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In-situ Measurement and Control of the Fermi Level in Colloidal Nanocrystal Thin Films during their Fabrication

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dots

ABSTRACT: In engineering a high-performance semiconductor device, understanding of the Fermi level position is critical. Here, we demonstrate that open-circuit potential (OCP) measurements can be used to quantify the Fermi level in nanocrystal thin films *in-situ* during their solution-based fabrication. We use this method to study the influence of (1) a metal contact and (2) nanocrystal surface termination on the Fermi level of the nanocrystal film, and find that oxidation or reduction of the nanocrystals as well as surface terminations with dipoles can be used to tune the Fermi level over large energy ranges. Finally, to emphasize the compatibility of the technique with device fabrication, we show that we can use blends of ligands to design the Fermi level landscape in a nanocrystal film. Our work highlights that OCP measurements can be

used to gain insights into existing device operation and direct further optimization of optoelectronic devices.

Colloidally-synthesized nanocrystals (NCs) exhibit size-dependent electronic structures, making them attractive for optoelectronic devices.^{1,2} In addition to size control, surface functionalization via ligand exchange provides a means to tune the electronic properties of NC-based thin films. The surface groups determine the electronic coupling between NCs and can strongly influence the electronic structure within thin films, with shifts in the band edges and Fermi level on the order of 1-2 eV.^{3,4} Here, we demonstrate how open-circuit potential (OCP) measurements can be used to quantify the Fermi level in a device during NC thin film fabrication⁴ to facilitate the development of record performing devices.^{5,6}

We begin by introducing the concept of surface dipole formation across a metal-semiconductor interface and how a measured voltage difference can be linked to the Fermi energy. **Figure 1a** illustrates how the electronic structure aligns across a metal-semiconductor interface. Separated by a finite distance, a metal and semiconductor (e.g., here a NC thin film) share the same vacuum level.⁷⁻⁹ After contact formation, the electrochemical potential equilibrates through electron transfer from the low work function material to high work function material.¹⁰ In equilibrium, the redistribution of charge causes a contact potential difference, offsetting the work function difference and shifting the vacuum level. This is often visualized as formation of an interface dipole. If the metal has a larger work function than the semiconductor, the induced surface dipole points away from the metal surface, lowering the vacuum level (**Figure 1a, right**). Thus, a metal substrate's work function is modified from Φ_1 to $\tilde{\Phi}_1$ with respect to the shifted vacuum level after deposition of a semiconductor thin film.

In the case of organic semiconductors deposited on metallic substrates, the shift in work function depends on both charge separation due to charge-transfer across the metal-organic interface as explained above and on the intrinsic molecular dipole of the molecular species itself.¹¹ For

example, self-assembled monolayers (SAMs) of alkanethiols and perfluorinated alkanethiols with opposite intrinsic molecular dipoles have been employed to increase^{12,13} and decrease^{12,14–16} the work function of the underlying transition metal substrates. Such shifts can be on the order of 1 eV and beyond as in the case of Ag (with a work function $\phi_{Ag} = 4.4$ eV), where surface modified samples are observed to have work functions in a range $\tilde{\phi}_{Ag} = 3.8$ eV – 5.5 eV.¹⁷ NC-based thin films, like organics, can exhibit both charge-transfer as well as dipoles, due to asymmetry of the NC or its surface functionalization.

Fermi levels in semiconductor thin films and induced work function shifts after their deposition on metals are commonly probed using x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS),^{4,6,18} scanning tunneling spectroscopy (STS),^{19,20} and Kelvin Probe microscopy⁶. As these techniques are best performed in ultra-high vacuum conditions, they are often applied *in-situ* to study thin films deposited in adjacent, connected system and are generally less compatible with solution-fabricated thin films. On the other hand, electrochemical (EC) techniques, which are themselves performed in solution, are an intuitive choice for measuring the electronic structure of NC thin films. Cyclic voltammetry,^{21–25} (energy-resolved) electrochemical impedance spectroscopy (ER-EIS, EIS),^{25–27} and differential pulse voltammetry^{28,29} have been employed to probe band onsets and quantify the density of states in NC thin films.²⁵ While these techniques determine the band onsets, they do not probe the Fermi level, which is important in understanding the electronic state occupation and junctions formation.

