Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange

Patrick R. Brown,†,‡ Donghun Kim,§,∥ Richard R. Lunt,∥ Ni Zhao,¶ Moungi G. Bawendi,∥ Jeffrey C. Grossman,‡,* and Vladimir Bulović†,*

†Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States, ‡Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States, §Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824, United States, ¶Department of Electronic Engineering, Chinese University of Hong Kong, Shatin, Hong Kong, ∥Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States, and #Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States. † These authors contributed equally to this work.

ABSTRACT The electronic properties of colloidal quantum dots (QDs) are critically dependent on both QD size and surface chemistry. Modification of quantum confinement provides control of the QD bandgap, while ligand-induced surface dipoles present a hitherto underutilized means of control over the absolute energy levels of QDs within electronic devices. Here, we show that the energy levels of lead sulfide QDs, measured by ultraviolet photoelectron spectroscopy, shift by up to 0.9 eV between different chemical ligand treatments. The directions of these energy shifts match the results of atomistic density functional theory simulations and scale with the ligand dipole moment. Trends in the performance of photovoltaic devices employing ligand-modified QD films are consistent with the measured energy level shifts. These results identify surface-chemistry-mediated energy level shifts as a means of predictably controlling the electronic properties of colloidal QD films and as a versatile adjustable parameter in the performance optimization of QD optoelectronic devices.

KEYWORDS: lead sulfide - ligands - quantum dots - nanocrystals - ultraviolet photoelectron spectroscopy - density functional theory - solar cells - photovoltaics

Colloidal quantum dots (QDs) possess a uniquely tunable set of electronic properties that has generated considerable interest in their use as active materials in solution-processed photovoltaics.¹ Synthetic techniques allowing reproducible control of QD size enable the preparation of strongly confined lead sulfide (PbS) colloidal QDs with bandgaps ranging from 0.7 to 2.1 eV, spanning the ideal range for single- and multijunction photovoltaic device applications.² In complement to the control over the QD bandgap afforded by modification of the nanocrystal size, the electronic properties of coupled colloidal QD solids can also be tuned through modification of the QD surface chemistry via ligand exchange.³ A wide variety of ligand chemistries have been utilized for PbS QDs, the highest-performance QD solar cell material to date,⁴ including bidentate aliphatic and aromatic thiols,⁵ primary amines,³ carboxylic acids,⁶ thiocyanate ions,⁷ and halide ions.⁸ For a given ligand, the different facets of the rock-salt-structure PbS nanocrystals present additional differences in steric opportunities and affinities for ligand binding.⁹ Ligand exchange can influence the carrier mobility by changing the inter-QD dielectric environment and tunneling distance; in the absence of other changes, mobility increases exponentially with decreasing ligand length.¹⁰ Appropriate ligands can also passivate electronic trap sites on the QD surface arising from structural aperiodicity and off-stoichiometry of the QD core, increasing carrier and exciton lifetimes and providing a degree of control over the doping level and type of the coupled QD film.¹¹–¹³ Changing the identity of the chemical binding group and dipole moment of the ligand should also change the strength of the QD-ligand surface dipole, shifting the

* Address correspondence to bulovic@mit.edu, jcg@mit.edu.

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vacuum energy and, in turn, the QD valence band maximum (VBM) and conduction band minimum (CBM). A number of studies have examined the influence of surface chemistry on QD energy levels; however, most energy-level studies performed on PbS QDs have been performed on QDs with oleic acid ligands that are too insulating for use in photovoltaic devices, or on QDs with a narrow subset of other ligands. Given the large shifts in energy levels observed for other species of QDs following ligand exchange, it is unlikely that the energy levels of oleic acid-capped PbS QDs are representative of the energy levels of the ligand-exchanged films used in PbS QD solar cells.

