere of radii *r*. Errors on last digit are between brackets.

	TA+ZnAc	**TC+ZnAc**
***r* [nm]**	2.2(2)	1.9(2)

Table S2: fitted SAXS parameters for a core@shell model sphere of radii of core r_c and shell thickness *t*. Errors on last digit are between brackets.

	TA+ZnAc	**TC+ZnAc**
r_c [nm]	1.0(3)	1.0(3)
***t* [nm]**	1.0(3)	0.5(5)

NOTE: The initial CdSe core size estimated by TEM is 2 ± 0.3 nm.

Figure S5: Correlation effect SAXS analysis (at low q values).

According to the analysis, the agglomeration or fractal structure of NCs in microemulsion can be avoided. In effect, as it can be observed in figure S5, the SAXS signal at low q for both samples present a clear slope at the beginning of the plot. The horizontal shape at low q values corresponds to isolated objects. Finally, after discarding the fractal structure formation of samples in microemulsion, we propose a rigid sphere model to obtain the interaction between NCs (correlation distance). More specifically, we obtained the characteristic distance between them and their density of packaging (see Table S1).

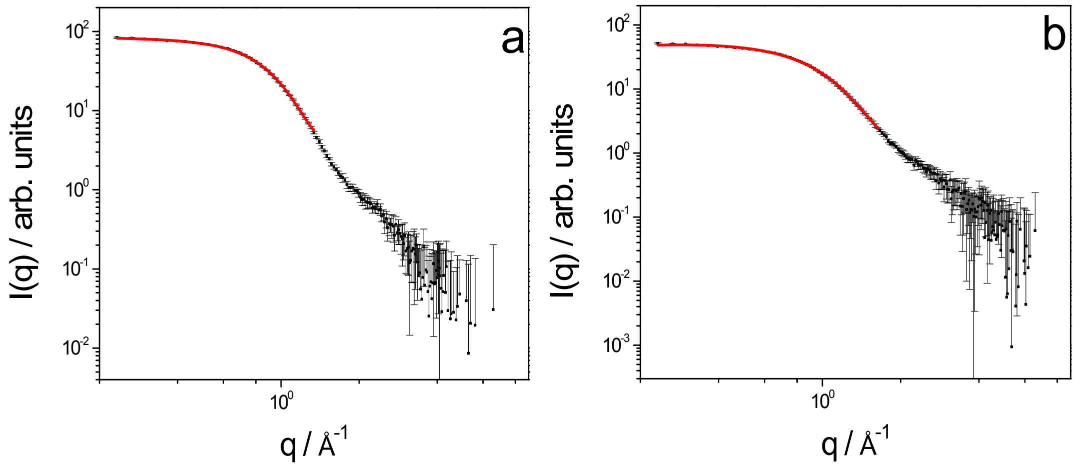


Figure S5. Experimental SAXS data (dotted line) and theoretical fits (full red lines) with a rigid spheres model on sample TA+ZnAc (a) and TC+ZnAc (b). Note the similarity between the slope of these curves which corresponds to isolated and not interacting spheres. See table S1 for fitted parameters

Table S3: best-fitted parameters obtained for a rigid spheres model on SAXS results showed in figure S5. R_{RS} is the radii of the rigid sphere proposed, ρ - ρ_{sol} is the electronic density contrast between sample and media (solvent), *Vol* is the fraction of occupancy of the sphere with R_{RS} radii and F is the scale factor fitted, which is proportional to the number of disperser object, N, as it is indicated in Ec. 1**.**

	TA+ZnAc	**TC+ZnAc**
R_{RS}	2.95 (1)	2.57(1)
$\rho - \rho_{sol}$	4.356	4.309
Vol	0.053(1)	0.027(1)
F	16175(287)	25174(75)

$(Vol)^2.(\rho - \rho_0)^2.N = F$ (Ec. 1)

According to the values for $r_C + t$ obtained from table S5 and R_{RS} obtained from Table S3, we can infer that the distance between NCs in microemulsion is about 2 nm for both samples TA+ZnAc and TC+ZnAc.

