

Article



Subscriber access provided by Queen Mary, University of London

N-Heterocyclic Carbenes as Reversible Exciton-Delocalizing Ligands for Photoluminescent Quantum Dots

Dana E. Westmoreland, Rafael Lopez-Arteaga, and Emily A. Weiss

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.9b13605 • Publication Date (Web): 14 Jan 2020

Downloaded from pubs.acs.org on January 15, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

N-Heterocyclic Carbenes as Reversible Exciton-Delocalizing Ligands for Photoluminescent Quantum Dots

Dana E. Westmoreland, Rafael Lopez-Arteaga, and Emily A. Weiss* Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208-3113

*corresponding author. Email: e-weiss@northwestern.edu

ABSTRACT

Delocalization of excitons within semiconductor quantum dots (QDs) into states at the interface of the inorganic core and organic ligand shell by so-called "exciton-delocalizing ligands (EDLs)" is a promising strategy to enhance coupling of QD excitons with proximate molecules, ions or other QDs. EDLs thereby enable enhanced rates of charge carrier extraction from, and transport among, QDs and dynamic colorimetric sensing. The application of reported EDLs – which bind to the QD through thiolates or dithiocarbamates - is however limited by the irreversibility of their binding and their low oxidation potentials, which lead to a high yield of photoluminescencequenching hole trapping on the EDL. This article describes a new class of EDLs for QDs, 1,3dimethyl-4,5-disubstituted imidazolylidene N-heterocyclic carbenes (NHCs), where the 4,5 substituents are either Me, H, or Cl. Post-synthetic ligand exchange of native oleate capping ligands for NHCs results in a bathochromic shift of the optical band gap of CdSe QDs (R = 1.17nm) of up to 111 meV while maintaining colloidal stability of the QDs. This shift is reversible for the MeNHC-capped and HNHC-capped QDs upon protonation of the NHC. The magnitude of exciton delocalization induced by the NHC (after scaling for surface coverage) increases with increasing acidity of its π -system, which depends on the substituent in the 4,5 positions of the imidazolylidene. The NHC-capped QDs maintain photoluminescence quantum yields of up to 4.2 \pm 1.8 % for shifts of the optical band gap as large as 106 meV.

INTRODUCTION

Exciton-delocalizing ligands (EDLs) are a class of molecules that couple quantum-confined electrons within semiconductor nanocrystals to their immediate environments.¹ The orbitals of an EDL with appropriate symmetry and energy mix with conduction or valence band orbitals of the nanocrystal, and thereby create new interfacial states into which the nanocrystal's exciton delocalizes. In a series of papers from 2010 to 2013, we introduced phenyldithiocarbamate (PTC) and its *para*-substituted derivatives as EDLs that decrease the optical bandgaps of Cd- and Pbchalcogenide quantum dots (QDs) by up to 1 eV without changing the physical structures of their cores.²⁻⁵ Our mechanistic studies on the QD-PTC complexes led to the conclusion that mixing of σ -character orbitals of PTC and the Cd²⁺ or Pb²⁺ s-orbitals of the QD conduction band, and mixing of π -character orbitals of PTC and the chalcogenide p-orbitals of the QD valence band, relax the quantum confinement of the exciton, primarily the excitonic hole.^{3-4, 6-9} This "through-bond" mechanism for exciton delocalization was substantiated and elaborated by a series of papers that combine experimental data with density functional theory calculations.^{2-4, 6, 10} ¹¹⁻¹² By increasing the permeation of the excitonic wavefunction through the dielectric interface separating the inorganic core and the organic ligand of the colloid, EDLs greatly enhance our ability to, for example, extract the otherwise highly localized excitonic hole from a QD¹³⁻¹⁵ (allowing us to achieve the fastest photo-reduction of a metal-chalcogenide OD recorded and the first photoreduction of the biexcitonic state of a QD),¹⁶ transport excitons through QD films,¹⁷⁻¹⁹ and perform multi-hole photo-oxidative reactions with QDs.^{16, 20}

Much of the physics of the EDL effect is fairly straightforward, but thiolates and PTC derivatives are problematic as EDLs due to their specific chemical structures. First, when bound to a metal cation on the QD surface, PTC is very chemically stable, even in air and light, but when freely diffusing as an acid or salt, PTC degrades within minutes-to-hours to the corresponding aniline, thiourea, and phenylisothiocyanate.⁶ Although these degradation products do not themselves delocalize the QD exciton, and therefore do not contribute to the observed spectral shift), the degradation makes ligand exchange inefficient, and complicates quantification of the yield of ligand exchange. Second, PTC is effectively an irreversible binder; once bound to Cd^{2+} or Pb^{2+} we have not found a way to displace it without also etching the QD core. The tight binding of PTC (and thiolates) makes their mechanism of delocalization difficult to prove because it is not straightforwardly reversible. Finally, and perhaps most importantly, PTC and thiolates adsorb in

more than one configuration on the QD surface, and some of these binding modes trap the excitonic hole on the ligand rather than delocalizing it through the ligand.^{7, 21-23} Hole trapping, when it occurs in high yield, efficiently quenches the photoluminescence (PL) of the QD ensemble by limiting electron-hole coupling. Sensing, photovoltaic, and photocatalytic applications of QDs require high photoluminescence quantum yields (QYs), or at least accessible excitonic charge carriers.