Here, the energy level shifts of PbS QDs treated with 12 different ligands are measured using ultraviolet photoelectron spectroscopy (UPS). The measured valence band maxima span a range of 0.9 eV. Atomistic simulations of the vacuum energy shift induced by the binding of five of these different ligands to pristine PbS slabs reproduce the observed trend in energy level modification. The impact of these energy level shifts on photovoltaic performance is determined through studies on devices employing 1,2-ethanedithiol (EDT), 1,2-benzenedithiol (1,2-BDT), and 1,3-benzenedithiol (1,3-BDT) ligands. Even between these chemically similar ligands, shifts in the VBM of more than 0.2 eV necessitate ligand-dependent adjustments of the electron- and hole-extracting contacts to achieve optimal performance. These results have recently guided the design and understanding of a certified 8.55% efficient PbS QD solar cell, a current record for this class of devices. These findings complement the known tunability of QD bandgap and highlight an important mechanism of control over the electronic properties of colloidal QDs.

RESULTS AND DISCUSSION

Ligand-Dependence of QD Energy Levels Measured by UPS.

Figure 1a shows a representative UPS spectrum of a
100 nm thick PbS QD film treated with 1,3-BDT without exposure to air. UPS measures occupied electronic states and thus provides information on the Fermi level (low-binding-energy cutoff) and VBM (high-binding-energy-cutoff) of a material. The energy $E_C$ of the CBM can be approximated by adding the electronic transition peak in solution to a published sizing curve.\(^\text{16,23}\) The PbS QDs used in this study are highly confined, with quantum-confined bandgaps 0.6–1.1 eV larger than the bulk bandgap of PbS. The confined electrons and holes therefore have a high kinetic energy, and the optical dielectric constant ($\varepsilon_{opt} = 17.2$) is a more suitable choice than the static dielectric constant ($\varepsilon = 169$).\(^\text{24}\)

Figure 1b shows a representative absorption spectrum of 1,3-BDT-treated PbS QDs on glass. The first absorption peak of the solid-state ligand-exchanged QDs is at energy $E_g = 1.23$ eV, corresponding to a transport bandgap of $E_g = 1.32$ eV. Figure 1c summarizes the energies of the VBM, Fermi level, and CBM determined from the measurements in Figure 1a,b for 1,3-BDT-treated PbS QDs. While the instrumental accuracy of UPS is $\sim 0.1$ eV,\(^\text{25}\) the standard deviation of our measurement (here across 4 different samples) is much smaller, in the range of 0.02 eV.

Figure 1d shows the chemical structure of the 12 ligands employed in this study, including thiols (benzenethiol (BT), 1,2-, 1,3-, and 1,4-benzene-dithiols (1,2-BDT, 1,3-BDT, and 1,4-BDT), 1,2-ethanedithiol (EDT), and 3-mercaptopropionic acid (MPA)), a primary amine (1,2-ethylenediamine (EDA)), ammonium thiocyanate (SCN), and halides (tetrabutyllammonium iodide (TBAl), bromide (TBABr), chloride (TBACl), and fluoride (TBAF)). Figure 1e shows the measured energy levels of a single batch of PbS QDs ($\lambda = 963$ nm absorption peak in solution) exchanged with these different ligands, sorted by decreasing VBM binding energy (complete photoemission and absorption spectra are given in the Supporting Information).

A maximum shift of 0.9 eV in the VBM is observed between QDs treated with TBABr and BT. Even among the chemically similar bidentate thiols, a shift of 0.3 eV is observed between PbS QDs treated with EDT and 1,4-BDT. Similarly large shifts in energy levels have been observed for conductors treated with thin layers of amine-containing polymers.\(^\text{26}\) Such large shifts are expected to have considerable influence on the operation of electronic devices fabricated using PbS QDs. We note that these energy levels are characteristic only of the specific size of PbS QDs studied here, and only under air-free fabrication and storage conditions; UPS measurements performed on PbS QD films fabricated in air indicate different values for the Fermi level and VBM.\(^\text{23}\) It is also notable that the majority of ligands tested in this study gave rise to VBM(s) significantly deeper than those reported for oleic-acid-capped PbS QDs in the literature (oleic acid ligands are too insulating to be employed in UPS, which requires adequate grounding of the emissive surface to prevent charging-induced shifts in the observed energy levels).\(^\text{16,18}\) This result highlights the importance of performing energy level measurements on QDs in a chemical environment that is as close as possible to the environment present in an operating device, taking into account both the solid-state ligand environment and the history of exposure to air, vacuum, and solvents.