Here, we demonstrate that OCP measurements can be used to quantify the Fermi level position in NC thin films during fabrication. To validate the technique, we use the model system of lead sulfide (PbS) NC thin films since their band structure has been extensively investigated and engineered to improve device performance.^{1,2,30} We show that both charge transfer to and from

the NC film (i.e., oxidation and reduction of the NCs) as well as the dielectric nature of the NC film play important roles in determining the Fermi level in a NC film. We then highlight that the OCP measurements can be performed *in-situ* by integrating it into a dip-coating assembly and using mixtures of surface ligands to engineer different Fermi levels throughout NC films.

In an OCP measurement, differences in electrochemical potential (i.e. differences in the work required to bring a unit charge from vacuum into the system) are measured with a voltmeter between the substrate/NC/electrolyte system (i.e., the working electrode (WE)) and the reference electrode (RE) (**Figure 1b**). The required amount of work changes with vacuum level shifts at the WE surface. These vacuum level shifts are equivalent to the Fermi level offset of the substrate and NC thin film before contact formation. Thus, we can quantify the Fermi level in the NC thin film by tracking the electrochemical potential difference of a modified WE with respect to a RE.

The electrolyte consists of a salt (e.g. 100 mM Tetrabutylammonium perchlorate (TBAP)) dissolved in anhydrous acetonitrile (anh ACN). 300 μ M ferrocene (Fc) is used to set the electrochemical potential of the supporting electrolyte. Indium tin oxide (ITO) in this Fc-containing electrolyte is used as a pseudo-reference electrode with an absolute electrochemical potential $E_{abs}^{ITO} = 4.9$ V versus vacuum (**Experimental Section**), as determined through calibration against an Ag/Ag⁺ reference electrode. TBAP and Fc concentrations are kept to a minimum to limit contamination of the NC thin film, but are large enough that ITO vs ITO OCP measurements show quickly vanishing (within seconds) measured voltage differences (< 10 mV) (**Figure 1c left, Supporting Information SI 1**). **Figure 1c** (right) shows the effect of a single monolayer of 1.3 eV band gap (as determined by the 1st exciton absorption feature in hexane) PbS NCs terminated with 1,2-Ethanedithiol (EDT) on ITO, deposited at ambient conditions.

Equilibration processes are visible within the first ~5 s. After this time, a stable voltage difference of about -285 mV with respect to ITO is observed.

Using the voltage difference measured with OCP, we can understand the energetic structure at an ITO/PbS:EDT interface (**Figure 1d**). Because ITO has a work function larger than that of the PbS NCs, the NCs oxidize, leading to charge separation and a surface dipole pointing away from the ITO surface. This results in a Fermi level of $E_F^{\text{ITO/PbS:EDT}} = -(4.9 \text{ eV} - 0.285 \text{ eV}) = -4.615 \text{ eV}$ in the ~5 nm thick film of PbS:EDT on ITO.

To confirm that oxidation or reduction of NCs and the resulting surface dipole at the metal-NC interface plays a key role in determining the Fermi level in a NC thin film, we investigate the same NC thin film on a series of substrates with different work functions. We select commonly used contacts in NC devices as substrates: ITO, ITO/Molybdenum Oxide (MoO_3), Al, and Al/LiF. On each of these substrates, we deposit a 20 nm PbS:EDT film, performing OCP measurements after every dip coating cycle (approximately every 4-5 nm, based upon atomic force microscopy (AFM)). The values (and error bars) shown in **Figure 2a** represent the mean and standard deviations of 20 seconds-long OCP time traces, recorded after 20 s to allow the system to first reach equilibrium. We measure substrate-dependent absolute potentials of $E_{abs}^{\text{ITO}} = 4.9 \text{ V}$, $E_{abs}^{\text{ITO/MoO}_3} = 4.97 \text{ V}$, $E_{abs}^{\text{Al/LiF}} = 3.54 \text{ V}$, and $E_{abs}^{\text{Al}} = 3.97 \text{ V}$, following the trend of literature values of their respective work functions (note, that we rule out the influence of standard potentials in the sense of mixed potential theory, **Supporting Information SI 2**).^{31–38}. In contrast to ITO and ITO/ MoO_3 giving rise to NC oxidation, Al or Al/LiF have work functions lower than that of the NCs such that the NCs are reduced and the surface dipoles point toward the metal substrate. The case of PbS:EDT on Al/LiF is shown in **Figure 2b**. First, in line with