Here, we introduce a new class of EDL: 1,3-dimethyl-4,5-disubstituted imidazolylidene N-heterocyclic carbene (NHC) ligands, with either hydrogen (H), methyl (Me), or chloride (Cl) substituents, **Scheme 1**, that address many of the issues with dithiocarbamate and thiolate EDLs. We targeted NHCs as EDLs because, much like dithiocarbamates and thiolates, NHCs interact through both s- and p-type orbitals located on the carbene carbon,²⁴⁻²⁶ which has the potential to bind to either cadmium²⁷⁻²⁹ or selenium³⁰⁻³² or both on the QD surface, and because of the literature precedent for NHCs as ligands for metal clusters³³⁻³⁵ and metal nanoparticles.³⁶⁻⁴¹ The imidazolylidene NHCs in particular are partially aromatic, so modification of substituents at the 4,5 positions affects their π -acidity, and should affect the degree of exciton delocalization enabled by the molecule.⁴² We find that all three NHC derivatives studied in this work delocalize the QD exciton; as expected for an EDL, the magnitude of the apparent increase in excitonic radius (ΔR) per bound NHC ligand depends on the substituent. Unlike PTC-capped QDs, (i) HNHC- and MeNHC-capped QDs maintain PL QYs of 0.6 ± 0.1 % and 4.8 ± 1.7 %, respectively, at an optical shift of 92 meV, and (ii) the exciton delocalization induced by HNHC- and MeNHC is *reversible* upon protonation and subsequent desorption of the NHC.

The spectral shift induced by CINHC is not reversible and its adsorption does not preserve the PL of the QDs (for reasons explained in the text). We nonetheless include it in our dataset, because comparison of its EDL effect to those of HNHC and MeNHC allows us to correlate the EDL effect of an NHC ligand with its π -acidity, a correlation that is consistent with our proposed mechanism for exciton delocalization by dithiocarbamates and thiolates.

RESULTS AND DISCUSSION

We synthesize CdSe QDs with an average radius of 1.17 nm and oleate capping ligands according to a previously published procedure⁴³ and purify the oleate-capped QDs by sequential precipitation with acetone followed by methanol (see the SI for details). We synthesize the

MeNHC and HNHC precursor salts according to a patented procedure,⁴⁴ and the ClNHC precursor salt according to a published procedure (see the SI for details).⁴⁵ Under an N₂ atmosphere, we deprotonate the 1,3-dimethyl-4,5-disubstituted imidazolium salts with a minimum of 1.2 equivalents of sodium hydride and 3 mol % cesium carbonate in anhydrous THF.⁴⁶ After allowing the reaction to proceed for at least four hours for the ClNHC and HNHC derivatives or between 13-18 hours for the MeNHC derivative, we filter the solution through celite and wash with additional THF. The resulting NHC derivatives exist predominantly as dimers in THF (see Figure S1 of the SI).⁴⁷⁻⁴⁸ All optical measurements of the NHC-capped QDs are performed using air-free cuvettes unless otherwise indicated, and all NMR measurements are performed using J Young tubes to ensure an air- and water-free environment.

Scheme 1 depicts the procedure that we use to exchange the native oleate ligands on the QDs for each type of NHC ligand. Under an N₂ atmosphere, we add an aliquot of the prescribed concentration of the XNHC dimer in a THF stock solution to an anhydrous toluene solution of 10 μ M CdSe QDs, and allow the ligand exchange to proceed for 12-18 hours (overnight) at RT. Upon addition of the NHC derivatives, a population of freely diffusing oleate (or oleic acid) appears in the ¹H NMR spectra of the samples; some residual QD-bound oleate remains (see the SI, Figure S2). It appears that MeNHC and CINHC react with the double bond of oleate, which prevents us from accurately quantifying the remaining coverage of oleate ligands (see the SI, Table S1). This reaction, which we have not characterized, does not appear to occur with HNHC, and we can determine that each added HNHC displaces 2.3 ± 0.3 oleate ligands from the QD surface (see the SI, Table S2). We do not wash out free oleate or unbound NHC dimers prior to characterization of the NHC-capped QDs to avoid stripping bound NHC ligands from the QD surface during washing. The resulting MeNHC-, HNHC-, and CINHC-capped QDs are colloidally stable in toluene under an N₂ atmosphere for at least two days (see the SI, Figure S3).



Scheme 1. The ligand exchange procedure. Varying equivalents (up to 120, depending on X) of XNHC dimer are added to 10 μ M oleate (OA)-capped CdSe QDs in toluene, and stirred at room temperature under an N₂ atmosphere. The cartoon of the NHC-capped QD is not to-scale.

Consistent with the effects of dithiocarbamate²⁻⁴ and thiolate^{7, 22-23} EDLs, ligand exchange from oleate to XNHC bathochromically shifts the absorbance spectrum of the QD ensemble; the shift corresponds to a decrease in the energy of the QD's first excitonic state by an amount (ΔE) that depends on (i) the coverage of XNHC and (ii) the substituent, X. **Figure 1A** shows the maximum achievable bathochromic shift of the ground state absorbance spectrum of 1.2 μ M CdSe QDs (physical radius of 1.17 nm) while maintaining colloidal stability, upon treatment of oleatecapped QDs (black) with MeNHC (red, $\Delta E = 115$ meV), CINHC (green, $\Delta E = 48$ meV), or HNHC (blue, $\Delta E = 111$ meV). The emission spectra for the data shown in **Figure 1A** show a corresponding bathochromic shift, except for the CINHC-capped QDs, which are non-emissive (see the SI, Figure S4). At >80 added equiv., the MeNHC-capped QDs precipitate from solution (see the SI, Figure S5A), as has been seen with Pd nanoparticles capped with NHCs with short chain aliphatic groups in the 4 and 5 positions of the imidazolylidene.⁴⁹ For the CINHC-capped QDs, precipitation occurs at >6 equivalents added, while for the HNHC-capped QDs, precipitation does not occur until >120 equivalents have been added (see the SI, Figures S5B,C).

