Supporting Information

for *Small*, DOI: 10.1002/smll.201302333

Optical and electronic properties of pyrite nanocrystal thin films: the role of ligands

Wei Li, Thomas Dittrich, Frank Jäckel,* Jochen Feldmann**

Dr. W. Li, Dr. F. Jäckel, Prof. J. Feldmann
Photonics and Optoelectronics Group, Department of Physics and Center for NanoSciences, Ludwig-Maximilians-Universität München, Amalienstr. 54, 80799 Munich, Germany
E-mail: feldmann@lmu.de
Dr. T. Dittrich
Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
E-mail: dittrich@helmholtz-berlin.de
Dr. W. Li, Dr. F. Jäckel
Present address: Department of Physics and Stephenson Institute for Renewable Energy, University of Liverpool, Oliver Lodge Building, Liverpool, L69 7ZE, United Kingdom
E-mail: fjaeckel@liv.ac.uk

Keywords: iron sulfides, solar cells, surface states, surface photo voltage spectroscopy, semiconductor nanocrystal solids

Additional experimental results

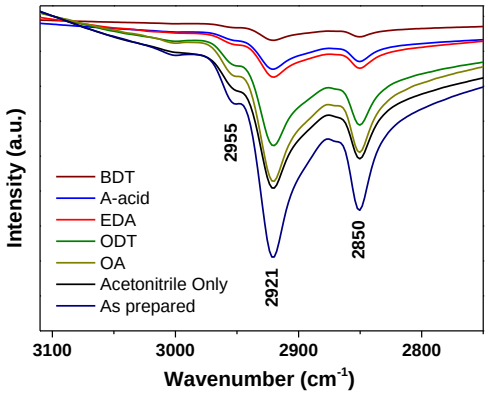

Fig. S1 *FT-IR spectra of ~500 nm thick pyrite nanocrystal films with OLA (as prepared), after washing with acetonitrile, and after ligand exchange with OA, OTD, EDA, A-acid, and BDT, respectively.*

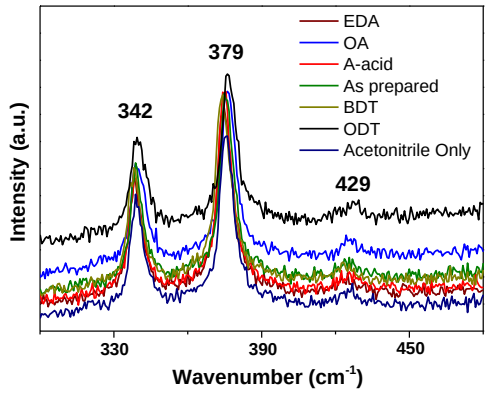

Fig. S2 *Raman spectra of ~500 nm thick pyrite nanocrystal films with OLA (as prepared), after washing with acetonitrile, and after ligand exchange with OA, OTD, EDA, A-acid, and BDT, respectively.*

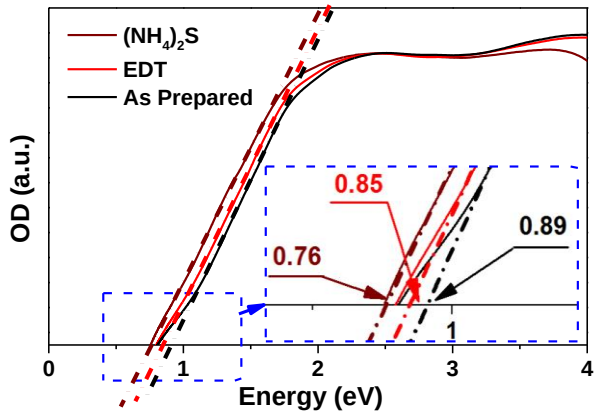

Figure S3. *Semi logarithmic plot of the absorbance in the absorption edge region as function of energy of as prepared (black) pyrite thin films and after ligand exchange to EDT (red) and $(NH_4)_2S$ (brown), respectively. The absorption edge is determined from extrapolation to zero absorbance. The zoom in shows the shift of the absorption edge for the different ligands.*