previous reports,^{37,38} a 3 nm thin LiF layer deposited on Al lowers the vacuum level by 430 meV, creating a dipole at the Al/ LiF interface.³⁵ Upon PbS:EDT deposition, the NCs are reduced and the vacuum level increases by 250 meV, corresponding to a Fermi level of -3.75 eV in the NC thin film.

Figure 2a shows that a single layer of NCs is sufficient to support a dipole of several hundred meV. About 80% of the overall measured voltage drop occurs within the first monolayer (measured voltage after first dipcoating cycling is -285 mV and after 5 cycles it is -360 mV). Transfer of a single electron per NC between the substrate and first NC monolayer layer leads to an estimated vacuum level shift of 325 meV (**Supporting Information SI 3**) consistent with the potential differences observed in **Figure 2a**. Density functional theory (DFT) calculations show that a positively or negatively charged PbS NC with thiol termination in vacuum exhibits a shift in energy levels on the order of 950 meV relative to a neutral NC (**Figure 2c**), and, due to charge screening effects, we expect the magnitude of the shift in energy levels to be smaller in a NC solid. Our measurements and calculations highlight that, when charge is localized on individual NCs, it is feasible to have dipole-induced shifts of several 100 meV. This may account for the contact metallurgy effects observed in transistors and diodes (**Supporting Information SI 4**).

The Fermi level of a NC thin film is also dependent on the surface-termination of the NCs. Surface-termination induced shifts of the electronic structure of capped NCs have been attributed either to the intrinsic dipole moment of the linker species itself⁸⁹ or to the NC-ligand interface dipole,¹⁹ and DFT calculations predict a combination of both.⁴ We perform OCP measurements on 20 nm-thick PbS NC thin films on ITO with 1,2-EDT, 3-Mercaptopropionic acid (MPA), 1,4-Butanedithiol (BDT), and Ammonium thiocyanate (NH_4SCN) ligands, and measure Fermi levels of $E_F^{\text{ITO/PbS:EDT}} = -4.56$ eV, $E_F^{\text{ITO/PbS:MPA}} = -4.59$ eV, $E_F^{\text{ITO/PbS:BDT}} = -4.64$ eV, and

$E_F^{ITO/PbS:NH_4SCN} = -4.89$ eV (**Figure 3a**). These findings are consistent with previous studies (**Supplementary Information SI 5**), highlighting that a solution-based electrochemical methodology can provide comparable information to that obtained by high-vacuum analytical techniques.

All the ligands studied attach via sulfur atom bonding to a Pb surface atom with a reported⁴ interface dipole between the NC and the S atom of 1.5 - 1.9 D; however, they differ in their effective molecular dipole moment. Assuming a primarily monodendate attachment, EDT and BDT exhibit a zero intrinsic dipole moment vertical to the NC surface due to molecular symmetry. Even though MPA as molecular monomer has a reported dipole moment of 2.25 D,⁴⁰ organic carboxylic acids are known to favor dimerization via hydrogen-bonding,^{41,42} which would result in a zero net dipole moment. The zero net dipole moment explains the similarity in the Fermi levels ($E_F^{ITO/PbS:EDT} = -4.56$ eV, $E_F^{ITO/PbS:MPA} = -4.59$ eV, $E_F^{ITO/PbS:BDT} = -4.64$ eV). In contrast, SCN⁻ surface termination (*via* NH₄SCN treatment, see Experimental Section) results in a much lower Fermi level ($E_F^{ITO/PbS:NH_4SCN} = -4.89$ eV). SCN₃⁻ with a reported dipole of 1.78 D⁴³ (pointing towards the PbS surface due to the strong electronegativity of N) lowers the electronic structure. Indeed, we confirm this by measuring the CB and VB onsets of SCN⁻-capped PbS NCs through ER-EIS²⁵ under nitrogen conditions and quantify a mean CB and VB shift of 202 meV compared to EDT (**Figure 3b**). The band onsets agree with XPS and UPS measurements,⁴ and the position of the Fermi level determined here with OCP is consistent with STS studies.⁴⁴ The lowering of the energy levels translates into a surface-dipole induced shift of 0.11 eV/D, equivalent to XPS studies by Kroupa et al. reporting 0.13 eV/D.³ We further observe that the Fermi level lies in close vicinity of the VB, in contrast to the Fermi level in PbS:EDT NC film, which is centered within the bandgap. We attribute this to the fact that