Table S4: P/Cd ratios for initial CdSe cores and samples treated with TA and TC.

Sample/ Ratio	**Initial CdSe**	**+TA**	**+TC**
P/Cd	1.3±0.3	0.4±0.1	0.4±0.1

Figure S6: Fourier Transform Infrared Spectroscopy (FTIR) of initial CdSe and treated NCs

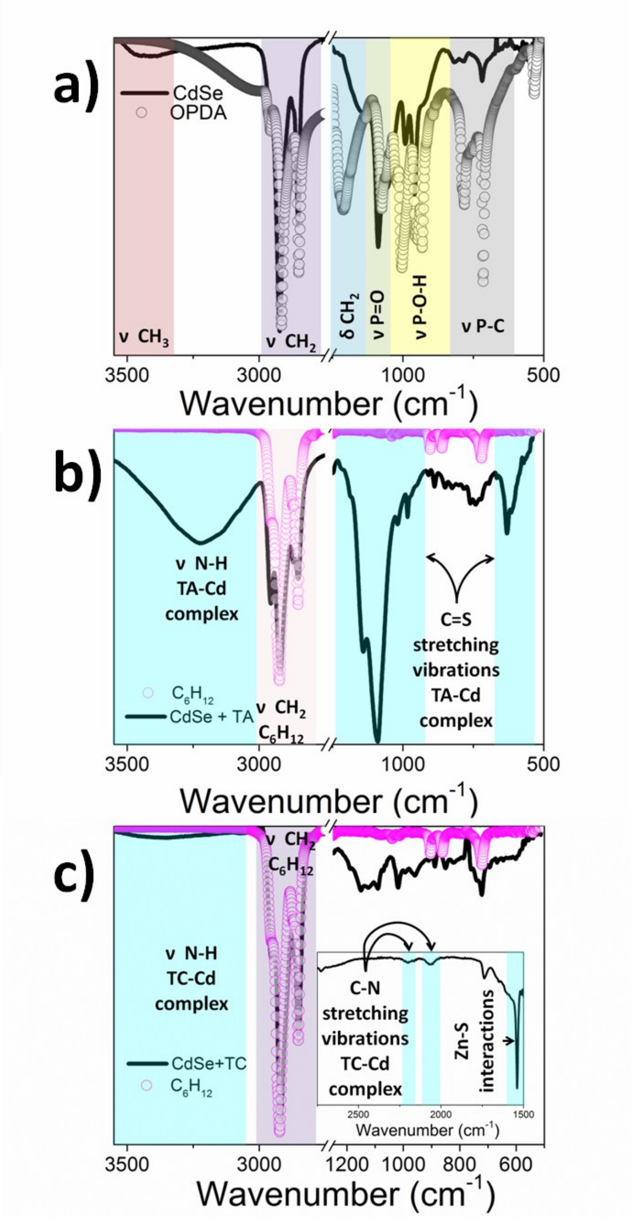


Figure S6. FTIR spectra of (a) initial NCs and ODPA, (b) TA+ZnAc treated NCs and cyclohexane and (c) TC+ZnAc treated NCs and cyclohexane

Figure S6 shows FTIR spectra of the initial CdSe NCs (a) and those of treated with TA+ZnAc (b) and TC+ZnAc (c), respectively. The spectrum of cyclohexane (used solvent) is also included. As evidenced the FTIR spectra of treated samples clearly differ from the initial ones. The vibrations corresponding to the original phosphonic species capping CdSe NCs are not present in the treated samples. From figure S6a we can deduce that the ligand sphere of the initial NCs is mainly formed by phosphonates, evidenced by the group of signals in the 3000-2800 cm^{-1} range which corresponds to the stretching vibrations of the ODPA aliphatic chain. The presence of signals at 950-900 cm^{-1}, corresponding to the P-O-H stretching modes, also confirms that these molecules are anchored to the surface as mono-dentated ligands, which does not exclude bi- or tri-dentated phosphonates.

