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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

Abstract:

Pyrite nanocrystals are currently considered as a promising material for large scale photovoltaic applications due to their non-toxicity and large abundance. While scalable synthetic routes for phase-pure and shape controlled colloidal pyrite nanocrystals have been reported, their use in solar cells has been hampered by the detrimental effects of their surface defects. Here, we report a systematic study of optical and electronic properties of pyrite nanocrystal thin films employing a series of different ligands varying both the anchor and bridging group. The effect of the ligands on the optical and electronic properties is investigated by UV-vis/NIR absorption spectroscopy, current voltage characteristic measurements and surface photovoltage spectroscopy. We find that the optical absorption is mainly determined by the anchor group. The absorption onset in the thin films shifts up to ~100 meV to the red. This is attributed to changes in the dielectric environment induced by different anchors. The conductivity and photoconductivity, on the other hand, are determined by combined effects of anchor and bridging group, which modify the effective hopping barrier. Employing different ligands, the differential conductance varies over four orders of magnitude. The largest redshift and differential conductance are observed for ammonium sulfides and thiolated aromatic linkers. Pyridine and long chain amines, on the other hand, lead to smaller modifications. Our findings highlight the importance of surface functionalization and interparticle electronic coupling in the use of pyrite nanocrystals for photovoltaic devices.

1. Introduction

Large scale utilization of renewable energy sources is essential to overcome the adverse effects of greenhouse gas emissions and to avoid problems associated with long term storage of nuclear waste and the limited supply of fossil fuels available. An essential criterion for selecting materials for such large scale applications is that they should be non-toxic and earth abundant, i.e. cheap.[1] In the area of solar cells this has led to renewed interest in materials such as pyrite or copper sulfide.[2-13] While pyrite has been studied as a solar cell material extensively in the 1980s the more recent studies focus on colloidal nanocrystals.[14-18] Colloidal nanocrystals hold the promise to combine the ease of solution processing with the advantages of inorganic semiconductors such as low exciton binding energy and high charge carrier mobility. At the same time, if the nanocrystal dimensions are small enough (i.e. below the exciton Bohr radius), quantum confinement effects can be used to tune the electronic and optical properties of the material over a wide range.[19-21]

Purely inorganic solar cells based on copper sulfide and silicon nanocrystals have already been reported.[11,22] Pyrite, on the other hand, has proven to be more challenging. There are only few reports of operating solar cells containing pyrite nanocrystals: hybrid system (i.e. combination with organic polymers) and dye sensitized solar cell with a pyrite nanocrystal based counter electrode.[23,24] The first challenge is the large number of crystal phases for iron sulfides, which makes it more difficult to prepare phase pure pyrite nanocrystals.[25] Successful reports of phase pure pyrite include hydrothermal and hot injection methods as well as synthesis from metal organic clusters. [6-8,23,26-28] Recently, we reported a scalable hot injection based procedure allowing for shape control of phase pure pyrite nanocrystals.[2] The second challenge for preparing photovoltaic devices from pyrite nanocrystals is the role of surface defects in particular sulfur vacancies.[3,29] While the precise mechanism involving the surface defects are still under debate their negative impact is amplified in nanocrystal based devices

due to the large surface area of the nanocrystals. Possible effects of the sulfur vacancies being discussed for the poor performance of pyrite nanocrystal solar cells include Fermi level pinning, and increased metal-like conductivity.[25,30] A well-established strategy to minimize effects of surface states or defects is their passivation with ligands. Therefore, the effects of *in-situ* ligand exchange/removal have recently attracted interest.[31,32] With respect to solar cells, such ligands should allow for intimate contact of pyrite nanocrystals in the thin films to enable sufficient electronic coupling for charge transport.

