

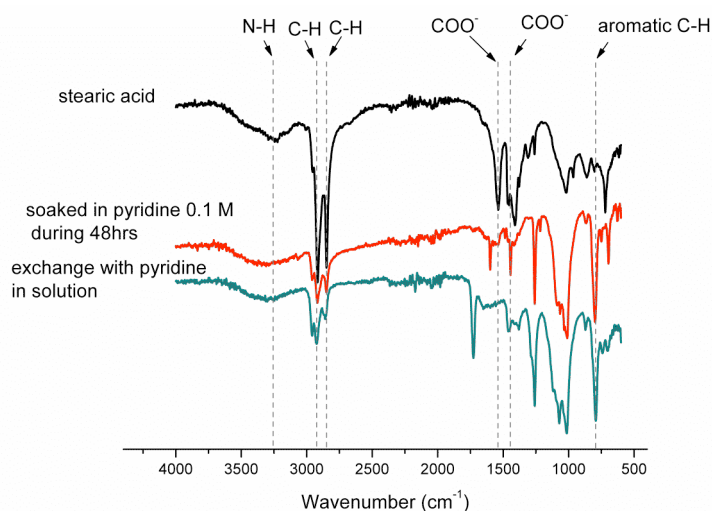
## Supporting Information

### Effect of the treatment with (di-)amines and dithiols on the spectroscopic, electrochemical and electrical properties of CdSe nanocrystals' thin films

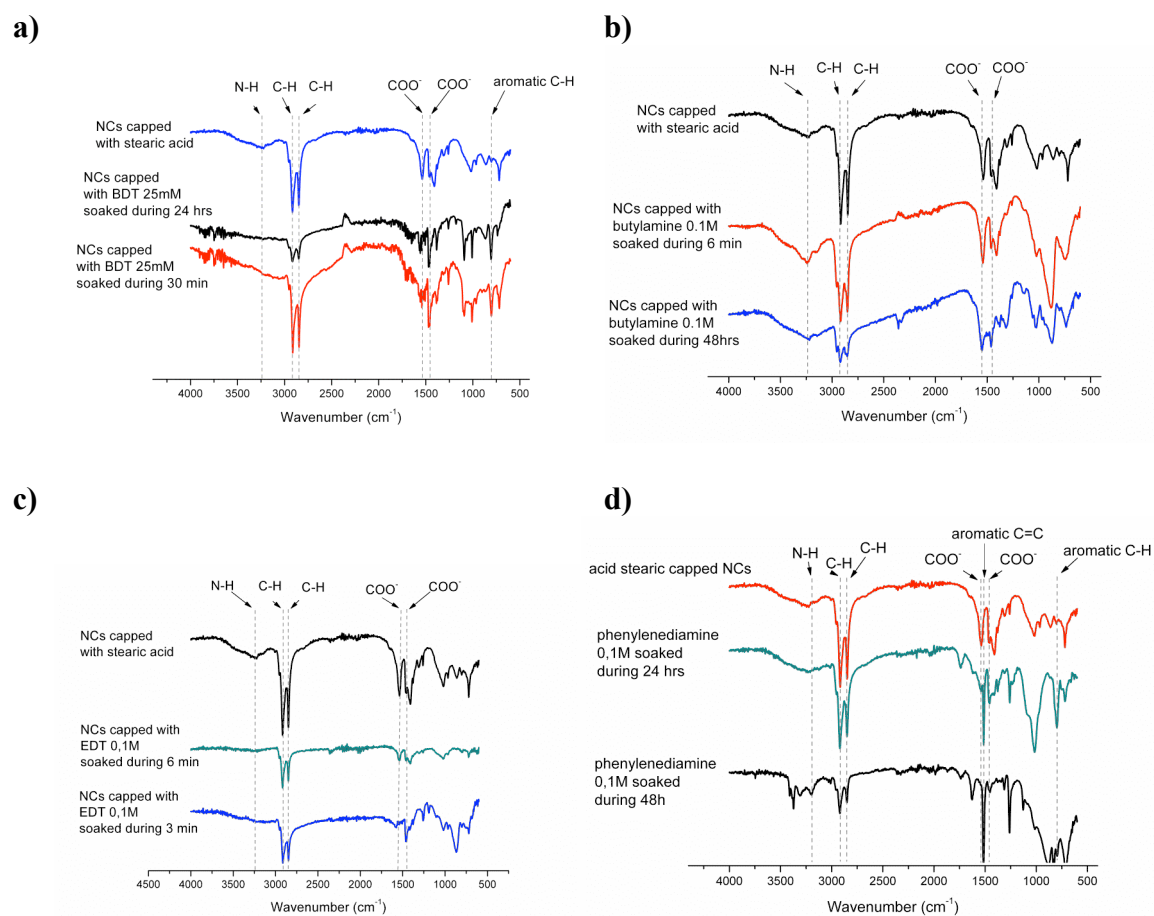
Aurélie Lefrançois, Elsa Couderc, Jérôme Faure-Vincent, Saïd Sadki,  
Adam Pron\*, Peter Reiss\*