We translate these ΔE values into " ΔR ", defined as the apparent increase in average excitonic radius of the QDs within the ensemble due to the EDL effect. The ΔR parameter is a convenient means of comparing EDL effects among different QD materials, ligand structures, and coverages. **Figure 1A** (inset) is a plot of ΔR versus added equivalents of each NHC derivative over the linear region of this plot (*i.e.*, before colloidal stability is compromised; see the SI, Figure S5). HNHC produces the largest ΔR without the loss of the QD colloidal stability, 0.165 nm; this value is on the order of the maximum ΔR value (0.175 nm) achieved by treating CdSe QDs with unsubstituted PTC.³ Addition of 50 equivalents of the protonated forms of MeNHC or ClNHC, or 400



Figure 1. A) Ground state absorbance spectra of 10 μ M oleate-capped CdSe QDs in toluene (black), and of those same QDs after treatment with 6 equiv. ClNHC (green), 78 equiv. MeNHC (red), or 120 equiv. HNHC (blue). All spectra are normalized to the first absorption maximum. We occasionally observed minor shifts in absorbance baseline due to a fraction of the QDs aggregating during ligand exchange; the SI describes how we manually subtract those baselines from the spectra before analyzing any spectral shift. (**Inset**): a plot of the apparent change in the average excitonic radius of the QD ensemble, " Δ R", vs. added equiv. of each NHC derivative. The datasets include measurements on at least three separately prepared sets of samples for each NHC derivative. **B**) ¹H NMR spectra of each NHC derivative in *ds*-toluene with and without 6.6 μ M CdSe QDs (45 equiv. MeNHC/QD), 7.6 μ M QDs (77 equiv. HNHC/QD), or 6.9 μ M QDs (2 equiv. ClNHC/QD). The quintet at 2.18 ppm (top) is a satellite peak of residual THF. The peaks at 4.02 ppm (middle) are due to impurities introduced during the deprotonation of the HNHC.

equivalents of the protonated form of HNHC, which should *not* bind to the QD surface, results in no shift of the absorbance or emission of the QDs (see the SI, Figure S6).

Figure 1B shows portions of the ¹H NMR spectra of each freely diffusing NHC in *d*₈-toluene, and the same compound upon addition of 7-8 µM QDs. We scale the NMR spectra with and without QDs to correct for dilution (see the SI for details). We know that the peaks in these six spectra are attributable to the dimer of each XNHC from ¹³C NMR (see the SI, Figure S7), and because their peak positions are not consistent with those previously reported for the monomeric species.⁴⁶ The top spectra show the MeNHC dimer peak for the backbone methyl groups at 2.26 ppm with QDs and at 2.20 ppm without QDs. In *d*₈-toluene, the wingtip protons are buried beneath residual THF at 3.54 ppm (see the SI, Figure S8). The middle spectrum shows the HNHC dimer peak for the wingtip protons at 4.00 ppm with QDs and at 3.95 ppm (and broadened) without QDs. The broadening of the peak for the freely diffusing HNHC dimer is due to the low solubility of this molecule in d_{δ} -toluene; the QDs, and associated oleate ligands, help to bring the HNHC into solution. The bottom spectrum in Figure 1B shows the CINHC dimer peak at 3.20 ppm with ODs and 3.19 ppm without QDs. A downfield shift and slight broadening of the peak upon addition of QDs is consistent with dynamic exchange of the molecule (through the monomer species) on and off the OD surface on a timescale faster than that of the NMR experiment.⁴⁹⁻⁵² We suspect, but have not proven, that the difference in chemical shift between the resonances for the bound monomer and freely diffusing dimer of CINHC is very small because this shift has a large contribution from NHC-NHC interactions on the QD surface, and we added only 2 equivalents/QD of CINHC (as opposed to the tens of equivalents of MeNHC and HNHC) in this experiment.

The inset of **Figure 1A** demonstrates that ΔR increases with increasing added XNHC, but does not account for the different binding equilibria of the various XNHCs, and therefore does not allow us to connect the molecular structure of each XNHC to the magnitude of its EDL effect. To probe the mechanism of exciton delocalization by NHCs, we need the value of ΔR per *bound* XNHC, which we denote ΔR_b . NMR is not useful for quantifying the number of XNHCs bound because excess MeNHC and CINHC dimer appear to react with oleate (see the SI, Table S1) and because freely diffusing HNHC dimer is only marginally soluble in *d*₈-toluene. We instead determine the value of ΔR_b by monitoring the position of the first excitonic peak of the QDs upon addition of various concentrations of *p*-toluene sulfonic acid (TsOH), which protonates XNHC molecules on the QD surface, induces their desorption, and causes the QD bandgap to shift back toward its original value (that corresponding to oleate-coated QDs).

This experiment relies on the reversibility of the EDL effect of the XNHCs; the lack of reversibility of the optical shift of dithiocarbamate-treated QDs was a notable weakness of tthis class of EDL ligands. **Figures 2A,B** show that the optical shift induced by 15 equiv. MeNHC is completely reversible upon addition of 30 μ L of 40 mM TsOH solution (50 equiv. TsOH/QD) in acetonitrile to 6 μ M QDs, and that the shift induced by addition of 64 equiv. HNHC is completely reversible upon addition of 100 μ L of 40 mM TsOH solution (122 equiv. TsOH/QD). The optical bandgap of the QDs returns to its value before NHC treatment; NMR evidence that this reversion is due to protonation of the NHC off the surface of the QD is in the SI, Figures S9, S10. The number of equivalents of MeNHC and HNHC we added in this experiment was limited by the amount of TsOH the QDs would tolerate before their emission was quenched, not the degree to which their EDL effect is reversible (see the SI, Figure S11). The shift in the QDs' optical bandgap by CINHC is not reversible upon addition of TsOH, **Figure 2C**, presumably due to stripping of both the CINHC and residual oleate from the QD surface, which results in aggregation and precipitation of the QDs after the addition of 36 equiv. of TsOH per QD (see the SI, Figure S12).