Here, we present a systematic study of the optical and electronic properties of pyrite nanocrystal thin films employing a series of ligands with different anchoring and bridging groups. The optical and electronic properties of the thin films are investigated with UV-VIS/NIR spectroscopy, current-voltage characteristics (*I-V*-curves) and surface photovoltage (SPV) spectroscopy. We find that the chemical nature of anchor groups leads shifts in the optical absorption edge of up to ~100 meV. The conductivity and photoconductivity in turn is determined by combined effects of anchoring and bridging groups of the ligands. Employing different anchor groups and both aliphatic and aromatic bridging groups, the differential conductance can be tuned over four orders of magnitude.

2. Results and Discussion

The main part of the paper is organized as follows. We first introduce the investigated ligands and discuss the film formation and ligand exchange process. We then address the effects of the length of the bridging groups for amine based ligands and finally compare different anchor groups and their impact on the optical and electronic properties of the thin films.

2.1. Ligand Exchange

Figure 1 displays the ligands investigated in this study. As synthesized pyrite nanocrystals are functionalized with oleylamine (OLA) as ligands. The ligands can be divided into five groups: first, amines, with bridging groups of different length, including OLA (as prepared), ethylenediamine (EDA), octylamine (OA) and dodecylamine. Second, thiols with aromatic

and aliphatic bridges including ethanedithiol (EDT), benzenedithiol (BDT), 1,8-octanedithiol

(ODT). Third, organic acids including acetic and decanoic acid (A- and D-acid, respectively).

Fourth, pyridine and, fifth, ammonium sulfide. The latter, has been shown to effectively re-

moved ligands and from metal sulfides on the nanocrystal surfaces.[31] Ligand exchange was

performed in spin coated films of ~200 nm thickness. Thicker films were prepared via itera-

tive cycles of spin coating and ligand exchange (for details see methods section). OLA was

chosen as the initial ligand since it is known to be readily displaced by other ligands.[5,33,36] In

addition, using the same initial ligand in all experiments assures a fair comparison between

the different ligands.

Figure 2 displays FT-IR and Raman spectra of as prepared films (OLA functionalization)

and representative spectra for each anchor group after ligand exchange (i.e. amine, thiol, acid,

pyridine and ammonium sulfide).[34] FT-IR spectroscopy is routinely used to monitor ligand

exchange on semiconductor nanocrystals both in solution and the solid state.[9,35-37] The FT-IR

spectra show the region of the antisymmetric (2955 and 2921 cm^{-1}) and symmetric (2850 cm^{-1}) C-H stretch vibrations of the aliphatic alkyl chains.[38] OLA contains the longest alkyl

chains while D-acid, DA, EDT, PD and $(NH_4)_2S$ contain much shorter or no alkyl chains at

all. Therefore, the reduced intensity/suppression of IR absorption in this region after the lig-

and exchange provides evidence for the successful replacement of the initial OLA ligands.

Careful analysis of the FT-IR spectra reveals that, with the exception of D-acid, more than

80% of the ligands have been exchanged (for details see supporting information). Ligands

with one amine function are likely to adsorb through monodentate bonding of the amine with

Cd^{2+}, while thiols may form direct Cd-S bonds or adsorb in sulphur vacancies.[39] Thus, thiols

may in fact reduce the surface defect density. Since such reduction in surface defect states

cannot be expected for the other ligands, we expect to also observe differences in the electron-

ic and optical properties. The shorter amine based ligands are believed to replace the long

chain OLA due to the lower entropic losses upon adsorption.[40]

The Raman spectra focus on the low wave number region where the characteristic Raman bands of pyrite are found at ~340 cm^{-1}, 380 cm^{-1} and 430 cm^{-1}.[41,42] The lack of observable differences between the samples before and after ligand exchange demonstrates the phase stability of the pyrite nanocrystal thin films during the ligand exchange.