CEA Grenoble, INAC-SPrAM (UMR 5819 CEA-CNRS-UJF) -LEMOH, 17 rue des Martyrs,  
38054 Grenoble cedex 9, France

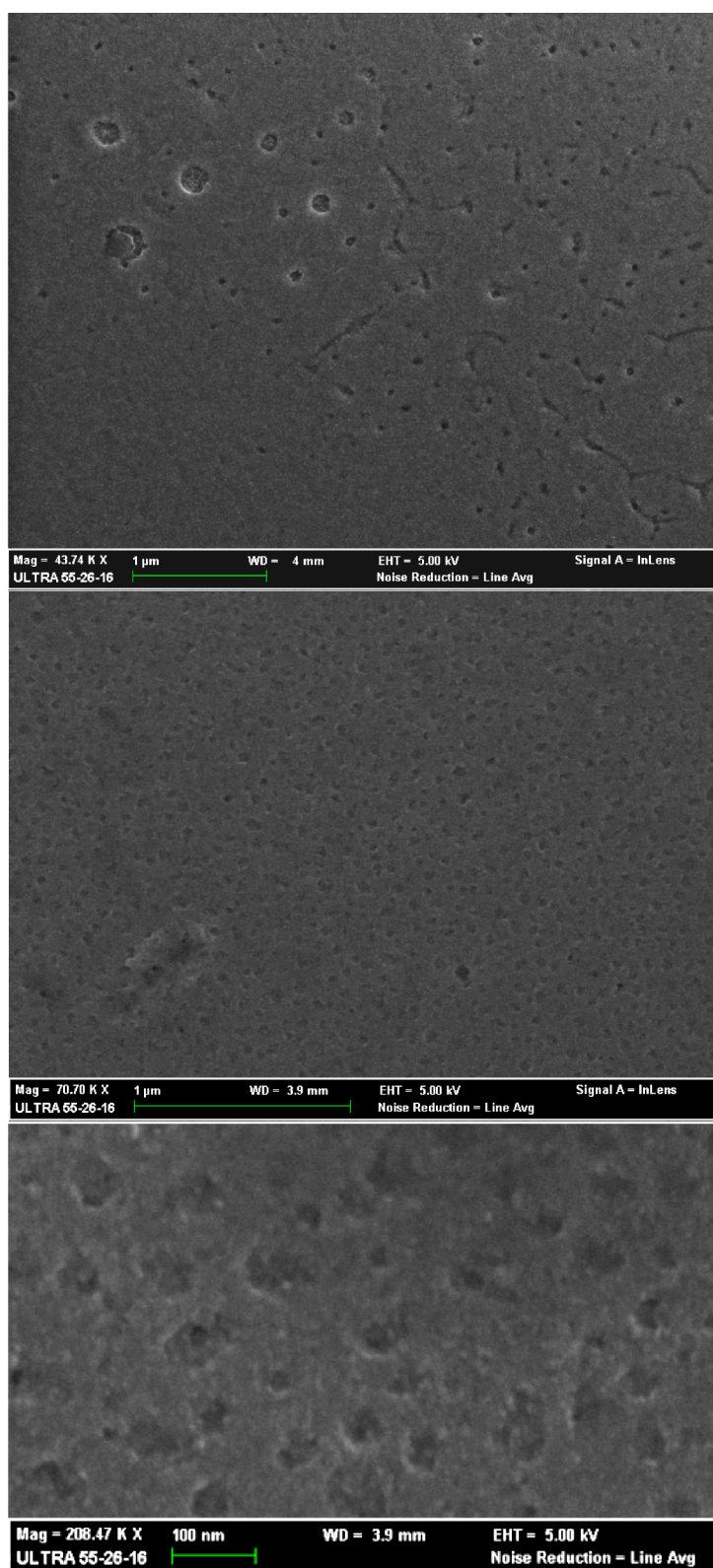
\*E-mail: [peter.reiss@cea.fr](mailto:peter.reiss@cea.fr), [adam.pron@cea.fr](mailto:adam.pron@cea.fr)