The FTIR spectrum of the TA+ZnAc treated NCs (Figure S6b) is formed by four main groups of peaks centered at 3384, 2919, 1121 and 610 cm^{-1}. The first group could be related to N-H stretching vibrations in a Cd-thioacetamide complex as previously reported by other authors

(*Int. J. Nanosci. Nanotechnol.*, 2013, **9**, 203-212). As evidenced in figure S6b, the signals at 3072 and 3261 cm^{-1} present in the free TA disappear and a broad signal at 3384 cm^{-1} is apparent. This change in the wavenumber is explained by the coordination of TA to the Cd atoms present at the NC surface. In this sense, it seems reasonable that the unreacted TA will be bonded to the NC surface by the NH_2 group and the C=S group will be free.

The groups of signals centered at 1121 and 610 cm^{-1} can be assigned to C=S stretching vibrations, whose signals are shifted compared to the free TA probably due to the interaction between TA and Zn-Ac during the second step of the reaction. The group of signals centered at 2919 cm^{-1} corresponds to cyclohexane, which is the oily part of the microemulsion, and its high viscosity and relatively high boiling point make difficult its complete removal during the washing procedure.

In the FTIR spectrum of TC+ZnAc treated NCs (Figure S6c) the absence of signals at 1405 and 726 cm^{-1}, corresponding to the stretching vibrations of C=S in the free TC, suggests that the unreacted TC is anchored to the NC surface by the sulfur and not by the amine. The presence of signals at 3418 cm^{-1} and from 1067 to 1200 cm^{-1}, corresponding to NH_2 and CN_2 the stretching vibrations, respectively, also supports the sulfur binding. These signals are quite shifted, compared to free TC, probably due to the interaction with the NC. In the TC+ZnAc treated NCs spectrum some new signals appear in the range of 2000-2200 cm^{-1} identifying as a Cd-thiocarbamide complex ($CdCN_2$), resulting product from the reaction of Cd with the H_2NCN coming from the TC or its polymerized decomposition, as previously reported (*J. Therm. Anal. cal.* 2003, **72**, 497-506). Also a new peak at 1539 cm^{-1} appears (see inset in Figure S6c) that shows a Zn-S interaction according to previously reported for Hybrid luminescent CdS@ZnS nanocomposites (*Ceramics Int.* 2015, **41**, 12930–12938).

Despite of the fact that these assignations are supported by the literature we cannot exclude the contribution to these spectra of sulfate species which stretching vibrations are centered close to 1200 cm^{-1} and their bending modes at 900 and 600 cm^{-1}. Although unequivocally identification could not be done, these species anchored to the NCs surface are probably contributing to the charge stabilization of the warm-like structures in polar solvents. As previously stated by EDX analysis, the comparison of these signals with the initial NCs spectrum discards from the presence of phosphonic acids proving the partial ligand removal.

Figure S7: HRTEM images of initial CdSe NCs

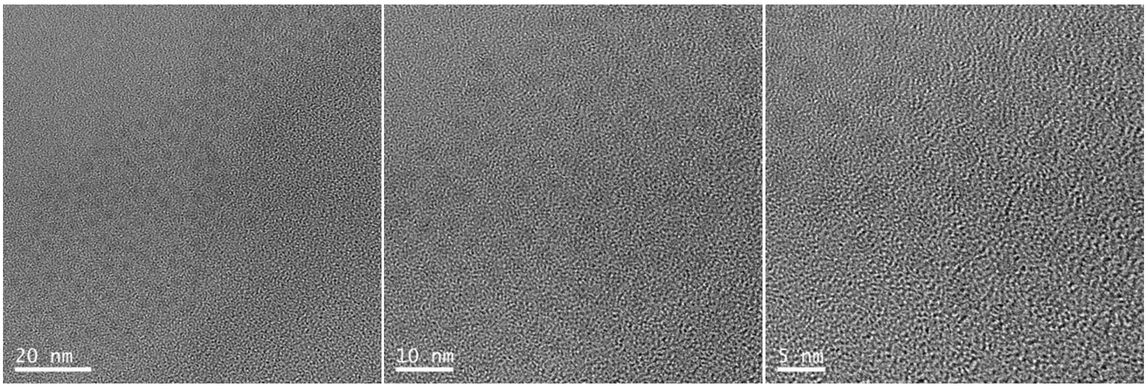


Figure S7. HRTEM images of initial CdSe NCs

Figure S8: CdSe core characterization by X-ray Absorption Spectroscopy.