Figure 3 displays SEM micrographs of thin films with one cycle of spin coating before (Figure 3A), and after ligand exchange with DA, EDT and $(NH_4)_2S$ (Figure 3B-D). Figure 3E and F shows a top view and cross sectional image of a thin film with 3 cycles of spin coating and ligand exchange with $(NH_4)_2S$. The SEM images provide additional evidence and more detailed insight into the successful ligand exchange process. The spin coated films of as pre-pared pyrite nanocrystals appear smooth and crack free (Figure 3A). After the ligand ex-change the films display holes and cracks. This is due to the shorter ligands replacing the comparably long OLA leading to a partial collapse of the smooth film structure. This effect apparently becomes stronger for shorter ligands (Figure 3B-D; a quantitative analysis of this effect is given in the supporting information). Additionally, in the case of linkers with two anchor groups cross linking of different nanocrystals increases the film collapse. Figs. 3E and F, on the other hand, provide evidence that smooth crack free films can be obtained by itera-tive cycles of spin coating and ligand exchange, which fill the cracks and holes and lead to smooth crack free films within three cycles.

2.2. Amine anchors with aliphatic bridging groups of different length

We now turn to the series of amine anchor group ligands which only differ in their bridging unit lengths, i.e. EDA, OA, DA and OLA. The total length of these ligands (fully elongated alkane chains) is 0.38 nm, 0.82 nm, 1.32 nm and 2.0 nm, respectively.

Figure 4 illustrates the optical and electronic properties of as-prepared thin films and after ligand exchange to EDA, OA and DA, respectively. Figure 4A displays extinction spectra of the films in the region of the pyrite band gap (0.95 eV). No significant differences in between the pristine and ligand exchanged films can be observed. Current voltage characteristics of as-

prepared films and, as a representative example, after exchange to EDA are displayed in Figure 4B. Apparently, the EDA treatment increases the conductivity by more than two orders of magnitude. Figure 4C summarizes the absorption edge positions and differential conductance data with and without illumination for all four ligands as a function of ligand length on linear and semi-logarithmic scale, respectively. The differential conductance was determined numerically from the *I-V*-curves at $0V$. Clearly, the absorption edges are virtually identical, while the differential conductance increases exponentially with decreasing ligand length. The ratios of the differential conductance with and without illumination, however, are ~1.5 independent of the ligand.

The two main observations are that ligand exchange of OLA with other amine anchor ligands does not change the optical properties of the thin films but that shorter ligands increase the differential conductance exponentially. The conservation of the optical properties can be explained by the following: Firstly, using amine anchors in all ligands does not change the interaction between the anchor group and the nanocrystal surface. Secondly, since our pyrite nanocrystals are larger in diameter than the pyrite exciton Bohr radius of ~1.3 nm no modification of optical properties through electronic coupling as observed in quantum dot solids is absent.[26,43] However, the reduced distances between the nanocrystals do modify the conductivity.

The charge carrier transport in disordered nanocrystal solids at room temperature, independently from the degree of quantum confinement, will be dominated by hopping of charge carriers between nanocrystals.[44] The hopping rate, and thus conductance, depends exponentially on the distance between the hopping sites. As with shorter ligands the average distance between the nanocrystals decreases, the conductance will increase exponentially. It should be noted that the exponential dependence of differential conductance on ligand length still holds for EDA despite the presence of two amine groups. This suggests that for comparably weakly binding amine groups the effect of interparticle distance is more important than the modifica-

tion of the surface electronic structure through the anchor group. [5,33,36] This is also in line with the virtually identical spectral position of the absorption edge for the amine-based ligands.

2.3. Different anchor groups and aliphatic vs. aromatic bridging groups

We now turn to the discussion of the remaining ligands that carry different anchor and bridging (i.e. aliphatic and aromatic) groups. **Figure 5** summarizes the optical and electronic properties of thin films for all ligands by displaying the differential conductance for each film as a function of the observed shift in the optical absorption edge. The following observations, which will be discussed in detail below, can be made: first, ligands with the same anchoring group (i.e. thiols, amines, acids) cluster, within experimental accuracy, at the same shift of the optical absorption edge but show very different conductance. Second, within a group of ligands the differential conductance can vary by more than an order of magnitude depending on the bridging unit. Third, $(NH_4)_2S$ and PD show the highest and lowest differential conductivity, respectively.