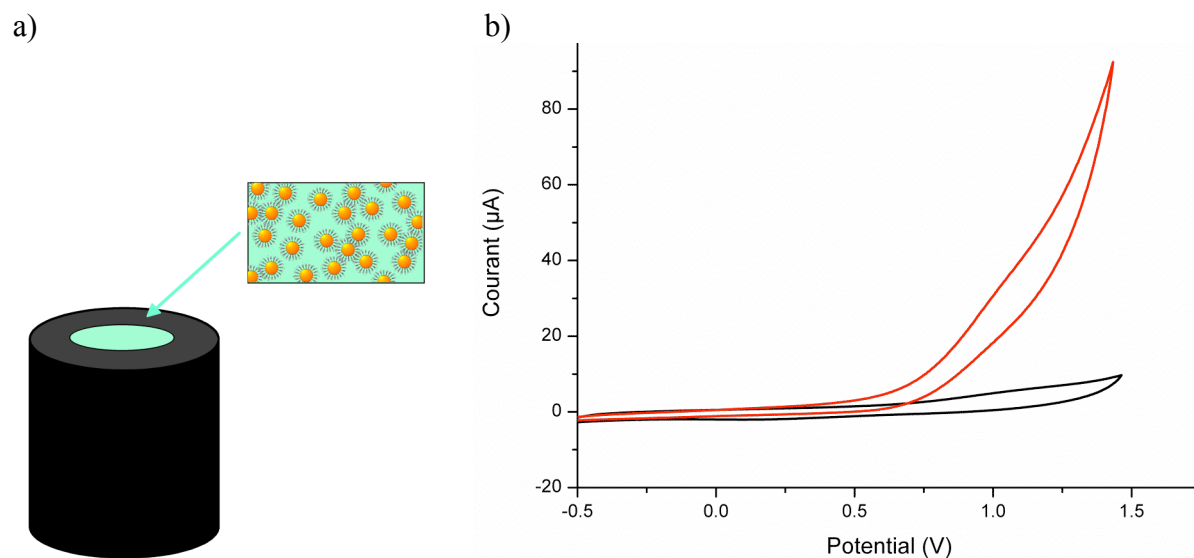
**Figure S1:** FTIR spectra of thin films of CdSe nanocrystals (NCs) treated with pyridine compared to the spectrum obtained with the initial capping ligands (stearic acid and oleylamine, black line). Red line: ligand exchange is carried out after film deposition using a 0.1 M solution of pyridine in acetonitrile. Green line: ligand exchange in solution achieved by heating a vial containing the nanocrystals dispersed in pyridine to 80°C for 1 hr, followed by precipitation with heptane and redispersion in chloroform. Both spectra show a very similar decrease of both the aliphatic C-H stretch and carboxylate stretch signal intensities. Therefore it can be assumed that the ligand exchange efficiency is similar in both cases and clearly below 100%. (As discussed in the text, we assume that preferentially the stearic acid ligands are replaced on the NCs' surface, while oleylamine ligands remain attached.) The introduction of the pyridine ligands on the NCs' surface is visible in both spectra by the appearance of a peak around 800 cm<sup>-1</sup>, characteristic for the out-of-plane deformation of the aromatic cycle.



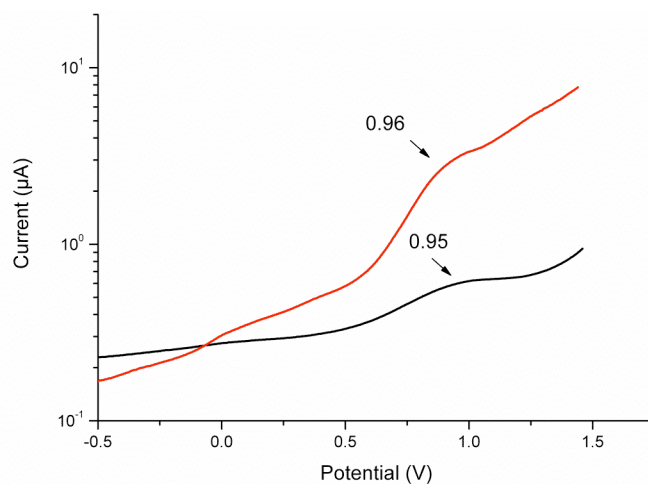
**Figure S2:** Evolution of the FTIR spectra of the NCs' films depending on the time treated with the ligand solutions in acetonitrile. *p*-enzenedithiol (BDT) 25 mM , b) *n*-butylamine 0.1 M, c) 1,2-ethanedithiol (EDT) 0.1 M, d) *p*-phenylenediamine 0.1M.