**Ligand Binding Simulations by Density Functional Theory.**

First-principles density functional theory (DFT) calculations provide insight into the origin of the band energy shifts measured by UPS. DFT calculations are widely used to simulate energy level shifts at interfaces between inorganic materials and organic molecules.\(^\text{9,17,13,27,28}\) As shown in Figure 2a, the surface of a PbS QD is approximated as a semi-infinite PbS (100) slab, as the (100) and (111) facets are known to be dominant for PbS QDs (similar trends in DFT results are obtained for binding to Pb-rich (111) facets, as shown in the Supporting Information).\(^\text{9,29,30}\) Modeling the QD surface as a semi-infinite quasi-two-dimensional slab is much more computationally efficient than modeling the entire three-dimensional QD/ligand system, and the electrostatic environment encountered by the electron or hole during transfer across the QD/ligand interface should be similar in both cases. A small dependence on the magnitude of the ligand-induced shift on QD size has been observed elsewhere for InAs QDs,\(^\text{14}\) but the direction of the trend in energy levels for different ligands is expected to be independent of QD size. As shown in Figure 2a, one side of the slab is passivated by ligands and one side by pseudohydrogen atoms for charge balance. Similar results are obtained when both sides of the slab are passivated by ligands (Figure S10 in the Supporting Information).

Five of the ligands employed above are simulated by DFT (BT, 1,2-BDT, 1,3-BDT, 1,4-BDT, and iodide), with the ligand coverage held constant at one ligand binding group per surface Pb atom (thus BT and iodide have twice the density of the benzene-dithiols). The ligands tested here are known to efficiently displace the original oleic acid ligands,\(^\text{8,31–34}\) but it is possible that some oleic acid remains bound to the QD surface, perhaps as a result of variations in binding affinity between the (100)
Figure 2. DFT calculations of ligand-induced energy shifts for PbS slabs. (a) Schematic diagram of modeled PbS slab. The left side of the slab is passivated by adsorbed ligands (1,2-BDT is shown here as an example), and the right side is passivated by appropriate pseudohydrogen atoms to ensure charge balance. Monodentate (BT, iodide) and bidentate (1,2-, 1,3-, and 1,4-BDT) ligands are employed here, with ligand density set at one binding atom per surface Pb atom (hence bidentate ligands have half the areal density of monodentate ligands). (b) Plane-averaged electrostatic potentials of PbS slabs with different ligands. The potential in the vacuum region far to the left of an unpassivated PbS slab is set to zero. (c) Density of states of the ligand (filled curve) and ligand-slab system (unfilled curve) for each of the five ligands considered. The vacuum level above each passivated PbS slab is set to zero. The vertical dashed lines signify the valence and conduction band edge energies. (d) Vacuum energy shifts (ΔE_{vac}) for each ligand and decomposition into interface (ΔE_{vac,1}, red arrows) and intrinsic ligand (ΔE_{vac,2}, blue arrows) dipoles.

and (111) facets.9,35,36 To facilitate comparison between the different ligands and simplify the DFT simulations, complete exchange of oleic acid is assumed.

Figure 2b shows the plane-averaged electrostatic potentials for these five ligands bound to PbS (100) slabs. Large shifts in these vacuum energy level (ΔE_{vac}) compared to the unpassivated PbS slab are observed. Figure 2c shows the electronic density of states of the ligand (filled curve) and ligand-slab system (unfilled curve) for each of the five ligands. The PbS bandgap remains relatively unchanged upon ligand adsorption, while the VBM and CBM shifts match the ΔE_{vac} observed in Figure 2b, indicating that the band edge shifts are electrostatic in origin. There is excellent agreement in the direction and ordering of band edge shifts observed by UPS and DFT, although the magnitude of the shifts is overestimated by DFT.