As discussed above for the case of amines, the shift of the absorption edge in absence of quantum confinement must solely be explained with the different nature of the anchor group. Different interaction/binding with the nanocrystal surface will lead to different degrees of interfacial charge redistribution. This changes the polarizability and dielectric environment of the nanocrystals which will lead to shifts in the optical absorption. The observed red shifts for thiols, blue shifts for pyridine and no shift for amines is in agreement with related studies of other (quantum confined) nanocrystals.[35, 36, 45] The differences in conductance for the different anchor groups (thiols show larger conductance than amines, which show larger conductance than acids) may result from the same effects that cause the shifts in the absorption. By changing the polarizability and dielectric environment between the nanocrystals the effective barrier for the hopping process may be modified leading to different hopping rates for the different anchors. In addition thiols may be more effective in passivating the sulfur vacancies

on the pyrite nanocrystal surfaces reducing charge carrier trapping. Related observations have been made for tunneling junctions of thiol, amine and carboxylic acid terminated alkanes. The same trend in conductivity of these molecules was observed and attributed to different electronic coupling of the anchors to the electrode, essentially modifying the tunneling barrier via the contact resistance.[46]

The variation of the differential conductance within each anchor group can be explained by the different bridging group. In addition to the above discussed length effect, the nature of the bridging unit needs to be taken into account. For instance, BDT leads to a larger conductivity than the alkane thiols, despite being longer than the EDT ligand for instance. This can be attributed to, firstly, a different dielectric environment and increased polarizability of the space between the nanocrystals provided by the aromatic benzene, and, second, additional hopping pathways provided by the molecular frontier orbitals of the aromatic linker.

The largest conductance is displayed by films containing $(NH_4)_2S$. This is attributed to the fact that ammonium sulfide provides a very short, inorganic linkage between the nanocrystals, which has been shown to drastically improve conductivity in PB and Cd based quantum dot solids.[31] PD on the other hand leads, as the only ligand, to an optical blue shift and displays the lowest conductivity. Following the above arguments this result indicates that the changes to the dielectric environment induced by PD are opposite to the other anchor group effectively leading to a larger hopping barrier. Additionally, PD may be less efficient in passivating sulfur vacancies on the nanocrystal surfaces.

It should be noted, that washing the thin films with acetonitrile only, already leads to an increased conductivity. This is due to ligand removal and thus decreased interparticle distances and hopping barriers.

Lastly, we turn to the SPV measurements of pyrite nanocrystal thin films that underwent ligand exchange. **Figure 6** displays SPV spectra (in-phase with the modulated light) of as prepared thin films and of films after ligand exchange to OA, EDT and (NH4)2S, respectively.

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The SPV signals are very weak and change sign at energies of about 1.5 eV. The appearance of SPV signals at photon energies below the band gap of pyrite shows the importance of defect states in this material. It is speculated that the negative sign of the sub band gap photovoltage can be related to the modulated excitation of holes trapped at surface states. The SPV signals of pyrite nanocrystals are about 2-3 orders of magnitude smaller than modulated SPV signals of conventional semiconductors (see, for example reference 47) indicating possibly large activation barriers. Therefore, improving the quality of the prepared pyrite thin films remains a critical challenge for the fabrication of solar cells. Promisingly, an increase of the modulated SPV signals has been observed after treatment with $(NH_4)_2S$. Further, the SPV signals passed the zero signal at lower photon energies for the pyrite nanocystals post-treated with EDT and $(NH_4)_2S$, which gives evidence that strong absorption sets on at reduced photon energy, i.e. that the band gap shifted to a lower value. This is line with the above observation of the red shifted absorption edge for these ligands.

3. Conclusion

In conclusion, using a systematic approach we investigated the effects of ligand anchor and bridging groups on the electronic and optical properties of pyrite nanocrystal thin films. In the absence of quantum confinement effects, the anchor group determines the optical shifts by modifying the dielectric environment in between the nanocrystals. The conductivity is determined by the combined effects of the chemical nature of the ligand and bridging group modifying the barrier for hopping transport. The SPV measurements show that charge separation occurs in pyrite nanocrystals and that the modulated SPV signals increased after surface treatments. However, the modulated SPV signals remained extremely small, which shows that improving the film quality remains a critical challenge for realizing pyrite nanocrystal-based solar cells. The largest red shift and highest conductivity is found for ammonium sulfide. Our findings highlight the importance of surface functionalization and interparticle electronic coupling in the use of pyrite nanocrystals for photovoltaic devices.