XANES and EXAFS Se-K edge results:

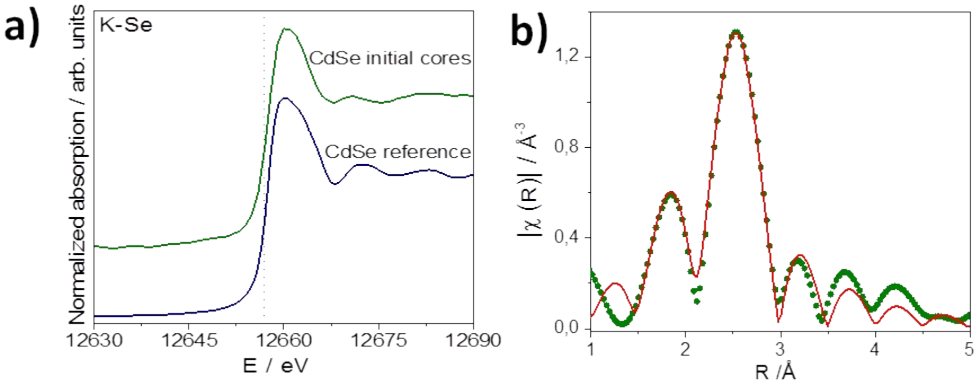


Figure S8. (a) Se K-XANES results obtained on CdSe initial cores. Vertical dotted lines indicates the energy position for Se K-edge and; (b) Fourier transform of EXAFS oscillation at Se K-edge, dotted line represent the experimental data and full red line the corresponding fit (see Table S5).

Figure S8 shows the chemical nature of the initial cores, which undoubtedly corresponds to CdSe according to XANES (Figure S8 a) and EXAFS fitting (Figure S8 b and Table S5).

Table S5: EXAFS fitted parameters for Se first coordination shell on CdSe initial cores samples in comparison with CdSe bulk reference compound. $N_{Se\text{-}Cd}$ is average coordination number which represent the number of Cd nearest neighbours of Se. R is interatomic distance and σ^2 the Debye-Waller factor. The smaller fitted value for CdSe initial cores respect to bulk reference material is associated with the nanometric dimensions of the cores.

	Fitted EXAFS Se K-edge parameters			
Sample	$\mathbf{N_{Se\text{-}Cd}}$	$\mathbf{R1_{Se\text{-}Cd}}$ **(Å)**	$\mathbf{R2_{Se\text{-}Cd}}$ **(Å)**	$\mathbf{\sigma^2_{Se\text{-}Cd}}$ **(Å^2)**
SeCd reference	4	2.610	2.702	-
SeCd initial cores	3.3(3)	2.62(1)	-	0.003(1)

Figure S9: Size histograms of initial and treated NCs.

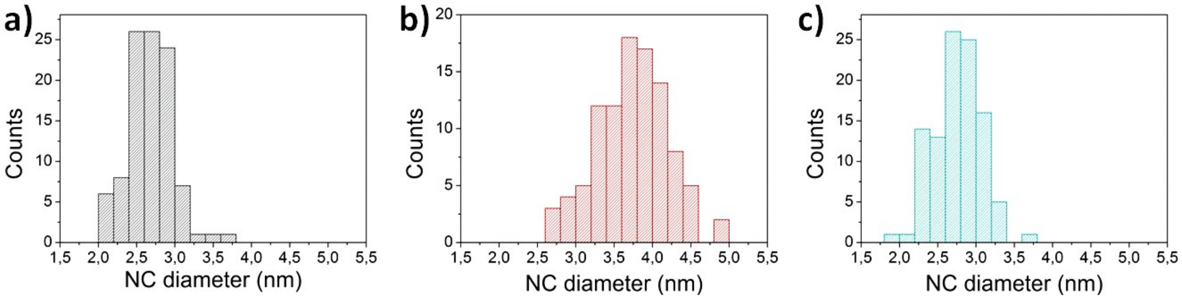


Figure S9. Size histograms of initial (a), TA+ZnAc (b) and TC+ZnAc (c)

These values correspond to the thickness of the worm-like structures. Length values depend on the degree of interconnection in the formed networks (See Figure 2b).