Shifts in the energy levels of QDs upon ligand adsorption can be conceptualized as the sum of two dipole contributions: a contribution from the dipole formed between the surface atom of the QD and the binding group of the ligand (here referred to as μ_{1}), and a contribution from the intrinsic dipole moment of the ligand itself (μ_{2}).28 For the Lewis-basic ligands studied here, μ_{1} points from the negatively charged ligand to the positively charged lead atom; μ_{2} depends on the chemical structure and binding orientation of the ligand. The z-component of the total dipole (μ_{total,z}) can be expressed as μ_{total,z} = μ_{1,z} + μ_{2,z}, to which ΔE_{vac} is related through the Helmholz equation:

$$\Delta E_{vac} = -\frac{\mu_{total,z}}{AE_{F0}} = -\left(\frac{\mu_{1,z}}{AE_{F0}} + \frac{\mu_{2,z}}{AE_{F0}}\right) = \Delta E_{vac,1} + \Delta E_{vac,2}$$

where A is the surface area of the ligand and ε_{r} is the dielectric constant of the ligand layer.27,37–39

Figure 2d shows ΔE_{vac} for each ligand and the decomposition of ΔE_{vac} into the opposing ΔE_{vac,1} and ΔE_{vac,2} terms. The ligand-intrinsic ΔE_{vac,2} terms follow trends predicted by simple electrostatics: iodide lacks an intrinsic dipole, while ΔE_{vac,2} for the thiol increases as the angle between C–S bonds decreases. The interfacial ΔE_{vac,1} term is large for the compact iodide and BT ligands and decreases for more sterically bulky ligands. The trend in ΔE_{vac} is dominated by the influence of the ligand dipole moment rather than the interfacial dipole, as ΔE_{vac} increases monotonically with decreasing |ΔE_{vac,2}|. The lack of an intrinsic dipole moment in opposition to the surface-ligand dipole moment is a general feature of the halide ligands and explains the large band energy shifts observed for this class of ligands in Figure 1e. The excellent agreement across multiple ligand classes with the trends observed in Figure 1e lends support both to the use of UPS to reliably measure QD energy levels and to the intuitive description of energy level shifts presented here.

Ligand-Dependent Photovoltaic Performance. To determine the importance of these shifts in QD energy levels for photovoltaic devices, PbS QDs exchanged with EDT, 1,2-BDT, and 1,3-BDT are incorporated into ZnO/PbS QD np heterojunction,40 Schottky junction,41 and donor–acceptor heterojunction42 photovoltaics. These ligands have been well studied in PbS QD optoelectronic devices to date4,34,44 and employ identical, reproducible ligand-exchange procedures, so they provide an ideal platform for comparison. All QD film preparation for the photovoltaics studied here is
performed under the same air- and water-free conditions as the film preparation for the UPS studies described above.

Figure 3 shows the dark and light J–V characteristics of indium tin oxide (ITO)/ZnO/PbS QD/MoO3/Au np-heterojunction (np-HJ) photovoltaics (Figure 2a) and ITO/Polyethylenedioxythiophene:polystyrene sulfonate (PEDOT:PSS)/PbS QD/LiF/Al Schottky junction (SJ) photovoltaics (Figure 2b) fabricated with EDT-, 1,2-BDT, and 1,3-BDT-exchanged PbS QDs ($\lambda = 905$ nm first absorption peak in solution) films. Two general performance trends are apparent. First, treatment with EDT results in a lower open-circuit voltage ($V_{OC}$) than treatment with BDT in both the np-HJ and SJ architectures. Second, the relative performance of 1,2-BDT and 1,3-BDT-exchanged QDs is reversed between the np-HJ and SJ architectures: 1,3-BDT exchange results in the best performance for the np-HJ architecture, while 1,2-BDT exchange results in the best performance for the SJ architecture. A straightforward comparison of trap distributions, carrier mobilities, and recombination rates could explain the first of these two trends, but not the second. As described in detail in the Supporting Information, while treatment with EDT leads to the highest carrier mobility of the three ligands studied, the high recombination rate and high trap density of EDT-treated PbS QD films lead to a lower $V_{OC}$ and power conversion efficiency ($\eta_{P}$) than treatment with BDT. However, changes in these properties do not explain the architecture-dependent performance of 1,2-BDT and 1,3-BDT-exchanged QDs. The difference in the energetic environment of the QD film between the np-HJ and SJ architectures suggests that a shift in the energy levels of the PbS QDs between the two different ligand treatments could explain this difference in performance.