4. Experimental Section

Materials. $FeCl_2$ (anhydrous, 99.99%, Sigma-Aldrich (S-A)), sulfur powder (99.998%, S-A), oleylamine (OLA) (80–90%, Acros), anhydrous ethanol (99.5%, Merck), chloroform (99.9%, S-A), anhydrous acetonitrile (99.8%, S-A), methanol (99.9%, Fluka), ethylenedia-mine (EDA) (99%, S-A), octylamine (OA) (99%, S-A), dodecylamine (DA) (99%, S-A), pyr-idine (99.8%, S-A), 1,2-ethanedithiol (EDT) (98%, Fluka), benzene-1,4-dithiol (BDT) (99%, S-A), 1,8-octanedithiol (ODT) (97%, S-A), $(NH_4)_2S$ (40–48 wt. % in H_2O, S-A), acetic acid (A-acid) (99.7%, S-A), decanoic acid (D-acid) (99.5%, Fluka). All chemicals were used as received. ITO substrates were purchased from PGO ($\leq$ 10 Ohms/sq.) and cleaned prior to use by ultrasonication in acetone (99.8%, Merck) and 2-proponal (99.7%, Merck) for 15 min each.

Pyrite FeS_2 nanocrystal synthesis. We used a slightly modified oleylamine-based synthesis that results in weakly bound ligands that are easily replaced.[2] In short, in a typical reaction, $FeCl_2$ (254 mg/2 mmol) was mixed with OLA (6 mL) in a three-neck flask and then reacted under a nitrogen atmosphere at 100 ºC for 1 hour to form the Fe–OLA complex. Afterwards, OLA solution of sulfur (6 mL) was quickly injected into the solution. The Fe/S-molar ratio was kept at 1/6. The resulting solution was heated to 220 ºC and kept at this temperature for 180 min. After the solution was cooled to room temperature, chloroform (10 mL) was injected into the solution and ethanol (10 mL) was added to precipitate FeS_2 nanocrystals. The precipi-tate was further purified by washing with 1:1 chloroform/ethanol mixture assuring that only surface bound ligands remained on the nanocrystal surface.[48] Finally, FeS_2 nanocrystals were collected.

Film preparation and ligand exchange. The obtained stable FeS_2 dispersions (30–100 mg mL^{-1}) were used as colloidal ink for spin coating onto clean glass or ITO coated glass sub-strates at 1000–2000 rpm. Film samples were immersed in 0.1 M EDA, OA, DA, pyridine,

EDT, BDT, ODT, $(NH_4)_2S$, A-acid, or D-acid solutions (acetonitrile or methanol as solvents), respectively, in a capped glass vials for 24 hours. After removing the samples from the vials, they were washed with acetonitrile or methanol. Again, this ensures the removal of excess ligands not bound to the surface of the nanocrystals. The described surface ligand exchange rendered the films insoluble in chloroform. To reduce the number of pinholes and cracks, multiple cycles of nanocrystal spin-coating and ligand exchange were employed. Ligand exchange in the solid state allows usage of bi-functional linkers which, in the case of ligand exchange in solution, would lead to destabilization of the colloidal suspensions.