thiocyanates are capable of decomposing at surfaces with strong affinity to S atoms, via cleavage of the S-C bond and dissociation to sulfide and cyanide monolayers.^{45–48} In contrast to EDT, where functional thiol groups bind to Pb surface atoms, the thiocyanate dissociation could partially result in single sulfur atoms being effectively incorporated into the PbS matrix, lowering the cation to anion ratio of the NC. Such a stoichiometry change could explain the positioning of the Fermi level close to the valence band onset as proposed in transport study measurements^{49,50} and predicted from theory.⁵¹ The decreasing Fermi level with increasing film thickness (**Figure 3a**) is consistent with more sulfur incorporation for an increasing number of dipcoating cycles. This highlights that NC is also a means to control the Fermi level position within the NC thin film.

In summary, a number of factors must be considered when designing an interface in a NC device. First, the workfunction difference between the metal and the NC thin film determines the charge state of the NC layer. The dielectric environment of the NCs – determined by the NCs themselves, their packing, and their ligands – determines how this charge is screened. The presence of intrinsic dipoles from the ligands can result in further shifts in the energy level. It can further be expected that a NC-film thickness dependence of the Fermi level may be observed, trending towards the Fermi-level of the NC material/ligand couple in vacuum. This thickness dependence will depend for example on how charge reorganizes over a given thickness (dependent on the electronic coupling between NCs and the energetic disorder of the thin film) as well as chemical changes to the film during deposition (e.g., deposition in air can lead to progressive oxidation).

NC thin films are typically processed from solution in a layer-by-layer procedure using spin coating, dipcoating, or spray coating.^{52–54} We integrate OCP measurements seamlessly into the

dipcoating procedure to monitor the potential landscape during device fabrication (**Experimental Section** and photograph in **Supporting Information SI 6**). To assess whether this technique can be used *in-situ*, we look at the effect of successive OCP measurements on the measured Fermi level values and on the subsequent device performance. First, we determine that after five subsequent measurement repetitions (in the extreme case without any sample rinsing), the OCP deviations are on the order of 30 mV (**Supporting Information SI 7**). Second, we analyze the impact of repetitive thin film exposure to the measurement environment on the performance of heterojunction SCs and find that the power conversion efficiency varies by less than 10% (**Supporting Information SI 8**). We note that selection of an electrolyte that does not interact strongly with the film is important (usage of Tetrabutylammonium hexafluorophosphate instead of Tetrabutylammonium perchlorate reduces the impact on the device performance parameters). Taken together, these results indicate that if a relatively non-interacting electrolyte is selected and if appropriate rinsing protocols during device fabrication are followed, this technique can be used *in-situ*, parallel to device fabrication.

Having shown that OCP measurements allow probing the electronic structure of NC thin films during fabrication, we demonstrate its potential to track the Fermi level within a several hundred nanometer thick NC film. Here we engineer the Fermi level by using combinations of EDT and NH₄SCN ligands. First, we investigate how the Fermi level shifts across an abrupt junction between EDT and NH₄SCN cross-linked PbS films. We deposit a 40 nm PbS:EDT film on ITO, followed by 60 nm PbS:NH₄SCN and measure the Fermi level approximately every 20 nm (**Figure 4a**). The Fermi level as a function of position x in the film can be approximated using an exponential power law $E_F(x) = c * e^{-\frac{x}{x_0}} + E_0$ with a characteristic length of $x_0 = 13$ nm, meaning that the Fermi level decays (or grows) to 37% of the final value across ~3-4 layers of

NCs.