Table S6: EXD data. To ensure that the elemental analyses were representative and statically valid, the atomic % has been estimated from EDX analyses from several observations spots at different magnifications.

%atomic	Initial CdSe	+TA	+TC	+TA+ZnAc	+TC+ZnAc
Cd	66±5	64±1	68±1	36±4	36±8
Se	34±5	15±1	22±1	11±1	21±4
S	-	21±1	11±2	34±2	10±1
Zn	-	-		18±3	33±12

After the addition of TA and TC there is an exchange of Se by S (the Se amount decreases in the same extent than S increases). S+Se/ Cd ratios after sulfur addition are almost constant being 0.51 for the initial CdSe NCs and 0.56 and 0.49 after TA and TC treatments, respectively, pointing to an alloyed structure $CdSe_{1-x}S_x$. This exchange is larger in samples treated with TA (almost double compared to TC), which is consistent with the formation of a thicker $CdSe_{1-x}S_x$ shell.

Figure S10: Photoluminescence response of TA+ZnAc and TC+ZnAc treated samples after one month.

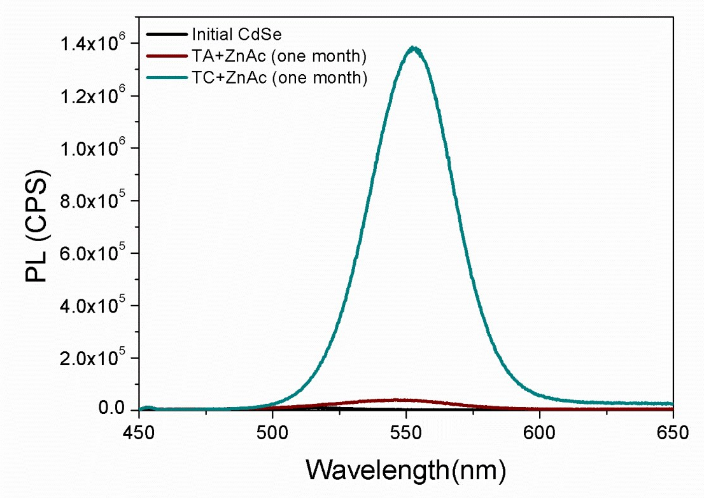


Figure S10. PL spectra of initial (black), TA+ZnAc (red) and TC+ZnAc (blue) NCs. All spectra were acquired in microemulsion after one month treatment

Figure S11: XPS measurements of TA+ZnAc and TC+ZnAc treated samples.