Characterization. To confirm the ligand exchange, Fourier transform infrared spectroscopy (FTIR, Bruker IFS 66 v/S) was performed. The crystal phase of pyrite and its stability were tested by a Raman microscope (Horiba, T64000) using a 514 nm laser. The optical density of the 500 nm thick thin films used in FTIR and Raman measurement exhibited transmissions of at least 10% at the experimental wavelength assuring that signal from the whole film was collected. UV-vis absorption spectra of FeS_2 nanocrystal films were recorded on a Cary 5000 UV-vis-NIR spectrophotometer. The film quality was investigated with scanning electron microscopy (SEM, Zeiss Ultra 55 Plus). For the electrical studies, FeS_2 nanocrystal films on ITO coated glass substrates were used. 100 nm Al electrodes were deposited onto the film surface. The current–voltage (I–V) characteristics of the films were measured with a Keithley 2400 source meter at room temperature. An Oriel solar simulator was used as light source for measurements under standardized AM1.5 illumination. SPV measurements were carried out in vacuum (10^{-5} mbar) in the fixed capacitor arrangement with a dielectric mica spacer between the sample electrode (nanocrystal layers spin cast on ITO) and the SnO_2:F electrode deposited on a quartz cylinder. Both electrodes were connected with a 10 GΩ resistance (RC time constant τRC about 100 ms). Spectral dependent SPV signals were coupled out via a high impedance buffer and measured with a two-phase lock-in amplifier (EG&G 5210). SPV

spectra were excited with light from a halogen lamp passing through a quartz prism mono-chromator and an optical chopper (chopping frequency 8 Hz).

Supporting Information

Supporting Information (additional FT-IR and Raman spectra, additional analysis of FT-IR spectra and SEM images) is available online from the Wiley Online Library.

Acknowledgements

[1]   C. Wadia, A.P. Alivisatos, D.M. Kammen, *Environ. Sci. Technol.* **2009**, *43*, 2072.

[2]   W. Li, M. Döblinger, A. Vaneski, A.L. Rogach, F. Jäckel, J. Feldmann, *J. Mater. Chem.* **2011**, *21*, 17946.

[3]   C. Steinhagen, T.B. Harvey, C.J. Stolle, J. Harris, B.A. Korgel, *J. Phys. Chem. Lett.* **2012**, *3*, 2352.

[4]   J.M. Lucas, C.-C. Tuan, S.D. Lounis, D.K. Britt, R. Qiao, W. Yang, A. Lanzara, A.P. Alivisatos, *Chem. Mater.* **2013**, *25*, 1615.

[5]   H.A. Macpherson, C.R. Stoldt, *ACS Nano* **2012**, *6*, 8940.

[6]   J. Puthussery, S. Seefeld, N. Berry, M. Gibbs, M. Law, *J. Am. Chem. Soc.* **2011**, *133*, 716.

[7]   C. Wadia, Y. Wu, S. Gul, S.K. Volkman, J. Guo, A.P. Alivisatos, *Chem. Mater.* **2009**, *21*, 2568.

[8]   D. Wang, Q. Wang, T. Wang, *CrystEngComm* **2010**, *12*, 3797.

[9]   D.-Y. Wang, Y.-T. Jiang, C.-C. Lin, S.-S. Li, Y.-T. Wang, C.-C. Chen, C.-W. Chen, *Adv. Mater.* **2012**, *24*, 3415.

[10]   Y. Wang, Y. Hu, Q. Zhang, J. Ge, Z. Lu, Y. Hou, Y. Yin, *Inorg. Chem.* **2010**, *49*, 6601.

[11]   Y. Wu, C. Wadia, W. Ma, B. Sadtler, A.P. Alivisatos, *Nano Lett.* **2008**, *8*, 2551.

[12]   I. Kriegel, J. Rodríguez-Fernández, E. Da Como, A.A. Lutich, J.M. Szeifert, J. Feldmann, *Chem. Mater.* **2011**, *23,* 1830.

[13]   M. Cabán-Acevedo, M.S. Faber, Y. Tan, R.J. Hamers, S. Jin, *Nano Lett* **2012,** *12*, 1977.

[14]   A. Ennaoui, H. Tributsch, *Sol. Energy Mater.* **1986**, *14*, 461.

[15]   A.K. Abass, Z.A. Ahmed, R.E. Tahir, *Phys. Status Solidi* **1986**, *97*, 243.

[16]   A.M. Karguppikar, A.G. Vedeshwar, *Phys. Status Solidi* **1986**, *95*, 717.

[17]   A.M. Karguppikar, A.G. Vedeshwar, *Phys. Status Solidi* **1988**, *109*, 549.