To control the Fermi level, we mix the two ligand exchange solutions in different ratios R , with $R = 0\%$ corresponding to a NH_4SCN ligand exchange solution and $R = 100\%$ corresponding to an EDT ligand exchange solution. **Figure 4b** shows a linear-logarithmic dependence of the Fermi level on R . This calibration curve can be used to design a linear E_F sweep throughout a NC thin film. Based on our finding of a characteristic length of 13 nm, we deposit five 20 nm layers with mixing ratios R of 0%, 1.7%, 8.4%, 38.8% and 100% (see intersection of equidistantly spaced horizontal gray lines with calibration curve in **Figure 4b**) to increase E_F from 4.91 eV to 4.65 eV (**Figure 4c**). Furthermore, it is possible to create a ratchet-style energy level structure. We start with a 20 nm thick layer of $\text{PbS}:\text{NH}_4\text{SCN}$ on ITO and progressively increase the EDT content in three successive 20 nm thin films (using ligand exchange solutions with mixing ratios $R = 2.6\%$, 27% to 100%). This sweep can be repeated multiple times as shown in **Figure 4d**. This *in-situ* character allows for precise tuning of the electronic structure and matching to contact metallurgy (**Supporting Information SI 4**).

In summary, we demonstrate OCP measurements as a method to quantify the Fermi level position in NC thin films. Unlike vacuum-based techniques for quantifying electronic structure, this electrochemical technique is well suited for NC-based thin films as it allows for *in-situ* assessment during the solution-based thin film fabrication. We show that oxidation and reduction of a single NC layer can lead to dipoles, giving rise to vacuum level shifts on the order of several hundreds of meV. Surface functionalization tunes the dielectric environment, and, by mixing ligand species, we can achieve a preselected Fermi level landscape within the NC thin film. This measurement technique and the insights into charge reorganization within NC thin films can be leveraged to further optimize electronic bandstructures in optoelectronic devices.

Methods:

Chemicals: Acetonitrile (anh. ACN, anhydrous, 99.8%), 1,2-Ethanedithiol (EDT, $\geq 98.0\%$), 1,4-Butanedithiol (BDT, $\geq 97.0\%$), 3-Mercaptopropionic acid (MPA, $\geq 99\%$), Ferrocene (Fc, 98%), Tetrabutylammonium perchlorate (TBAP, $\geq 98.0\%$), Tetrabutylammonium tetrafluoroborate (for electrochemical analysis, $\geq 99.0\%$), Ammonium hexafluorophosphate (99.99% trace metal basis), Tetraethylammonium hexafluorophosphate (for electrochemical analysis, $\geq 99.0\%$), Tetrabutylammonium hexafluorophosphate (for electrochemical analysis, $\geq 99.0\%$), Tetrahexylammonium hexafluorophosphate (gravimetric, $\geq 97.0\%$) are purchased from Sigma-Aldrich. N-Hexane (95+%, extra pure, Acros Organics) and Ammonium thiocyanate (NH_4SCN , +99%, extra pure, Acros Organics) are purchased from Fisher Scientific.

Synthesis of the NCs: The synthesis of PbS NCs is carried out using the hot injection method according to Hines and Scholes.⁵⁵ To prepare PbS NCs with 1.3 eV band gap, 1.8 g of PbO is mixed with 5 ml of oleic acid and 75 ml of 1-octadecene in a three-neck flask. At 140 °C 40 ml of 0.1 M hexamethyldisilathiane solution in octadecene is quickly injected to the purified lead oleate. The reaction mixture is cooled down to 90 °C and kept at this temperature for another 5 min. Obtained PbS NCs are purified three times using a mixture of hexane and ethanol and centrifugation. The cleaned NCs are dispersed in hexane at a concentration of 5 mg/ml.

Substrate preparation: ITO substrates are cleaned through two sonication steps (5 min each) in Mucasol solution (10 vol%), deionized water and acetone followed by a 5 min immersion in hot isopropanol, followed by oxygen plasma cleaning. For other substrates than ITO, metals are evaporated on top of ITO. Electrical connection legs (Ossila, E241) are clipped onto the substrate for connection to external circuits. A drop of silver paste is applied on the contact area of the

connection legs/ substrate and backed-out for 30 min at 100 °C. All metallic parts are isolated with PDMS to only expose an approximately 1 cm² window to the electrolyte solution. PDMS is cured for 60 min at 120 °C.

Solution preparation: 300 µM Ferrocene and 100 mM Tetrabutylammonium perchlorate or 100 mM Tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile are prepared in a nitrogen glovebox and exposed to air just before usage.

Thin film fabrication: Thin films are fabricated using a programmable and custom-built, automated dipcoater setup at ambient conditions or in nitrogen glovebox (if OCP measurements are paired with ER-EIS). Films are built up by immersing the substrate into a 5 mg/ml solution of PbS NCs in Hexane followed by a crosslinking step in a 5 mM EDT (or alternatively 5 mM BDT, 5 mM MPA) solution in anh. ACN, or 30 mM NH₄SCN in anh. Methanol. A third rinsing step washes-off excess ligands. Typically, layers of 4 nm thickness are deposited in one cycle. Atomic force microscopy analysis reveals the NC films to be continuous. This is confirmed by the ER-EIS measurement, where the electronic structure of the NC film, not the underlying substrate is observed.

Thin film potential measurement: Potential differences are measured with a Keithley 2602A SMU between reference electrode and the working electrode, formed by NC thin film deposition. In addition to the three-step dip-coating process, we add four more steps (4. additional rinsing, 5. potential measurement, 6. & 7. rinsing in anh. ACN) to automate and migrate the potential measurements into the fabrication line. After immersing the working electrode into the electrolyte, we allow the system 20 s to reach an equilibrium state and we record time traces over 20 s to calculate mean values and standard deviations. All measurements are performed under

ambient conditions, except for the OCP and ER-EIS datasets in **Figure 3b** due to the necessity of an oxygen and humidity-free measurement environment for impedance measurements under applied potentials.

Energy-resolved electrochemical impedance spectroscopy: Charge-transfer between ITO and a NC thin film (same sample fabrication as for OCP measurements) is analyzed using impedance measurements with a perturbation amplitude $E_a = 25$ mV in the frequency range from 1 kHz to 3 Hz at 2 pts./decade in logarithmic spacing in the potential range OCP $\rightarrow$ -1.7 V vs Ag/Ag⁺ (+0.5 V vs Ag/Ag⁺, fresh samples for each measurement) with a typical energy-resolution of 10 mV. A standard Randles circuit consisting out of double layer capacitance in parallel to a charge-transfer resistance, both in series to a series resistance, is used to analyze the charge-transfer event. The inverse charge-transfer resistance is approximated with Gaussian distributions (accounting for the energy spread of the first state) and their means taken as band onsets.²⁵

Assignment of electrochemical to physical scale: The relationship between absolute E_{abs}^M and the relative single electrode E_{rel}^M potentials can be written as:⁵⁶

$$E_{abs}^M = E_{rel}^M + \kappa,$$

where the constant term κ depends on the chosen reference system. To match semiconductor energy levels with the electrochemical potential scale, we follow Trasatti⁵⁷ and define an electron in vacuum just outside the electrolyte phase as a reference point matching the origins of the physical and electrochemical scales. Thus, the Fermi energy of the Ag/Ag⁺ redox-system E_F^{Ag/Ag^+} can be expressed as:

$$-E_F^{Ag/Ag^+} = eE_{abs}^{Ag/Ag^+} = e(E_{SHE}^{Ag/Ag^+} + E^0(H^+/H_2))$$

with the relative potential of the Ag/Ag⁺ pair $E_{SHE}^{Ag/Ag^+} = 0.542$ V versus the standard hydrogen electrode (SHE),⁵⁸ the elementary charge e , and the absolute electrode potential of SHE $E^0(H^+/H_2)$. The reported values for the absolute SHE potential span 4.73 to 4.44 V^{56,57,59} and $E^0(H^+/H_2) = 4.5$ V is chosen in this study. The negative sign in front of E_F^{Ag/Ag^+} comes from the fact that the physical scale points into opposite direction as the absolute electrochemical scale.

Electrode potentials: We emphasize that we are not measuring the redox potential associated with ion transfer to or from the film of interest (i.e., the working electrode (WE)), which would not necessarily correlate with its work function. Instead, the electrochemical potential of the Fc/Fc⁺ couple at the electrode surface is measured. Due to the much larger carrier concentration in the ITO (both forming RE and WE), the electrochemical potential of the Fc/Fc⁺ couple locally equilibrates with the Fermi levels of the metal.

Estimation of surface dipole due to charge transfer event: A PbS:EDT (3.1 nm diameter) inter-NC spacing $r_{inter} = 1.43$ nm has been reported in a previous study²⁵ based upon small-angle X-ray scattering in agreement with literature.⁶⁰ Nanoparticle radius r_{NC} is determined via 1st exciton absorption peak in hexane. PbS:EDT NC networks are reported to form BCC superlattice with the [100] facet parallel to the substrate,⁶⁰ which simplifies the effective area of a NC to $(NC-NC \text{ distance})^2$.

DFT calculations: The atomistic model employed for the $r \sim 1.2$ nm PbS NCs were identical to those used previously,^{25,61,62} constructed following the atomistic model proposed by Zhrebetskyy et al.⁶³ In place of the more computationally demanding ethanedithiol ligands, we used methanethiol (mth) ligands, which capture the chemistry of the Pb-S bond. The final NC

had $N_{Pb} = 199$ lead atoms, $N_S = 140$ sulfur atoms, and $N_L = 118$ ligands. Electronic structure calculations and geometry optimizations are performed within the CP2K program suite utilizing the quickstep module.⁶⁴ A dual basis of localized Gaussians and plane-waves,⁶⁵ with a 300Ry plane-wave cutoff, Double-Zeta-Valence-Polarization (DZVP),⁶⁶ Goedecker–Teter–Hutter pseudopotentials⁶⁷ for core electrons, and the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional are used. Convergence to 10^{-8} in Self-Consistent Field calculations is always enforced. For both the structure and the potential, non-periodic boundary conditions are employed, which is solved using the Wavelet Poisson solver.^{68,69} A cubic unit cell of dimensions 4nm×4nm×4nm was employed. Geometry optimization is performed with the Quickstep module utilizing a Broyden–Fletcher–Goldfarb–Shannon (BFGS) optimizer, with maximum force of 24 meVÅ⁻¹ is used as convergence criteria. The charge state of the NC was achieved by adding/removing an electron from the system. All atoms in all systems are relaxed.

Figure 1. Principle of open-circuit potential (OCP) measurements. a) Schematic of a metal-semiconductor interface. Left: metal and semiconductor a finite distance apart. Here, the metal exhibits a larger work function ϕ_1 with respect to the surface vacuum level than the semiconductor. The semiconductor Fermi level (E_F), conduction (CB) and valence band (VB) are indicated. Right: in contact, Fermi level equilibration between the solids takes place through electron charge-transfer from the semiconductor to the metal. As a result, an electric double layer forms, reflected in a surface vacuum level step Δ , equivalent to the difference $\phi_1 - \phi_2$ between the metal and semiconductor work functions before they are brought into contact. The electric double layer can be interpreted as a surface dipole $\mathbf{p}$ pointing away from the metal surface, that lowers its work function to $\tilde{\phi}_1$. This sketch shows the interface and does not include band bending (**Supporting Information, SI 2**). b) In an OCP measurement, the electrochemical potential differences between a working electrode (the film under measurement such as PbS nanocrystals (NCs) terminated with ethanedithiol (EDT) ligands on ITO, immersed in electrolyte) and the reference electrode (an ITO film) are measured at open-circuit conditions. c)

OCP time traces of (left) ITO versus ITO (showing a vanishing potential difference) and (right) NC film on ITO substrates versus ITO showing a -285 mV potential differences reflective of a surface dipole formation between the PbS and the ITO. d) Bandstructure of a PbS:EDT thin film deposited on ITO. The Fermi level is deduced from the OCP measurement results in panel c). Inset: for quantitative assessment of the magnitude of dipole p and surface vacuum level shift, we assume charges to be separated by the sum of the interparticle distance r_{inter} and nanoparticle radius r_{NC} . The surface dipole can be explained by charge-transfer of 1 electron per NC between substrate and the first NC layer.

Figure 2. Effect of nanocrystal (NC) oxidation or reduction on Fermi level. a) Fermi levels measured before and during deposition of a PbS:EDT NC thin films on substrates typically used in NC-based optoelectronic devices. b) Schematic illustration of surface dipoles formed after deposition of a 3 nm thin LiF layer (which decreases Al work function by 450 meV) and deposition of 20 nm-thick PbS:EDT, where reduction of the NC thin film gives rise to a surface

dipole pointing towards the substrate and increases the vacuum level by 250 meV. c) Density functional theory on a thiol-terminated PbS NC in vacuum shows that an excess negative or positive charge (i.e., reduction or oxidation of the NC) shifts the energy levels by 950 meV compared to that of a neutral NC (center). This shift decreases by a factor of three for simulations performed on NC networks, indicating that oxidation and reduction of a single NC layer can explain Fermi level shifts as seen in a).

Figure 3. Effect of surface termination. a) Fermi levels determined from open circuit potential (OCP) measurements on ITO and during subsequent deposition of PbS nanocrystal films using ethanedithiol (EDT), mercaptopropionic acid (MPA), and butanedithiol (BDT), and Ammonium thiocyanate (NH₄SCN) as ligands. Schematics of these surface terminations are shown on the right. b) Bandstructure of PbS:EDT and PbS:NH₄SCN thin films fabricated and measured under nitrogen conditions. Fermi levels are obtained from OCP measurements and conduction band (CB) and valence band (VB) onsets are determined from energy-resolved electrochemical impedance spectroscopy measurements.

Figure 4. Controlling the Fermi level through ligand mixtures. a) Fermi level measured every 20 nm for a 40 nm thin film with an EDT crosslinked solution followed by a 60 nm film with NH_4SCN cross linker solution (black). The data points are fit with an exponential curve (gray) indicating a characteristic length scale of $x_0 = 13$ nm. The Fermi level for a 100 nm thick PbS cross linked with EDT (blue dashed) or NH_4SCN (red dashed) are also provided. b) Using different mixtures of the two stock ligand exchange solutions (5.5 mM EDT in anh. ACN or 30 mM NH_4SCN in anh. MeOH, respectively) different nanocrystal (NC) films are fabricated and measured to develop the calibration curve. c) A linearly changing Fermi level is achieved depositing 20 nm thick films with the $R = 0\%$, 1.7% , 3.8% , 8.4% , and 100% . d) A ratchet style Fermi level across a 250 nm thick NC film is achieved by selecting three energy-equidistant mixing ratios, deduced from the calibration curve in panel b).

Supporting Information:

SI 1) Electrolyte concentration optimization, **SI 2)** Note on Fermi level pinning and band bending in NC thin films immersed in electrolyte, **SI 3)** Discussion of substrate work functions, **SI 4)** Estimation of surface vacuum level shift based upon single electron charge transfer, **SI 5)** Reported bandstructures in NC thin films, **SI 6)** Photograph of measurement setup integrated in fabrication line, **SI 7)** Impact of electrolyte exposure on measured Fermi level, **SI 8)** Electrolyte impact on device performance, **SI 9)** Discussion of contact metallurgy

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Author Contributions: SV performed the experiments. OY and MY synthesized the material. NY performed DFT simulations. SV, DB and VW envisioned the experiments. The manuscript was written through contributions of all authors.

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