In the SJ architecture, the interfacial energetics can be tuned in a controlled manner through modification of the electron- and hole-extracting contacts. A common modification to the simple ITO/PbS/cathode structure is to insert a layer of PEDOT:PSS as a hole-extracting layer between the ITO and the PbS QDs. This PEDOT:PSS is known to aid in hole injection into, and hole extraction out of, organic semiconductors with deep highest occupied molecular orbitals (HOMOs) as a result of its deep work function ($E_F = 5.0$ eV for PEDOT:PSS, vs $4.7$ eV for ITO). As shown in Figure 4, the inclusion of a PEDOT:PSS hole-extracting layer results in a 3.2-fold improvement in $\eta_{P}$ for a SJ photovoltaic fabricated with 1,3-BDT-exchanged PbS QDs, while it has a negligible effect on a 1,2-BDT-exchanged SJ photovoltaic. This observation matches what would be expected from the energy levels reported in
Figure 1e: 1,3-BDT-treated QDs, with their deeper VBM, benefit more from the high-work-function PEDOT:PSS hole transport layer than do the 1,2-BDT-treated QDs. Similarly, a thin layer of LiF is commonly inserted between the cathode and the electron transport layer in organic LEDs and solar cells, where it is shown to increase the efficiency of electron injection and extraction.49,50 This effect is commonly attributed to a lowering of the effective cathode work function as a result of a strong interface dipole induced by the LiF, resulting in a reduced barrier height for electron injection.51 In the PbS QD SJ architecture described here, a reduction in the cathode work function should result in a greater benefit for PbS QDs with a shallower VBM and CBM by strengthening the Schottky junction at the interface and increasing the driving force for electron extraction. Indeed, as shown in Figure 4b, the insertion of LiF results in a 2.2-fold improvement in ηP for 1,2-BDT-treated QDs of different size paired with C60 (f) 1,2-BDT and 1,3-BDT-treated QDs of a given size paired with C60 and (g) 1,2-BDT-treated QDs paired with PTCBI and C60.

Figure 5. Ligand- and QD-size-induced changes in DA-HJ photovoltaic performance. (a) Device structure of the donor–acceptor heterojunction and (b) schematic band diagram of the donor–acceptor pair, showing a conduction band offset ΔECB that is favorable for photocurrent extraction. (c) Measured energy levels of three different sizes of PbS QDs, with LUMO energies of C60 and PTCBI from the literature. The conduction band energy Ec corresponds to the transport gap; the optical gap is omitted here for clarity. The experimental uncertainty of the QD energy levels determined by UPS is 0.1 eV; the uncertainty of the LUMOs of the organic materials determined by inverse photoelectron spectroscopy in the literature is 0.5 eV.25 (d–g) Dark current (dashed curves), light current (solid curves), and photocurrent (dotted curves) of DA-HJ photovoltaics, comparing (d) 1,2-BDT-treated QDs of different size paired with C60 (e) 1,3-BDT-treated QDs of different sizes paired with C60 (f) 1,2-BDT and 1,3-BDT-treated QDs of a given size paired with C60 and (g) 1,2-BDT-treated QDs paired with PTCBI and C60.

Figure 5c shows the measured energy levels of three different sizes of PbS QDs (λ = 725, 905, and 1,040 nm). Dark current (dashed curves), light current (solid curves), and photocurrent (dotted curves) of DA-HJ photovoltaics, comparing (d) 1,2-BDT-treated QDs of different size paired with C60 (e) 1,3-BDT-treated QDs of different sizes paired with C60 (f) 1,2-BDT and 1,3-BDT-treated QDs of a given size paired with C60 and (g) 1,2-BDT-treated QDs paired with PTCBI and C60.
METHODS