Estimate of ligand exchange efficiency

The efficiency of the ligand exchange can be estimated from the FTIR spectra as follows: Assuming that after the washing procedure of the nanocrystals only surface bound ligands are present in the as-prepared films, the measured transmittance in the IR is converted to absorbance and normalized by the film thickness. Considering the antisymmetric and symmetric C-H stretch vibrations (2955, 2921 and 2850 cm^{-1}, respectively) and the different number of C-H bonds in each ligand, Lambert-Beer's law allows for estimating the percentage of replaced original ligands. The results of this analysis are summarized in the table below. With the exception of D-Acid more than 80% of the original ligands are found to be replaced in all cases within this analysis. This is additional significant evidence for successful ligand exchange.

Sample	Absorbance of C-H at 2921 cm^{-1}	Film thickness, nm	Normalized Absorbance, μm^{-1}	Percentage of exchanged ligand
As prepared (OLA)	0.03099	490	0.063	N. A.
DA	0.01655	330	0.0502	83 %
D-acid	0.01631	345	0.0476	58 %
EDT	0.00574	495	0.0116	87 % ~ 93 %
PD	0.00366	480	0.0076	88 %
$(NH_4)_2S$	0.00249	475	0.0052	92 %

Quantitative analysis of SEM images

The increasing formation of cracks and holes after ligand exchange with decreasing length of the ligands can be quantified from the SEM images. Since cracks and holes usually appear darker, an estimate of the crack and hole proportion can be obtained by converting the SEM images to black and white images (ImageJ version 1.45), as illustrated in Figure S4 for data from Fig. 3D of the manuscript. The percentage of black pixels is then calculated from the images as a measure of crack and hole formation and reported in the table below. Clearly, an increase of crack and hole formation can be observed for shorter ligands confirming the qualitative statement in the paper.

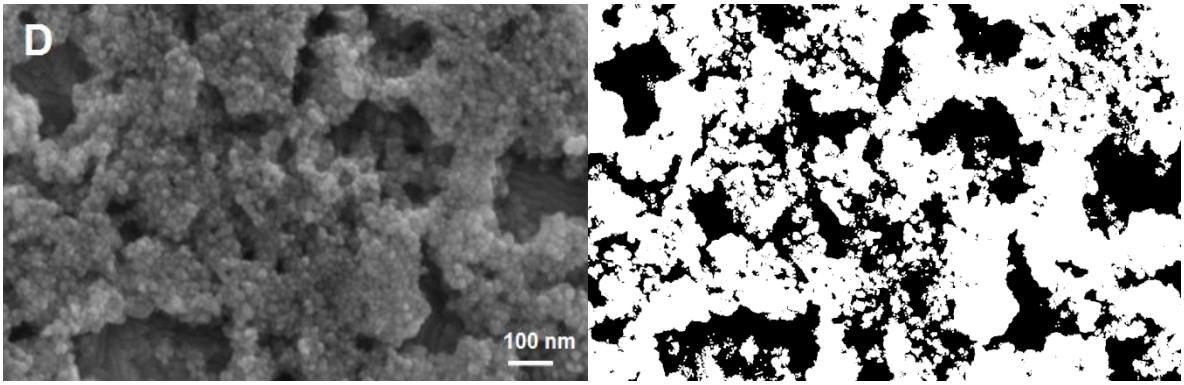

Figure S4. *SEM image of a pyrite thin films after ligand exchange to $(NH_4)_2S$ (left, Figure 3D from the paper) and the same image after conversion to black and white (right).*

Sample	Ligand length, L/nm	area of holes and cracks/area of film
As prepared (OLA)	2.0	5 ± 3 %
DA	1.32	11 ± 2 %
EDT	0.45	24 ± 3 %
$(NH_4)_2S$	0.2	30 ± 4 %