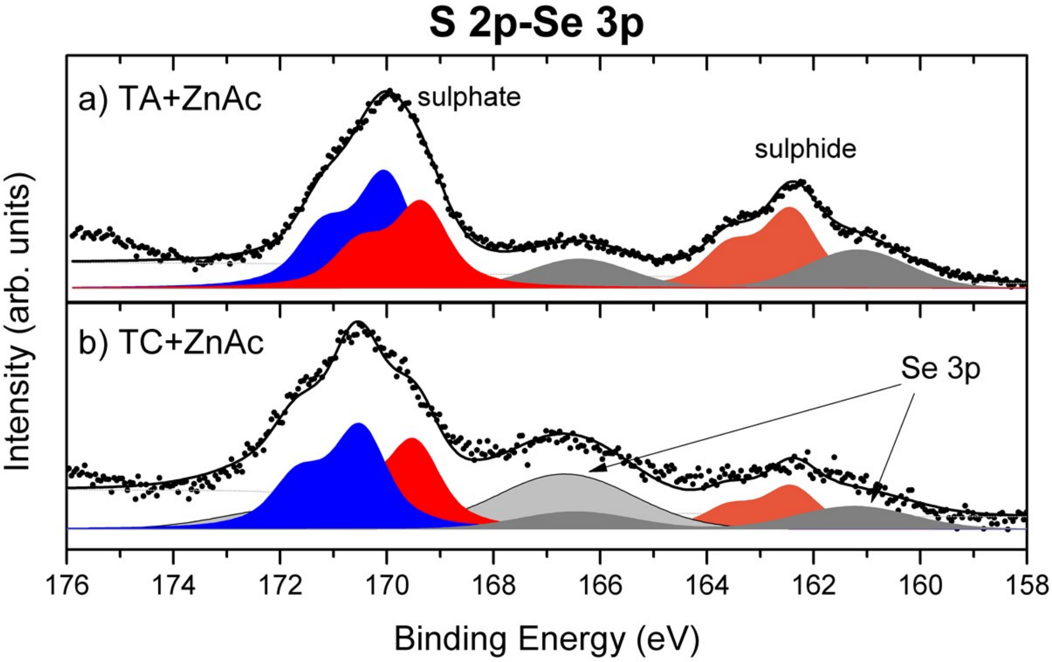


Figure S11. XPS results measured at the S 2p region for TA+ZnAc (a) and TC+ZnAc (b) treated samples. The samples were prepared in microemulsion, washed in ethanol/chloroform and dropcasted on highly oriented pyrolytic graphite (HOPG) prior to their insertion into the XPS chamber.

Table S7: fitted values to Zn K-edge EXAFS oscillations of first coordination shell, showed in figure 5-d, for the average coordination number (N), interatomic distance (R) and Debye-Waller factor (σ^2). Structural parameters values for reference compounds are showed for comparison.

	Zn-O shell		
Samples	**Average N**	**Average R (Å)**	**Average σ^2 (Å^2)**
TA+ZnAc	5.0(8)	2.00(3)	0.012(3)
TC+ZnAc	4.3(7)	2.00(2)	0.011(3)

	Zn-O shell						Zn-S shell		Zn-Zn shell	
References	**N_1**	**R_1 (Å)**	**N_2**	**R_2 (Å)**	**N_3**	**R_3 (Å)**	**N**	**R (Å)**	**N**	**R (Å)**
ZnO	1	1.796	3	2.042	-	-	-	-	6	3.208
ZnS	-	-	-	-	-	-	4	2.342	12	3.824
$ZnSO_4$	2	1.947	2	2.042	2	2.344	4	3.182	-	-
ZnAc	2	1.987	2	2.179	2	2.188	-	-	-	-

Figure S12: K-Se and K-Zn EXAFS oscillation fitting of first coordination shell on initial and treated NCs.

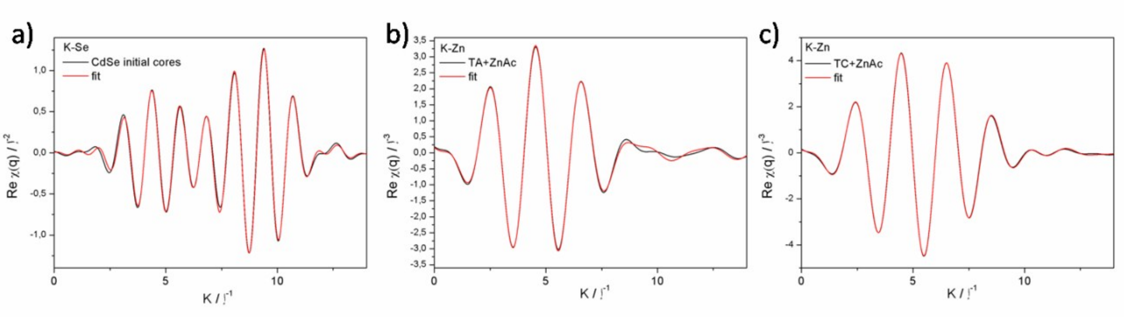


Figure S12. K-Se and K-Zn EXAFS oscillation fitting of first coordination shell on CdSe initial cores (a), TA+ZnAc (b) and TC+ZnAC (c)