To estimate the average number of XNHC ligands that desorb from each QD for each added amount of TsOH – and therefore determine the number of bound XNHC ligands that correspond to a certain shift in the absorption spectrum, ΔE – we measure the number of freely diffusing XNHC molecules that are protonated upon addition of various equivalents of TsOH (in the absence of QDs). We measure this number through the disappearance of dimer signal in the NMR spectra in *d*₈-toluene of each XNHC (see the SI, Figure S13), since the protonated NHCs with *p*-toluene sulfonate counterions are insoluble in toluene. We then assume that the p*K*_a of the QD-associated NHC derivatives is similar to that of the free NHC dimers in solution, since the species are in equilibrium, such that we can convert "equivalents of TsOH added" to an XNHC-capped QD sample to "equivalents of XNHC desorbed" for that sample. We then determine the energy by which the bandgap of the QDs increases (decreases) upon desorption (adsorption) of a given number of XNHC ligands, and plot $\Delta R vs$. equivalents of MeNHC and HNHC bound to the QD surface in **Figure 3**. The slope of this line is ΔR_b , the value of ΔR per *bound* XNHC.



Figure 2. Normalized and baseline-subtracted absorbance spectra for 10 μ M CdSe QDs treated with 15 equiv. MeNHC (**A**), 64 equiv. HNHC (**B**), or 4 equiv. ClNHC (**C**) upon addition of various equivalents per QD (up to 50 equiv. for MeNHC-capped QDs, 122 equiv. for HNHC-capped QDs, and 36 equiv. for ClNHC-capped QDs) of 40 mM *p*-toluene sulfonic acid (TsOH) in acetonitrile solution. The ClNHC-capped QDs precipitate upon addition of TsOH, as described in the text.

We cannot do such an analysis for ClNHC because its binding is not reversible under conditions where the QDs remain colloidally stable, due to the initial displacement of the majority of the oleate ligands during the ligand exchange with ClNHC (see the SI, Figure S2). We therefore plot in **Figure 3** Δ R *vs*. equiv. ClNHC added. The value of Δ R_b extracted from this plot is a lower limit for the actual Δ R_b value for this ligand.

From **Figure 3**, we conclude that (i) ΔR_b for XNHC depends on X, a result consistent with the dependence of ΔR_b of *para*-substituted phenyldithiocarbamate ligands on their substituents;⁴ and (ii) $\Delta R_b(\text{CINHC}) > \Delta R_b(\text{MeNHC}) > \Delta R_b(\text{HNHC})$. NHC ligands are strong σ donors, but may also show significant π -acidity depending on the nature of the backbone substituents.⁵³ Density functional theory calculations of the orbital energies of cadmium complexes of each XNHC suggest that exciton delocalization could occur through ground state electron transfer from the QD valence band to the π -type LUMO+1 of the Cd²⁺-bound XNHC (see the SI, Figures S14, S15). Such a mechanism would imply that the strongest π -acceptor NHC of the series should also be the most strongly exciton-delocalizing ligand (and have the largest ΔR_b). One measure of π -acidity is the Hammett resonance parameter, σ_R , for a given substituent. The values of σ_R for the three substituents in our study are listed in the legend of **Figure 3**: $|\sigma_R|(\text{Cl}) \ge |\sigma_R|(\text{Me}) > |\sigma_R|(\text{H}).^{54-55}$ This trend explains our result: $\Delta R_b(\text{CINHC}) \ge \Delta R_b(\text{MeNHC}) > \Delta R_b(\text{HNHC})$. Additionally, ⁷⁷Se



Figure 3. The change in the apparent excitonic radius of the QDs, " ΔR ", versus the number of equivalents of MeNHC (red squares), ClNHC (green triangles), and HNHC (blue circles) per QD. For MeNHC and HNHC, the *x*-axis is "Equivalents of NHC *bound* per QD", as determined from the TsOH titration described in the text. For ClNHC, the *x*-axis is "Equivalents of NHC *added* per QD". The data are fit with lines with slopes of ΔR_b , defined as ΔR per equivalent of NHC bound (or added, in the case of ClNHC). Since the equivalents of ClNHC added per QD are upper bounds for ClNHC bound per QD, the value of ΔR_b for ClNHC listed in the legend is a lower limit for the actual value of ΔR_b . We can therefore conclude that ΔR_b (ClNHC) $\geq \Delta R_b$ (MeNHC) > ΔR_b (HNHC). " σ_R " is the Hammett resonance parameter for the correspondingly substituted benzoic acid: $|\sigma_R|$ (ClNHC) $\geq |\sigma_R|$ (MeNHC) > $|\sigma_R|$ (HNHC). The datasets include measurements on at least three separately prepared sets of samples for each NHC derivative.

NMR studies of Se-XNHC adducts, where the NHC is a H- or Cl-disubstituted imidazolylidene with dipp wingtip groups, support our conclusion that ClNHC is a stronger π -donor than HNHC.³⁰ There is no report comparing the π -acidities of HNHC, ClNHC, and MeNHC; methods involving changes in the CO stretching frequency *trans* to an NHC ligand for a metal center do not isolate the influence of the π -acidity of the NHC ligand on this frequency.

The results in **Figure 3** are consistent with our picture of the interfacial electronic structure of phenyldithiocarbamate-capped QDs,⁴ in that the σ interaction between the EDL and a metal cation on the QD surface allows for adsorption of the EDL, while mixing of orbitals within the valence band of the QD and a π -type orbital or orbitals on the ligand mediates the ground state charge transfer-type interaction necessary for exciton delocalization. The degree of this charge transfer, dictated by the electron accepting ability of those ligand π -type orbitals, determines the magnitude of the EDL effect and the degree to which the optical spectrum of the QD shifts.

Unlike with PTC ligands, we detect PL of the NHC-capped QDs without the addition of a cadmium salt, which, in the PTC case, was needed to precipitate excess PTC that would otherwise bind as a hole trapping ligand.²¹ **Figure 4** shows the photoluminescence quantum yield (PL QY) of the QDs as a function of increasing equiv. of each XNHC bound to the QD surface, plotted as the Δ R value for each sample.⁵⁶ We observe an initial increase in the PL QY upon the addition of MeNHC and HNHC, followed by a decrease. Addition of CINHC results in quenching of the PL QY even upon addition of <1 equivalent. We suspect this quenching is due to decreased surface passivation upon oleate desorption and subsequent aggregation of these particles (see the SI, Figures S2,S5B).



Figure 4. Fractional photoluminescence quantum yields (PL QY) of a set of samples of QDs in toluene, relative to that of quinine sulfate in 0.1 M aqueous H₂SO₄, after treatment with various concentrations of MeNHC, CINHC, or HNHC, *vs.* the values of ΔR for those samples. The excitation wavelength used to acquire the emission spectra, which are in the SI, Figure S16, is 450 nm.

CONCLUSIONS

In summary, we demonstrate the use of 1,3-dimethyl-4,5-disubstituted imidazolylidene XNHC (X = H, Me, Cl) ligands as exciton-delocalizing ligands (EDLs) for CdSe QDs; the magnitude of the delocalization effect, which appears as a bathochromic shift of the absorption and emission spectra of the QDs of up to 0.165 eV, increases with the π -acidity of the XNHC ligand. This trend is consistent with the mechanism proposed for exciton delocalization by phenyldithiocarbamate and thiolate EDLs in that the σ interaction between the ligand and a surface Cd²⁺ enables binding of the NHC ligands to the surface, but the mixing of π orbitals on the carbene carbon with the QD valence band enables the exciton delocalization to occur.

This work broadens the scope of colloidal nanoparticle applications of NHCs, which until now has been limited to NHC-capped metal nanoparticles³⁶⁻⁴¹ and clusters³³⁻³⁵ and the synthetic precursors of coinage-metal chalcogenide QDs.⁵⁷ It also broadens the scope of EDLs beyond those containing thiolate binding groups, and simultaneously overcomes two of the major limitations of sulfur-containing EDLs: the lack of reversibility of exciton delocalization (due to lack of reversible binding to the QD surface) and the of lack of PL without the addition of excess cadmium salts to solution following ligand exchange. In contrast, titration of MeNHC- and HNHC-capped QDs with

Page 13 of 17

TsOH results in full reversibility of the bathochromic shift induced upon ligand exchange with these NHC derivatives, which we attribute to protonation and subsequent desorption of the MeNHC and HNHC ligands from the QD surface. The NHC-capped QDs maintain photoluminescence quantum yields of up to 4.2 ± 1.8 % for shifts of the optical band gap as large as 106 meV. The conservation of PL of the QDs at coverages of MeNHC and HNHC that display a change in PL peak position that is 87% of the PL linewidth suggests that NHC-capped QDs may be useful as colorometric sensors. The lack of hole-trapping by these EDLs also suggests that they may greatly enhance the rates of direct charge carrier extraction to NHC-linked molecular acceptors in, for instance, photocatalytic applications.

Supporting Information. Details of QD and XNHC syntheses, ligand exchange procedure, ¹H NMR experiments, and ground state spectroscopy experiments, including Figures S1-S16 and Tables S1 and S2.

Acknowledgements. This work was supported by the National Science Foundation (grant # CHE-1664184) and the National Institutes of Health (grant # R21GM127919). We utilized instrumentation in the IMSERC facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the NIH (1S10OD012016-01 / 1S10RR019071-01A1), the state of Illinois, and the International Institute for Nanotechnology (IIN). We kindly thank Mark Maskeri, Dan Laorenza, Dr. Agnes Thorarinsdottir, and Dr. Andrea D'Aquino for helpful discussions.

REFERENCES

1. Frederick, M. T.; Amin, V. A.; Weiss, E. A., Optical Properties of Strongly Coupled Quantum Dot–Ligand Systems. *J. Phys. Chem. Lett.* **2013**, *4* (4), 634-640.

2. Frederick, M. T.; Weiss, E. A., Relaxation of Exciton Confinement in CdSe Quantum Dots by Modification with a Conjugated Dithiocarbamate Ligand. *ACS Nano* **2010**, *4* (6), 3195-3200.

3. Frederick, M. T.; Amin, V. A.; Cass, L. C.; Weiss, E. A., A Molecule to Detect and Perturb the Confinement of Charge Carriers in Quantum Dots. *Nano Lett.* **2011**, *11* (12), 5455-5460.

4. Frederick, M. T.; Amin, V. A.; Swenson, N. K.; Ho, A. Y.; Weiss, E. A., Control of Exciton Confinement in Quantum Dot–Organic Complexes through Energetic Alignment of Interfacial Orbitals. *Nano Lett.* **2013**, *13* (1), 287-292.

5. Teunis, M. B.; Dolai, S.; Sardar, R., Effects of Surface-Passivating Ligands and Ultrasmall CdSe Nanocrystal Size on the Delocalization of Exciton Confinement. *Langmuir* **2014**, *30* (26), 7851-7858.

6. Harris, R. D.; Amin, V. A.; Lau, B.; Weiss, E. A., Role of Interligand Coupling in Determining the Interfacial Electronic Structure of Colloidal CdS Quantum Dots. *ACS Nano* **2016**, *10* (1), 1395-1403.

7. Amin, V. A.; Aruda, K. O.; Lau, B.; Rasmussen, A. M.; Edme, K.; Weiss, E. A., Dependence of the Band Gap of CdSe Quantum Dots on the Surface Coverage and Binding Mode of an Exciton-Delocalizing Ligand, Methylthiophenolate. *J. Phys. Chem. C* **2015**, *119* (33), 19423-19429.

8. Aruda, K. O.; Amin, V. A.; Thompson, C. M.; Lau, B.; Nepomnyashchii, A. B.; Weiss, E. A., Description of the Adsorption and Exciton Delocalizing Properties of p-Substituted Thiophenols on CdSe Quantum Dots. *Langmuir* **2016**, *32* (14), 3354-3364.

9. Giansante, C., Surface Chemistry Control of Colloidal Quantum Dot Band Gap. J. Phys. Chem. C 2018, 122 (31), 18110-18116.

10. Li, W.; Lu, T.-F.; Ren, W.; Deng, L.; Zhang, X.; Wang, L.; Tang, J.; Kuznetsov, A. E., Influence of an exciton-delocalizing ligand on the structural, electronic, and spectral features of the Cd33S33 quantum dot: insights from computational studies. *J. Mater. Chem. C* **2018**, *6* (32), 8751-8761.

11. Azpiroz, J. M.; De Angelis, F., Ligand Induced Spectral Changes in CdSe Quantum Dots. *ACS Appl. Mater. Interfaces* **2015**, *7* (35), 19736-19745.

12. Giansante, C.; Infante, I.; Fabiano, E.; Grisorio, R.; Suranna, G. P.; Gigli, G., "Darkerthan-Black" PbS Quantum Dots: Enhancing Optical Absorption of Colloidal Semiconductor Nanocrystals via Short Conjugated Ligands. *J. Am. Chem. Soc.* **2015**, *137* (5), 1875-1886.

13. Lian, S.; Weinberg, D. J.; Harris, R. D.; Kodaimati, M. S.; Weiss, E. A., Subpicosecond Photoinduced Hole Transfer from a CdS Quantum Dot to a Molecular Acceptor Bound Through an Exciton-Delocalizing Ligand. *ACS Nano* **2016**, *10* (6), 6372-6382.

14. Lee, J. R.; Li, W.; Cowan, A. J.; Jäckel, F., Hydrophilic, Hole-Delocalizing Ligand Shell to Promote Charge Transfer from Colloidal CdSe Quantum Dots in Water. *J. Phys. Chem. C* **2017**, *121* (28), 15160-15168.

15. Xie, Y.; Teunis, M. B.; Pandit, B.; Sardar, R.; Liu, J., Molecule-like CdSe Nanoclusters Passivated with Strongly Interacting Ligands: Energy Level Alignment and Photoinduced Ultrafast Charge Transfer Processes. *J. Phys. Chem. C* **2015**, *119* (5), 2813-2821.

16. Lian, S.; Christensen, J. A.; Kodaimati, M. S.; Rogers, C. R.; Wasielewski, M. R.; Weiss, E. A., Oxidation of a Molecule by the Biexcitonic State of a CdS Quantum Dot. *J. Phys. Chem. C* **2019**, *123* (10), 5923-5930.

17. Azzaro, M. S.; Le, A. K.; Wang, H.; Roberts, S. T., Ligand-Enhanced Energy Transport in Nanocrystal Solids Viewed with Two-Dimensional Electronic Spectroscopy. *J. Phys. Chem. Lett.* **2019**, *10* (18), 5602-5608.

18. Azzaro, M. S.; Dodin, A.; Zhang, D. Y.; Willard, A. P.; Roberts, S. T., Exciton-Delocalizing Ligands Can Speed Up Energy Migration in Nanocrystal Solids. *Nano Lett.* **2018**, *18* (5), 3259-3270.

19. Zotti, G.; Vercelli, B.; Berlin, A.; Virgili, T., Multilayers of CdSe Nanocrystals and Bis(dithiocarbamate) Linkers Displaying Record Photoconduction. *J. Phys. Chem. C* **2012**, *116* (49), 25689-25693.

