THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

Cite This: J. Phys. Chem. Lett. 2019, 10, 5602−5608

pubs.acs.org/JPCL

Ligand-Enhanced Energy Transport in Nanocrystal Solids Viewed with Two-Dimensional Electronic Spectroscopy

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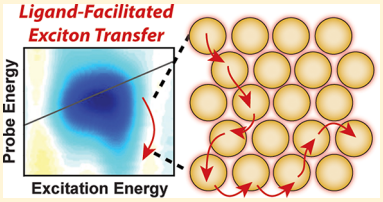
Supporting Information

ABSTRACT: We examine CdSe NCs functionalized with the exciton-delocalizing ligand phenyldithiocarbamate (PDTC) using two-dimensional electronic spectroscopy (2DES). PDTC forms hybrid molecular orbitals with CdSe's valence band that relax hole spatial confinement and create potential for enhanced exciton migration in NC solids. We find PDTC broadens the intrinsic line width of individual NCs in solution by ∼30 meV, which we ascribe to modulation of NC band edge states by ligand motion. In PDTC-exchanged solids, photoexcited excitons are mobile and rapidly move to low-energy NC sites over ∼30 ps. We also find placing excitons into high-energy states can accelerate their rate of migration by over an order of magnitude, which we attribute to enhanced spatial delocalization of these states that improves inter-NC wave function overlap. Our work demonstrates that NC surface ligands can actively facilitate inter-NC energy transfer and highlights principles to consider when designing ligands for this application.



Due to their size-tunable electronic properties, quantum-confined semiconductor nanocrystals (NCs) hold promise for solution-processable optoelectronics.[1−4] Yet a persistent challenge in realizing NC-based devices is the termination of NC surfaces with long aliphatic ligands introduced during synthesis to halt NC growth and impart colloidal stability. In solids, such ligands create insulating barriers that hinder carrier migration,[5] driving development of ligand exchange approaches[6−10] to replace these ligands with shorter ones that reduce tunneling barriers for electron and hole transfer.[11] A complementary strategy to build on this approach is to functionalize NCs with short exciton delocalizing ligands (EDLs), molecules possessing frontier molecular orbitals that can readily hybridize with states situated at a NCs' valence or conduction band edges.[12,13] Such hybridization can relax carrier spatial confinement, making them more accessible for extraction. Indeed, EDLs have successfully been used to achieve subpicosecond hole transfer from CdS/CdSe NCs and nanorods to molecules at their surface,[14,15] improve carrier mobility and photoconductivity within NC solids,[9,16] and speed exciton transport in CdSe NC solids by facilitating concerted electron and hole transfer.[17]

However, a key challenge in using EDLs to enhance energy and charge transport is understanding how structural heterogeneity within NC solids impacts these processes. Unlike atomically precise molecules, even the best synthetic routes typically yield NCs with a size distribution of ∼3−5%.[18] As NC electronic structure varies with their size, this distribution yields an inhomogeneously broadened line shape for both NC absorption and emission spectra. Ligand exchange with EDLs can further increase inhomogeneous broadening due to heterogeneity in the number of EDL molecules exchanged.[19] In addition to these static broadening sources, dynamic processes, such as spectral diffusion tied to fluctuations of a NC's structure and environment[20,21] and line shape contributions from exciton fine structure[22,23] and electron−phonon coupling,[12,24] can each act to homogeneously broaden the line shape of individual NCs.

Here, we use two-dimensional electronic spectroscopy (2DES) to evaluate the impact of both static and dynamic electronic disorder on exciton transport within CdSe films treated with the exciton delocalizing ligand phenyldithiocarbamate (PDTC). 2DES is well-suited to this task as it has both the time resolution to resolve exciton transfer between NCs and spectral resolution to separate contributions to these dynamics from electronically inhomogeneous sites within a NC solid. In a 2DES experiment, spectral information is encoded along two axes−excitation (E_{pump}) and emission (E_{probe}), allowing one to disentangle effects such as energy transfer,[25] electronic coupling between quantum states,[26,27] spectral diffusion,[28] and homogeneous and inhomogeneous broadening of absorption line shapes,[29−32] each of which can be obscured in commonly employed techniques such as absorption spectroscopy or transient absorption (TA). By correlating the energy of photoexcited excitons with their ensuing dynamics, we build a fuller picture for how energy migrates in EDL-treated NC solids.