**Figure S3:** Top: SEM image showing the formation of cracks upon solid state ligand exchange with *p*-benzenedithiol (BDT). Middle: Filling the cracks and voids by a second cycle of NCs' deposition via spin-coating followed by surface ligand exchange with BDT. Bottom: zoom into the previous image, showing that the ITO substrate is no longer visible after the second step of NCs' deposition and BDT treatment.



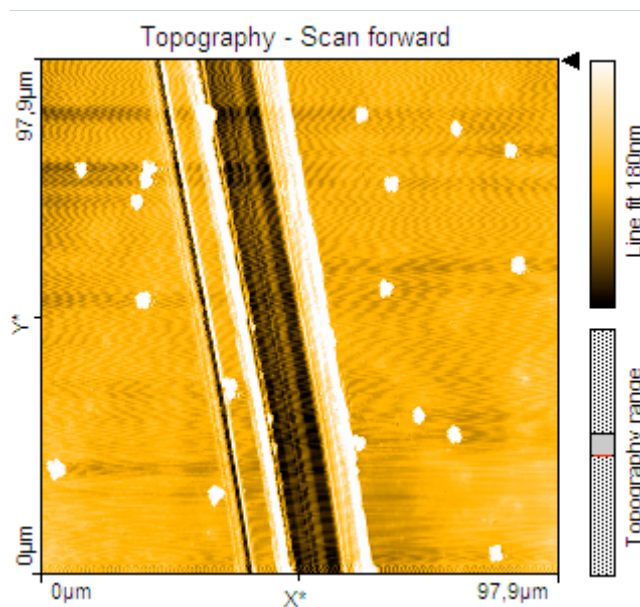
**Figure S4:** a) Scheme of the working electrode (Pt) covered with a thin film of CdSe nanocrystals obtained by solvent evaporation. b) Cyclic voltammograms of *n*-butylamine in acetonitrile solution (red curve); a thin layer of 4.8 nm CdSe nanocrystals capped with *n*-butylamine (black curve). Electrolyte: 0.1 M tetrabutylammoniumhexafluorophosphate in acetonitrile, potential vs  $\text{Fc}/\text{Fc}^+$ , scan rate: 60 mV/s.



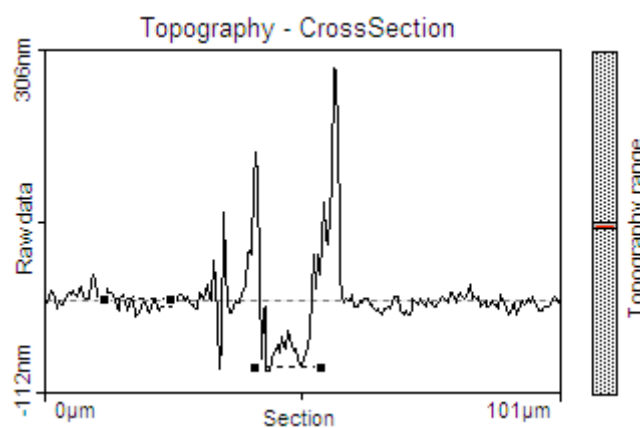
**Figure S5:** DPV curves of *n*-butylamine in solution (red curve); a thin layer of 4.8 nm CdSe nanocrystals capped with *n*-butylamine (black curve). Electrolyte: 0.1 M tetrabutylammoniumhexafluorophosphate in acetonitrile, potential vs.  $\text{Fc}/\text{Fc}^+$ , scan rate: 10 mV/s.

Measurement of the NCs' film thickness (films thicker than 100 nm were measured with a profilometer).

a)



b)



**Figure S6:** a) AFM image of a CdSe NCs' film spin-coated from hexane solution with a concentration of  $80 \text{ mg}\cdot\text{mL}^{-1}$  (10s @4,000 rpm, acceleration 3,000 rpm/s) onto an ITO substrate. A straight scratch was made with a steel tip in order to get a height step between the NCs' film and the ITO substrate. b) Cross-section of the image above. Around 15 cross-sections were analyzed for each film, resulting in the present case in a mean value of  $70 \pm 20$  nm for the film thickness.