[18]   G. Smestad, A. Ennaoui, S. Fiechter, H. Tributsch, W.K. Hofmann, M. Birkholz, W. Kautek, *Sol. Energy Mater.* **1990**, *20*, 149.

[19]   P. Cozzoli, T. Pellegrino, L. Manna, *Chem. Soc. Rev.* **2006**, *35*, 1195.

[20]   C. de Mello Donegá, P. Liljeroth, D. Vanmaekelbergh, *Small* **2005**, *1*, 1152.

[21]   A. Rogach (Ed.) *Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications*, Springer, Wien, Austria, New York, USA **2008**.

[22]   C.-Y. Liu, Z.C. Holman, U.R. Kortshagen, *Nano Lett.* **2009**, *9*, 449.

[23]   Y.-Y. Lin, D.-Y. Wang, H.-C. Yen, H.-L. Chen, C.-C. Chen, C.-M. Chen, C.-Y. Tang, C.-W. Chen, *Nanotechnology* **2009**, *20*, 405207.

[24]   Y.-C. Wang, D.-Y. Wang, Y.-T. Jiang, H.-A. Chen, C.-C. Chen, K.-C. Ho, H.-L. Chou, C.-W. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6694.

[25]   A. Ennaoui, S. Fiechter, C. Pettenkofer, N. Alonso-Vante, K. Büker, M. Bronold, C. Höpfner, H. Tributsch, *Sol. Energy Mater. Sol. Cells* **1993**, *29*, 289.

[26]   J.P. Wilcoxon, P.P. Newcomer, G.A. Samara, *Solid State Commun.* **1996**, *98*, 581.

[27]   P.V. Vanitha, P. O'Brien, *J. Am. Chem. Soc.* **2008**, *130*, 17256.

[28]   X. Chen, Z. Wang, X. Wang, J. Wan, J. Liu, Y. Qian, *Inorg. Chem.* **2005**, *44*, 951.

[29]   Y. Bi, Y. Yuan, C.L. Exstrom, S. A. Darveau, J. Huang, *Nano Lett.* **2011**, *11*, 4953.

[30]   L. Yu, S. Lany, R. Kykyneshi, V. Jieratum, R. Ravichandran, B. Pelatt, E. Altschul, H.A.S. Platt, J.F. Wager, D.A. Keszler, A. Zunger, *Adv. Energy Mater.* **2011**, *1*, 748.

[31]   H. Zhang, B. Hu, L. Sun, R. Hovden, F.W. Wise, D.A. Muller, R.D. Robinson, *Nano Lett.* **2011**, *11*, 5356.

[32]   E. Zillner, S. Fengler, P. Niyamakom, F. Rauscher, K. Köhler, T. Dittrich, *J. Phys. Chem. C* **2012**, *116*, 16747.

[33] N. Pradhan , D. Reifsnyder , R. Xie , J. Aldana , X. Peng, *J. Amer. Chem. Soc.* **2007**, *129*, 9500.

[34]   Similar results were obtained for ligands with the same anchor groups but different bridging units (see supporting information for details).

[35]   A. Lefrançois, E. Couderc, J. Faure-Vincent, S. Sadki, A. Pron, P. Reiss, *J. Mater. Chem.* **2011**, *21*, 11524.

[36]   Y. Gao, M. Aerts, C.S.S. Sandeep, E. Talgorn, T.J. Savenije, S. Kinge, L.D.A. Siebbeles, A.J. Houtepen, *ACS Nano* **2012**, *6*, 9606.

[37] G. Sarasqueta, K.R. Choudhury, F. So, *Chem. Mater.* **2010**, *22*, 3496.

[38]   H. Günzler, H.-U. Gremlich, *IR Spectroscopy*, Wiley, Weinheim, Germany **2002**.

[39] G.C. Lisensky, R.L. Penn, C.J. Murphy, A.B. Ellis, *Science* **1990**, *248*, 840.