Upon exchange with PDTC in solution, we find 2DES spectra show fast modulation of the transition energy of CdSe's lowest exciton band that we attribute to PDTC ligand motion. When applied to PDTC-exchanged NC films, 2DES reveals that the average energy of photoexcited excitons decreases over ∼30 ps following their generation. No such energy decrease is seen in oleate-capped NC solids, indicating this behavior

Received: July 13, 2019
Accepted: September 1, 2019
Published: September 1, 2019

DOI: 10.1021/acs.jpclett.9b02040
J. Phys. Chem. Lett. 2019, 10, 5602−5608

results from PDTC ligand exchange and is assigned to exciton migration. Importantly, we find hot excitons with ∼0.8 eV of excess energy migrate with rates that are an order of magnitude faster relative to excitons that occupy band-edge states in PDTC-exchanged NC solids. We ascribe this to enhanced spatial delocalization of high-energy NC electron states as this is consistent with prior reports of the electronic structure of PDTC-functionalized CdSe NCs.[33] Our work constitutes the first use of 2DES to examine energy migration in NC solids and confirms EDLs can improve electronic coupling in these materials.

Details regarding NC synthesis, film preparation, our 2DES spectrometer, and processing of 2DES spectra are provided in sections SI and SII of the Supporting Information. In brief, our 2DES spectrometer uses a pump−probe geometry[34−37] wherein the excitation pulse pair is produced by shaping the output of a home-built noncolinear optical parametric amplifier via an acousto-optic programmable dispersive filter (Fastlite Dazzler) and the time-delayed probe is derived from a temporally compressed white light supercontinuum. Figure 1

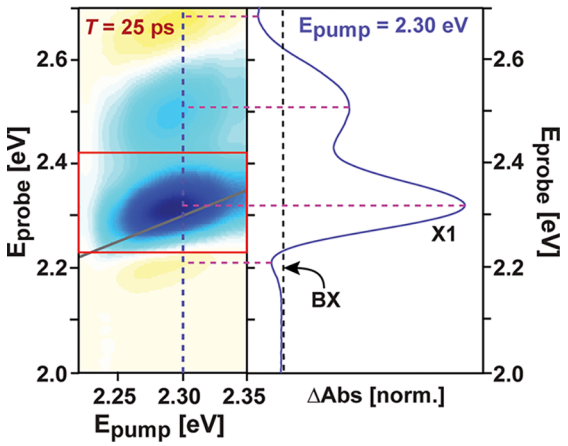


Figure 1. (Left) 2DES spectrum of oleate-functionalized CdSe NCs dispersed in dichloromethane at T = 25 ps. The X1 band used for analysis throughout this report is highlighted by a red box. (Right) slice of the 2DES surface taken at E_{pump}= 2.30 eV.

shows a representative 2DES spectrum of oleate-terminated CdSe NCs collected at a waiting time (T) of 25 ps. Spectra measured during a 2DES experiment are analogous to ones collected in a series of transient absorption (TA) experiments wherein the photon energy of the excitation pulse is scanned. As such, vertical slices of a 2DES line shape can be thought of as a TA spectrum recorded for a given pump photon energy. For example, if we take a slice along E_{pump} = 2.30 eV (Figure 1, right), this data can be interpreted as the TA spectrum produced 25 ps after sample excitation by a 2.30 eV photon. This spectrum displays a photobleach attributed to CdSe's lowest energy CdSe exciton transition (X1) and a photo-induced absorption (BX) associated with excitation of excitons produced by the pump to a higher energy biexciton state. These features have been labeled as the B1 and A1 bands in prior TA work.[38,39]