2	
3	20. Wolff, C. M.; Frischmann, P. D.; Schulze, M.; Bohn, B. J.; Wein, R.; Livadas, P.;
4	Carlson M T · Jäckel F · Feldmann J · Würthner F · Stolarczyk J K All-in-one visible-light-
5	driven water splitting by combining nanoparticulate and molecular co. catalysts on CdS
6	anven water splitting by combining hanoparticulate and molecular co-catalysis on Cus
7	nanorods. Nat. Energy 2018, 3 (10), 862-869.
8	21. Jin, S.; Harris, R. D.; Lau, B.; Aruda, K. O.; Amin, V. A.; Weiss, E. A., Enhanced Rate
9	of Radiative Decay in CdSe Quantum Dots upon Adsorption of an Exciton-Delocalizing Ligand.
10	Nano Lett. 2014, 14 (9), 5323-5328.
11	22. Buckley, J. J.; Couderc, E.; Greaney, M. J.; Munteanu, J.; Riche, C. T.; Bradforth, S. E.;
12	Brutchey R. L. Chalcogenol Ligand Toolbox for CdSe Nanocrystals and Their Influence on
13	Exciton Relayation Pathways ACS Nano 2014 8 (3) 2512-2521
14	22 Liong V: Therma I E: Derkinson D A Controlling the Electronic Coupling between
15	25. Liang, F., Filome, J. E., Farkinson, B. A., Controlling the Electronic Coupling between
16	Case Quantum Dots and Thiol Capping Ligands via pH and Ligand Selection. Langmuir 2012,
17	28 (30), 11072-11077.
18	24. Nelson, D. J.; Nolan, S. P., Quantifying and understanding the electronic properties of N-
19	heterocyclic carbenes. Chem. Soc. Rev. 2013, 42 (16), 6723-6753.
20	25. Huynh, H. V., Electronic Properties of N-Heterocyclic Carbenes and Their Experimental
21	Determination. Chem. Rev. 2018, 118 (19), 9457-9492.
22	26. Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F., An overview of N-heterocyclic
23	carbenes Nature 2014 510 (7506) 485-496
25	27 Arduango Anthony I: Coorlight Iong P: Davidson E: Marshall William I. Carbona
26	Advista of Directly log during In 7 Naturfaugel, D 1000, Vol. 54 a 1250
27	Adducts of Dimethylcadmium. In Z. Naturjorscn. B, 1999; Vol. 54, p 1550.
28	28. Roy, M. M. D.; Ferguson, M. J.; McDonald, R.; Rivard, E., Investigation of N-
29	Heterocyclic Carbene-Supported Group 12 Triflates as Pre-catalysts for
30	Hydrosilylation/Borylation. Chem. – Eur. J. 2016, 22 (50), 18236-18246.
31	29. Bellan, E. V.; Poddel'sky, A. I.; Protasenko, N. A.; Cherkasov, A. V.; Bogomyakov, A.
32	S.; Cherkasov, V. K.; Abakumov, G. A., Bis-o-semiquinonato cadmium(II) complexes with o-
33	quinonato and N-heterocyclic carbene neutral ligands. <i>Inorg. Chem. Commun.</i> 2014 , <i>50</i> , 1-3.
34	30 Verlinden K · Buhl H · Frank W · Ganter C Determining the Ligand Properties of N-
35	Heterocyclic Carbones from 77Se NMR Parameters <i>Fur I Inorg Cham</i> 2015 (14) 2416-
36	$\frac{1}{2}$
37	21 Duhl II. Verlinden K. Center C. Nevelsević S. D. Derdenević C. A. Electrostatio
38	51. Buni, H.; verlinden, K.; Ganter, C.; Novakovic, S. B.; Bogdanovic, G. A., Electrostatic
39	Properties of N-Heterocyclic Carbenes Obtained by Experimental Charge-Density Analysis of
40	Two Selenium Adducts. <i>Eur. J. Inorg. Chem.</i> 2016 , <i>2016</i> (21), 3389-3395.
41	32. Liske, A.; Verlinden, K.; Buhl, H.; Schaper, K.; Ganter, C., Determining the π -Acceptor
42	Properties of N-Heterocyclic Carbenes by Measuring the 77Se NMR Chemical Shifts of Their
45	Selenium Adducts. Organometallics 2013, 32 (19), 5269-5272.
44 15	33. Smith, C. A.; Narouz, M. R.; Lummis, P. A.; Singh, I.; Nazemi, A.; Li, CH.; Crudden,
45 46	C. M. N-Heterocyclic Carbenes in Materials Chemistry, <i>Chem. Rev.</i> 2019 , <i>119</i> (8), 4986-5056.
40	34 Narouz M R : Osten K M : Unsworth P I : Man R W V : Salorinne K : Takano S :
48	Tomihara D : Kaanna S : Malala S : Dinh C T : Dadmas I D : Ayaa K : Carrett D I :
49	Namba M. Hartan I. H. Sanzant F. H. Häldingen H. Taylanda T. Crudden C. M. N
50	Nambo, M.; Horton, J. H.; Sargeni, E. H.; Hakkinen, H.; Isukuda, I.; Crudden, C. M., N-
51	heterocyclic carbene-functionalized magic-number gold nanoclusters. Nat. Chem. 2019, 11 (5),
52	419-425.
53	35. Narouz, M. R.; Takano, S.; Lummis, P. A.; Levchenko, T. I.; Nazemi, A.; Kaappa, S.;
54	Malola, S.; Yousefalizadeh, G.; Calhoun, L. A.; Stamplecoskie, K. G.; Häkkinen, H.; Tsukuda,
55	
56	
57	
58	15
59	

T.; Crudden, C. M., Robust, Highly Luminescent Au13 Superatoms Protected by N-Heterocyclic Carbenes. J. Am. Chem. Soc. **2019**, 141 (38), 14997-15002.

36. Tegeder, P.; Freitag, M.; Chepiga, K. M.; Muratsugu, S.; Möller, N.; Lamping, S.; Tada, M.; Glorius, F.; Ravoo, B. J., N-Heterocyclic Carbene-Modified Au–Pd Alloy Nanoparticles and Their Application as Biomimetic and Heterogeneous Catalysts. *Chem. – Eur. J.* **2018**, *24* (70), 18682-18688.

37. Martínez-Prieto, L. M.; Rakers, L.; López-Vinasco, A. M.; Cano, I.; Coppel, Y.;
Philippot, K.; Glorius, F.; Chaudret, B.; van Leeuwen, P. W. N. M., Soluble Platinum
Nanoparticles Ligated by Long-Chain N-Heterocyclic Carbenes as Catalysts. *Chem. – Eur. J.*2017, 23 (52), 12779-12786.

38. Rakers, L.; Martínez-Prieto, L. M.; López-Vinasco, A. M.; Philippot, K.; van Leeuwen, P. W. N. M.; Chaudret, B.; Glorius, F., Ruthenium nanoparticles ligated by cholesterol-derived NHCs and their application in the hydrogenation of arenes. *Chem. Commun.* **2018**, *54* (51), 7070-7073.

39. Möller, N.; Rühling, A.; Lamping, S.; Hellwig, T.; Fallnich, C.; Ravoo, B. J.; Glorius, F., Stabilization of High Oxidation State Upconversion Nanoparticles by N-Heterocyclic Carbenes. *Angew. Chem. Int. Ed.* **2017**, *56* (15), 4356-4360.