PbS QD Synthesis and Film Preparation. All synthesis, fabrication, and testing are performed under oxygen- and water-free conditions unless otherwise stated. Oleic acid-capped PbS QDs are synthesized via standard literature methods and purified three times by precipitation and centrifugation in a mixture of acetone and 1-butanol, followed by resuspension in hexane. After the final round of purification, the QDs are dissolved in octane at a concentration of 25 mg mL\(^{-1}\). All solid QD films are prepared by sequential spin-casting. For each layer, ~15 μL of QD solution is dispensed through a 0.02 μm filter (Anotop) onto a 12.5 mm × 12.5 mm substrate and spin-cast at 1500 rpm for 15 s. Roughly 200 μL of ligand solution is then dispensed through a 0.1 μm filter (PTFE) onto the substrate, allowed to sit for 30 s, and spun dry. The substrate is then flooded with the solvent used for ligand exchange and spun dry three times to remove unbound ligand, and the entire process is repeated; each complete iteration results in the deposition of ~20 nm of QDs. The ligand concentrations and solvents used in this study are representative of well-characterized ligand exchange conditions from the literature: benzenethiol and 1,2-, 1,3-, and 1,4-benzenedithiol, 1.7 mM in acetonitrile (ACN); 3-mercaptopropionic acid, 115 mM in methanol (MeOH); ethylenediamine, 1 M in MeOH; ammonium thiocyanate, 30 mM in MeOH; and tetrabutylammonium fluoride, chloride, bromide, and iodide, 30 mM in MeOH. All chemicals are purchased from Sigma-Aldrich at the highest purity available.

Ultraviolet Photoelectron Spectroscopy. UPS spectra are collected using an Omicron ultrahigh vacuum system with a base pressure of 10\(^{-10}\) mbar. The substrates for the UPS measurement are 12.5 mm × 12.5 mm glass slides coated with...
Cr(10 nm)/Au(100 nm) anodes by thermal evaporation and stored in air-free conditions without further surface treatment. Five sequential spin-casting cycles of PbS QDs with various ligand treatments, performed as described above, result in a QD film thickness of ~100 nm. Electrical contact from the steel sample plate to the Cr/Au anode is made using carbon tape. Samples for UPS are transported from an inert-atmosphere glovebox (<1 ppm of O2) to the UPS system without exposure to air using a load-locked transfer system. During the UPS measurement, illumination at 21.22 eV is provided by the He(I) emission line from a helium discharge lamp, and the chamber pressure increases to 10^{-7} mbar. The samples are biased at ~5.0 V to ensure accurate determination of the low-kinetic energy cutoff, and electron emission is collected at 0° from normal. Single kinetic energy scans are completed in <45 s to minimize charging. Cutoff energies are determined from the intersection of a linear extrapolation of the cutoff region to a linear extrapolation of the baseline.

Density Functional Theory Calculations. DFT calculations are performed using the Vienna Ab Initio Simulation Package (VASP)67 with the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE)68 for the exchange and correlation functional. The projector-augmented-wave method is adopted to describe the core electrons. Our recent work has shown that variations in ligand coverage density can significantly affect electronic properties;13 surface coverage here is held constant for two consecutive ionic steps is less than 10^{-4} eV, and (ii) the maximum Hellmann–Feynman forces acting on each atom are less than 0.02 eV Å^{-1}. Dipole corrections are included to remove the spurious electrostatic interactions between neighboring supercells.

Photovoltaic Device Fabrication. Photovoltaic devices are deposited onto ITO-coated glass substrates (Thin Film Devices) that have been cleaned by ultrasonication in micro-90 soap solution, deionized water, acetone, and 2-propanol, followed by treatment with ozone plasma. The device area is defined by the anode–cathode overlap to be 1 mm². Zinc oxide (Plasmaterials) is deposited by rf-sputtering as described in ref 43. Molybdenum oxide (C49), 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI), bathocuproine (BCP), aluminum, silver, and gold are deposited by thermal evaporation at 0.5 mtorr, with the gold being deposited by thermal evaporation at 0.5 mtorr. The sample plate to the Cr/Au anode is made using carbon tape. The samples are biased at ~5.0 V to ensure accurate determination of the low-kinetic energy cutoff, and electron emission is collected at 0° from normal. Single kinetic energy scans are completed in <45 s to minimize charging. Cutoff energies are determined from the intersection of a linear extrapolation of the cutoff region to a linear extrapolation of the baseline.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Ultraviolet photoelectron spectra and absorption spectra of QD-ligand complexes. Ligand binding simulations on Pb-rich PbS(111) surface, monodentate and bidentate ligand binding simulations on PbS(100) surface, and double-sided ligand binding simulations on PbS(100) slab. Field-effect mobility, recombination rate, and density of states of ligand-exchanged PbS QDs, and solar cell spectral mismatch. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES


