Heavily doped n-type PbSe and PbS nanocrystals using ground-state charge transfer from cobaltocene

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Colloidal nanocrystals (NCs) of lead chalcogenides are a promising class of tunable infrared materials for applications in devices such as photodetectors and solar cells. Such devices typically employ electronic materials in which charge carrier concentrations are manipulated through "doping;" however, persistent electronic doping of these NCs remains a challenge. Here, we demonstrate that heavily doped n-type PbSe and PbS NCs can be realized utilizing ground-state electron transfer from cobaltocene. This allows injecting up to eight electrons per NC into the band-edge state and maintaining the doping level for at least a month at room temperature. Doping is confirmed by inter- and intra-band optical absorption, as well as by carrier dynamics. Finally, FET measurements of doped NC films and the demonstration of a p-n diode provide additional evidence that the developed doping procedure allows for persistent incorporation of electrons into the quantum-confined NC states.

Electronic devices often achieve maximum performance by using electronic doping of their constituent electronic materials to exert control over charge carrier behavior. A powerful example is the use of the internal fields within the p-n junction of many common types of photovoltaic solar cells to achieve efficient carrier separation. Colloidal semiconductor nanocrystals (NCs) are the subject of vigorous and widespread investigation for use in low-cost, efficient electronic devices1–3. Increasingly, focus is shifting to realizing and exploiting electronic doping in these materials, particularly in infrared NCs, like the lead chalcogenides, which are of direct importance for solar cells. Reported approaches to NC-doping have utilized incorporation of metal ions4, chemical treatments5,6, or electrochemical charge injection7, but "heavy doping" of lead chalcogenide NCs (persistent introduction of multiple charges into the quantum-confined band-edge states) still represents a significant challenge.

Apparent n- and p-type behaviors have been imparted via surface treatment of PbS and PbSe NCs with chemical species such as hydrazine or ethanedithiol (EDT)1,8, and effective carrier densities within p-type films of EDT-treated NCs can be further manipulated by charge injection from chemical redox agents9. However, studies of field-effect transistors (FETs) based on EDT-treated PbS NCs indicate that these procedures introduce charges not into the NC quantum-confined band-edge states, but rather into surface trap sites within the NC assembly7. While this approach can improve dark conductivity, it does not allow for precise control of the doping level, and the resulting emergence of a band of mid-gap states causes unwanted phenomena such as fast trapping of minority carriers and pinning of the open circuit voltage in photovoltaic cells9. Likewise, introduction of metal-impurity “dopants” into InAs NCs, another infrared-active material, has also resulted in n- or p-type conductivity based transport of carriers through trap states8, which at extreme doping levels may form distinct impurity-based sub-bands9. On the other hand, adding carriers directly into the quantum-confined band-edge NC states offers better control of device performance, as these states reside at predictable, size-tunable energies, and exhibit well-understood degeneracies and recombination dynamics.

Injection of electrons into band-edge NC states has been accomplished in relatively wide-gap materials, such as CdSe or ZnO NCs, by reaction with strong reducing agents such as sodium biphenyl. However, attempts to reproduce these effects in lead chalcogenide-based materials are frustrated by severe degradation of the NCs, as these materials are considerably less chemically robust toward redox chemistry8, ion-exchange32, and more complex processes associated with disruption of the ligand shell33. An alternative approach suitable for PbSe is to inject charges into NCs deposited on an electrode within an electrochemical cell33. This method offers excellent...
control over doping levels, and thus is very useful for, e.g., spectroscopic studies in a laboratory setting; however, the necessity of maintaining an additional externally applied bias to preserve the NC-doping is impractical in a functional device. Thus, there is still a need for a simple, non-destructive method for persistent addition of charge carriers into the band-edge states of lead chalcogenide NCs.

Here, we report the chemical doping of these materials with molecules of cobaltocene, a mild, non-polar-soluble reducing agent. Typically, \(n\)-type PbSe and PbS NCs are prepared by simple mixing of NC dispersions with various concentrations of cobaltocene in toluene (see Methods for details). Ground-state electron transfer from cobaltocene to quantized NC band-edge states is confirmed using optical absorption and photoluminescence (PL) spectroscopy, as well as transient absorption (TA) spectroscopy. As true electronic doping of the NCs can be achieved by this approach, we also study the effect of incorporated charges into the quantum-confined states within the NC core by FETs and \(p-n\) junction diode measurements.

**Results**

The effect of doping on inter-band and intra-band optical absorption. The reduction potential of cobaltocene is \(-0.69\) V vs. SHE\(^{14}\) which lies above the conduction band edge of both bulk PbSe (0.2 V vs. SHE) and PbS (0.1 V vs. SHE)\(^{15}\). Importantly, the driving force for electron transfer in NCs is modified by the effects of quantum confinement: as the conduction band edge of the NCs shifts up in energy with decreasing NC dimensions (Fig. 1a), the driving force decreases, and the process becomes unfavorable at very small sizes. On the basis of size-dependent band energies from a recent report by Jasieniak, \textit{et al.}\(^{16}\), we should expect that electron transfer from cobaltocene to the PbSe and PbS NCs is energetically favorable for particle sizes greater than \(\sim 3.2\) nm and \(\sim 4.2\) nm, respectively.

Once electrons are transferred to the 1S\(_e\) conduction band state, the amplitude of the 1S peak is expected to be reduced (bleached; Fig. 1b) due to Pauli blocking, by an amount \((\Delta N)\) that scales directly with the number of electrons injected into the NC (\(N\)). In the case of PbSe and PbS NCs with an 8-fold degenerate 1S\(_e\) state\(^{16}\), this scaling can be described by \(\Delta N = 8N\), where \(N\) is the number of electrons injected into the NC. For \(N\) electrons, the 1S\(_e\) peak is completely bleached, indicating that the NC contains at least 8 electrons.

By using different concentrations of cobaltocene, we can control the level of doping. As illustrated in Fig. 2a, the increase in the amount of cobaltocene from 20 \(\mu\)m to 5 \(\mu\)m for the same concentration of the PbSe NCs (7.9 nm diameter), the amplitude of the 1S peak at 0.60 eV (Fig. 2a) decreases monotonically. Interestingly, we also observe simultaneous partial bleaching of the second absorption peak at 0.60 eV (Fig. 2a) decreases monotonically. Interestingly, we also observe simultaneous partial bleaching of the second absorption peak, while the third absorption feature remains virtually unchanged.

To analyze these results in quantitative terms, we fit the band-edge absorption to the sum of three Gaussian peaks (Fig. 2b). A plot of the amplitudes of the peaks (\(\alpha_1\), \(\alpha_2\), and \(\alpha_3\)) as a function of cobaltocene concentration (Fig. 2c) reveals clear correlations in the bleaching of the first and second absorption features. Specifically, if we plot the normalized bleach amplitude of the second peak \(\Delta \alpha_2/\alpha_{02}\) vs. \(\Delta \alpha_1/\alpha_{01}\), we see that they are related by a factor of \(-0.5\) (inset of Fig. 2c).

This observation can be explained if we assume that the second absorption feature is due to the two nominally parity forbidden transitions 1P\(_h\) – 1S\(_e\) and 1S\(_e\) – 1P\(_e\). It has been suggested that parity conservation in lead chalcogenide NCs can be broken due to internal electric field and/or asymmetry in the distribution of atoms with

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**Figure 1** Cobaltocene doping of PbSe and PbS NC solutions. (a) The redox potential of cobaltocene (dashed gray line) in comparison to the conduction band states in PbSe (solid black line) and PbS (dashed-dotted black line) NCs. Symbols correspond to samples from the present study. (b) The effect of electron injection from cobaltocene on optical absorption of a NC. NC-size dependent absorption spectra of PbSe (c) and PbS (d) NCs before (solid lines) and after (dashed lines) treatment with cobaltocene; color coding matches that in panel a.
regard to the NC center, allowing these forbidden transitions<sup>20</sup>.
Because of mirror symmetric valence and conduction bands in PbSe, these transitions have the same energy and strength, and should overlap in the absorption spectrum; hence, $\alpha_2$ can be presented as $\alpha_{02} = \alpha_0(1P_h,1S_e) + \alpha_0(1S_h,1P_e) = 2\alpha_0(1P_h,1S_e)$. If electrons are introduced into the $1S_e$ state, the contribution to $\alpha_2$ from the $1S_h - 1P_e$ transition is unchanged, while the contribution due to the $1P_h - 1S_e$ transition is bleached according to $\Delta\alpha(1P_h,1S_e) = (N_e/8)\alpha_0(1P_h,1S_e)$<sup>8</sup>; see Fig. 1b. As a result, $\Delta\alpha_2/\alpha_{02} = N_e/16$, that is, $\Delta\alpha_2/\alpha_{02} = 0.5\Delta\alpha_1/\alpha_{01}$. This is exactly what is seen experimentally.

Along with bleaching of inter-band absorption peaks, doping is expected to activate a new absorption feature in the mid-infrared due to the allowed intra-band transition of the injected electrons from the $1S_e$ to the $1P_e$ level<sup>23</sup> (Fig. 1b). If, as stated above, the second peak in inter-band absorption is due to the $1S_{he} - 1P_{eh}$ transition, its separation from the 1S peak provides a measure of the energy of the intra-band $1S_{he} - 1P_{eh}$ transition, which for 7.9 nm PbSe NCs is 165 meV (Fig. 2d, black solid line). Indeed, along with 1S bleaching, cobaltocene-treatment of these NCs produces a new mid-infrared feature located exactly at 165 meV (Fig. 2d, red dashed line), which cannot be attributed to absorption by cobaltocenium counterion (Supplemental Fig. S1).

**The effect of doping on photoluminescence.** Doping of quantum-confined band-edge states should also have a dramatic effect on the dynamics of photoexcited charges in NCs, and thus on PL quantum yield. On the basis of statistical considerations<sup>25-27</sup>, the radiative lifetime of an exciton in the presence of $N_e$ extra charges ($\tau_{XXX}$) is shorter than that of a neutral exciton ($\tau_{XX}$, typically 100s of ns<sup>28</sup>) by a factor of $(N_e + 1)$. In reality, if even one additional electron is introduced into the NC, the measured lifetime of the singly-charged exciton ($\tau_{XX}$) — a state known as a negative trion — is characterized by sub-ps time constants<sup>25</sup>. This is due to activation of efficient, nonradiative Auger decay, whereby the recombination energy of an electron-hole pair is transferred to the extra carrier within the NC. The Auger decay lifetime ($\tau_a$) scales inversely with the number of available recombination pathways<sup>24</sup>. In the case of a single exciton generated in the NC doped with $N_e$ electrons, $\tau_{XXX}$ can be expressed in terms of the well-established biexciton Auger lifetime ($\tau_{XXX}$) as $\tau_{XXX} = (8\tau_{XXX})/(N_e(N_e + 1))$.

The effect of the combined contributions of radiative and Auger recombination to overall PL efficiency within doped NCs can be described in terms of the PL suppression factor, $\beta$. For an individual NC with $N_e$ extra electrons, $\beta = Q_{Ne}/Q_0 = (8/N_e)\tau_{XXX}/\tau_{XX}$, where $Q_0 = \tau_{XX}/\tau_{XX}$ is the neutral exciton PL quantum yield ($\tau_{XX}$ is its total lifetime), and $Q_{Ne} = \tau_{XXX}/(N_e + 1)\tau_{XX}$ is the charged exciton PL quantum yield. Based on these expressions, a single excess charge is expected to suppress PL by a factor of at least 1000, due to the dramatic difference between the single-exciton radiative lifetime and biexciton Auger lifetime. This is in sharp contrast to the effect on the band-edge absorption feature, which is only bleached by a factor of $N_e/8$ (i.e., 12.5% for a single excess electron).

We use the above considerations to model the effect of injected electrons on PL assuming that extra charges are distributed across the NC sample according to Poisson statistics: $p_i = (<N_e>/i)!\exp(-<N_e>)$, where $p_i$ is the probability of having $i$ electrons in a given NC if the average number of injected electrons is $<N_e>$. In this case, the ensemble-averaged PL suppression factor can be presented as $<\beta> = p_0 + (8\tau_{XXX}/\tau_{XX})\sum_{i=1}^{\infty} p_i i^{-1}$. As $\tau_{XXX}/\tau_{XX} \ll 1$, the ensemble PL quenching factor can be approximated by the fraction of uncharged NCs, that is, $<\beta> = p_0$. In Fig. 3a, we apply this approximation to model the PL quantum yield of the sample with $F_g = 0.60$ eV. Using $<N_e>$ from the bleach of the 1S absorption peak, we obtain excellent agreement with the measured data (inset of Fig. 3a; compare symbols and solid line) without any adjustable parameters. This correlation holds true for all NC sizes, which is to say that smaller NCs that exhibit less 1S bleach also show less PL suppression (Supplemental Fig. S2).

**The effect of doping on carrier dynamics.** Next, we directly monitor photoexcited NC dynamics as a function of doping level using TA experiment<sup>29</sup>. We first measure the pristine sample and find $\tau_{XXX}$ to
be 104(4) ps. Then we treat the sample with cobaltocene to obtain ~55% bleaching of the 1S feature (Fig. 3b), which corresponds to injection of ~4 electrons per NC. The 1S feature gradually recovers with a timescale of approximately 3.4 hours to a final value of about 76% of its original amplitude (inset of Fig. 3b). As the 1S bleach recovers, we observe TA dynamics (Fig. 3c) which also recover, approaching that of the untreated sample (black symbols). To capture the exciton lifetimes in the most heavily and most lightly doped NCs, we apply a two-exponential fit. The results are plotted in Fig. 3d and compared with the Auger lifetimes for X 1-, X 2-, X 3- and X 4- (horizontal lines in Fig. 3d), which were calculated using statistical scaling from biexciton lifetime, $t_{\text{XX}}$. The comparison indicates that the shortest time constant measured for the freshly treated sample is close that of X 4-, as expected for NCs doped with 4 electrons. During the 1S bleach recovery, the initial time constant becomes progressively longer due to discharging of the NCs and eventually approaches the value expected for a trion (X 1-). The long time constant in the freshly treated sample lies in between the values expected for X 1- and X 2-, while the sample which has recovered to the steady state shows values of ~360 ps which is close to the lifetime (416 ps) expected for a negative trion (exciton plus one excess electron). In addition to providing additional evidence for charge injection into NCs, these results represent the first direct measurement of charged exciton dynamics in lead chalcogenide NCs.

### Stability of doped charges

As mentioned above, the data in the inset of Fig 3b shows that in standard core-only PbSe NCs, the majority of injected charges seem to escape from the NC on the timescale of tens of hours. Shim et al. described a similar recovery in n-doped CdSe NCs, which was reported to be mediated by trace amounts of air or water, and accompanied by etching of the NCs. This is not likely to be the operative mechanism in our study: our samples are kept rigorously air- and water-free because we have found that even brief exposure of a doped-NC solution to air leads to complete recovery of spectral features within seconds, well before any sign of the spectral blue-shift associated with air-oxidation of the NCs is observed. Moreover, as can be seen in Fig. 3c, recovery of the 1S absorption is accompanied by a similar recovery in the TA dynamics, which show no sign of the type of efficient recombination centers that generally arise during etching or other degradative processes. One might expect that injected electrons in PbSe NCs are instead slowly quenched at electron trap sites at the surface, or perhaps on the ligands themselves. Such a mechanism could be suppressed by growing an outer shell of a wider-gap semiconductor, which is an effective and much more stable passivation method that would effectively reduce formation of surface trap states. To verify this hypothesis, we encapsulated the PbSe core (diameter = 7.3 nm) with a CdSe shell (0.3 nm thick) using a previously reported method (Fig. 4 a, b). We observe that even very thin CdSe shell can indeed dramatically extend the lifetime of charges in the PbSe core. As illustrated in Fig. 4c, the PbSe/CdSe core/shell samples maintain a nearly complete bleaching of the 1S feature (that is, a 8 electrons per NC) for at least a month at room temperature. This is a record-long lifetime for injected charges in samples doped via chemical treatments, to be compared to previously reported lifetimes for CdSe NCs that did not exceed a few days.

### The effect of doping on conductivity of NC films

Using these core/shell NCs, we investigated the feasibility of using cobaltocene to dope NCs within already-deposited solid films. PbSe/CdSe NC solutions were drop-cast onto quartz substrates and dried under argon atmosphere; no subsequent ligand exchange or removal steps were applied, so the NCs maintained their native oleate passivation. The substrate-bound NCs were then immersed in a 50 mM solution of cobaltocene in acetonitrile for periods varying from 1 hour to 1 day. The absorption spectra of the PbSe/CdSe NC film following exposure to cobaltocene (Fig. 4d) show the bleach of the 1S feature typical of...
doping. This bleach, however, develops much more slowly than in solution samples: after 1 hour of treatment its magnitude is 30%, and it takes a full day to reach a 60% bleach. This is consistent with the reduced access of cobaltocene in solution to NCs within the film because of the need to diffusively penetrate the thick film. Nonetheless, these bleach levels indicate injection of up to 5 electrons per NC on average, demonstrating that with cobaltocene we can produce very high doping levels in both solution and solid-state samples.

Strikingly, these doped PbSe and PbSe/CdSe NC films show a dramatic increase in their conductivity even without ligand exchange. For instance, while traditional EDT-treatment of an undoped PbSe/CdSe NC film can increase conductivity roughly by 2 orders of magnitude (Fig. 4c, $3.0 \times 10^{-10}$ S cm$^{-1}$ → $7.7 \times 10^{-8}$ S cm$^{-1}$), a cobaltocene-doped PbSe/CdSe NC film, without EDT, shows a reversible conductivity enhancement of over 4 orders magnitude (Fig. 4f, $3.2 \times 10^{-10}$ S cm$^{-1}$ → $3.3 \times 10^{-6}$ S cm$^{-1}$). Importantly, TEM images (inset of Fig. 4f), FT-IR (Fig. S3a), and SAXS data (Fig. S3b) confirm that the surface ligand is still oleic acid, and that the interparticle spacing (~1 nm) has not been measurably altered in the conductive cobaltocene-doped NC films. In contrast, both our TEM measurements (inset of Fig. 4e) as well as previous studies$^{26}$ have shown that treatment of films with short ligands clearly reduces the average interparticle spacing between NCs (typically to ~4 Å), which is necessary to reduce the barrier for trap-mediated hopping-based transport of charge carriers. This implies that the mechanism of charge transport in doped-NC films is inherently different from that in an EDT-treated film; specifically, we suggest that it occurs instead via charge hopping between quantum-confined band-edge states, which are known to have much greater spatial extent than the relatively localized trap states and therefore are somewhat less sensitive to interparticle spacing. Finally, we find that cobaltocene doping is reversible: conductivity of a doped NC film can be decreased nearly to that of the original film.
by even quick, gentle washing with pure acetonitrile solvent, further
demonstrating that conductivity enhancement is not due to surface
trap formation and/or reduction in the inter-particle spacing, both of
which would be expected to persist after room-temperature washing.

In order to demonstrate that the enhanced conductivity is a result
of the high level of doping in the band-edge states, rather than from
any other consequence (e.g., increased carrier mobility) that could
result from cobaltocene treatment, we further studied transport in
FET devices based on PbSe NC films before and after cobaltocene
doping (Fig. 5a). To facilitate these measurements, we have deve-
loped a two-step protocol to first reduce interparticle spacing via
mild hydrazine treatment and then $n$-dope via treatment with cobal-
tocene. Interestingly, attempts to use EDT treatment as the first step
were not successful, likely because EDT introduces surface traps that
typically impart $p$-type behavior on PbSe NC films and interfere with
cobaltocene doping; thus instead, we used short (~1.5 hr exposure
time) treatment with hydrazine.

Heavy treatment with hydrazine has been observed to impart $n$-
type doping to PbSe NC films; however, because of the volatility of
hydrazine molecules, mild treatment with these species did not pro-
duce any doping effect. Specifically the films, that have undergone
this type of treatment, show ambipolar and highly symmetric beha-
vior and positive and negative gate voltages in both $I_D$ vs. $V_DS$
(Fig. 5b) and $I_D$ vs. $V_GSc$ (Fig. 5d, black trace) measurements, typical
of an intrinsic (i.e., undoped) semiconductor with the Fermi level
near the mid-gap position (Fig. 5a; cartoon on the left); $I_D$ is the drain
current, and $V_DS$ and $V_GSc$ are the drain-source and the gate-source
voltages, respectively.

In sharp contrast, $I_D$ vs. $V_DS$ (Fig. 5c) and $I_D$ vs. $V_GSc$ (Fig. 5d, red
trace) measurements of a cobaltocene-treated NC film show unipolar
behavior and an almost linear dependence of $I_D$ on $V_DS$ in the
manner expected for an $n$-type conductor with the Fermi level tuned
within the conduction band (Fig. 5a; cartoon on the right). Further,
in contrast to the pronounced gating effect seen in undoped films
(Fig. 5b), changes in $V_GSc$ only modify the slope of the $I_D$ vs. $V_DS$
dependence, consistent with the situation where the conductance changes
due to the $V_GSc$-induced variation in the concentration of conduction
band electrons. This is also suggested by the $I_D$ vs. $V_GSc$ measure-
ments in Fig. 5d (red trace). Importantly, the measurements of both
intrinsic and $n$-doped films are highly reproducible over multiple
voltage sweeps, and therefore are not associated with any chemical
modifications in the NC film during the measurements.

We can use the results of transport studies to derive the doping
level of cobaltocene-treated NC films, and then compare the
obtained values with those inferred from optical studies. From the
FET measurements in Fig. 5d, we calculate an electron mobility ($\mu_e$)
of $7.2 \times 10^{-4}$ cm$^2$/Vs (see Methods). The fact that this value is much
lower than the record mobilities in films comprising NCs re-capped
with very short inorganic ligands or films infilled via atomic layer
deposition is not surprising. The charge mobilities in NC assem-
bles are defined by the overlap of wave functions localized on adja-
cent NCs and are strongly dependent on parameters such as NC-NC
separation and NC-matrix energy band offsets. In our experiments, we did not attempt to improve conductivity by improving mobilities, but instead tried to demonstrate the dramatic effect of cobaltocene doping on charge transport which occurs despite fairly low values of μ. For a greater contrast, we start with an undoped film comprising widely spaced NCs. As indicated by measurements in Figs. 5b, d without applied gate bias this film is essentially insulating (see estimated charge densities below). However, upon treatment with cobaltocene the film turns into an n-type conductor. Specifically, the $I_{FET}$-Vs-D dependence measured for zero gate bias shows a nearly Ohmic behavior (Fig. 5c), which allows us to derive Ohmic resistance and then the channel conductivity (see Methods). On the basis of data in Fig. 5c, σ = 4.1 x 10^−5 S cm^−1 ($V_G$ = 0). From this value and the measured mobility, we can calculate a free electron density ($n_e$) in the NC film, which yields $n_e = \sigma(e\mu) = 3.6 \times 10^{10}$ cm^−2. If we assume a random close-packing of NCs in the film, we can estimate the concentration of the NCs in the channel (n_{NC}) from n_{NC} = 0.64/ $V_{SCON}^2$, where $V_{SCON}$ is the effective NC volume, accounting for the outer ligand shell. From this expression, n_{NC} = 2.1 x 10^{10} cm^−2.

Finally, we obtain that the average number of electrons per NC, $<N_e>$, = n_{NC}/n_{NC}, is 1.7, which is comparable to the values derived from optical studies of samples that have undergone a similar treatment with cobaltocene. Interestingly, the same analysis applied to hydrazine treated films (Fig. 5b, d) indicates that at $V_G$ = 0, the density of free charges is only ~0.01 per NC and even under very large gate bias of 40 V it is still below ~0.5 charge per NC.

In the above FET studies, we used core-only PbSe NCs. As we have shown earlier, doping is preserved on much longer timescales in NCs coated with a thin CdSe layer. One concern in the practical application of such structures is a possible detrimental effect of the external shell on charge conductance. However, as we indicated before, due to the large spatial extent of band-edge states, transport via these states is expected to be not significantly hindered by a thin passivating layer. To test the device applicability of core/shell nanostructures, we fabricate p-n junction diodes using a NiO p-type layer and an n-type layer made from PbSe/CdSe NCs treated with the same two-step hydrazine/cobaltocene procedure applied previously to FETs. In Fig 5e, we can see that a p-n junction diode of doped NCs indeed shows rectifying behavior in the I-V curve (red trace). This is in marked contrast to the response of an undoped hydrazine-treated film (black trace), confirming again that the cobaltocene doping is responsible for the n-type behavior and further suggesting that stabilization of dopants with the inorganic passivating shell does not prohibit the use of doped NCs in functional devices.

**Methods**

Cobaltocene treatment of NC solution and film samples. All syntheses and manipulations were carried out under dry argon using standard Schlenk-line and glove-box techniques. PbSe NCs, PbSe/CdSe, and PbS NCs were prepared by previously reported methods. Typically, a dispersion of NCs in toluene (0.5 ml, ~1.5 μM) was mixed with an equal amount of a solution of cobaltocene in toluene (~5 mM ~ 20 μM). For the FT-IR measurements (as shown in Fig 2d), mixed solutions of NCs (~1.5 μM) and cobaltocene (~25 mM) were drop-cast onto a zinc selenide window and dried under argon atmosphere. For the cobaltocene treatment of PbSe/CdSe NC films (as shown in Fig 4d), NC solutions were drop-cast onto quartz substrates and dried under argon atmosphere. The sample was then immersed in a solution of cobaltocene in acetonitrile (5 mM) for a period of time ranging from one hour to one day (see main text). Then, it was transferred into a customized sealed quartz cell to prevent air exposure. We observed that even brief exposure to air resulted in a quick bleach recovery indicating the loss of doping (inset of Fig. 5).

Visible-near-infrared absorption, PL, and Fourier transformed infrared (FT-IR) spectroscopies. Absorption spectra were taken in transmission mode on a Perkin-Elmer Lambda 1050 UV/vis/NIR spectrophotometer at 2 nm spectral bandwidth. The absorption spectra were measured for NC films on quartz, and NC dispersions in standard air-free quartz cuvettes with airtight seals. The concentration of NCs solutions were calculated using the molar extinction coefficients $\varepsilon$ at 400 nm $=$ 0.0277 $d^{-1}$ cm $^{-1}$ μM $^{-1}$ and 0.0233 $d^{-1}$ cm $^{-1}$ μM $^{-1}$ for PbSe and PbS NCs, respectively, where $d$ is the NC diameter in nm. The steady-state PL spectra were collected using a monochromator and detected by a liquid N$_2$ cooled InSb detector using an 808 nm diode laser for excitation. FT-IR spectra were taken in transmission mode on a Thermo-Fisher 6700 FT-IR spectrometer at a spectral resolution of 4 cm$^{-1}$. Spectra of NC films were taken in a demountable liquid cell with zinc selenide windows and 0.1 mm Teflon spacers (Ike technologies).

TA spectroscopy. The TA setup used here has been discussed in detail previously. Briefly, samples are excited with ~100 fs (FWHM), 1.55 eV pulses from a 1 kHz Ti–sapphire amplifier. Pump-induced changes in the absorption spectra are then associated with state-filling of the 1S transition. The size of this bleach is directly proportional to the number of electrons in the 1S state and monitoring this state as a function of time reveals carrier dynamics.

Sample preparation for conductivity measurements. For conductivity measurements, NC films were spin-coated from a solution of NCs in hexane at 2500 rpm onto clean glass substrates with interdigitated source and drain electrodes (30 nm thick Au) spaced 50 μm apart. They were immersed in either a 1,2-ethanedithiol solution in acetonitrile (~1% v/w) for 30 sec, or cobaltocene in acetonitrile solution (5 mM) overnight.

FET measurements. The $m$ = 3 periods of 30 nm thick Au interdigitated electrodes (length $L$ = 50 μm and spacing $w$ = 10 mm) were thermally deposited using a shadow mask on oxidized Si wafers with a thermally grown 250 nm thick layer of SiO$_2$. A PbSe NC (diameter $d$ = 6.9 nm) film was deposited by casting a NC layer onto the surface of acetonitrile and then transferring it to the electrode-patterned substrate by the method described in a previous report. After deposition of each layer, the whole substrate was immersed in 1 M hydrazine in acetonitrile for 30 min. The layer transfer and hydrazine treatment were then repeated three times to produce crack-free films (total thickness $h$ of ca. 50 nm), which were subsequently immersed in 5 mM cobaltocene in toluene for 20 min.

Device characterization was performed using a semiconductor analyzer (B1500A, Agilent). The mobilities $\mu$ were calculated using the gradual channel approximation.
equation in the linear regime, \( \frac{V_{DS}}{V_{GS}} = \frac{W}{L} \frac{g_m}{g_d} \), where \( C = 138 \text{ nF/cm}^2 \) is the capacitance per unit area of the gate oxide, and \( W \) and \( L \) are the channel width and length, respectively; in the case of interdigitated electrodes, \( W = (2m-1)w \), which yields \( W = 50 \text{ mm} \) for our structures.

The \( V_{DS} \)-\( V_{GS} \) characteristics of cobaltocene doped films are nearly Ohmic, which allows us to derive from them the usual Ohmic resistance, \( R = \frac{V_{DS}}{V_{GS}} \), and subsequently, using the geometrical parameters of our FETs, the conductivity \( \sigma = L \frac{R_{th}(2m-1)}{w} \).

Fabrication of \( p-n \) diodes: \( p\)-NiO (10 nm thick) was deposited onto an ITO substrate by spin coating 100 nm nickel acetate in 2-ethoxyethanol at 4000 rpm, and annealed at 130°C for 5 min, 250°C for 5 min, and 350°C for 30 min, sequentially. PbSe/CdSe NC (core \( 5 \) nm thick) and aluminium oxide (80 nm thick) were thermal deposited using a shadow mask. Device measurements were carried out with Keithley 2400 SourceMeter.

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