[40] P. Samorí, N. Severin, K. Müllen, J.P. Rabe, *Adv. Mater.* **2000**, *12*, 579.

[41]   H. Vogt, T. Chattopadhyay, H.J. Stolz, *J. Phys. Chem. Solids* **1983**, *44*, 869.

[42]   A.K. Kleppe; A.P. Jephcoat, *Miner. Mag.* **2004**, *68*, 433.

[43]   J. Zhang, A.A. Lutich, A.S. Susha, M. Döblinger, C. Mauser, A.O. Govorov, A.L. Rogach, F. Jäckel, J. Feldmann, *J. Appl. Phys.* **2010**, *107*, 123516.

[44]   A.J. Houtepen, D. Kockmann, D. Vanmaekelbergh, *Nano Lett.* **2008,** *8*, 3516.

[45]   Y. Liu, M. Gibbs, J. Puthussery, S. Gaik, R. Ihly, H.W. Hillhouse, M. Law, *Nano Lett.* **2010**, *10*, 1960.

[46]   F. Chen, X. Li, J. Hihath, Z. Huang, N. Tao, *J. Am. Chem. Soc.* **2006**, *128*, 15874.

[47]   T. Dittrich, A. Gonzáles, T. Rada, T. Rissom, E. Zillner, S. Sadewasser, M. Lux-Steiner, *Thin Solid Films* **2013**, *535*, 357.

[48] D. Celik, M. Krueger, C. Veit, H.F. Schleiermacher, B. Zimmermann, S. Allard, I. Dumsch, U. Scherf, F. Rauscher, P. Niyamakom, *Sol. Energy Materials & Solar Cells* **2012**, *98*, 433.

Figure captions

Figure 1. Overview of ligands studied. Oleylamine (OLA), the ligand present after nanocrystal synthesis and film preparation, was replaced by ethylenediamine (EDA), octylamine (OA), dodecylamine (DA), pyridine (PD), ethanedithiol (EDT), benzenedithiol (BDT), 1,8-octanedithiol (ODT), ammonium sulfide ($(NH_4)_2S$), acetic acid (A-acid) or decanoic acid (D-acid), respectively.

Figure 2. (A) FT-IR and (B) Raman spectra of ~500 nm thick pyrite nanocrystal films with OLA (as prepared) and after ligand exchange with DA, D-acid, EDT, PD, and $(NH_4)_2S$, respectively. Spectra are off-set vertically for clarity.

Figure 3. SEM images of pyrite layers (one cycle of spin coating and ligand exchange) with (A) OLA (i.e. as-prepared); and after ligand exchange with (B) DA; (C) EDT; (D) $(NH_4)_2S$; and of multilayers with (E) $(NH_4)_2S$, three cycles spin coating and ligand exchange; and (F) cross sectional SEM of the sample in panel (E).

Figure 4. (A) Absorption spectra of pyrite nanocrystal films with OLA (as prepared), and after ligand exchange to DA, OA and EDA, respectively. Spectra are off-set vertically for clarity. (B) *I-V*-curves of pyrite nanocrystal films with OLA (as-prepared; inset) and after ligand exchange to EDA with and without illumination (AM1.5). (C) Shifts of the optical absorption edge and differential conductance (at $0V$) for pyrite nanocrystals films with OLA (as prepared), EDA, OA and DA, respectively. Open and closed symbols represent differential conductance with and without illumination, respectively.

Figure 5. Differential conductance (at $0V$) vs. shift of the optical absorption edge for pyrite nanocrystal films for all ligands investigated. Open and closed symbols represent differential conductance with and without illumination, respectively.

Figure 6. SPV spectra of pyrite nanocrystal thin films with OLA (as prepared) and after ex-

change with OA, EDT and (NH$_4$)$_2$S.

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The influence of ligand anchor and bridging groups on the optical and electronic properties of pyrite nanocrystal thin films is investigated systematically. The thin film absorption onset shifts up to 100 meV to the red and the differential conductance varies over four orders of magnitude for the different ligands with ammonium sulfides and thiolated aromatic linkers showing the largest effects.

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

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