Looking at the 2DES line shape, we observe a noticeable tilt of the X1 band along the diagonal axis (E_{pump} = E_{probe}). As this line reflects X1 electronic transitions that do not shift on photoexcitation, the diagonal elongation of the 2DES spectrum reflects the distribution of NCs within our sample with different X1 energies. By looking at dynamics measured at different values of E_{pump} as T is scanned, we can understand how excitations produced in NCs with X1 energies that differ, due to either variations in size or EDL coverage, evolve with time. This allows us to extract both the NC homogeneous line width as a function of their X1 energy, given by the antidiagonal line width of the X1 band,[40] and the rate of energy transfer between NCs in films, which give rise to cross-peaks below the diagonal axis. Such information is often obscured in traditional TA experiments as the resulting transient spectra are integrated across the spectral bandwidth of the excitation pulse along the E_{pump} axis.

Figure 2A displays 2DES spectra of the X1 band of oleate-capped and PDTC-exchanged NC suspensions at T = 25 ps.

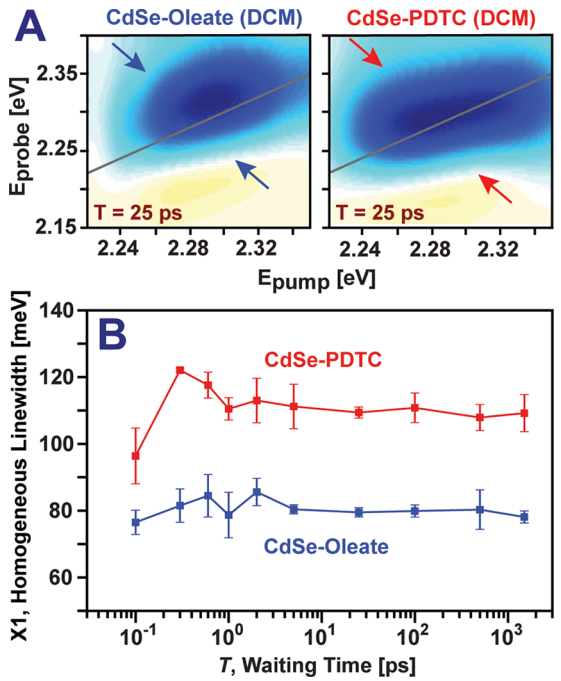


Figure 2. (A) 2DES spectra of the X1 band of CdSe-oleate (left) and CdSe-PDTC (right) in dichloromethane at T = 25 ps highlighting differences in their antidiagonal line width. (B) fwhm values of Lorentzian fits to the antidiagonal line width of 2DES spectra measured for CdSe-oleate (blue squares) and CdSe-PDTC solutions (red squares) as a function of waiting time, T.

Looking at the two spectra, we note several differences. First, the inhomogeneous line width along the diagonal axis is broader for the PDTC-exchanged solution than for CdSe-oleate. This is consistent with our prediction that ligand exchange with PDTC introduces energetic disorder due to a nonuniform distribution of these ligands throughout the NC ensemble. More interestingly, we find the antidiagonal line width, which reflects the intrinsic homogeneous absorption line width of the X1 exciton state, also differs between the two samples, increasing by ∼30 meV following PDTC ligand exchange (Figure 2B). This broadening displays a slight time variation on the subpicosecond time scale, increasing from 95 to 120 meV over 300 fs, followed by a 10 meV narrowing over 1 ps.

There are several effects that may underlie this broadening upon PDTC functionalization: (1) alteration of exciton-fine structure due to hybrid orbital formation between CdSe valence band states and PDTC's HOMO; (2) increased

DOI: 10.1021/acs.jpclett.9b02040
J. Phys. Chem. Lett. 2019, 10, 5602−5608

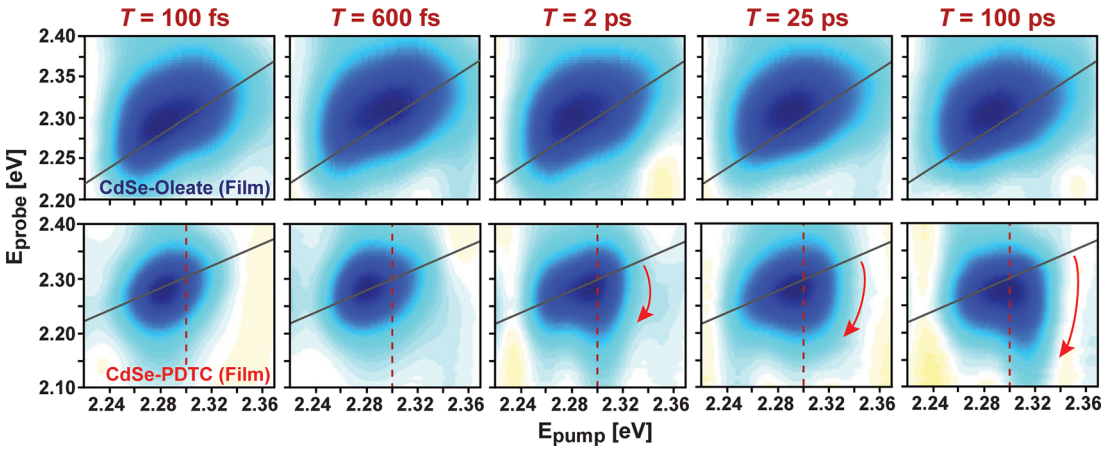


Figure 3. Normalized 2DES spectra of the X1 band of CdSe-oleate (top) and CdSe-PDTC films (bottom) for waiting times ranging from T = 100 fs to T = 100 ps. Red arrows highlight changes in 2DES spectra attributed to downhill energy migration.

exciton−phonon coupling due to changes in NC phonon modes upon PDTC binding; (3) spectral diffusion induced by modulation of a NC's X1 energy by PDTC ligand motion. While the first two effects should provide a relatively constant contribution to the X1 homogeneous line width with increasing T, spectral diffusion tied to ligand motion is expected to lead to a time-dependent modulation of a NC's bandgap as ligands re-equilibrate following excitation, a process expected to occur over a few hundred femtoseconds to a few picoseconds. Modulation of the X1 energy of CdSe NCs by PDTC motion has also been observed in Car−Parrinello molecular dynamics simulations, which have found that while oleate ligands bound to CdSe remain relatively immobile, PDTC exhibits fluxional behavior on NC surfaces, shifting between bidentate bridging, chelating, and tilted chelating geometries.[33] Similar conclusions regarding the fluxional nature of PDTC on NC surfaces were reached in a DFT study.[41] Such motion is expected to modulate PDTC's ability to accept charge from a NC to which it binds, leading to a transient polarization that can shift a NC's X1 energy. While spectral diffusion does not appear to play a role in homogeneously broadening the line width of CdSe-oleate, our data, together with these simulation results, suggest PDTC ligand motion homogeneously broadens the X1 line width of CdSe NCs over time.

To examine how the photoexcited dynamics of CdSe NCs are altered by inter-NC coupling, 2DES spectra of NC solids were measured as a function of T (Figure 3). 2DES spectra of oleate-capped films (Figure 3, top) exhibit little evolution of the X1 band as T increases from 100 fs to 100 ps and resemble spectra of isolated NCs in dichloromethane, indicating their electronic dynamics are unchanged by film formation. In sharp contrast, 2D spectra of PDTC-exchanged NC films (Figure 3, bottom) change drastically as T increases, gaining intensity below the diagonal axis at E_{pump} = 2.30 eV and E_{probe} = 2.20 eV. Such an asymmetric line shape change is reminiscent of relaxation-induced cross-peaks in 2DES spectra of photosynthetic bacteria,[42] lead halide perovskites,[43] and electronically coupled dye molecules,[44] wherein cross-peaks appearing below the diagonal axis signal energy transfer from species that absorb high-energy photons to ones absorbing at lower energy. In the case of CdSe-PDTC solids, exciton transfer along an energetic gradient, moving from smaller NCs featuring less PDTC ligands (large X1 energies) to larger NCs with a higher degree of PDTC substitution (low X1 energies) is expected to yield such asymmetric broadening of 2DES spectra. Support for this interpretation comes from the absence of this cross-peak in 2DES spectra of dispersed CdSe-PDTC NCs in solution, indicating it does not arise from internal relaxation mechanisms within individual CdSe-PDTC NCs but rather requires close association between them.

We also note that this cross-peak is indicative of exciton transfer rather than charge transfer between NCs. The X1 band selectively reports on the excited electron population of CdSe rather than excited holes,[45,46] indicating the X1 dynamics we observe result from rapid electron migration. However, PDTC reduces the quantum confinement of excited holes rather than excited electrons,[33,47,48] creating the expectation that it should aid hole transfer. We can rationalize these two seemingly at odds observations if the electron and hole migrate through CdSe-PDTC solids in a concerted manner, as an exciton. One mechanism that can explain why hole delocalization alone would enhance exciton transfer was recently proposed by Reich and Shklovskii,[11] who noted charge transfer-mediated coupling induced by wave function overlap of either electrons or holes between NCs can aid exciton transfer.

We next examine the time dependence of this exciton migration by plotting the average energy of photoexcited X1 excitons produced with different amounts of initial energy as a function of time. This information is extracted from the 2DES data by measuring the minimum position of the X1 band for different excitation energies, E_{pump}. Prior work examining exciton migration in CdSe NC solids[17] and carrier migration in PbS NC solids[49,50] used TA to extract analogous information, but dynamics retrieved in these measurements are effectively averaged over the full NC ensemble.

Figure 4 plots the time dependence of the X1 band center position following excitation of CdSe-oleate and CdSe-PDTC films by photons of different energies. For comparison, we also plot the center position of the X1 band measured in TA experiments that report the average behavior of the full NC ensemble following X1 photoexcitation. For CdSe-oleate (Figure 4A), TA data (gray circles) show two time-dependent changes in the center position of the X1 band. Seen first is a subtle blue shift of ∼7 meV over ∼10 ps, which we assign to a loss of stimulated emission contributing to the low-energy side of the X1 line shape on the basis of prior ultrafast measurements of CdSe-oleate NCs.[17] Over longer delays

DOI: 10.1021/acs.jpclett.9b02040
J. Phys. Chem. Lett. 2019, 10, 5602−5608

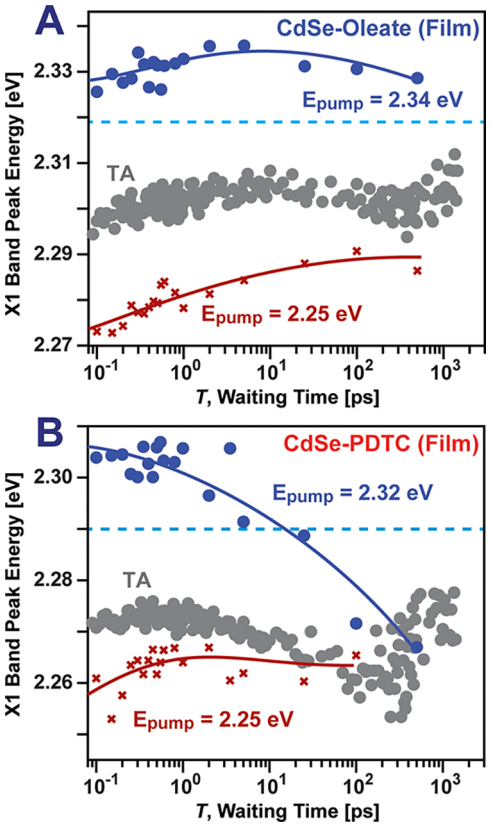


Figure 4. Spectral peak of the X1 band seen in 2DES (colored shapes) and TA spectra (gray circles) for (A) CdSe-oleate and (B) CdSe-PDTC films as a function of time delay. The X1 absorption max for each sample is shown as a dashed blue line. Solid lines overlaid on 2DES data are guides to the eye.

(~100 ps), a slight red shift is seen that we attribute to exciton migration along a downhill energy gradient as this behavior is not seen for CdSe-oleate NCs dispersed in solution.

X1 dynamics measured by exciting CdSe-oleate films at specific E_{pump} energies via 2DES reveal heterogeneous exciton behavior averaged over in TA experiments. Data acquired by exciting the red side of the X1 peak (E_{pump} = 2.25 eV, Figure 4A, red crosses) display a blue shift with increasing T consistent with the loss of stimulated emission seen in TA. As T increases, however, this blue shift continues, unlike in the TA data, indicating migration of carriers from low-energy NC sites to ones higher in energy. The magnitude of this energy shift, ~15 meV, is less than k_BT at room temperature, suggesting this uphill energy migration is entropically driven and reflects the larger number of NCs in the film with X1 energies at the peak of the X1 steady-state absorption band (2.32 eV, Figure S5). Excitons produced by photons with energies on the blue side of the X1 band (E_{pump}= 2.34 eV) also display an initial slight blue shift due to stimulated emission loss, but at long times show a red shift signaling exciton migration from high-energy NC sites to lower energy ones (Figure 4A, blue circles). Importantly, our data indicate the extent of exciton migration occurring by 500 ps is minimal as dynamics initiated at different initial energies have yet to relax to similar asymptotic values.

Turning to CdSe-PDTC, X1 dynamics captured by TA (Figure 4B, gray circles) show a red shift signaling downhill exciton migration, but with a rate that significantly increased relative to CdSe-oleate, completing within 100 ps. We note such rapid migration cannot be explained by an enhancement of Förster resonance energy transfer due to a decrease in spacing between NCs upon PDTC exchange,[17] suggesting this speedup results from improved wave function overlap between NCs.[17,33,47,51] At T > 100 ps, a blue shift of the X1 band appears that we have noted in prior work.[17] Briefly, PDTC-substitution increases the density of states of CdSe NCs near their band edge, leading to an enhancement of their exciton decay rate.[17,51,52] This causes the average X1 energy to increase at sufficiently long times as NCs substituted with smaller amounts of PDTC (and larger X1 energies) come to represent the largest fraction of surviving excitations.

Moving to X1 dynamics extracted from 2DES spectra, excitons produced by exciting on the X1 band's red edge (E_{pump} = 2.25 eV) show a lack of appreciable change in their energy following their generation (Figure 4B, red crosses). This lies in contrast to excitons produced by photons centered on the high-energy side of the X1 band (E_{pump}= 2.32 eV), which undergo a clear decrease in their energy as they funnel to low-energy NC sites (Figure 4B, blue circles). While the energetic downshift due to exciton migration in CdSe-oleate films was relatively small (<10 meV) and occurred over >500 ps, 2DES spectra reveal much faster exciton migration over a larger energetic scale in PDTC-exchanged films. At the largest E_{pump} value examined (2.32 eV), we observe an energetic downhill shift of nearly 40 meV in 100 ps.