40. Ernst, J. B.; Muratsugu, S.; Wang, F.; Tada, M.; Glorius, F., Tunable Heterogeneous Catalysis: N-Heterocyclic Carbenes as Ligands for Supported Heterogeneous Ru/K-Al2O3 Catalysts To Tune Reactivity and Selectivity. *J. Am. Chem. Soc.* 2016, *138* (34), 10718-10721.
41. Ernst, J. B.; Schwermann, C.; Yokota, G.-i.; Tada, M.; Muratsugu, S.; Doltsinis, N. L.; Glorius, F., Molecular Adsorbates Switch on Heterogeneous Catalysis: Induction of Reactivity

by N-Heterocyclic Carbenes. J. Am. Chem. Soc. 2017, 139 (27), 9144-9147.
42. Heinemann, C.; Müller, T.; Apeloig, Y.; Schwarz, H., On the Question of Stability, Conjugation, and "Aromaticity" in Imidazol-2-ylidenes and Their Silicon Analogs. J. Am. Chem.

Soc. **1996**, *118* (8), 2023-2038.

43. Flamee, S.; Cirillo, M.; Abe, S.; De Nolf, K.; Gomes, R.; Aubert, T.; Hens, Z., Fast, High Yield, and High Solid Loading Synthesis of Metal Selenide Nanocrystals. *Chem. Mater.* **2013**, *25* (12), 2476-2483.

44. Ren, R. X.; Koch, V. R. One-step process for the preparation of halide-free hydrophobic salts. U.S. Patent 20040225131A1, Nov. 11, 2004.

45. Solovyev, A.; Ueng, S.-H.; Monot, J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P., Estimated Rate Constants for Hydrogen Abstraction from N-Heterocyclic

Carbene–Borane Complexes by an Alkyl Radical. Org. Lett. 2010, 12 (13), 2998-3001.

46. Arduengo, A. J.; Dias, H. V. R.; Harlow, R. L.; Kline, M., Electronic stabilization of nucleophilic carbenes. *J. Am. Chem. Soc.* **1992**, *114* (14), 5530-5534.

47. Jolly, P. I.; Zhou, S.; Thomson, D. W.; Garnier, J.; Parkinson, J. A.; Tuttle, T.; Murphy, J. A., Imidazole-derived carbenes and their elusive tetraazafulvalene dimers. *Chem. Sci.* **2012**, *3* (5), 1675-1679.

48. Alder, R. W.; Blake, M. E.; Chaker, L.; Harvey, J. N.; Paolini, F.; Schütz, J., When and How Do Diaminocarbenes Dimerize? *Angew. Chem. Int. Ed.* **2004**, *43* (44), 5896-5911.

49. Richter, C.; Schaepe, K.; Glorius, F.; Ravoo, B. J., Tailor-made N-heterocyclic carbenes for nanoparticle stabilization. *Chem. Commun.* **2014**, *50*, 3204-3207.

50. Donakowski, M. D.; Godbe, J. M.; Sknepnek, R.; Knowles, K. E.; Olvera de la Cruz, M.; Weiss, E. A., A Quantitative Description of the Binding Equilibria of para-Substituted Aniline Ligands and CdSe Quantum Dots. *J. Phys. Chem. C* **2010**, *114* (51), 22526-22534.

58 59

60

1	
2	
3	51. Moreels, I.; Martins, J. C.; Hens, Z., Ligand Adsorption/Desorption on Sterically
4	Stabilized InP Colloidal Nanocrystals: Observation and Thermodynamic Analysis
5	Cham Dhug Cham 2006 7 (5) 1028 1021
6	Chemi F hyschem 2000, 7 (5), 1026-1051.
7	52. Kohlmann, O.; Steinmetz, W. E.; Mao, XA.; Wuelfing, W. P.; Templeton, A. C.;
8	Murray, R. W.; Johnson, C. S., NMR Diffusion, Relaxation, and Spectroscopic Studies of Water
9	Soluble, Monolayer-Protected Gold Nanoclusters. J. Phys. Chem. B 2001, 105 (37), 8801-8809.
10	53. Khramov, D. M.: Lvnch, V. M.: Bielawski, C. W., N-Heterocyclic Carbene–Transition
11	Metal Complexes: Spectroscopic and Crystallographic Analyses of π -Back-bonding
12	Interactions, Oregonometallies 2007, 26 (24), 6042, 6040
13	$\frac{1}{2} = \frac{1}{2} = \frac{1}$
14	54. Swain, C. G.; Lupton, E. C., Field and resonance components of substituent effects. J.
15	Am. Chem. Soc. 1968, 90 (16), 4328-4337.
16	55. Hansch, C.; Leo, A.; Taft, R. W., A survey of Hammett substituent constants and
17	resonance and field parameters. Chem. Rev. 1991, 91 (2), 165-195.
18	56. Eastman, J. W., OUANTITATIVE SPECTROFLUORIMETRY-THE FLUORESCENCE
19	OUANTUM VIELD OF OUININE SULFATE Photochem Photobiol 1967 6(1) 55-72
20	57 Delsen A. M. Weisend E. Thens. A. Stillmen M. L. Carrison, J. E. A. N. Heterosyelie
21	57. Polgar, A. M.; weigend, F.; Zhang, A.; Sulliman, M. J.; Corrigan, J. F., A N-Helerocyclic
22	Carbene-Stabilized Coinage Metal-Chalcogenide Framework with Tunable Optical Properties. J.
23	Am. Chem. Soc. 2017, 139 (40), 14045-14048.
24	
25	
26	
27	For Table of Contents Only:
28	Y Y
29	
30	
31	
32	
33	
34	
35	
36	
37	
38	
39	
40	
41	
42	
43	