While PDTC primarily impacts states within CdSe's valence band while leaving states at its conduction band edge largely

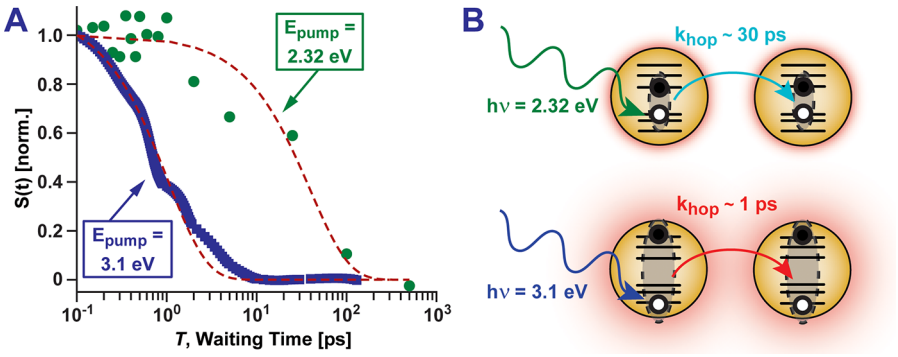


Figure 5. (A) Normalized X1 band center position for CdSe-PDTC films following excitation at 2.32 eV (green circles, from 2DES) and 3.1 eV (blue squares, from TA). (B) Data in (A) indicate the rate of exciton hopping increases with exciting photon energy, which we hypothesize results from increased spatial delocalization of carrier states further from CdSe's valence and conduction band edges.

DOI: 10.1021/acs.jpclett.9b02040
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unchanged, calculations have predicted PDTC to strongly hybridize with high-energy states within the conduction band that fall closer into energetic resonance with PDTC's LUMO.[33] Excitation into these high-energy states would create potential for delocalization of both the photoexcited electron *and* hole, further speeding exciton transfer. While limitations of our pulse shaper's spectral range prevent us from using excitation pulses containing 3.1 eV (400 nm) photons for 2DES, we can compare the results of our X1-pumped 2DES experiments to TA experiments performed with 3.1 eV photons with ∼0.8 eV in excess of the NC bandgap. This comparison allows us to characterize the degree of mixed NC-ligand character of high-energy conduction band states through their influence on exciton mobility.

Figure 5A compares the time dependence of the X1 band center position for PDTC films excited at 3.1 eV and at the blue side of the X1 band (E_{pump}= 2.32 eV). To highlight changes in the exciton migration rate viewed during these experiments, we have plotted our data analogous to a time-dependent Stokes shift:[53−55]

$$S(t) = \frac{B(t) - B(\infty)}{B(0) - B(\infty)} \quad (1)$$

where $B(t)$ represents the center energy of the X1 photobleach. Thus, the normalized shift, $S(t)$, starts at 1 and decays to zero. Data for X1 and 3.1 eV excitation display clear differences in the rate of exciton migration. For the X1-pumped data (Figure 5A, green circles) the X1 shift can be well fit with an exponential decay with a time constant of ∼30 ps. In contrast, when the same film is excited at 3.1 eV, this shift occurs 30× faster, with a time constant of ∼1 ps (Figure 5A, blue squares). A red shift of the X1 band is not seen for dispersed PDTC-functionalized NCs in solution following 3.1 eV excitation, indicating the spectral shift seen in films does not result from internal NC relaxation dynamics. Thus, our data indicate imparting excess energy to excitons in PDTC-functionalized solids leads to a substantial acceleration of their migration.

One scenario that can rationalize the increase in exciton hopping rate with increasing excitation photon energy is that the wave functions associated with both the photoexcited electron and hole are more spatially delocalized when these carriers are placed into high-energy states above the valence and conduction band edges (Figure 5B). This result is expected for a simple particle in a sphere picture where the edges of the sphere present a finite confinement potential, although experiments that examined high-energy states within PbS NCs have questioned this picture by noting these states can behave akin to ones not subject to exciton confinement.[56] This suggests that any relaxation of exciton confinement involving highly excited states in PDTC-functionalized CdSe NCs likely stems from direct involvement of PDTC itself in modifying the NC's electronic structure. Indeed, this is consistent with prior electronic structure calculations that have shown PDTC's LUMO mixes with high-energy states within CdSe's conduction band, allowing PDTC to enhance both electron and hole delocalization upon excitation.[33]

As this extended delocalization involves hot excitons, this creates a situation where carrier cooling will act to effectively slow the rate of exciton transfer. We have previously measured hole and electron cooling rates for PDTC-functionalized NCs in solution[51] and found they occur over a few hundred femtoseconds. Examining the center position of the X1 band following 3.1 eV excitation, we see that our exponential fit noticeably overestimates the rate with which this band shifts after a delay of 1 ps, indicating a slowing of exciton migration on this time scale. As hot carrier relaxation is expected to largely be complete after this delay, this supports a physical picture wherein hot excitons hop faster than ones wherein the electron and hole occupy states near CdSe's valence and conduction band edges.

We note our present findings lead us to slightly reinterpret results we previously reported wherein exciton hopping between NCs in CdSe-PDTC films was found to unfold with a ∼200 fs hopping rate on the basis of TA and kinetic Monte Carlo simulations.[17] In this prior report, a pump photon energy of 3.1 eV was used, causing a portion of the exciton transport we observed to involve hot carrier migration. While we have yet to revisit our simulation model to parametrize it to account for the effects of exciton cooling on transport, our results here suggest that excitons occupying states at CdSe-PDTC's valence and conduction band edges exhibit hopping rates that appear to be an oder of magnitude slower, on the picosecond time scale. We note this rate is still faster than hopping rates reported for NC solids featuring short linkers with limited EDL character, wherein hopping time scales as fast as ∼30 ps have been reported.[57−59]

Our work also suggests clear means by which EDL structure can be reconfigured to improve exciton transport. We observe a speedup of exciton hopping when both photoexcited electrons and holes can access states that involve partial ligand character. Comparison of our work to our prior results[17] further supports this conclusion as our two studies examined CdSe NCs of different diameters (2.8 nm in the present work vs 2.3 nm in ref 17). We find the X1 band shift we observe under 3.1 eV excitation is slowed by ∼2.5× and reduced in magnitude for the larger 2.8 nm diameter NCs we examine in this report. Altering CdSe NC size is known to tune a NC's redox properties,[13,33,47,48,52,60] which can change the energetic alignment of states in both their valence and conduction bands relative to PDTC's frontier molecular orbitals. Moving to a larger diameter NC is expected to detune the edge positions of both the valence and conduction band relative to PDTC, reducing hybridization between PDTC and CdSe NC band edge states.[60] Our work suggests this reduced hybridization also leads to a slowing of exciton transfer. If rapid exciton transport is a desired goal for a NC solid, then designing ligands with frontier molecular orbitals that lie in better energetic resonance with NC band edge states is desirable.

In summary, our work demonstrates that the EDL PDTC can enhance electronic coupling of CdSe NCs to their environment. 2DES spectra reveal that PDTC attachment both increases the homogeneous line shape of individual CdSe NCs in solution and allows for picosecond exciton migration in NC solids. The initial rate of this migration depends on the energy imparted to an exciton, which we in part ascribe to PDTC's ability to better relax the spatial confinement of electrons placed into high-energy states within CdSe's conduction band. Our work shows that electronic coupling between a NC and molecules within its ligand shell can aid energy transport in NC solids, but care must be taken to control electronic disorder within these materials and to properly match the energetic structure of the ligand to the NC to achieve maximal transport.

DOI: 10.1021/acs.jpclett.9b02040
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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b02040.

Details regarding materials synthesis and experimental measurements, schematic of our 2DES spectrometer, excitation pulse sequence for 2DES, general description of 2DES line shapes, characterization of 2DES excitation pulses via frequency resolved optical gating (FROG), steady-state absorption spectra and X1 homogeneous line width of CdSe-oleate and CdSe-PDTC films, brief discussion of PDTC degradation, transient absorption spectra of CdSe-oleate and CdSe-PDTC films (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Work performed at UT Austin was supported by the National Science Foundation under award CHE-1610412 and the Welch Foundation under award F-1885. The authors also acknowledge the Texas Materials Institute at the University of Texas at Austin, which made available instrumentation for characterization of NC films.

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